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Heavy Metal Accumulation by Freshwater Hydrobionts in a Mining Area in the South of the Russian Far East

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Abstract—The contents of heavy metals (HMs) were studied in freshwater hydrobionts from the south of the Russian Far East, including the area of wastewater discharge from a lead smelter (the village of Rudnaya Pristan, Primorye). The results showed that most invertebrates disappeared from the ecosystem as the toxicity of the aquatic environment increased. Mollusks of the genus *Lymnaea* proved to be most tolerant of HM pollution. As the contents of Pb, Mn, Cd, and Zn in bottom sediments increased, the amounts of these metals in mollusk bodies increased as well but to a much lesser extent, with the intensity of HM accumulation decreasing at their higher concentrations in the environment. The range of HM concentrations accumulated in the bodies of limneids noticeably broadened with an increase in technogenic impact. This is evidence for differences in the efficiency of mechanisms regulating the contents of trace elements in individuals of the same species under conditions of extreme pollution.

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Key words: Russian Far East, the Rudnaya River, heavy metals, mollusks, amphipods, may flies, caddis flies.

Studies on specific features of heavy metal (HM) accumulation by hydrobionts help resolve issues concerning regulation of anthropogenic load on ecosystems (Volkov et al., 1996). However, environmental monitoring in mountain regions of Russia, where ore manifestations are observed most frequently, deals mainly with the state of land biocenoses (Koval'skii, 1974; Elpat'evskii, 1993). Aquatic organisms of mountain rivers, among which larval amphibiontic insects prevail (Bogatov, 1994), have unfortunately received little attention from Russian researchers (Volkov et al., 1996).

The purpose of this study was to determine HM accumulation level in mass species of aquatic invertebrates inhabiting rivers and lakes in mountain areas of Primorye and to estimate prospects for using these hydrobionts for HM monitoring at mining sites.

MATERIAL AND METHODS

An assessment of HM contents in aquatic invertebrates from the lower part of the Rudnaya River basin (near the village of Rudnaya Pristan, Dalnegorsk raion) was made in August 1985 and 1986. This region is exposed to gaseous emissions and industrial wastewater discharge from the lead smelter (PO Dalpolymetal), which has been in operation since 1930. Consequently, a critical ecological situation involving profound changes in environmental quality developed there already in the mid-20th century (Kachur, 1981; Bogatov et al., 1987; Kachur et al., 1992; Elpat'evskii, 1993). Our observations covered water bodies exposed to direct impact of industrial discharge (three sedimentation basins and the channel connecting them with the Rudnaya River) or to moderate pollution, mainly with gas and smoke emissions (a stream in the Koreiskaya Pad' valley), and control (unpolluted) aquatic objects: Vas'kovskoe Lake used as a source of drinking water for the village and a stream in the Vas'kovskaya Pad' valley, which flows into this lake (Fig. 1). Additional studies (in 1986, 1999, and 2003) were performed on Yaponskoe Lake (Terneiskii raion); Kedrovaya, Alimovka, and Izvestkovaya rivers (Khasanskii raion); and the Bol'shaya Ussurka River and its right tributary, the Dalnyaya River (Krasnoarmeiskii raion).

The objects of this study included gastropods *Lymnaea pacifampla* (Krugl. et Star.) with a shell height of 22–28 mm; bivalves *Kunashiria coptzevi* (Zatr. et Bog.) with a shell length of 7–8 cm; mature amphipods *Gammarus* sp.; larvae of different mayfly species, including *Cinygmula* sp.; and larvae of caddis flies *Neophylax ussuriensis* (Mart.) and *Glossosoma altaicum* Mart. The contents of Fe, Mn, Zn, Pb, and Cd in their bodies

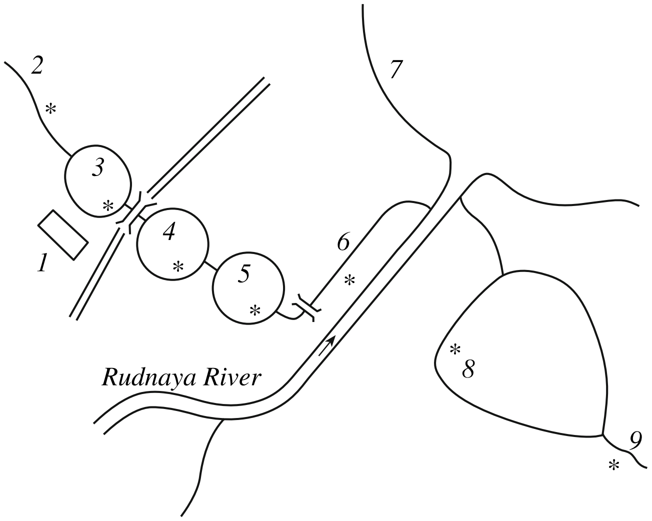

Fig. 1. Scheme of the study area: (*1*) lead smelter; (*2*) stream in Koreiskaya Pad'; (*3–5*) sedimentation basins 1–3; (*6*) channel connecting sedimentation basins with the Rudnaya River; (*7*) Rudnaya Bay; (*8*) Vas'kovskoe Lake; (*9*) stream in Vas'kovskaya Pad'. Asterisks indicate sampling sites.

were determined with regard to specific features of local pollution (Kachur, 1981). The same HMs were measured in the water, suspended matter, and bottom sediments. At background stations, we additionally estimated Cu contents in bottom sediments and Ni, Co, and Cu contents in hydrobionts.

Concentrations of HM ions were measured with a Hitachi 180-70 atomic absorption spectrometer. On the whole, about 3500 hydrobionts were used for the analysis. The samples were prepared following a standard procedure. Mollusks were cleaned of fouling and kept for up to 2 days in distilled water to evacuate the gut contents, and HMs were determined in the mollusk body without the shell. Other hydrobionts—amphipods and larvae of aquatic insects—were washed in distilled water before analysis. All specimens were dried at 85°C to constant weight, homogenized, and wet-ashed with a mixture of concentrated nitric and perchloric acids (2 : 1). Each sample was analyzed in five replications. The correctness of metal determination was checked in periodic tests with standard samples, and possible sample contamination during analysis was controlled in regular blank tests.

The degree of HM accumulation by hydrobionts was assessed using the biological accumulation coefficient (K_d) calculated as the ratio of HM concentrations in their bodies to those in bottom sediments. Animals with $K_d > 2$, $K_d = 1–2$, or $K_d < 1$ were classified as macroconcentrators, microconcentrators, and deconcentrators, respectively.

RESULTS AND DISCUSSION

The composition of HM ions in hydrobionts from different unpolluted habitats was relatively stable. Thus, HM concentrations in *Gammarus* sp. from the upper and middle reaches of the Kedrovaya River and from the Alimovka and Izvestkovaya rivers differed bi a factor of only 1.2–1.4 (Table 1). Under moderate pollution, the accumulation of some HMs by invertebrates proved to be increased. For instance, the concentrations of Pb, Ni, and Cd in amphipods from the stream in Koreiskaya Pad' appreciably exceeded the background values. Such changes in the chemical composition of amphipod bodies are explained by the fact that these crustaceans feed mainly on leaf litter (Bogatov, 1991), in which HM contents are increased (Elpat'evskii, 1993). High Pb, Ni, and Cd concentrations in a polluted stream were also observed in *Cinygmula* sp. mayfly larvae feeding on detritus (Tiunova, 2006); moreover, Fe and Zn concentrations in their bodies were also relatively high. The concentrations of Pb, Ni, and Cd ions exceeding the background values were observed in the larvae of caddis flies *N. ussuriensis* and *G. altacium* feeding on periphyton (Kocharina, 2005).

In bottom sediments of water bodies and streams exposed to discharge from the lead smelter, excess over the background concentration was the highest for Fe and Mn, and the lowest for Cd. The concentrations of HMs in bottom sediments and suspended matter at clean and heavily polluted stations on the Rudnaya River differed as follows: Fe, by factors of 4.6 and 3.5; Mn, by factors of 50 and 2.7; Zn, by factors of 70 and 5; Pb, by a factor of 86 and from 0.0 to 8300 μg/g dry suspension; and Cd, by a factor of 3.3 and from 0.0 to 50 μg/g dry suspension. It is apparent that Fe, Mn, and Zn concentrations in suspension were more stable than those in bottom sediments at different stations, while those of Pb and Cd were less stable. HM concentrations in water at different stations also varied widely: by factors of 3.3 for Fe, 60 for Mn, 13 for Zn, 40 for Pb, and 11 for Cd.

The distribution of HMs with respect to their average concentrations in bottom sediments, suspended matter, and water proved to change noticeably with an increase in technogenic load:

Bottom sediments:	
Control	Cd < Pb < Zn < Mn < Fe
Moderate pollution	Cd < Zn < Pb < Mn < Fe
Sedimentation basins	Cd < Mn < Pb < Zn < Fe
Suspended matter	
Control	Cd = Pb < Zn < Mn < Fe
Moderate pollution	Cd < Zn < Pb < Mn < Fe
Sedimentation basins	Cd < Zn < Mn < Pb < Fe
Water	
Control	Cd < Pb < Mn < Zn < Fe
Moderate pollution	Cd < Pb < Zn < Mn < Fe
Sedimentation basins	Cd < Pb < Zn < Fe < Mn

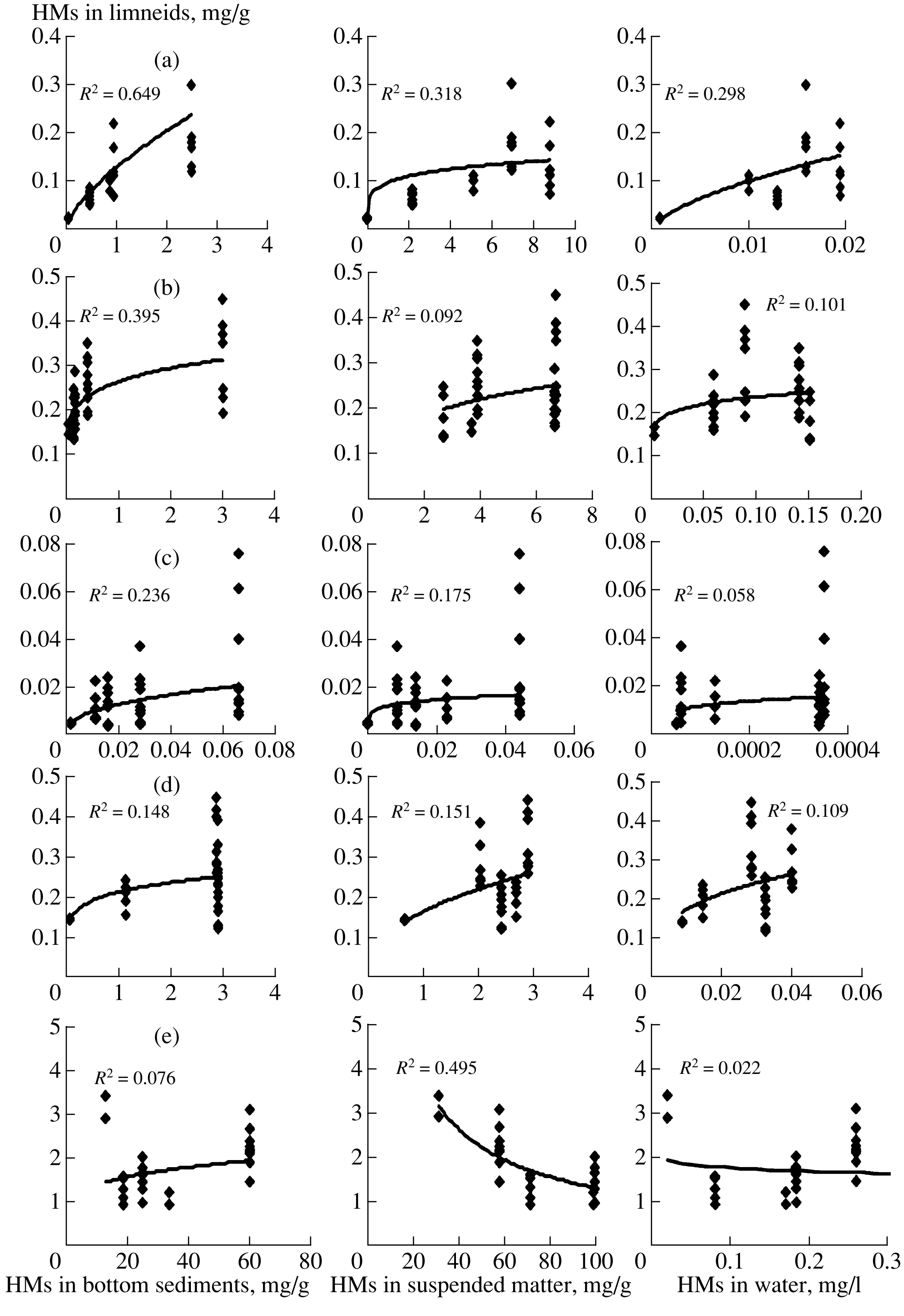

Fig. 2. Relationship between concentrations of HMs in bottom sediments, suspended matter, and water and their concentration in limneids (based on sample average values): (a) Pb, (b) Mn, (c) Cd, (d) Zn, and (e) Fe.

Thus, at higher pollution levels, the content of Pb appreciably increased in bottom sediments and suspended matter, with that of Mn increasing in water. In addition, Zn prevailed over Mn and Pb in bottom sediments from the most polluted site. Iron was the main HM pollutant in all three environments, except for

Table 1. Concentrations of HMs in bottom sediments and bodies of hydrobionts, μg/g of dry weight

Sample name	Fe	Mn	Zn	Pb	Ni	Co	Cu	Cd
Koreiskaya Pad', stream								
Sediments	30000	450	90	135	–	–	8.6	28
Gammarus sp.	–	–	76	146	83	9.4	40	5.0
Cinigmula sp.	3700–5300	155–310	290–435	70–100	20–22	3.2	24–27	7.3–7.5
N. ussuriensis	–	190–520	180–200	30–36	2.6–3.6	1.4–1.3	17.6	1.0
G. altaicum	1500–1600	690–720	180–185	40–60	6.8–8.9	1.8	10.3	6.3
Vas'kovskaya Pad', stream								
Sediments	25000	550	40	30	–	–	4.0	1.8
Cinigmula sp.	1400–2400	115–180	170–190	Not found	Not found	Not found	17.4–18.3	0.9–1.3
N. ussuriensis	190–260	120–140	134–162	″	0.0–0.8	0.8–1.2	12.2–13.4	0.1–0.3
G. altaicum	3000	800	183	″	Not found	Not found	5.4	1.4
Lake Vas'kovskoe								
Sediments	13000	130	70	42	–	–	4.6	2.0
Mayfly larvae	1600–2000	100–110	570–670	27–29	7–25	5.4	50–55	14.5–18.7
L. pacifampla	2800–3900	160–170	145–150	21.0–25.0	5.5–9.5	2.7–3.0	–	3.4–5.5
K. coptzevi	4300–8200	2600–8100	430–850	30–40	3.5–20	2.0–4.8	6.7–9.1	4.8–8.5
Lake Yaponskoe								
K. coptzevi	5400–7500	6500–7000	270–310	5.1–6.7	6.3–6.9	–	5.1–5.3	2.6–2.9
Kedrovaya River								
Gammarus sp.	1500–1600	34–38	73–75	12–14	7.2–8.8	5.4–6.1	44–52	2.6
G. altaicum	4400	22	50–51	3.7	1.8	1.4	7.1	0.6
Alimovka River								
Gammarus sp.	1200–1400	26–33	64	12	6.9	4.8–5.4	48–58	1.9
Izvestkovaya River								
Gammarus sp.	1600	35.5	64	11	6.1	5.4	54	2.1
Bol'shaya Ussurka and Dalnyaya rivers								
Cinigmula sp.	1500–2700	170–190	120–150	3.7–6.6	1.1–3.5	9–10	27–32	3.0–3.4
L. pacifampla	1100–6000	95–570	35–90	16–23	11–15	11–13	18–34	3.3–4.0

Note: (–) not analyzed.

Table 2. Concentrations of Pb, Cd, Zn, and Mn in bottom sediments and bodies of pond snails, μg/g dry weight

HM concentration in sediments, station name	Range of HM accumulation in snails	Average HM concentration in snails	K_{min}/K_{max}	N	K_d
		Lead			
42 (Vsk)	21.0–25.0	23.3 ± 1.9	0.84	16	0.55
480 (channel)	31.6–99.2	64.0 ± 17.1	0.32	30	0.13
880 (SB3)	59.3–128.7	90.9 ± 19.0	0.46	23	0.10
950 (SB1)	63.2–231.6	139.5 ± 62.5	0.27	37	0.15
2470 (SB2)	118.9–727.7	326.7 ± 198.0	0.16	34	0.13
		Cadmium			
2 (Vsk)	3.4–5.5	4.85 ± 0.73	0.62	16	2.42
11 (SB3)	4.7–24.0	11.7 ± 6.1	0.20	23	1.06
16 (channel)	3.9–27.2	14.4 ± 7.1	0.14	30	0.90
28 (SB1)	4.8–40.1	16.0 ± 10.2	0.12	34	0.57
66 (SB2)	6.9–93.3	30.5 ± 25.7	0.07	32	0.46
		Zinc			
70 (Vsk)	140–150	145.8 ± 4.1	0.93	16	2.08
1130 (SB3)	143–260	205.0 ± 35.6	0.55	22	0.18
2830 (channel)	188–544	361.4 ± 102.7	0.35	30	0.12
2875 (SB1)	113–268	178.7 ± 45.5	0.42	36	0.06
2880 (SB2)	175–422	302.0 ± 74.3	0.41	33	0.10
		Manganese			
128 (Vsk)	150–172	165.9 ± 7.2	0.87	16	1.30
310 (SB3)	135–255	193.4 ± 42.8	0.53	21	0.62
380 (SB2)	152–290	204.1 ± 30.8	0.52	28	0.53
860 (SB1)	165–385	258.7 ± 53.9	0.43	36	0.30
5900 (channel)	171–482	304.6 ± 80.6	0.35	30	0.05

Note: K_{min}/K_{max} is the minimum-to-maximum HM concentration ratio in mollusk bodies; (*N*) number of measurements, (Vsk) Vas'kovskoe Lake, (SB1–SB3) sedimentation basins.

the water from sedimentation basins, where Mn concentrations were even higher. The observed HM distribution pattern is indicative of fairly active washing of Mn out of the pollution zone with simultaneous accumulation of Pb and Zn in bottom sediments.

Macroconcentrator species are considered to be most informative for monitoring fresh waters. At background stations in the Rudnaya River basin, these were mussels (for Mn, Zn, and Cd), pond snails (for Zn and Cd), mayfly larvae (for Zn and Cu), *N. ussuriensis* larvae (for Zn and Cu), and *G. altaicum* larvae (for Mn and Zn) (Table 1). Among all HMs studied, the most active accumulation was characteristic of Mn in bivalves. At a background Mn concentration of 130 μ/g in bottom sediments, its content in *K. coptzevi* averaged 4500 ± 880 μg/g (K_d = 32), reaching a peak of 8100 μg/g dry weight. A similar capacity of mussels for Mn accumulation was also observed beyond the Rudnaya Basin. For instance, Mn concentration in *K. coptzevi* from Yaponskoe Lake (in the protection zone of the Sikhote Alin Nature Reserve) reached 6500–7000 μg/g of dry weight (Table 1).

At high concentrations of environmental HMs, a considerable proportion of hydrobionts—first of all, amphipods and the larvae of stone flies, mayflies, and caddis flies—disappear from the aquatic ecosystem (Bogatov et al., 1987). In such case, it is expedient to assess the state of environment by analyzing changes in the structure of benthic communities (Woodiwiss, 1964; Bogatov and Bogatova, 1986; Alimov and Teslenko, 1988; and others). Thus, studies performed in the Rudnaya River showed that increasing pollution resulted in structural simplification of the benthic community and in an increasing ratio of production to expenditures for metabolism in the bottom biocenosis (Teslenko, 1986; Alimov and Teslenko, 1988).

Among the invertebrates studied, gastropods *L. pacifampla* proved to be most tolerant to extreme pollution.

As environmental Pb, Cd, Zn, and Mn concentrations increased, their contents in these mollusks increased as well but to a much lesser extent, with the intensity of HM accumulation decreasing at their higher concentrations in the environment (Fig. 2). In particular, when the concentrations of Pb, Cd, Zn, and Mn in bottom sediments increased by factors of approximately 60, 30, 40, and 46, their average concentrations in *L. pacifampla* increased by factors of only 15, 6, 2.5, and 1.8, respectively. The correlation between the degree of HM accumulation in the mollusks and HM concentrations in different media (bottom sediments, suspended matter, and water) was strongest in the case of bottom sediments, especially for Pb ($R^2 = 0.65$). This is readily explicable by the fact that pond snails feed mainly on bottom detritus and periphyton (Kruglov, 2005). Moreover, bottom sediments not only show the highest capacity for HM accumulation but also have "memory," i.e., contain information on the state of a biotope over a fairly long period of time (Stumm and Morgan, 1996). It is noteworthy that no definite relationship between the level of HM accumulation in limneids and its concentration in the environment was revealed in the case of Fe (Fig. 2).

In the zone of increased pollution, we revealed a consistent decrease in K_d values calculated from the average concentrations of trace elements (including Fe) in pond snails (Table 2). Thus, under extreme pollution of the aquatic environment, pond snails proved to become deconcentrators with respect to HMs. Note that, for instance, at background and moderately polluted stations in the Dnieper basin (Ukraine), freshwater mollusks of different systematic groups (bivalves, prosobranchs, and pulmonates) functioned only as macroconcentrators of HMs (Cd, Pb, Cu, and Zn) (Kirichuk, 2006). Obviously, the reduced intensity of Pb, Mn, Cd, and Zn accumulation by limneids in mining areas may be regarded as a major adaptation of these hydrobionts to living under conditions of technogenic anomalies.

It is noteworthy that the error of mean values of HM concentrations in mollusks proved to increase with the accumulation of HMs in bottom sediments (Table 2). This was because the range of variation in the amounts of these elements accumulated by different individuals (from minimal to maximal values) broadened at more heavily polluted stations. For instance, in Lake Vas'kovskoe (a drinking water source), individual Pb concentrations in limneids differed by a factor of 0.8, compared to 6.1 at the most polluted station (the second sedimentation basin). The minimum-to-maximum HM concentration ratios in the bodies of mollusks from clean and heavily polluted stations differed as follows: for Pb, 0.84 vs. 0.16; for Cd, 0.62 vs. 0.07; for Zn, 0.93 vs. 0.35–0.41; and for Mn, 0.87 vs. 0.35.

Thus, under conditions of extreme technogenic load, at the most polluted stations, mollusks (pond snails) were found in which HM concentrations only slightly exceeded background values. This is evidence that some individuals in their population were capable of preventing excessive accumulation of trace elements, whereas another part of this population was highly susceptible to penetration of HMs into their bodies. An increase in the range of variation in the accumulation of HM ions in mollusks living in a heavily polluted aquatic environment indicates that the efficiency of mechanisms regulating HM contents may differ in individuals of the same species. This should be taken into account in biomonitoring studies.

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REFERENCES

Alimov, A.F. and Teslenko, V.A., Structural and Functional Characteristics of River Zoobenthos in the Zone of Anthropogenic Impact, *Gidrobiol. Zh.*, 1988, vol. 24, no. 2, pp. 27–30.

Bogatov, V.V., Growth and Production of Amphipods in Rivers of Southern Primorye, *Gidrobiol. Zh.,* 1991, vol. 27, no. 1, pp. 39–46.

Bogatov, V.V., *Ekologiya rechnykh soobshchestv rossiiskogo Dal'nego Vostoka* (Ecology of River Communities in the Russian Far East), Vladivostok: Dal'nauka, 1994.

Bogatov, V.V. and Bogatova, L.V., Assessment of Water Pollution in the Lower Amur by the Composition of Benthos, in *Donnye organizmy presnykh vod Dal'nego Vostoka* (TRANSLATION), Vladivostok: DVNTS Akad. Nauk SSSR, 1986, pp. 128–133.

Bogatov, V.V., Bogatova, L.V., and Kachur, A.N., Heavy Metal Monitoring in Background and Polluted Freshwater Ecosystems, *Sostoyanie i perspektivy razvitiya metodologicheskikh osnov khimicheskogo i biologicheskogo monitoringa poverkhnostnykh vod sushi: Tez. dokl. XXIX Vsesoyuz. gidrokhimich. soveshch.* (Methodological Bases of Chemical and Biological Monitoring of Land Surface Waters: Current State and Prospects for Development. Abstr. XXIX All-Union Conf.), Rostov-on-Don, 1987, vol. 2, pp. 5–6.

Elpat'evskii, P.V., *Geokhimiya migratsionnykh potokov v prirodnykh i prirodno-antropogennykh geosistemakh* (Geochemistry of Migration Flows in Natural and Natural–Anthropogenic Geosystems), Moscow: Nauka, 1993.

Kachur, A.N., Some Specific Features of Constructing Landscape–Geochemical Maps of Regions with Intensive Technogenesis, *Sikhote-Alinskii biosfernyi raion: printsipy i metody ekologicheskogo monitoringa* (The Sikhote Alin Biosphere Region: Principles and Methods of Ecological Monitoring), Vladivostok: Dal'nevost. Nauchn. Tsents Akad. Nauk SSSR, 1981, pp. 136–145.

Kachur, A.N., Bogatov, V.V., Kosolapov, A.V., et al., Sanitary–Ecological Problems in Primorye, *Dolgovremennaya programma okhrany prirody i ratsional'nogo ispol'zovaniya prirodnykh resursov Primorskogo kraya do 2005 goda (Ekologicheskaya programma)* (Long-Term Program of Nature Conservation and Rational Use of Natural Resources in Primorye for the Period to the Year 2005: Ecological Program), Vladivostok: Dal'nauka, 1992.

Kirichuk, G.E., Specific Features of Accumulation of Heavy Metal Ions in Freshwater Mollusks, *Gidrobiol. Zh.*, 2006, vol. 42, no. 4, pp. 99–110.

Kocharina, S.L., Trophic Structure of Invertebrates in Some Streams of the Pravaya Sokolovka River Basin (Verkhneussuriiskii Station, Primorye), in *Chteniya pamyati Vladimira Yakovlevicha Levanidova* (Vladimir Yakovlevich Levanidov Memorial Lectures), Vladivostok: Dal'nauka, 2005, issue 3, pp. 49–61.

Koval'skii, V.V., *Geokhimicheskaya ekologiya* (Geochemical Ecology), Moscow: Nauka, 1974.

Kruglov, N.D., *Mollyuski semeistva prudovikov (Lymnaeidae, Gastropoda, Pulmonata) Evropy i Severnoi Azii* (Mollusks of the Pond Snail Family (Lymnaeidae, Gastropoda, Pulmonata) in Europe and Northern Asia), Smolensk: Smolensk. Gos. Ped. Inst., 2005.

Stumm, W. and Morgan, J.J., *Aquatic Chemistry,* New York: Wiley, 1996.

Teslenko, V.A., Assessment of Hydrobiological Regime in the Rudnaya River by the Composition of Benthic Invertebrates, in *Donnye organizmy presnykh vod Dal'nego Vostoka* (Benthic Organisms in Fresh Waters of the Far East), Vladivostok: Dal'nevost. Nauchn. Tsentr Akad. Nauk SSSR, 1986, pp. 116–127.

Tiunova, T.M., Trophic Structure of Invertebrate Communities in Ecosystems of Salmon Rivers in the Southern Far East, *Ekologiya*, 2006, no. 6, pp. 457–463.

Volkov, I.V., Zalicheva, I.N., Shustova, N.K., and Il'mast, T.B., The System of Federal Maximum Admissible Concentrations for the Fishing Industry: Does It Make Ecological Sense?, *Ekologiya*, 1996, no. 5, pp. 350–354.

Woodiwiss, F.S., The Biological System of Stream Classification Used by the Trent River Board, *Chem. Ind.*, 1964, vol. 11, pp. 443–447.