

Assessing the Influence of the Mining Operations on the State of Streams in the Northern Part of the Red River Basin (Viet Nam)

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Abstract—A study was made of the influence of extraction of lead and zinc ores in the northern part of Vietnam (the Red river basin, Chodon district of Bac Can Province, and the basins of the Dai, Ban Thi, Ta Dieng and Cau rivers). Background concentrations of macro- and microelements and biogenic elements are determined in the river waters and water extracts from bottom sediments of small streams of the study area. A significance exceedance of background concentrations was revealed in stretches of the headwaters of the Ban Thi and Dai rivers caused by a combination of natural and anthropogenic factors. It is established that the river waters near the pollution sources contain increased (compared with the geochemical background) concentrations of Zn, Pb, Fe, Ni, Co, As, Bi, Cd, Cs, Sb, Ag, NO₃⁻ and SO₄²⁻. The waters are estimated as moderately and heavily polluted, and at the other points as minimally polluted. It is determined that the level of accumulation of matter in water extracts from bottom sediments with respect to the geochemical background in the vicinity of the ore dressing factories corresponds to weakly and heavily polluted bottom sediments, and further downstream, to the minimum level of pollution. It is shown that the influence of extraction of lead and zinc ores on the state of small streams is observed in stretches as long as 11–12 km (with a maximum in stretches of up to 4.5 km). The mathematical model of Pb and Zn distribution in the river waters of the study area has been developed and tested.

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INTRODUCTION

Hydroecological investigations with a focus of the study of the status of water bodies and natural-anthropogenic conditions for its formation constitute an important stage of planning and implementation of measures for the rational utilization of natural resources and environmental protection. The current significance of such research is especially high in Southeastern Asia where the supply of water of adequate quality increases many times in importance because of a high population density and the existence of a number of outstanding water-economy problems.

With this in mind, we examined the status of the river waters and bottom sediments in the northern part of the Socialist Republic of Viet Nam. Administratively, the study area corresponds to the Chodon district of the Bac Can province and geographically, to the interfluvium of number of large tributaries of the Red (Hong Ha): the Loa and Cau rivers (Fig. 1). Deposits and occurrences of Pb and Zn have been discovered within its boundaries. The most intense extraction of lead-zinc ores (mostly by the mine method) is concentrated in the drainage area of the Ban Thi river (the tributary of

the Gam river flowing into the Lo river); a somewhat smaller volume of mining production corresponds to the drainage areas of the Ta Dieng (flows into Lake Ba Be) and Dai (the tributary of the Lo river). Other mineral resources have also been discovered [1].

Based on this, the objective of this study is to determine the influence of the extraction of solid mineral resources on the status of water bodies with a different degree of anthropogenic pressure. We examined the Dai river and its tributaries Pho Dai and Namdu, the Ban Thi and its tributary the Chengu, and the Ta Dieng and Cau rivers. Anthropogenic pressure is minimal on the Cau river in its upstream section, and maximal on the Dai and Ban Thi rivers.

METHODS AND INITIAL DATA

The primary goals of this study are to determine the background chemical composition of the river waters on the territory under consideration, assess the deviations from the hydrochemical background caused by the extraction of lead-zinc ores, and to analyze the self-purification conditions of the rivers experiencing the influence from the mining industries. In view of

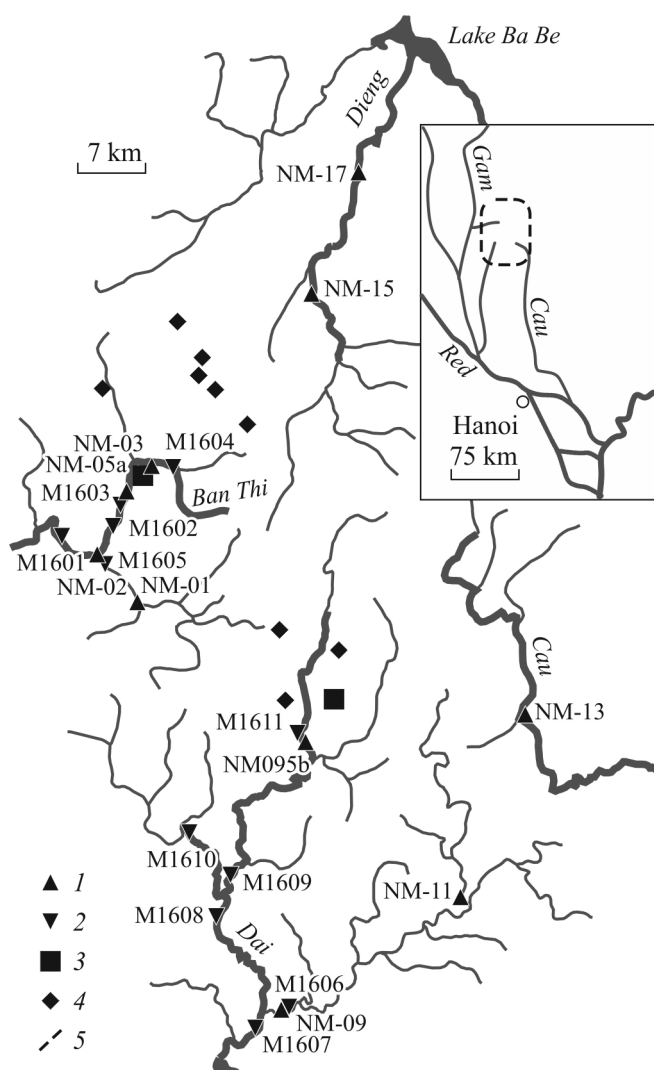


Fig. 1. Schematic map showing the location of the objects under study in the interfluve of the Lo and Cau rivers.
 1 – water sampling locations in 2015; 2 – water and bottom sediment sampling locations in 2016; 3 – ore-dressing plants; 4 – mines; 5 – study area.

the aforementioned goals, the techniques included field work involving selection of river water and bottom sediment samples, measurements of water discharges of the rivers under investigation, analytical procedures of determining the chemical composition of river water samples and aqueous extracts from river bottom sediments, a statistical analysis of data obtained, thermodynamical calculations, and the development and testing of the mathematical model for migration of trace elements in the river waters.

River water samples (simultaneously with water temperature and pH measurements) were collected on February 14–16, 2015 (10 samples from the Dai, Pho Dai, Cau, Ban Thi and Ta Dieng rivers) and on February 19–20, 2016 (11 samples from the Dai, Pho Dai, Namdu, Ban Thi and Chengu rivers) along the fairway of the

river from the layer of 0.3–0.5 m from the surface into specially prepared reservoirs, in accordance with the requirements reported in [2, 3]. Bottom sediments in the streams (river sediments) were only collected in 2016 at the same locations as used for river water sampling (see Fig. 1), having regard to the recommendations in [4], from the upper layer of about 0.2 m by using the bottom sampler. Bottom sediment samples were dried at 100°C and reduced in size to a fraction with particles less than 0.5 mm in diameter. Flow velocities were measured in accordance with the instructions in [5] by means of surface floats, by converting to the mean velocity. The time of sampling corresponded to the low-water period lasting, on the average, from November to April and characterized by atmospheric precipitation amounts in the range from 1 to 5% of the annual amount [6].

Analytical work was done in the certified Hydrogeochemical Laboratory of Tomsk State University (state certification No. ROSS RU. 0001.511901 of 7.12.2011). The analyses used the potentiometric, titrimetric, turbidimetric, photometric, inversion volt-ampere and atomic absorption methods, ion chromatography and inductively coupled plasma mass spectrometry (PerkinElmer NexION 300D mass spectrometer).

Data obtained were processed having regard to the requirements in [7]; it included the estimation of the statistical parameters, the exclusion of extreme values, and correlation and regression analyses. The first stage of statistical analysis revealed extreme values according to the conditions:

$$\frac{C_{\max} - C_a}{\sigma} \geq K_{\text{ex}} \quad (1),$$

$$\frac{C_a - C_{\min}}{\sigma} \geq K_{\text{ex}} \quad (2)$$

where C_a , C_{\max} , and C_{\min} are the mean (arithmetic), maximum and minimum concentrations of matter, σ – is the root-mean-square deviation of the values of the concentration of matter, and K_{ex} is the value determined according to the sample size N [7]. Whenever at least one of the conditions of (2) and (3) is not satisfied, the extreme value was excluded from the sample, and the statistical parameters were recalculated. As the characteristic of background concentrations, according to [8], we used the mean geometric C_G and the upper limit of its determination C_{GUP} :

$$C_{\text{GUP}} = C_G \exp\left(\frac{3\sigma_{\ln C}}{\sqrt{N}}\right), \quad (3)$$

where $\sigma_{\ln C}$ – is the root-mean-square deviation of the concentration logarithm. According to [9], we assigned the values to abnormal ones, which exceed C_{GUP} twice or more. The overall estimation of the geochemical state of the environmental component was carried out according to the index:

$$Z = \sum \frac{C}{C_{\text{GUP}}} - (N_m - 1), \quad (4)$$

where N_m is the number of cases when $C/C_{\text{GUP}} > 2$ [9].

The correlation between the values of X and Z was considered significant (at 5% significance level) if the condition (5) was satisfied, and the coupling equation was considered satisfactory subject to the condition (6)

$$r_{X,Z} \geq 2 \frac{1 - r_{X,Z}^2}{\sqrt{N-1}}, \quad (5)$$

$$\frac{S}{\sigma} = \frac{1}{\sigma} \sqrt{\frac{\sum_{i=1}^N (Z_{1,i} - Z_{2,i})^2}{N - m}} \leq 0.8, \quad (6)$$

where $r_{X,Z}$ is the correlation coefficient, N is the sample size, m is the number of parameters in the relation, Z_1 and Z_2 are the measured and calculated values of Z , and σ is the root-mean-square deviation of Z_1 [10, 11].

The concentration index η was calculated by using the Solution+ software package [12]:

$$\eta = \lg PA - \lg K_{\text{neq}}, \quad (7)$$

where PA is the product of the activities of a group of substances, and K_{neq} is a non-equilibrium constant. The technique of thermodynamical calculations with regard to the territory under consideration is given in [13].

The self-purification conditions of the rivers were analyzed by comparing the geochemical indicators obtained for the sections of the rivers with different anthropogenic pressure as well as by developing and testing the mathematical model for the distribution and transformation of substances in the river waters (by taking into account the process having a significant influence on the correspondence of modeling results with observational data). The model is based the analytical solution of the equation of turbulent diffusion in the flow [14–16] by including in the source function the content of a given substance in bottom sediments and a regional dependence of the specific rate of variation in the concentration of matter in the river waters on the modulus of water discharge and hydraulic conditions.

RESULTS AND DISCUSSION

Analysis of data obtained showed that, according to background values of the hydrochemical indicators, the river waters of the territory under investigation (according to O.A. Alekin's classifications [17]) are characterized, on the average, as fresh waters with low and moderate mineralization, hydrocarbonate calcium waters of the second and third types; according to [18]: in terms of pH – weakly alkaline, hardness – very soft, index of permanganate oxidability – with a very low oxidability, and in terms of content of

organic and biogenic matter – from the oligotrophic to beta-mesosaprobic class [13]. Aqueous extracts from bottom sediments in the rivers, like the river waters, are fresh, hydrocarbonate calcium, of the third type but are characterized by higher content of organic matter corresponding to the waters with an increased permanganate oxidability (Table 1).

A violation of the Russian regulations on the water quality in the water bodies of economic-household purposes [19] is observed with respect to Si, Fe, Al, As and Pb content levels. In most cases, a violation of the Russian Fisheries regulations [20] is recorded with respect to NO_2^- , Fe, Al, Mn, Cu, Zn and Pb concentrations. Exceedances of the Vietnamese regulations on the economic and drinking water quality [21] were recorded with respect to Fe, Al, As and Pb content levels; in water bodies for fisheries purposes [22] – with respect to NO_2^- and Pb content levels. Overall, the status of the river waters is estimated, in view of [9] as unsatisfactory because of an exceedance of the regulations on the quality for Pb by more than a factor of 5 as well as Al – more than twice and As – by more than a factor of 1.5.

In most cases, increased background concentrations of Pb, Zn, Cd, Ag, Hg, As and a number of other elements in the river waters as well as in aqueous extracts from bottom sediments were observed in the sources of the Ban Thi (location M1603, see Fig. 1 and Table 2) and Dai (location M1611, see Fig 1 and Table 2), especially near the dressing plants where the index of combined excess of the geochemical background Z is 26.1 and 82.7 for the river waters and 54.4 and 13.0 for bottom sediments, respectively. To a first approximation, this permits us to attribute the resulting high values of the geochemical indicators to the extraction of lead-zinc ores. Thus, a twofold exceedance of the value of CGUP in February 2016 on the Ban Thi river was observed with respect to the Zn and Pb content levels about 1 km downstream from the dressing plant, and on the Dai river – on the section from 3 to 12 km.

For studying in greater detail the influence of the mining industries we examined the model for the distribution of pollutants in the water flow in the form

$$C = \frac{k_s}{k_c} S + \left(C_0 - \frac{k_s}{k_c} S \right) \exp \left(x \frac{v}{2D} \left(1 - \sqrt{1 + \frac{4k_c D}{v^2}} \right) \right), \quad (8)$$

where C and C_0 are the concentrations of matter in the river water at a distance x from the pollution source and in the section line of waste water discharge, S is the concentration of matter in the aqueous extract from bottom sediments, v is the mean flow velocity, D is the coefficient of hydrodispersion, and k_c and k_s are the specific rates of variation in concentration of matter in the river water and in bottom sediments,

Table 1. Statistical parameters of chemical composition of the river waters and aqueous extracts from bottom sediments in the interfluvium of the Lo and Cau rivers in 2015–2016

River waters					Aqueous extract from bottom sediments				
Indicator	C_G	C_{GUP}	C_{max}	N	Indicator	C_G	C_{GUP}	C_{max}	N
pH, units	7.65	7.81	8.03	21	pH, units	7.70	7.87	8.00	11
S	218.4	300.9	335.7	21	S	661.8	883.4	1922.4	10
Ca ²⁺ , mg/dm ³	44.6	69.5	83.2	21	Ca ²⁺ , mg/kg	183.3	257.5	540.0	10
Mg ²⁺ , mg/dm ³	5.0	5.9	7.3	21	Mg ²⁺ , mg/kg	5.9	7.9	23.5	9
Na ⁺ , mg/dm ³	2.0	2.9	4.1	21	Na ⁺ , mg/kg	5.0	7.6	9.4	11
K ⁺ , mg/dm ³	1.3	1.9	3.5	21	K ⁺ , mg/kg	25.5	34.0	61.0	10
HCO ₃ ⁻ , mg/dm ³	150.9	209.5	238.0	21	HCO ₃ ⁻ , mg/kg	320.2	387.1	415.0	11
SO ₄ ²⁻ , mg/dm ³	8.8	12.9	26.2	21	SO ₄ ²⁻ , mg/kg	104.3	225.9	870.0	10
Cl ⁻ , mg/dm ³	1.4	1.6	2.0	21	Cl ⁻ , mg/kg	3.0	4.5	6.5	11
NO ₃ ⁻ , mg/dm ³	1.716	2.583	4.340	21	NO ₃ ⁻ , mg/kg	0.250	0.250	2.000	10
NO ₂ ⁻ , mg/dm ³	0.017	0.026	0.500	20	NO ₂ ⁻ , mg/kg	0.541	0.934	2.500	10
NH ₄ ⁺ , mg/dm ³	0.060	0.111	0.210	21	NH ₄ ⁺ , mg/kg	12.769	31.284	39.000	11
PO ₄ ³⁻ , mg/dm ³	0.025	0.025	0.080	18	PO ₄ ³⁻ , mg/kg	0.554	1.560	6.100	10
P, mg/dm ³	0.006	0.015	0.050	10	P, mg/kg	0.317878	0.479356	0.630000	11
Si, mg/dm ³	6.05	7.50	11.29	21	Si, mg/kg	10.93	13.69	15.56	11
Fe, mg/dm ³	0.127	0.172	0.662	18	Fe, mg/kg	2.144	3.891	12.540	10
Al, mg/dm ³	0.0308	0.0784	0.4640	19	Al, mg/kg	0.8598	2.0086	3.0300	11
PO, mgO ₂ /dm ³	0.42	0.64	1.13	21	PO, mg/kg	188.56	325.15	460.00	11
BO, mgO ₂ /dm ³	3.83	5.64	8.20	11	BO, mg/kg	355.86	402.16	400.50	11
Ti, µg/dm ³	0.341	0.539	0.808	11	Ti, mg/kg	0.01214	0.02603	0.11000	10
V, µg/dm ³	0.309	0.518	0.591	11	V, mg/kg	0.00555	0.00816	0.02300	10
Cr, µg/dm ³	0.636	0.830	0.838	11	Cr, mg/kg	0.00339	0.00484	0.00570	11
Mn, µg/dm ³	31.154	55.811	73.942	11	Mn, mg/kg	3.92434	11.09017	17.32000	11
Co, µg/dm ³	0.073	0.076	0.164	11	Co, mg/kg	0.04430	0.07697	0.23000	10
Ni, µg/dm ³	0.032	0.046	0.771	10	Ni, mg/kg	0.02211	0.03764	0.04400	11
Cu, µg/dm ³	0.978	1.623	2.495	21	Cu, mg/kg	0.08822	0.12628	0.34000	10
Zn, µg/dm ³	13.08	34.07	140.00	20	Zn, mg/kg	0.14037	0.63410	3.69000	10
As, µg/dm ³	3.556	8.193	17.855	11	As, mg/kg	0.04689	0.09869	0.72000	9
Se, µg/dm ³	0.304	0.537	0.786	11	Se, mg/kg	0.00700	0.01358	0.02200	11
Rb, µg/dm ³	2.409	5.179	7.737	11	Rb, mg/kg	0.066984	0.088728	0.210000	10
Sr, µg/dm ³	103.43	135.53	141.34	11	Sr, mg/kg	0.29053	0.40768	0.91000	10
Ag, µg/dm ³	0.0067	0.0103	0.0664	8	Ag, mg/kg	0.000046	0.000087	0.002000	7
Cd, µg/dm ³	0.0513	0.0907	0.4974	18	Cd, mg/kg	0.001183	0.003699	0.019000	9
Sn, µg/dm ³	0.0221	0.0566	0.0868	11	Sn, mg/kg	0.000087	0.000243	0.000900	9
Sb, µg/dm ³	0.2865	0.7025	1.5059	11	Sb, mg/kg	0.010526	0.019870	0.035000	11
Ba, µg/dm ³	20.405	31.533	33.640	11	Ba, mg/kg	0.13062	0.22263	0.73000	9
La, µg/dm ³	0.0800	0.1892	0.2452	11	La, mg/kg	0.003007	0.004181	0.012000	8
Ce, µg/dm ³	0.1503	0.3437	0.5006	11	Ce, mg/kg	0.010232	0.017224	0.027000	11
Sm, µg/dm ³	0.0112	0.0297	0.0417	11	Sm, mg/kg	0.000804	0.001432	0.002300	11
Eu, µg/dm ³	0.0051	0.0083	0.0096	11	Eu, mg/kg	0.000165	0.000233	0.000660	9
Yb, µg/dm ³	0.0035	0.0098	0.0115	11	Yb, mg/kg	0.000208	0.000299	0.001000	11
Au, µg/dm ³	0.0025	–	0.0025	11	Au, mg/kg	0.000037	0.000074	0.000170	10
Hg, µg/dm ³	0.0025	–	0.0025	5	Hg, mg/kg	0.000299	0.000578	0.006700	8
Pb, µg/dm ³	2.490	5.024	58.690	19	Pb, mg/kg	0.158401	0.571616	4.070000	10
Bi, µg/dm ³	0.0022	0.0045	0.1705	10	Bi, mg/kg	0.000222	0.001161	0.002100	11

Note. \sum_{mi} – sum of major ions; PO and BO – permanganate and bichromatic oxidability; C_G – geometric mean; C_{GUP} – upper limit of the error of determining the geometric mean by formula (3).

Table 2. Geochemical anomalies in the river waters and aqueous extracts from bottom sediments in the interfluvium of the Lo and Cau rivers

Sample number	River	Distance from source, km	Substances and ratio of exceeded background concentrations	
			in river waters	in aqueous extracts from bottom sediments
M1604	Ban Thi	3.7	Ag 3.2; Z = 3.2	Zn 3.2; Pb 2.5; Fe 3.2; As 7.3; Cd 2.2; Sn 2.1; La 2.9; Eu 2.8; Z = 24.9
M1603	Ban Thi	7.8	Zn 2.2; Pb 2.4; NO ₂ ⁻ 19.0; Ag 2.1; Cd 4.4; Z = 26.1	Zn 2.7; Pb 7.1; Cu 2.7; As 2.4; Ag 23.0; Au 2.3; Hg 5.5; Cd 5.1; Sn 3.7; La 2.1; Yb 2.5; Z = 54.4
M1602	Ban Thi	9.0	Zn 2.1; Z = 2.1	Zn 2.4; Pb 2.7; Ag 7.8; Z = 10.9
M1601	Ban Thi	13.14	Z = 1	NO ₂ ⁻ 2.7; Hg 2.1; Z = 3.8
M1605	Chengu	8.0	Z = 1	NO ₂ ⁻ 8.0; Z = 8.0
M1611	Dai	16.1	Zn 2.6; Pb 11.7; SO ₄ ²⁻ 2.0; P 3.2; Ni 16.8; As 2.2; Ag 6.4; Cd 5.5; Bi 37.6; Z = 82.7	S
M1609	Dai	29.6	Z = 1	Ba 2.0; Hg 11.6; Z = 12.6
M1607	Dai	41.7	Fe 2.1; Z = 2.1	Co 3.0; Z = 3.0
M1610	Namdu	11.3	Sb 2.1; Z = 2.1	Ag 4.9; Z = 4.9
M1606	Pho Dai	32.9	Fe 3.9; Co 2.1; Z = 5.0	Ti 4.2; Z = 4.2

Note. Z – index of geochemical state of the environmental component by formula (4); the geochemical indicators used are given in Table 1; at the point M1608 Z = 1 for water and aqueous extract.

respectively [14–16]. The concentrations of substances (in mg/dm³), the flow velocities and the depths of the rivers were adopted according to February 2016 observational data, the values of k_C and k_s were determined by suitable selection for each section line used, and the values of D were calculated by the formulas:

$$D = \frac{9.81vh}{k_M k_{Ch}}, \quad (9)$$

$$k_M = \begin{cases} 0, 7k_{Ch} + 6, & 10 \leq k_{Ch} \leq 60, \\ 48, & k_{Ch} > 60 \end{cases}, \quad (10)$$

where k_{Ch} – is the Chézy coefficient, and h – is the mean depth of the river [23].

The model (8)–(10) is complemented by equation (11) in order to determine the specific rate of variation in concentration of matter depending on the modulus of water discharge and hydraulic conditions. In view of [22], this dependence can be interpreted as a coupling function between k_C and the area of contact of the water and solid particles A :

$$k_C = k_{C,0} \left(\frac{Q}{F} \right)^{k_1} \left(\frac{k_M k_{Ch}}{v^2} \right)^{k_2} = k_{C,0} A, \quad (11)$$

where Q – is the water discharge, F – is the drainage area, $k_{C,0}$ – is the specific rate of variation in concentration of matter in the river water in the absence of water flow, and k_1 and k_2 – are empirical coefficients. The component

$\left(\frac{Q}{F} \right)^{k_1}$ serves as the characteristic of the total amount of suspended and transported sediments, and $\left(\frac{k_{Ch}}{v^2} \right)^{k_2}$ – as a function that is the reverse of the diameter of particles of river sediments [23].

First, an analysis of modeling results and their comparison with observational data confirmed the possibility of using the model (8)–(11) to calculate changes in Zn and Pb concentrations (Fig. 2). And, second, the model (8)–(11) was used to obtain a more accurate assessment of the influence of the dressing plants on the status of the rivers under investigation. Thus, a decrease in Zn concentrations to the $2C_{GUP}$ level in the waters of the Ban Thi river is observed on the section about 4.2–4.5 km in length, a decrease in Pb content with a change in the area of contact of water with solid particles at 3.3 km from the pollution source and, for a constant area, at 11.3 km. In the waters of the Dai river, a decrease in Zn concentrations to the $2C_{GUP}$ level is observed at 3.2–3.3 km from the pollution source, and Pb – at 11.2–12.2 km (see Fig. 2 and Table 2).

Hence, a statistically significant anthropogenic influence was detected on the sections of up to 11–12 km long, and the most clearly pronounced influence on the sections of up to 4.5 km long. It should also be noted that the existing mining industries are, by definition, concentrated at natural geochemical anomalies. Accordingly, the geochemical anomalies in the river waters and bottom sediments of the territory under consideration can be regarded as natural-anthropogenic

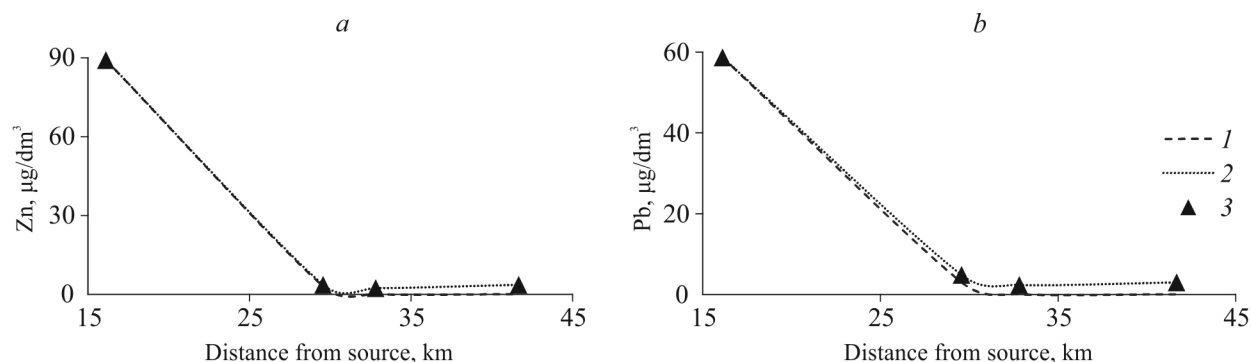


Fig. 2. Calculated and measured Zn (a) and Pb (b) concentrations in the waters of the Dai river in February 2016.

1 – calculation in terms of the model (8) at a constant value of k_c for the section line 4.9 km from the source; 2 – calculation in terms of the model (8) at variable values of k_c (11); 3 – measured values.

ones. This is indicated, first, by an exceedance of the local geochemical background at the M1604 location on the Ban Thi river 1.2–1.4 upstream from the dressing plant (see Table 2). Second, the concentrations of a number of substances in the river waters and in areas with a clearly pronounced anthropogenic influence as well as beyond them obey the general regularities in the distribution of substances in water flows (in the river waters and, especially, in bottom sediments) which, under certain assumptions, can be roughly described by the equation:

$$C = C_0 \frac{Y_0}{Y} \left(\frac{F_0}{F} \right)^b, \quad (12)$$

where C and Y are the concentration of matter and the layer of water discharge for the river under investigation, C_0 and Y_0 are the concentration of matter and the layer of water discharge in the upper reaches of the river without a pronounced river network, and b is the coefficient representing the set of hydrogeochemical and geomorphological conditions of the catchment [25].

In the streams of the interfluvium of the Lo and Cau rivers used in this study, such a dependence was revealed in 2015 for the river waters [13] and in 2016 for bottom sediments. An analysis of them suggested the following conclusions: 1) the Zn concentrations measured near the pollution sources and at a significant distance upstream and downstream from them produce, in fact, a single assembly, and 2) the points corresponding to natural anomalies and areas with the largest anthropogenic influence are located predominantly in the upper part of the plot of dependencies of the form (12).

A decline in concentrations of Zn, Pb and a number of other chemical elements in the waters of the Dai and Ban Thi rivers downstream from the mines and dressing plants, according to [26], is due to a set of processes of interaction of the river waters with bottom sediments and river sediments, including deposition of poorly soluble compounds of heavy metals and their

codeposition with hypergenic new formations. This is confirmed by results from validating the model (8)–(11) and by hydrodynamical calculations. The former indicates there are linkages between concentrations of substances in the river waters and contents in bottom sediments and hydraulic parameters; the latter give evidence for the potential of the river waters to dissolve primary aluminosilicates to produce clay minerals and oversaturation of the waters with respect to quartz (the mean value of the saturation index for all of the streams studied, $\sigma = 0.39$), and compounds of calcium and magnesium with humic acids ($\sigma = 0.65$ – 0.88). It must be remarked in this case that the waters of the Dai and Ban Thi rivers are generally closer to an equilibrium or are more oversaturated with respect to carbonate minerals ($\sigma = 0.31$ – 0.64) than the waters of the other rivers studied, with lower anthropogenic pressure ($\sigma = -0.47$).

CONCLUSIONS

Background concentrations have been obtained for major ions, biogenic substances and trace elements in the waters and bottom sediments of small streams in the northern part of the Red river basin (see Table 1). A significant exceedance of background concentrations corresponding to geochemical anomalies was observed primarily in the upstream reaches of the Ban Thi and Dai rivers, and it is associated with a combination of natural and anthropogenic factors. A crucial anthropogenic factor is input of pollutants to the water bodies from the extraction of lead-zinc ores. The influence of this factor on the small rivers is observed along the length of 11–12 km (and a maximal influence occurs in the river sections of up to 4.5 km).

As contrasted to the river waters, bottom sediments are characterized by the fact that the distribution of concentrations of trace elements is more uneven along the length of the rivers. Aqueous extracts from bottom sediments showed increased contents of Zn, Pb, Fe, Co, Ti, As, Cd, Sn, Ag, Rb, Sr, Hg, Ba, La, Eu, Yb, NO_2^- , Ca_2^+ ,

Mg²⁺ and SO₄²⁻, while the accumulation level of substances relative to the geochemical background, according to [9], corresponds near the ore-dressing plants to weakly and heavily contaminated bottom sediments. Downstream from the plants, bottom sediments correspond to the minimal level of pollution (see Table 2). The river waters near the pollution sources contain increased (compared to the geochemical background) concentrations of Zn, Pb, Fe, Ni, Co, As, Bi, Cd, Cs, Sb, Ag, NO₂⁻ and SO₄²⁻ and are estimated as moderately and heavily polluted, and at other locations as minimally polluted. The pollution level of the river waters decreases with the distance of the water masses from the pollution sources due to the dilution of waste waters and the processes of deposition and codeposition of pollutants.

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