Man-Caused Pollution under Gold Mining and the Reaction of Ecosystems in the Permafrost Zone

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ABSTRACT

Pollution of the ecosystems of downstream tailing dumps of gold extracting factories in the permafrost zone is considered. Primary and secondary toxic effects of cyanide technologies are distinguished. The conclusion is made that the ecological risk of pollution with heavy metals and arsenic is the most significant. Geological environment is of great importance in formation of man-caused anomalies: silicate medium prospers their expansion, carbonate one decreases man-caused effect on conjugate ecosystems. The data on the reaction of ecosystems to man-caused pollution are obtained using bioindicative method of fluctuating skewness. When pollution of ecosystems occurs, fluctuating skewness of vegetation increases, or, in other words, reaction to pollution is reflected on their physiologo-morphological level.

INTRODUCTION

The study of man-caused pollution and of reaction of the living constituent of cryolite zone ecosystems to it is one of the most urgent problems of geoecology. The north ecosystems are characterized by lower stability and weaker restitution potential in comparison with the ecosystems of middle latitudes [1–3].

The goal of the present study is to reveal particularities of man-caused pollution under gold mining employing cyanide technologies in permafrost zone in different geological states and to estimate the reaction of vegetation to this pollution. The integrated ecologo-geochemical investigations were carried out in 1996–2000.

The Aldan mining region of South Yakutia is chosen as a subject of investigation where two large man-made objects are situated within the B. Kuranakh river basin: the Kuranakh and Lebedinsk gold extracting factories (GEF). The Lebedinsk one is in the very riverhead of the B. Kuranakh; the Kuranakh one is down stream. The B. Kuranakh flows from south to north and falls into the Seligdar – the right tributary of the Aldan river (Fig. 1).

The riverhead of the B. Kuranakh is a raised upland where mountain type ecosystems with continuous and focus permafrost are developed. Low placors with plain medium-taiga ecosystems with discontinuous occurrence of permafrost rocks prevail in the lower course of the B. Kuranakh river [4].

The B. Kuranakh runs among silicate rocks of the Aldan sheet in the river head, among carbonate ones of the Lena-Aldan platform in the lower part. This specifies not only landscape-geomorphological but also geological-geochemical features of the basin. The silicate

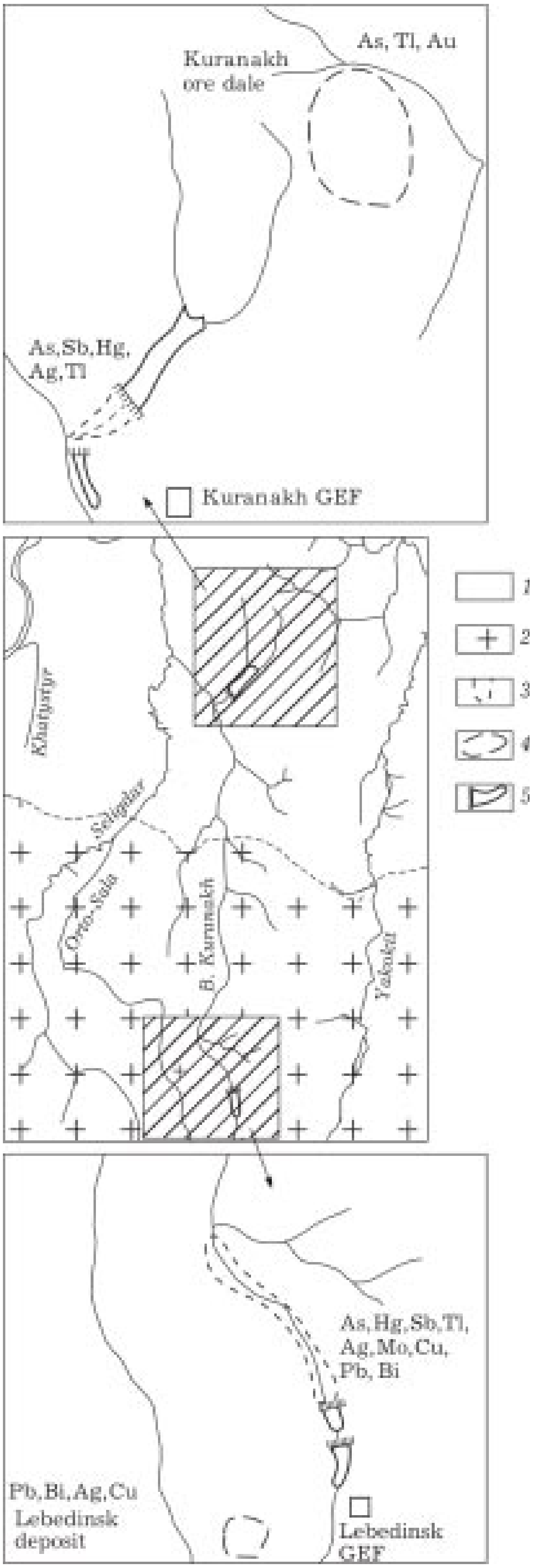

Fig. 1. Scheme of the region under investigation: *1,2* – carbonate and silicate media, respectively; *3* – man-caused anomalies in the GEF downstream tailing dump; *4* – natural-technogenic anomalies of ore deposits; *5* – GEF tailing dumps.

rocks of the B. Kuranakh riverhead are represented by the bottom ones: gneisses, crystal schists and granites of Archean period, and also by the Mesozoic (J–K) and alkaline syenites spread in the zones of overthrust fractures [5, 6]. Gold-sulphide ores of the Lebedinsk deposit are mostly represented by the layer potash feldspar metasomatites and, to a less extent, by the quartz lodes [6].

In the lower part of the B. Kuranakh, the bottom-covering sedimentary rocks of the sheeting – strongly karst and cracked limestones, limestone dolomites of Vend–Lower Cambrian period with the thickness of ~600–650 m – are spread. The terrigenous sediments of Lower Jurassic period with the thickness of 0 to 100 m occur as the horizontal discrete cover on the eroded surface of Cambrian rocks. The gold-quartz oxidated ores of the Kuranakh ore dale are confined to the karst caverns of limestones and are the products of weathering and redeposition mostly of quartz lodes and conformable solids developed in the zones of overthrust fractures [5–7].

The content of admixture elements, including heavy metals, in silicate rocks is considerably higher than that in limestones and dolomites [8]. The biogeochemical organisation of ecosystems of silicate and carbonate media differ; consequently, two geochemical backgrounds exist within the B. Kuranakh basin (Table 1). Pb–Bi–Ag–Cu natural abnormal geochemical zone is distinguished at the Lebedinsk deposit, As–Tl one at the Kuranakh deposit (see Fig. 1) [8].

Since the middle 1960-ies the technology of vat cyanidation of ores was employed at the Kuranakh and Lebedinsk GEF. The Lebedinsk GEF was restrained in 1994; at the Kuranakh GEF the cyanide production continues and consists in the following. When ore stamped to 0.16 mm, 0.01 % NaCN solution is added, and CaO to maintain alkaline medium. Gold is extracted by the sorption lixiviation procedure according to the following scheme:

$$4Au + 8NaCN + 2H_2O + O_2 \Rightarrow 4Na[Au(CN)_2] + 4NaOH \text{ (lixiviation)}$$

$$2Na[Au(CN)_2] + \text{ion exchange resin} \Rightarrow Na_2[(CN)_4]^{2-} + 2Au^{2+} \text{ (sorption on the ion exchange resin)}$$

TABLE 1

Background concentrations of elements in soils (g/t) and plant tissues (mg/kg of dry mass)

Element	Soils			Moss			Larch coniferous needles		
	BL	BU	BL/BU	BL	BU	BL/BU	BL	BU	BL/BU
Ti	3000 ± 550	7750 ± 1400	2.6	29 ± 7.7	81.8 ± 21.7	2.8	11.8 ± 3.1	42.6 ± 11.3	3.6
V	60 ± 11	99 ± 18	1.7	0.11 ± 0.02	0.45 ± 0.08	4.1	0.09 ± 0.02	0.38 ± 0.07	4.2
Cr	48 ± 10	84 ± 18	1.8	0.3 ± 0.1	0.6 ± 0.2	2.6	0.6 ± 0.2	0.7 ± 0.2	1.2
Mn	550 ± 90	720 ± 120	1.3	25 ± 4	50 ± 7	2.0	130 ± 40	322 ± 99	2.5
Co	13 ± 2.6	15 ± 3.1	1.2	n/d	0.05 ± 0.02		0.03 ± 0.01	0.05 ± 0.02	1.5
Ni	23 ± 4.7	22 ± 4.5	1.0	0.12 ± 0.03	0.28 ± 0.06	2.3	0.08 ± 0.02	0.27 ± 0.06	3.4
Cu	28 ± 5.6	55 ± 11.1	2.0	0.74 ± 0.17	2.04 ± 0.39	2.8	1.18 ± 0.23	2.39 ± 0.46	2.0
Zn	65 ± 10	100 ± 40	1.4	3.5 ± 1.6	8.2 ± 2.5	2.4	5.0 ± 1.5	13.0 ± 4.1	2.6
Ga	14 ± 2.9	24 ± 5	1.7	0.05 ± 0.02	0.39 ± 0.12	7.8	0.03 ± 0.01	0.17 ± 0.05	5.7
Ge	1.1 ± 0.2	2.1 ± 0.4	1.9	n/d	0.03 ± 0.01		n/d	n/d	
As	n/d	n/d		»	n/d		»	n/d	
Y	30 ± 10	<30 up to 30 ± 10		<1.7 up to 1.7 ± 0.3	<1.7 up to 1.7 ± 0.3		<1.7 up to 1.7 ± 0.3	n/d	
Nb	10 ± 4	20 ± 6	2.0	0.2 ± 0.1	0.5 ± 0.1	2.5	0.3 ± 0.1	0.5 ± 0.1	1.7
Mo	1.3 ± 0.3	1.75 ± 0.41	1.4	0.06 ± 0.01	0.17 ± 0.04	2.8	0.04 ± 0.009	0.13 ± 0.03	3.3
Ag	0.05 ± 0.01	0.59 ± 0.12	11.8	0.01 ± 0.003	0.04 ± 0.01	4.0	0.006 ± 0.002	0.023 ± 0.006	3.8
Sn	1.6 ± 0.3	6.9 ± 1.4	4.3	n/d	0.06 ± 0.02		n/d	0.03 ± 0.01	
Sb	n/d	<10 up to 10 ± 1.2		»	<0.5 up to 0.5 ± 0.06		»	n/d	
Pb	10 ± 2	30 ± 6	3.0	0.62 ± 0.11	4.4 ± 0.76	7.1	0.37 ± 0.07	2.3 ± 0.42	6.2
Tl	n/d	<1 up to 1 ± 0.25		n/d	0.06 ± 0.01		n/d	0.05 ± 0.01	
Hg	0.0085 ± 0.00001	0.0155 ± 0.00002	1.8	No data	No data		No data	No data	

Notes. BL is the background of carbonate medium (lower part of the B. Kuranakh), BU is the background of silicate medium (upper part of the B. Kuranakh); here and in Tables 2–4: n/d means not detected.

Formaldehyde (the input is 0.4 kg/t of ore) is added to the mash for the purpose of cyanide neutralization, then the mash is discharged into the tailing dump. Till 1996 $FeSO_4$ solution was employed for neutralization of cyanides:

$$6FeSO_4 + 30CN^- + 6Fe^{3+} \Rightarrow Fe_3[Fe(CN)_6]_2 + Fe_4[Fe(CN)_6]_3 + 6SO_4^{2-}$$

which resulted in sedimentation of insoluble salts of iron cyanides.

The 2 % solution of H_2SO_4, which is merged into the tailing dump together with the mash contents, is used for elimination of metal admixtures, gold desorption and regeneration of the ion exchange resin.

Only 500 thousand tonn of ore per year were processing at the Lebedinsk GEF, at the same time the annual input of NaCN accounted for ~400 t, $FeSO_4$ about 3500 t. Ore from the deposits of the Kuranakh ore dale was supplied in addition to ores of the quickly exhausting Lebedinsk deposit. The amount of accumulated waste products at the Lebedinsk tailing dump (LTD) accounts for ~15.6 mln m^3.

Up to 3360 thousand t of ore per year is processed at the Kuranakh GEF; the annual consumption of NaCN accounts for ~605 t, that of formaldehyde up to 1344 thousand tonn, that of $FeSO_4$ (till 1996) up to 10 080 t. Beside that, 11 500 m^3 of H_2SO_4 solution annually enter the tailing dumps. By the end of 2001 43 mln m^3 of solid wastes were accumulated in the Kuranakh tailing dump (KTD).

High contents of As (~70 g/t), Sb (~30 g/t) were also detected in the wastes of KTD; the same contents of As, Sb plus those of Cu and Pb (up to 300 g/t) were detected in the wastes of LTD.

The tailing dumps of both GEF were built in the B. Kuranakh valley: from three sides these are natural boards and the head pool with catch channels; from the forth side, downstream, the tailing dumps are restrained by the drainage dams, a natural relief surface serves as a bottom.

EXPERIMENTAL

For geochemical studying by standard procedures [9, 10], 43 water, 63 bottom sediment and 95 soil samples were picked.

Water samples were taken from the sources and mouths of tailing dump drainage grooves and from the rivers, which the drainage sewers enter at the distances of 100, 500, 1000 m, and further at 2–3 km from the groove inflows. The samples were taken at the 0.4 m depth into polyethylene bottles, previously rinsed three times at a sampling site. After filtering through a 0.45 mm filter, a sample was preserved by distilled nitric acid to pH ~ 2. The samples were kept in a refrigerator at the temperature of 5–8 °C before analysis.

Bottom sediments were taken into polyethylene parcels by the same scheme as water samples: from the drainage grooves and rivers with the help of a scraper, preferably in the sites with slow current. The samples were dried at the site, then packed hermetically.

Soils were tested at the adjoining territory by the profiles, directed across and maximally characterising the effect of the tailing dumps on the adjoining territories. The length of each profile accounted for 1.5–2 km. The samples were picked from the illuvial horizon B1 at the depth of 5 to 20 cm from the surface into canvas sample sacks, then they were dried under field conditions to air-dry state [9, 10].

Total chemical analysis of the water samples was carried out by standard procedures in the laboratory of the Institute of Applied Ecology of the North (Yakutia). The concentration of main ions was determined by titration, sodium and potassium ions by flame photometry, sulphate ions by turbidimetric method. The determination accuracy for HCO_3^- is not more than 12 %, for SO_4^{2-} 23 %, Cl^- 16 %, Ca^{2+} 2 %, Mg^{2+} 10 %, $Na^+ + K^+$ 25 %. The content cyanides, both free and bound in integrated compounds, excluding ferrocyanides (II) and (III), in the water samples was determined by a photocolorimetrical pyridin-barbiturate procedure (the lower CN^- detection limit is not less than 0.02 mg/l). Trace elements in the water samples were analyzed with the help of ICP–MS Element in the Interdepartmental Analytic Centre YaSC, SB RAS, with the relative root-mean-square deviation not more than 10 %. Mean content in the water samples from the Seligdar, Khatystyr, Yakokit rivers – the main currents of the Aldan mining region (the B. Kuranakh is one of the right-hand tributaries of the Seligdar) – was accepted as the surface water background.

The content of trace elements in the soil and bottom sediment samples and in the vegetation ash was determined by the spectrum analysis in the laboratory of The Sakha Republic (Yakutia) State Committee of Geology and Use of Mineral Resources. The atomic absorptive method with the relative root-mean-square deviation equal to 0.12 % was used to determine mercury in the water and bottom sediment samples. The content of trace elements in plant tissue was obtained by recalculating their concentrations in ash by the ash content factor of the corresponding sample.

Geological background values in soils and vegetation of silicate and carbonate media were determined at the two reference sections of watershed landscapes, far from natural geochemical anomalies and from the man-made objects under investigation. The size of both sections was ~500 × 500 m, where 10 samples of soil and vegetation were taken through out a regular net over each section. Mean element contents in these samples were considered as the geological background. Man-caused concentrations of elements were normalised according to the geological background: LTD zones according to silicate one, KTD zones according to carbonate one. When the content of analysed elements in the background area was lower the detection limit, normalisation was performed with respect to clarkes in soils [11].

For integral estimation of the reaction of ecosystems of the downstream tailing dumps to man-caused pollution, the bioindicative vegetation fluctuating skewness (FS) method was chosen. Plants permit estimating integral atmospheric and water effects characteristic of the given ecosystem area in whole. Stronger the reaction to stress effect and lower the level of homeostasis of plant development, higher its degree of fail in ontogenesis, which is expressed in a skewness increase. In the zone of technogenesis under almost the same microclimatic and landscape conditions, FS variations of one plant species are usually linked with man-caused factor [12, 13]. The FS measurement was carried out on the leaves of flat-leaf *birch (Betula platyphylla* Sukacz.) and of bush alder (*Duschekiia fruticosa* (Rupr.) Pouzar). In each site under study, 10 sheets of 10 nearly growing trees of the same age, equally irradiated, with the same landscape occurrence (100 sheets in one sample) were picked. A sample was preserved in ethyl alcohol. The scale of plant FS was determined by the integral indicator – a value of mean relative difference per a sign:

$$\mathrm{FS} = (\sum_{j=i}^{n}\left(\sum_{i=1}^{100}\frac{(l_{ij}-P_{ij_i})}{(l_{ij}+P_{ij_i})}\right)/(100n)$$

where l_{ji} and P_{ji} are the leaf sizes, measured by j sign from the left and right, respectively; i is the serial number of a leaf in a sample, n is the number of signs, in the given case equal to 7. The error of measurement accounts for not more than 3 %. In total 9 samples (900 leaves) were studied. Sampling sites for geochemical and bioindicative study were the same.

RESULTS AND DISCUSSION

Surface water of the B. Kuranakh and other currents of the Aldan region refer to low mineralized hydrocarbonate-calcium type (according to Kurlov [14]):

$$190\,\frac{\mathrm{HCO_3^-}\,92\,\mathrm{SO_4^{2-}}\,4\,\mathrm{Cl^-}\,3\,\mathrm{NO_3^-}\,1}{\mathrm{Ca^{2+}}\,68\,\mathrm{Mg^{2+}}\,27(\mathrm{Na^+},\mathrm{K^+})5}$$

Noticeable increase in surface water salinity is observed in the LTD and KTD pools: up to 600 and 390 mg/l, respectively, under the 340 mg/l mean salinity of the B. Kuranakh water (Table 2). In comparison with background levels, the mean content $\mathrm{HCO_3^-}$ in water of the downstream tailing dumps increase about 1.5-fold, $\mathrm{Ca^{2+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Cl^-}$ ~ 2-fold, nitrogen-containing ions 60-fold. Concentrations [$\mathrm{Na^+}$ + $\mathrm{K^+}$] and [$\mathrm{SO_4^{2-}}$] increase by an order of magnitude and more in the LTD zone and from 2.5 to 6 in the KTD zone.

Water content of the Lebedinsk downstream tailing dump according to Kurlov's formula is equal to:

$$380\,\frac{\mathrm{HCO_3^-}\,64\,\mathrm{SO_4^{2-}}\,20\,\mathrm{NO_3^-}\,14\,\mathrm{Cl^-}\,3}{\mathrm{Ca^{2+}}\,53(\mathrm{Na^+},\mathrm{K^+})25\,\mathrm{Mg^{2+}}\,22}$$

in the zone of the Kuranakh one –

TABLE 2

Total chemical composition of the Aldan mining region surface water, mg/l

Sampling sight (site number)	pH	Rigidity, mg-eqv/l	Mineralization, mg/l	Ca^{2+}	Mg^{2+}	Na^+, K^+	HCO_3^-	SO_4^{2-}	Cl^-	NH_4^+	NO_2^-	NO_3^-
The Seligdar river (4)	7.70	1.5	130	17.0	7.6	1.3	90	4.0	4	0.07	0.012	0.78
Lake Seligdar (1)	7.73	2.4	190	27.0	12.6	3.0	130	11.4	4	0.15	0.009	1.06
The Orto-Sala (2)	8.22	2.8	230	32.1	14.3	3.0	160	4.3	6	0.06	0.021	0.78
The Yakokit (4)	7.65	2.2	180	30.6	8.5	1.5	120	9.7	2	0.10	0.255	0.00
The Khatystyr (2)	8.0	2.6	210	28.0	9.1	1.6	160	n/d	1	0.04	0.033	0.97
Mean (background water)	7.86	2.3	190	26.9	10.4	2.0	130	5.9	4	0.09	0.066	0.72
0.2 km from LTD	8.48	7.0	600	100.2	23.7	58.6	210	162.0	11	0.09	0.789	148.80
0.5 km from LTD	9.15	4.0	320	45.1	20.6	14.5	200	24.0	9	0.07	0.049	34.10
2.1 km from LTD	8.78	3.7	330	38.1	21.3	19.0	180	59.9	9	0.21	0.112	19.57
2.2 km from LTD	8.8	5.0	410	63.1	23.1	16.5	230	60.5	7	0.51	0.381	32.55
3.0 km from LTD	8.56	3.5	330	28.0	24.9	22.3	200	41.0	7	0.08	0.079	11.51
7.5 km from LTD	9.0	3.0	280	36.1	15.8	14.8	170	28.4	6	0.11	0.037	7.44
8.0 km from LTD	7.56	2.6	220	32.1	11.5	6.5	150	13.3	6	0.07	0.013	1.37
Mean over the LTD zone (to 7.5 km)	8.80	4.3	380	51.8	21.6	24.3	200	62.6	8	0.18	0.24	42.33
28 km from LTD* (5)	8.23	3.8	290	39.5	19.2	2.6	210	12.8	2	n/d	n/d	0.66
0.8 km from KTD (3)	8.2	n.d.	350	No data	No data	No data	No data	65.3	No data	0.14	No data	24.14
1.2 km from KTD	8.4	4.9	390	57.1	24.3	5.8	250	31.3	10	0.11	0.009	7.79
2.1 km from KTD	9.05	3.4	280	39.1	17.6	4.5	190	15.8	6	0.10	0.131	17.85
7.6 km from KTD	8.22	3.5	270	38.1	19.4	1.0	200	3.0	6	0.07	0.007	0.84
8.3 km from KTD* (2)	7.8	3.9	310	42.1	21.3	4.0	220	11.5	4	n.d..	0.20	0.00
Mean over the KTD zone (to 2.1 km)	8.55	4.1	340	48.1	21.0	5.1	220	37.5	8	0.11	0.07	16.59
Mean over the B. Kuranakh	8.48	4.0	340	46.6	20.2	14.2	200	40.7	7	0.12	0.15	23.59

Note. See Table 1.

TABLE 3

Cyanide content in the lake of the Kuranakh tailing dump and in surface water of its pool, mg/l

Date	In the mash output	KTD channel	0.8 km from KTD	1 km from KTD	Trouble section of KTD	2.1 km from KTD	2.6 km from KTD
05.01.1996	22.0	24.25	<0.02	No data	No data	No data	No data
26.01.96	20.63	23.25	<0.02	»	»	»	»
05.02.96	16.75	15.60	<0.02	»	»	»	»
05.03.96	22.23	12.50	No data	»	»	»	»
05.04.96	18.25	13.50	0.09	»	»	»	»
16.04.96	22.40	23.75	<0.02	»	»	»	»
07.05.96	No data	15.75	No data	»	1.1	»	»
05.06.96	»	No data	<0.02	»	0.32	<0.02	<0.02
05.07.96	21.73	<0.02	<0.02	<0.02	0.07	0.04	No data
30.07.96	9.38	0.67	<0.02	No data	0.22	<0.02	<0.02
26.08.96	2.75	0.58	<0.02	»	n.d.	<0.02	<0.02
06.09.96	8.70	0.46	<0.02	<0.02	0.17	<0.02	<0.02
26.09.96	4.75	0.53	<0.02	<0.02	0.06	<0.02	No data
16.10.96	No data	0.30	No data	<0.02	No data	<0.02	»
18.11.96	<0.02	No data	<0.02	<0.02	»	No data	»
19.12.96	21.5	»	<0.02	No data	»	»	»

Note. See Table 1.

$$340\frac{HCO_3^- 78SO_4^{2-} 13NO_3^- 6Cl^- 3}{Ca^{2+} 65Mg^{2+} 28(Na^+,K^+)7}$$

The ratio $[HCO_3^-]/[SO_4^{2-}]$ in background water is ~22.0; in water of the tailing dumps it decreases: in the LTD zone ~3.2, in the KTD one 5.9 – as a result of increase in sulphate concentration. The ratio $[Ca^{2+}]/[Na^+ + K^+]$ in background water equal to 13.5, decreases to 2.1 in the LTD zone, whereas it remains close to background value – 9.4 – in the KTD zone.

Salinity and concentrations of main ions decrease with an increase in the distance from the tailing dumps and approach the background level: in the LTD zone – at the distance more than 7.5 km, in the KTD zone at 2 km.

The content of cyanides varies within the limits of 0.027–0.058 mg/l in the LTD bed. The same level of cyanide concentrations is observed in the drainage sewers and in surface water at the distance of 100 m from the LTD dam in May and August after affluent rains. Cyanides are not observed in the samples of surface water of the LTD pool at the distance of more than 500 m from the dam. The cyanide content achieves values characteristic of raw mash – 24–25 mg/l in KTD waste in winter (December – April) period (Table 3). The cyanide content in the tails sharply decreases – to 0.67–0.3 mg/l with the approach of heat (in July). The cyanide concentration was low – hundredth and mil parts of milligram per litre in surface water of the KTD pool during the whole observation period. A single case of the excess of maximum permissible concentration [15] – 0.04 mg/l – was revealed 2.1 km lower the KTD dam. Cyanides were not detected in surface water at a distance of 2.6 km from KTD.

Mercury, cadmium, in the KTD zone – thallium contents exceeding maximum permissible concentration for economical and for potable water purposes [15], and also increased molybdenum concentrations are observed in some water samples from the LTD and KTD pools (Table 4).

Man-caused anomalies of As, Sb and heavy metals were revealed in bottom sediments and soils of the downstream tailing dumps. Associations of elements, accumulating in concentrations, several times exceeding the background levels were distinguished in the tailing dump – downstream tailing dump system (Figs. 2, 3).

TABLE 4

Element content in surface water of the Aldan mining region, μg/l

Sampling site (site number)	Fe^{3+}	Si^{4+}	$P_{\text{общ}}$	Zn	As	Cd	Hg	Pb	Mo	Tl
The Seligdar river (4)	20	4900	10	20.0	0.50	0.67	0.00	1.25	1.50	n/d
Lake Seligdar 1)	21	4000	8	50.0	0.70	0.88	n/d	4.00	2.00	»
The Orto-Sala (2)	25	4350	20	27.0	0.65	0.68	1.20	0.00	3.50	»
The Yakokit (4)	20	No data	No data	No data	n/d	n/d	No data	No data	No data	No data
The Khatystyr (2)	No data	»	11	»	»	»	»	»	»	»
0.2 km from LTD	530	3600	8	36.0	0.70	0.67	n/d	2.80	20.00	»
0.5 km from LTD	23	2500	7	29.0	0.80	0.70	»	n/d	2.00	»
2.1 km from LTD	11	3000	3	30.0	1.10	0.60	»	»	5.00	»
2.2 km from LTD	86	3200	3	38.0	0.80	0.96	»	»	31.00	»
3.0 km from LTD	30	3200	3	43.0	0.80	4.03	7.48	4.70	5.00	»
7.5 km from LTD	27	4000	6	48.0	0.80	4.09	n/d	4.10	77.00	»
8.0 km from LTD	23	4400	7	29.0	0.90	0.63	»	n/d	3.00	»
28 km from LTD (5) [10]	220	No data	n/d	9.0	n/d	n/d	No data	»	0.00	»
0.8 km from KTD (3) [10]	1710	»	»	18.4	2.40	1.93	0.001	1.20	2.20	0.25
1.2 km from KTD	93	2500	3	15.1	3.80	1.88	0.001	1.10	7.10	0.10
2.1 km from KTD	5	2800	3	47.0	3.40	2.00	0.001	1.90	6.30	0.08
7.6 km from KTD	20	2500	1	43.0	0.70	0.65	n/d	2.70	23.00	No data
MPC [3]	300	10 000	0.1	5000	50	1	0.5	30	250	0.1

Note. See Table 1.

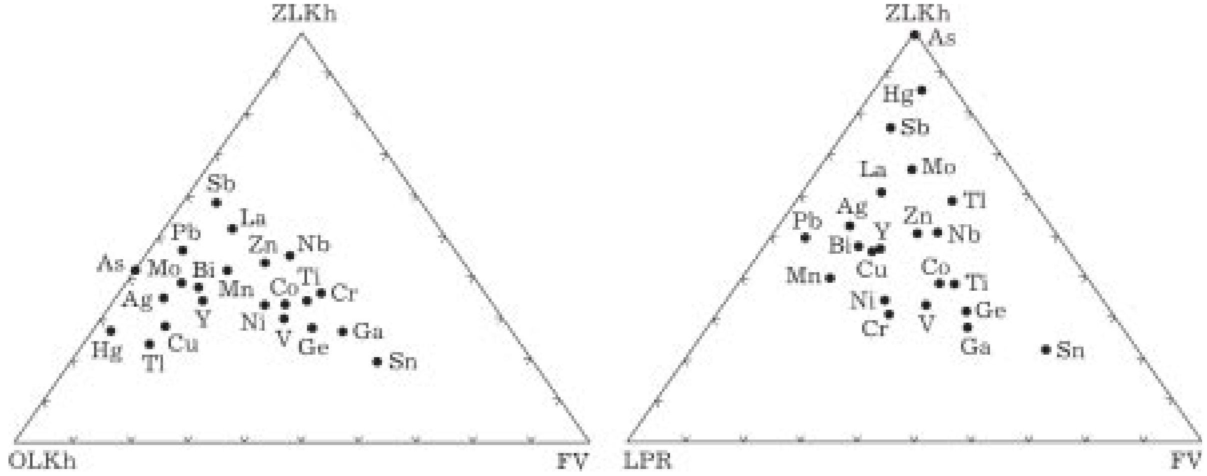

Fig. 2. Associations of chemical elements in the zone of the Lebedinsk tailing dump. Marks: OLKh – the tailing dump waste, ZLKh – floodplain soils of the downstream tailing dump (over 7 km from the dam), FV – a geological background in the soils of the B. Kuranakh, LRP – the soil of the Lebedinsk deposit.

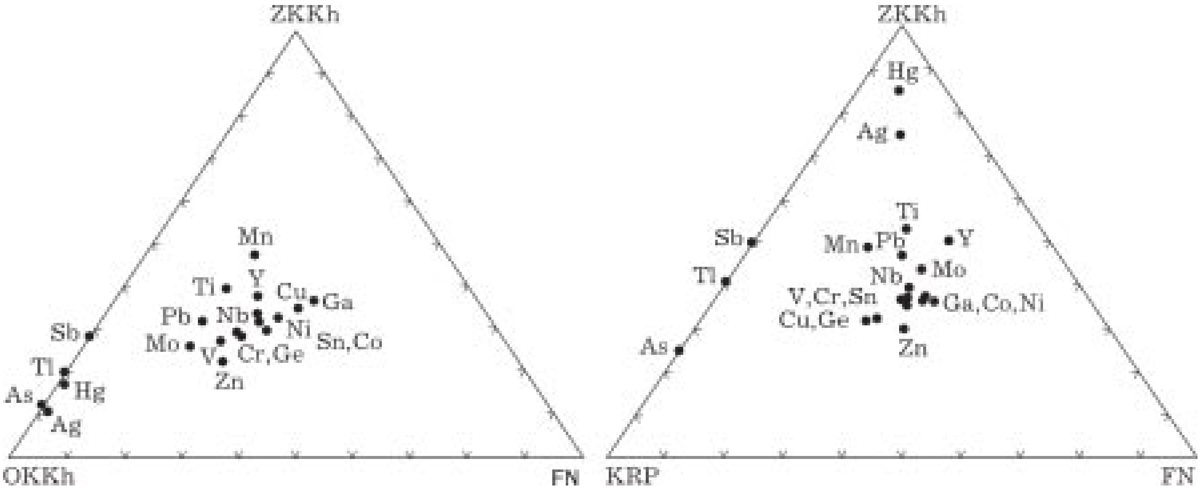

Fig. 3. Association of chemical elements in the zone of the Kuranakh tailing dump. Marks: OKKh – the tailing dump waste, ZKKh – floodplain soils of the downstream tailing damp (over 2 km from the dam), KRP – geological background in the soils of the B. Kuranakh low part, KRP – the Kuranakh ore dale's soils.

The following elements are accumulated, gph*: As – up to 29, Hg – to 5, Tl – 2.4, Cu – 2.7, Ag – 5.3, Mo – 5.5, Sb – 12, La – 7, Bi – 3, Y – up to 3, Mn – up to 2.6, Pb – up to 10.6 in the man-caused the Lebedinsk tailing dump – pool system. A man-caused group of elements – {As, Hg, Tl, Mo} migrating and being accumulated only in the downstream tailing dump is revealed among them. The other elements {Cu, Ag, Sb, La, Bi, Y, Mn, Pb} are considered as a natural man-caused group, since they migrate and are accumulated in abnormal (but less than in the LTD zone) concentrations in the natural-man-caused zone of the Lebedinsk deposit – conjugated landscapes system. The Pb concentration in soils of the Lebedinsk deposit zone reaches 7 gph, W – 1.3 gph (see Figs. 2, 4).

The contents of the elements of the man-caused group in floodplain soils and bottom sediments of the LTD pool and reference current (the Seligdar river) does not exceed the geological background of silicate medium. Floodplain soils of the LTD pool turned out to be toxic due to As (~25 maximum permissible concentrations for soils [16], Sb (~2.5 MPC) and Pb (~10 MPC).

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*Geological background of silicate medium.

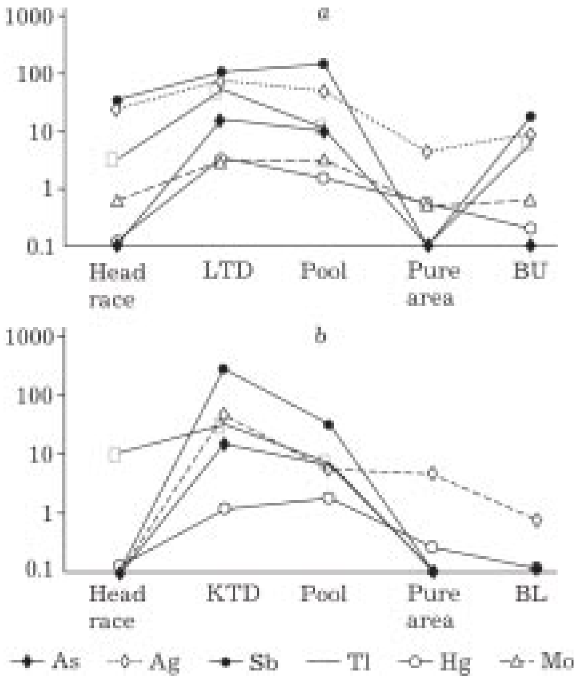

Fig. 4. Man-caused anomalies in the soils of the pools of the Lebedinsk *(a)* and Kuranakh *(b)* tailing dumps, standardized over soil clarkes [3].

The following elements: As (up to 6 soil clarkes [11]), Ag (5.2 clarkes), Hg (1.7 clarkes or 15.5 gph of carbonate medium), Tl (6.7 clarkes), Sb (up to 30 clarkes) are accumulated in the Kuranakh tailing dump – pool man-caused system (see Figs. 3, and 4, *b*). Here {Hg, Ag} are referred to the man-caused group; {As, Tl, Sb} are also appropriate to the natural anomaly of the Kuranakh ore dale – conjugated landscape system (see Fig. 3). Floodplain soils of the KTD tail race turned out to be toxic due to high concentrations of As (7 MPC) and Sb (2.5 MPC).

With moving away from the tailing dumps, the man-caused contents of heavy metals, As and Sb in water samples decrease gradually, approaching background values – at the distance of 7 km from LTD and 2 km – from KTD.

Man-caused pollution of the soils of the downstream tailing dumps affects the trace element content of plant tissues. The problems of man-caused transformation of chemical composition of plant tissues will be considered in a special article.

Bioindicative study revealed that the alder fluctuating skewness values on the referred areas of silicate and carbonate media are approximately equal and account for 0.029 and 0.026, respectively. The birch FS values on the referred areas also have almost no difference: in carbonate medium – 0.04, in silicate one – 0.047 (Table 5). This is the evidence of successful choice of referred areas on carbonate and silicate media, as far as here the external stress factors of the effect to ecosystems are absent.

The FS absolute values and their variability for different species of plants are individual. The FS indicator for the alder leaves changes far stronger than for the birch ones. The alder FS accounts only for 0.029 in the reference of silicate medium, whereas its value accounts for 0.06–0.07 at the strongly polluted area of the LTD pool, *i. e.* the alder FS increases more than two times under man-caused pollution within the limits of single (silicate) medium.

The birch FS at the average polluted area of the KTD pool almost does not differ from the birch FS at the referrence area of carbonate medium and accounts for 0.045–0.039. The birch FS indicator is equal to 0.062 at the strongly polluted area of silicate medium [17]. Negative effect of man-caused pollution to birches is not expressed in carbonate medium, as far as an increase in the birch FS indicator is fixed in silicate one.

The drainage sewers from the GEF tailing dumps cause a three times increase in total salinity of the pool surface water in comparison with the background level due to an increase in the concentrations of all main cations and anions.

Change in the composition of surface water of the downstream tailing dumps occurs in different ways under different geologo-geochemical conditions.

Surface water in the LTD zone turns somewhat softer and more acidic. Quartz-ankerite-orthoclase rocks of the Lebedinsk deposit in the LTD wastes are the rich Na^+ and K^+ sources. The sulphide component of those ores in the result of hypergene oxidation supplies sulphates in addition to the disposals of technological sulphuric acid. Sulphate content in surface water at the LTD foot is nearly two times higher than at the KTD foot and ~10 times higher than the background level. These conditions ensure the change in the surface water

TABLE 5

Fluctuating skewness (FS) values of vegetation of the Aldan mining region (sampling in 2000)

Sample cipher	Plant (number of leaves)	Mean value of FS (range)	Root-mean-square deviation	Degree of the growth area pollution
LTD1	Alder tree (100)	0.060 (0.128–0.021)	0.024	Strong, 0.5 km zone from LTD
LTD2	Alder tree (99)	0.065 (0.172–0.018)	0.028	The same, 6 km
LTD3*	Alder tree (99)	0.07 (no data)	0.032	Medium, zone of ~10 km from LTD
BL1	Alder tree (100)	0.026 (0.099–0.008)	0.019	Reference within the carbonate geological medium, the Seligdar mouth
BU1*	Alder tree (100)	0.029 (no data)	0.02	The same, silicate medium, the M. Kuranakh basin
KTD1	Birch (100)	0.045 (0.124–0.015)	0.023	Weak, zone of 0.1 km from KTD
KTD2	Birch (100)	0.039 (0.233–0.018)	0.036	The same, 0.8 km
BL2	Birch (99)	0.041 (0.227–0.003)	0.025	Reference within the carbonate geological medium, the Seligdar river
BU2*	Birch (100)	0.047 (no data)	0.03	The same, silicate medium, the M. Kuranakh basin

* Sampling in August, 1999.

composition and the sharp decrease in the ratios $[Ca^{2+}]/[Na^+ + K^+]$, $[HCO_3^-]/[SO_4^{2-}]$.

The sources rich with Na^+ and K^+ ions are absent in the KTD gold-quartz ore wastes. The sulphide forms of minerals in these completely oxidated ores are not retained, therefore the formation of sulphates under the hypergene oxidation of wastes is excluded. Sulphates enter the KTD zone surface water substantially due to the disposals of technological sulphuric acid. Surrounding limestones are intensively dissolved by the KTD drainage water; hydrocarbonate concentration in the KTD zone water is higher than that in the LTD one, and on average accounts for 220 and 200 mg/l, respectively. These mentioned factors cause the change of the ratios $[Ca^{2+}]/[Na^+ + K^+]$, $[HCO_3^-]/[SO_4^{2-}]$ in the KTD zone by lesser extent than in the LTD one.

Low temperatures in winter period slow down the processes of cyanide decomposition in wastes; their content remains the same as in the KTD row mash (see Table 3). Summer onset causes a several times enhancement of the cyanide neutralization under the influence of heat, sunshine, biological decomposition; their content decreases by up to 40 times, which is consistent with the results of the studies under the conditions of North America [18]. By 1996 a two-year break of output at the Lebedinsk GEF brought a decrease in cyanide concentration in the tails to 0.058 mg/l that is hardly higher than the maximum permissible concentration (0.035 mg/l). Cyanides are absent in surface water of the downstream tailing dump. This is the evidence of their instability in the given medium and the fast transformation into other compounds. Thus, the existing climate conditions and technological characteristics provide rather efficient neutralization of cyanides. In spite of that, casual detection of cyanides in the samples of drainage and surface water after floods and affluent rains points to the possibility of durable preservation of cyanide salts in soils and wastes.

Just as there are no agricultural objects in the B. Kuranakh basin – active sources of nitrogen compounds – so we link multiple increase in the nitrate concentration in the tailing dump tail races with the oxidation of cyanides according to the following reactions:

$$2CN^- + O_2 + \text{catalyst (minerals, bacteria, sunshine)} \rightarrow 2CNO^-$$

$$HCNO + H_2O \rightarrow NH_3 + CO_2$$

$$2NH_4^+ + 3O_2 + \text{(bacteria nitritosomonas)} \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 + \text{nitrobacter} \rightarrow 2NO_3^-$$

Their regular spacial distribution (maximal under the tailing dumps' dam and decreasing with an increase in the distance from them) points to the possible linkage of nitrates with cyanides.

The effect on fine ore bulk of the solution of cyanides possessing an expressed ability to dissolve metals, and also of sulphuric acid, activates the migration of heavy metals and arsenic from the wastes according to the following principal scheme:

$$n\text{Me}^+(\text{Me}^{2+}, \text{Me}^{3+}) \text{ (I)} + m\text{CN}^- \ (i\,\text{SO}_4^{2-}) \rightarrow k\text{Me}_i(\text{CN})_j + j\text{Me}_i\ (\text{SO}_4)_j \rightarrow u\text{Me}^+(\text{Me}^{2+}, \text{Me}^{3+}) \text{ (II)}$$

$$n\text{Me}^+(\text{Me}^{2+}, \text{Me}^{3+}) \text{ (I)} + \text{catalyst } (\text{SO}_4^{2-}, \text{CN}^-) \rightarrow n\text{Me}^+(\text{Me}^{2+}, \text{Me}^{3+}) \text{ (II)}$$

where (I) means heavy metals in the stable difficultly water-soluble compounds, (II) – heavy metals in the less stable, water-soluble compounds and complexes.

This process results in the formation of metal cyanide compounds (simple and complex): easily soluble $Ba(CN)_2$, $Hg(CN)_2$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $Na_4[Fe[CN_6]$, $Ca_2[Fe[CN)_6]$, $KPb[Fe(CN)_6]$, $TlCo(CN)_6$, $ZnTl_2(CN)_4$, *etc.*; medium-soluble $CuCN$, $Zn(CN)_2$, $K_3Cu(CN)_4$, $K_4Co(CN)_6$, $K_2Ni(CN)_4$, *etc.*; difficultly soluble (stable) $Cd(CN)_2$, $Ni(CN)_2$, $Fe_3[Fe(CN)_6]_2$, $Fe_4[Fe(CN)_6]_3$, $Ag_3Fe(CN)_6$, $Cu_2Fe(CN)_6$, $Zn_2Fe(CN)_6$, $K_5Mn(CN)_6$, $AgCN$, *etc.* [19].

Arsenic and antimony sulphides do not react directly with cyanides. Antimonite and orpiment in alkaline medium (pH > 10) maintained during cyanidation easily dissolve with the formation of hydroxy- and thiosalts:

$$As_2S_3 + 6OH^- = AsO_3^{3-} + AsS_3^{3-} + 3H_2O \qquad (1)$$

$$2AsS_3^{3-} + 12OH^- = 2AsO_3^{3-} + 6S^{2-} + 6H_2O \qquad (2)$$

Realgar firstly oxidizes:

$$3As_4S_4 + 3O_2 = 2As_2O_3 + 4As_2S_3 \qquad (3)$$

then it dissolves in alkali according to the reactions (1), (2) and (4):

$$As_2O_3 + 6OH^- = 2AsO_3^{3-} + 3H_2O \qquad (4)$$

The formed thiosalts can react with cyanide and oxygen with the formation of thiacyanates and hydroxysalt:

$$2AsS_3^{3-} + 6CN^- + 3O_2 = 6SCN^- + 2AsO_3^{3-} \qquad (5)$$

As a result of these reactions arsenic does not only acquire the ability to migrate but also becomes a transporter of metals bound with their hydroxysalts in the tailing dump wastes.

Arsenic is not characteristic of natural soils of silicate medium and the Lebedinsk deposit. The wastes of the Kuranakh ore dale's ores imported to the Lebedinsk GEF are the source of As accumulated in its pool, *i.e.*, As plays the role of element-indicator of man-caused pollution in the zone of LTD.

Sulphide minerals of chalcophile metals in the process of cyanidation and later on in wastes oxidize, turning into thiosulphides, sulphides and thiocyanates by the reactions

$$2S^{2-} + 2O_2 + H_2O = S_2O_3^{2-} + 2OH^-$$

$$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O$$

$$2S^{2-} + 2CN^- + O_2 + 2H_2O = 2SCN^- + 4OH^-$$

The reactions listed above lead to dilution and migration of metals, As, Sb with drainage water into the downstream tailing dumps ant their sedimentation in bottom sediments and floodplain soils.

The local geologo-geochemical situation determines the scale and intensity of the development of man-caused anomalies in the downstream tailing dumps. Enclosing LTD low-permeability silicate rocks stimulate the sink of surface and ground waters into the river valley and the accumulation of natural and man-caused matter in the valley. Mixed wastes of gold-sulphide and gold-quartz ores in LTD are the rich source of elements-toxicants able to migrate in water medium. Silicate rocks due to their physicochemical inertness in contrast to limestones do not counteract to the formation of expanded man-caused anomaly (up to 7 km) in the LTD tail race.

Enclosing KTD limestones and dolomites act as a geochemical barrier for its drainage sinks. High sorption properties decreasing the rate and scale of the elements-toxicants' migration are characteristic of these rocks. Chemical binding of metal ions and formation of insoluble carbonates can not be also excluded. Beside this, the wastes of oxidized gold-quartz ore in KTD deliver less high-mobile elements-toxicants in comparison with LTD since they are the product of weathering (all their water-soluble compounds were washed away by water long ago). The main man-caused sinks of KTD are merged into high fissured and karst limestones and dolomites, because of this their effect to surface water, hence to ecosystems of the downstream tailing dumps in whole is not significant. In this regard, the questions arise about the effect of the KTD sinks to underground water-bearing horizon, about the behaviour of cyanides and heavy metals in underground water and the risk of their pollution. The above-mentioned geologo-geochemical factors explain the formation of short and weak man-caused anomaly in the KTD pool, despite the fact that the bulk of wastes in the KTD is about 3 times higher that in LTD, and there is the constant inflow of raw mash and the disposal of technological sulfur acid.

The 7 km area of the Lebedinsk downstream tailing dump is considered as the most polluted one; the 2 km long area of the Kuranakh downstream tailing dump – as the medium-polluted one.

An indirect indicator of the reaction of the living component of ecosystem is one of fluctuating skewness in vegetation. More the man-caused pollution, more the failures in plant ontogenesis and higher the skewness of plant bodies. The variationrange of fluctuating skewness differs for each kind of plants, but for aldar tree it is considerably larger, which makes it the most suitable object for bioindicative study.

CONCLUSIONS

1. In the warm time of a year (spring-summer period) the neutralization of disposals specified by the standing orders of cyanidation technology at the Kuranakh and Lebedinsk GEF practically provides sufficiently secure ecological protection of surface water from cyanide pollution.

2. At low temperatures the decay of cyanide slows down, which makes ecological risk of short-time and local pollution of floods by these compounds, especially in spring and during shower rains.

3. Along with the direct danger of cyanides, they play significant role in dilution, transfer and sedimentation of heavy metals in the form of integrated compounds in the downstream tailing dumps. Beside this, alkaline medium provided by the cyanidation technique furthers the dissolution of arsenic and antimony minerals.

4. The specific effect of carbonate and silicate media on the character of man-caused pollution was established: the first one is a geochemical barrier, the second furthers the formation of more expanded aureoles.

5. One of the indirect reactions of the biotic component of ecosystems to man-caused pollution is an increase in the skewness degree of birch and alder leaves.

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REFERENCES

1 S. I. Mironova, Tekhnogennye suksetsionnye sistemy rastitel'nosti Yakutii (na primere Zapadnoy i Yuzhnoy Yakutii), Nauka, Novosibirsk, 2000.

2 Problemy ispol'zovaniya i okhrany prirodnykh resursov Sibiri, Nauka, Novosibirsk, 1980.

3 Yu. V. Shumiliv, D. D. Savvinov, V. V. Ivanov *et al.*, Problemy i praktika ekologicheskogo normirovaniya na Severe, Yakutsk, 2001.

4 Yu. V. Shumiliv, A. I. Bozhedonov, V. V. Samsonova *et al.*, Otsenka izmeneniy ekologicheskogo sostoyaniya Aldanskogo ulusa za period promyshlennogo osvoyeniya i prognoz evolyutsii prirodnoy sredy k 2015 godu: Otchet IPES AN RS(Ya), Yakutsk, 1997.

5 E. Altunin, L. Sergeeva, A. Yarlov, Podschet zapasov mestorozhdeniy Kuranakhskogo rudnogo polya po sostoyaniyu na 1.01.1978 g.: Otchet AK "Aldanzoloto", Nizhniy Kuranakh, 1979.

6 N. P. Chibisov, *Geologiya rudnykh mestorozhdeniy*, 16, 4 (1974) 77.

7 L. V. Razin, I. S. Rozhkov, Geokhimiya zolota v kore vyvetrivaniya i biosfere zolotorudnykh mestorozhdeniy kuranakhskogo tipa, Nauka, Moscow, 1966.

8 A. A. Seleznev, V. A. Timchenko, V. N. Makarov, Geokhimicheskoye oprobovaniye na territorii Yuzhnoy Yakutii s sostavleniyem geokhimicheskoy karty masshtaba 1 : 500 000: Otchet Tsentral'noy kompleksnoy ekspeditsii Tsentral'noy geokhimicheskoy partii PGO "Yakutskgeologiya", Yakutsk, 1980.

9 Instruktsiya po geokhimicheskim metodam poiskov rudnykh mestorozhdeniy, Nedra, Moscow, 1965.

10 Metodicheskiye rekomendatsii po provedeniyu polevykh i laboratornykh issledovaniy pochv i rasteniy pri kontrole zagryazneniya okruzhayushchey sredy metallami, in N. G. Zyrin and S. G. Malakhov (Eds.), Gidrometeoizdat, Moscow, 1981.

11 A. P. Vinogradov, Geokhimiya redkikh i rasseyannykh khimicheskikh elementov v pochvakh, Izd-vo AN SSSR, Moscow, 1950.

12 V. M. Zakharov, V. I. Borisov, A. S. Baranov, A. V. Valetskiy, Stabil'nost' razvitiya. Posledstviya Chernobyl'skoy katastrofy: Zdorovye sredy, Tsentr ekologicheskoy politiki Rossii, Moscow, 1996, pp. 65–77.

13 V. M. Zakharov, T. A. Chubinishvili, S. G. Dmitriev *et al.*, Zdorovye sredy: praktika, otsenki, Tsentr ekologicheskoy politiki Rossii, Moscow, 2000.

14 Spravochnik po gidrokhimii, Gidrometeoizdat, Leningrad, 1989.

15 Gosudarstvennaya sistema sanitarno-epidemiologicheskogo normirovaniya RF.2.1.5. Vodootvedeniye naselennykh mest, sanitarnaya okhrana vodoemov. Predel'no-dopustimye kontsentratsii (PDK) khimicheskikh veshchestv v vode vodnykh obyektov khozyaystvenno-pityevogoi kul'turno-bytovogo vodopol'zovaniya. Gigiyenicheskiye normativy GN 2.1.5.689–98, Izd-vo Minzdrava RF, Moscow, 1998.

16 Poryadok opredeleniya razmerov ushcherba ot zagryazneniya zemel' khimicheskimi veshchestvami, Ministerstvo okhrany okruzhayushchey sredy i prirodnykh resursov RF, Komitet RF po zemel'nym resursam i zemleustroystvu, Moscow, 1993.

17 V. A. Danilov, E. G. Shadrina, Ya. L. Volpert, *Nauka i obrazovaniye*, 1 (2001) 30.

18 D. H. Rubisov, V. G. Papangelakis, P. D. Kondos, Fundamental Kinetic Models for Gold Ore Cyanide Leaching, *Canadian Metallurgical Quarterly*, 35, 4 (1996) 353.

19 Spravochnik po rastvorimosti, Izd-vo AN SSSR, Moscow – Leningrad, 1961.