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THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA
CENTER FOR ECOLOGICAL-NOOSPHERE STUDIES

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«___» November 2005

REPORT ON THE PROJECT

«ASSESSING ENVIRONMENTAL IMPACT OF TAILING STORAGE SITES FROM MINING AND DRESSING PRODUCTION ON THE TERRITORY OF KAJARAN TOWN (SYUNIK MARZ)»

Principal investigator

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Yerevan 2005

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1. INTRODUCTION

This research “Assessing environmental impact of tailing storage sites from mining and dressing production on the territory of Kajaran town (Syunik Marz)” has been performed based on the Agreement with the Organization for Security and Cooperation in Europe Office in Yerevan.

Pilot investigations in Kajaran’s area were funded by the city municipality, which, too, got interested in the research.

To complexly investigate territories exposed to the impact of mining enterprises, the application of versatile methodic approaches including both the assessment of the state of basic components of the ecosystem (soil cover, surface waters, vegetation, agricultural crops, etc.) and conjugated analysis of data obtained, are required. All this allows getting a comprehensive picture of ecological state of urban sites from positions of sanitary-hygienic, eco-toxicological, functional, and sustainable development of the territory.

In Armenia, it is northern and southern portions of the republic, which are attributed to mining centers in the first turn. Of particular interest is South Armenia where a whole set of mining enterprises is focused. There, the cities of Kapan, Kajaran, Meghri, Agarak etc. are located. This research covers the areas both of Kajaran and 3 tailing repositories: Darazami, Pkhrut, Voghchi.

Ecologically valuable data for this territory are scarce and disintegrated. Basic investigations were conducted in the context of ore deposit prospecting. In first turn, one should stress the researches of D. P. Malyuga [1958] who conducted bio-geochemical surveys on Kajaran’s territory in the 1950s for the purpose of molybdenum prospecting. Later, based on D. A. Malyuga’s works V. V. Kovalskiy [1974] described the territory as natural bio-geochemical province enriched by molybdenum.

No detailed or comprehensive ecological studies of the territory have been conducted, yet.

The research was performed by

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The agreement-based works were performed from 1.07.05 to 31.11.05.

1.1. Brief description of the territory of Kajaran City

The city of Kajaran is one of Armenia's largest mining centers. On its territory the Zangezur mining and dressing group of enterprises is located which specializes in the obtaining of copper-molybdenum concentrate.

The city is situated in River Voghchi gorge. Mean annual amount of precipitation is 600*mm*. The relief is sharply cut. For geological composition of the region tertiary volcanogenic, intrusive rocks (porphyrites, porphire granites, and monzonites) are common. The major portion of the territory (up to 80%) is covered by layers of soil and deluvium (1-5*m*). Up to a height of 1800m a.s.l., soil cover is mainly represented by brown soils, at 1800-2400*m* a.s.l. – by chestnut soils. Northern slopes are covered by mountain-forest gray skeletal soil. Southern slopes are covered by mountain-xerophile vegetation, and northern – *Quercus macranthera, Carpinus betulus* L. shrub shoots, and so on.

The territory of Kajaran lies in the area of sulfide copper-molybdenum deposit and is a natural bio-geochemical province described for the first time by D. P. Malyuga [1958] and V. V. Kovalskiy [1974].

1.2. The project goal and tasks

The project goal was to assess ecological state of Kajaran's territory with regard for the impact of the Zangezur copper-molybdenum group of enterprises and adjacent tailing repositories. The **tasks** to achieve the stated goal were

- to assess pollution level of basic natural environments (surface waters, soils, plants) on Kajaran's territory and give their sanitary-hygienic assessment,
- to provide eco-toxicological assessment of agricultural crops grown in the city and tailing repository sites,
- to suggest a set of actions for functional tree planting on the city's territory and rehabilitation of tailing repositories.

1.3. Research materials and methods

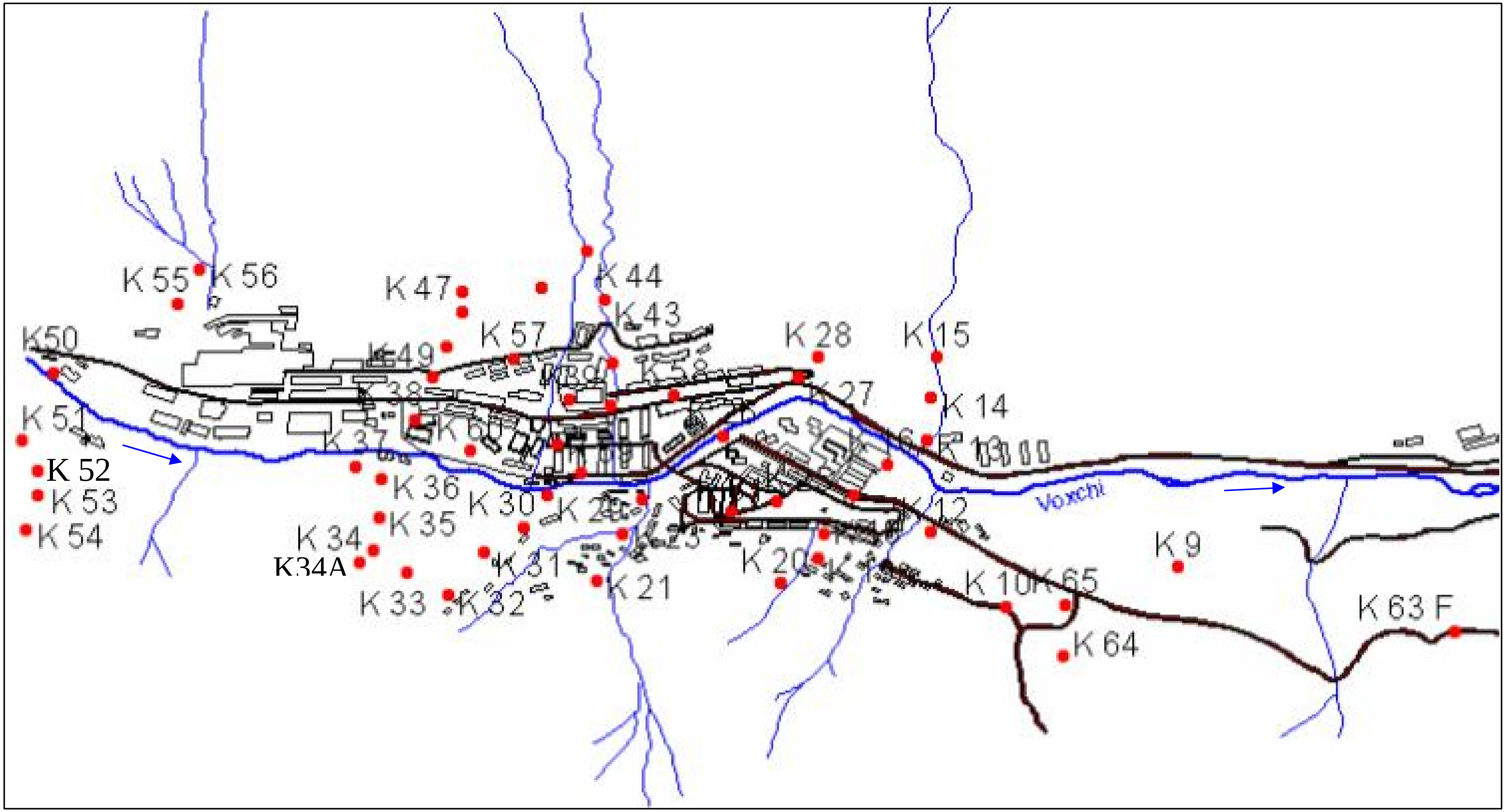
Soil samples were collected from the city's territory following a topographic plan (Sc. 1:5000) applying GPS (for getting precise geographical coordinates of sampling points). On "potentially clean" sites sampling network got rarefied. Total amount of sampling points was 66 (*Fig. 1*), the amount of samples being 140.

Water samples were collected from River Voghchi, its mouth and main tributaries as well as from some springs (at the suggestion of Kajaran municipality). Total amount of points was 16 (*Fig. 2*).

The soil, water, vegetation samples (*Fig. 3*) were collected and processed through methods developed in IMGRE and the V. V. Dokuchaev Soil Institute [Methodic…, 1981, 1982].

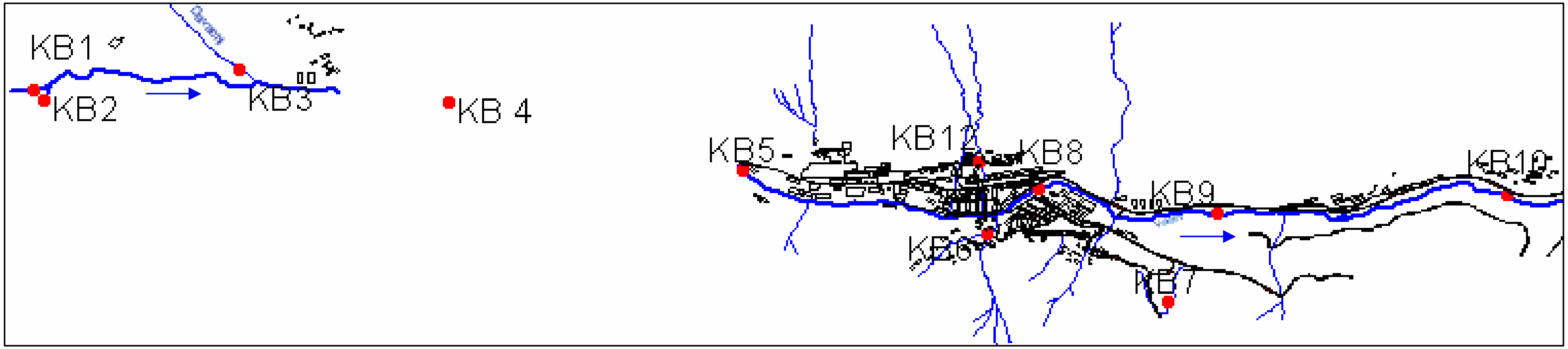
Fig. 3. Sample collection procedure

Fig. 1. **A schematic map of soil and plant sampling.**



Sampling points, index (K) and ordinal number

***Fig. 2.* A schematic map of water sampling.**



Sampling points, index (KB) and ordinal number.

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The work frame included bioindication investogations, too. The material for indication investigations was the most widely spread tree species, for eco-toxicological studies – vegetable species and herbs (on tailing repository sites).

In field conditions, basic physical and chemical indices of water (T, pH, mineralization, salinity, dissolved oxygen, conductivity) were measured through a Horriba U-10 multi-analyzer. The collected soil, water, plant samples were analyzed in CENS laboratory (*Tab. 1*).

Table 1. The scope of analyses of separate environmental components

Parametrs / Environ-mental components	pH	Eh	T^0C	Salinity	Dissolved oxygen	Minera-lization	Ions	Total N	Heavy metals, element/analysis	Gross - radioactivity
Waters	16	12	12	12	12	12	238	-	240	-
Soil	72	-	-	-	-	-	37	-	1008	54
Plants	-	-	-	-	-	-	37	223	1080	-

Heavy metal contents were determined by the methods of quantity spectral (ДФС-13) and atomic-absorption analyses (Perkin Elmer 800). Ion composition and total sulphur contents were determined through accepted methods [Arinushkina, 1970] keeping ISO international standards. In soils, water soluble (1:2) form of elements was determined as well.

Gross -radioactivity in soils was measured on a -radiometer РКБ4-1еМ. As standard, KCl was used.

Total nitrogen in dry vegetation material was determined through the express-method [Margaryan, Hovhannisyan, 1979] on the basis of formation of a complex with the Nessler's reagent and further colorimetric measurements on a KFK-2-UKhL 4.2 photo-electrocolorimeter, wave length – 413.

Accumulation level of chemical elements in separate environments was determined through the method of collation of actual concentrations with data on background plots and Maximum Acceptable Concentrations (MAC) [Kloke A., 1980; MPC, 1982; Dueck et al., 1984; Temporary…, 1987; List..., 1990; Ecology..., 1993].

For cartographic reflection of sampling points and results of further material processing, digital 4-layer maps of the territory were developed, sc.1 : 5000.

Ecological and geochemical mapping of the territory was performed based on the compiled computer database of chemical element contents in soils and plants applying the licensed program package ArcView 3.2a. While collating mono-element schematic maps, a 3-fold grade scale was used.

2. ASSESSING POLLUTION LEVEL OF SURFACE WATERS

Assessing pollution levels of surface waters is important both in sanitary-hygienic, and ecological aspects. In short terms, high concentrations and activation of majority of heavy metals and ions in water environment may lead to pollution of environmental components (soils, plants, etc.) and enter the human organism through food chain.

As background contents, mean values of ion and heavy metals concentrations in the water of Rivers Kaputjukh (КВ1) and Kajarants (КВ2) tributaries were accepted (*Fig. 4*).

Fig. 4. River Voghchi tributaries – the Kaputjugh (КВ1, to the left) and the Kajarants (КВ2, to the right) confluence site

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2.1. Physical and chemical indices of waters

Table 2 gives the results of measurement of basic physical and chemical indices of Kajaran's surface waters.

Table 2. Physical and chemical indices of surface waters

N°	pH	Eh	T^0C	Salinity, %	Dissolved oxygen, *mg/L*	Mineralization, *mg/L*
Drinking water						
KB2	7,72	160	13,7	-	13,83	121,72
River Voghchi						
KB1	5,48	220	14,2	-	13,58	125,196
KB3	8,21	150	17,0	-	11,89	284,216
KB4	7,78	180	14,7	-	13,16	155,769
KB5	7,79	190	15,7	-	12,97	228,038
KB8	7,96	180	17,8	-	12,70	202,8
KB9	8,05	180	19,0	-	11,71	219,46
KB10	8,03	160	20,1	-	12,58	235,97
KB11	7,85	180	20,4	-	12,91	255,116
KB12	7,84	180	18,8	-	13,12	267,37
Aqueducts						
KB6	7,58	210	16,1	0,05	12,76	978,44
KB7	8,07	200	17,6	0,08	12,70	1443,53

As seen, except point KB1 (pH=5.48), the waters are attributed to weak alkaline and alkaline category (pH=7.7-8.2).

Measurements of redox potential (Eh) show that waters are in the standard limits.

By salinity index, the waters from 2 points (*Fig. 5*) only may be noted: KB6 (from colliery) and KB7 (aqueduct from Darazami tailing repository). In the rest points salinity index is under sensibility of the instrument.

Fig. 5. Water sampling points: KB6 (stream from the colliery, near Kajaran's old TV tower, to the right) и KB7 (aqueduct from Darazami tailing repository, to the left)

Measurement results for dissolved oxygen in all the waters do not overstep MAC (4*mg/L*).

By water mineralization index, River Voghchi waters are attributed to low (up to 200*mg/L*) and middle (200-500*mg/L*) mineralization. The basic share in mineralization falls to carbonates and to sulfates for points KB6 and KB7 (*Tab. 3*). Mineralization level of these waters is attributed to elevated and high category (500-1000, 1000 and more *mg/L*). In point KB7 (aqueduct from Darazami tailing repository) mineralization values (1443.5 *mg/L*) are 1.4 times higher vs. MAC (1000 *mg/L*).

2.2. Ion composition of waters

According to ion composition formulae (*Tab. 3*), the waters are mainly attributed to hydrocarbonate-calcium and here and there to hydrocarbonate-magnesium and sodium classes; the waters from points KB6 (a stream flowing out from the colliery) and KB7 (an aqueduct from Darazami tailing repository) belong to sulfate-calcium class. The presence of sulfate ions in these waters is conditioned by its high concentrations in the materials of colliery and tailing repository. A supposition may be made that in these points heavy metal migration processes might actively run and thus be really harmful from sanitary-hygienic positions.

Table 3. Ion contents in Kajaran's surface waters (in *mg/L*).

Samples	Na^+	K^+	Ca^{2+}	Mg^{2+}	PO_4^{3-}	NO_2^-	NO_3^{2-}	NH_4^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ion composition formulae
Drinking water													
KB2	2,0	0,7	12,0	3,6	-	-	0,99	-	-	56,1	28,4	18,9	$\frac{HCO_3^-54\ Cl^-27\ SO_4^{2-}18\ NO_3^{2-}1}{Ca^{2+}66\ Mg^+20\ Na^+11\ K^+3}$
KB14	6,8	2,2	24,1	7,3	-	0,034	3,05	0,076	-	124,4	28,4	12,8	$\frac{HCO_3^-74\ Cl^-17\ SO_4^{2-}7\ NO_3^{2-}2}{Ca^{2+}60\ Mg^+18\ Na^+17\ K^+5}$
KB15	440	34,0	299,3	91,2	0,15	0,066	-	0,77	-	1830	255	228	$\frac{HCO_3^-79\ Cl^-11\ SO_4^{2-}10}{Na^+51\ Ca^{2+}35\ Mg^+10\ K^+4}$
KB16	6,8	7,2	19,1	10,5	0,15	0,022	2,8	0,038	10,2	166	19,5	44,0	$\frac{HCO_3^-69SO_4^{2-}18\ Cl^-8\ CO_3^-4\ NO_3^{2-}1}{Ca^{2+}44\ Mg^+24\ Na^+16\ K^+16}$
Waters for fish breeding purposes													
MAC	120	50	180	40	-	0,08	40	0,5	-	-	300	100	
KB3	26,0	1,3	37,1	11,6	0,38	-	0,37	0,039	12,0	134,2	35,46	38,68	$\frac{HCO^-{}_3 61\ SO_4^{2-}\ 18\ Cl^-\ 16\ CO_3^-5}{Ca^{2+}49\ Na^+34\ Mg^+15\ K^+2}$
River Voghchi waters													
KB1	3,7	1,0	15,0	4,3	0,15	0,022	1,12	-	-	61,0	21,3	18,9	$\frac{HCO_3^-60\ Cl^-\ 20\ SO_4^{2-}\ 19\ NO_3^{2-}\ 1}{Ca^{2+}63\ Mg^+18\ Na^+15\ K^+4}$
KB4	3,5	1,0	18,0	6,1	0,38	-	1,49	-	-	73,2	35,5	18,5	$\frac{HCO_3^-57\ Cl^-\ 27\ SO_4^{2-}\ 15\ NO_3^{2-}\ 1}{Ca^{2+}63\ Mg^+21\ Na^+12\ K^+4}$
KB5	5,4	1,6	30,6	9,7	0,11	-	2,53	-	-	104,9	35,5	40,3	$\frac{HCO_3^-57\ SO_4^{2-}\ 22\ Cl^-20\ NO_3^{2-}\ 1}{Ca^{2+}65\ Mg^+21\ Na^+11\ K^+3}$
KB8	5,5	1,7	32,1	4,9	0,15	0,022	2,94	0,039	2,4	82,9	35,5	43,2	$\frac{HCO_3^-50\ SO_4^{2-}\ 26\ Cl^-\ 21\ NO_3^{2-}2\ CO_3^-1}{Ca^{2+}73\ Na^+12\ Mg^+11\ K^+4}$
KB9	5,8	1,9	27,1	9,7	0,11	0,011	3,46	0,039	-	97,6	35,5	42,0	$\frac{HCO_3^-55\ SO_4^{2-}\ 23\ Cl^-20\ NO_3^{2-}2}{Ca^{2+}61\ Mg^+22\ Na^+13\ K^+4}$
KB10	6,2	1,9	28,1	14,6	0,31	0,044	4,02	0,46	-	104,9	35,5	44,9	$\frac{HCO_3^-56\ SO_4^{2-}23\ Cl^-19^-\ NO_3^{2-}2}{Ca^{2+}55\ Mg^+29\ Na^+12\ K^+4}$
KB12	6,1	7,3	43,1	10,3	0,996	0,066	6,26	0,039	14,4	131,8	35,5	33,3	$\frac{HCO_3^-60\ Cl^-16\ SO_4^{2-}15\ CO_3^-6\ NO_3^{2-}3}{Ca^{2+}64\ Mg^+16\ K^+11\ Na^+9}$
Aqueducts													
KB6	11,6	4,5	163,3	80,9	0,115	0,033	23,66	0,077	16,8	146,4	42,6	529,2	$\frac{SO_4^{2-}70\ HCO_3^-19\ Cl^-6\ NO_3^{2-}3\ CO_3^-2}{Ca^{2+}63\ Mg^+31\ Na^+4\ K^+2}$
KB7	14,0	5,2	250,5	113,7	0,383	0,022	24,03	0,19	24,0	185,4	49,6	825,1	$\frac{SO_4^{2-}\ 74\ HCO_3^-17\ Cl^-5\ NO_3^{2-}2\ CO_3^-2}{Ca^{2+}65\ Mg^+30\ Na^+4\ K^+1}$
KB11	6,8	2,2	33,1	10,9	0,27	0,18	4,58	0,039	-	112,2	42,6	47,3	$\frac{HCO_3^-54\ SO_4^{2-}23\ Cl^-21\ NO_3^{2-}2}{Ca^{2+}62\ Mg^+21\ Na^+13\ K^+4}$

Sampling sites:

KB1 – R. Kaputjugh tributary
KB2 – R. Kaputan (Kajarants) tributary
KB3 – R. Davachi tributary
KB4 – R. Voghchi
KB5 – R. Voghchi, near the tunnel
KB6 – stream from the colliery, near Kajaran's old TV tower
KB7 – aqueduct from Darazami tailing repository
KB8, KB9 – R. Voghchi, in the city
KB10 – R. Vighchi, beyond the city
KB11 – large stream from Voghchi tailing repository
KB12 – R. Voghchi tributary, behind the hotel
KB14 – mineral water "Ttu jur"
KB15 – mineral water "Esentuki"
KB16 – spring

The analysis of ion composition of the waters of River Voghchi, its tributaries and aqueducts from tailing repositories allows the following conclusions:

1. Ion contents in the waters of R. Kaputjugh tributary (KB1) meet the accepted standard (*Fig.6*). The water is applicable for economic and household purposes and possibly for drinking.
2. The waters of River Voghchi tributary – the Davachi (KB3, *Fig. 7*) were specially investtigated to use them for fish breeding purposes, as today a relevant organization functions. The results of investigations indicated in-MAC ion contents in the Davachi waters (*Tab.3*) and thus the waters are quite appropriate for fish breeding purposes.

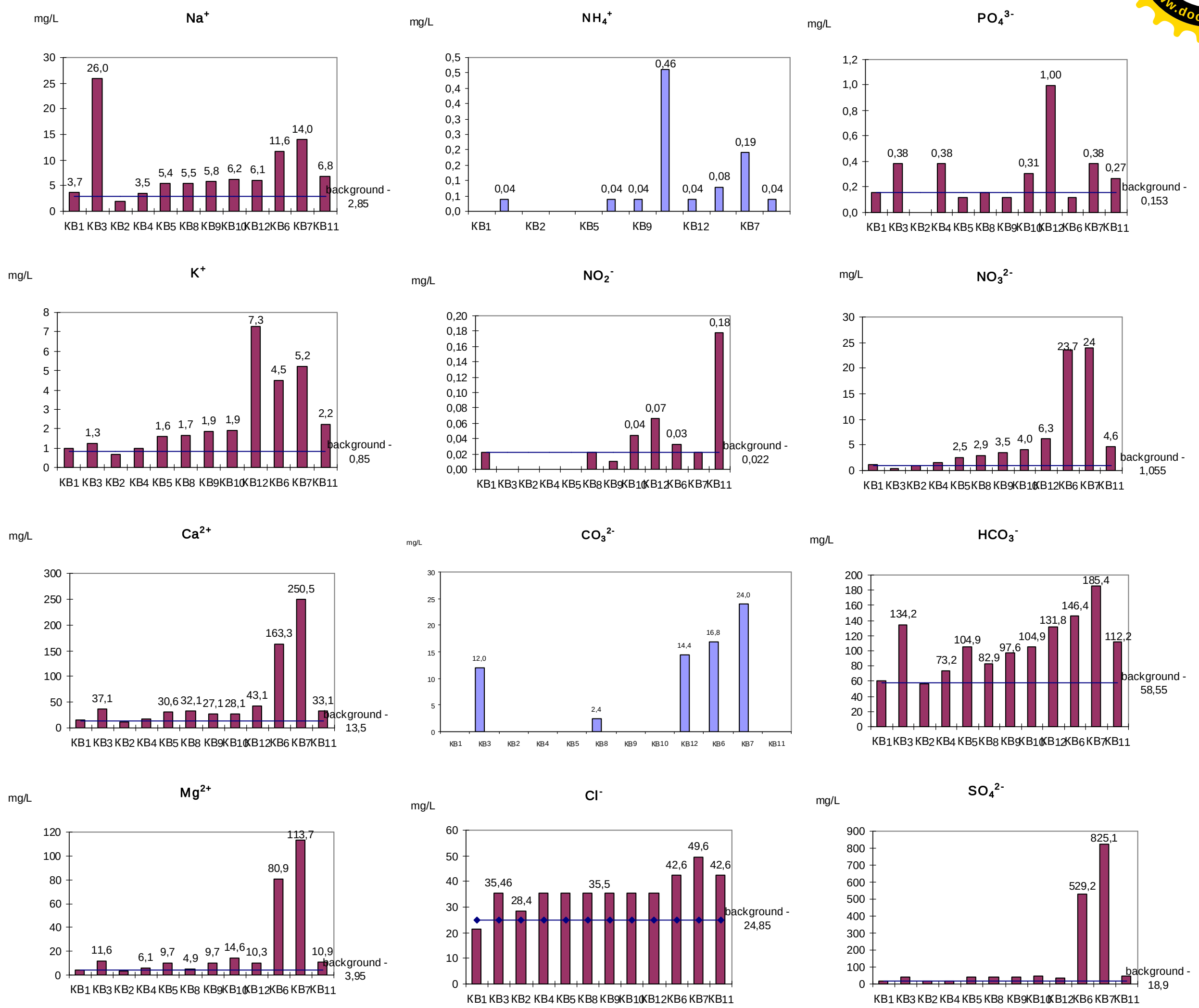

Fig. 6. Ion contents in the waters of River Voghchi and aqueducts from tailing repositories.

Sampling sites:

KB1 – R. Kaputjugh tributary KB2 – R. Kaputan (Kajarants) tributary KB3 – R. Davachi tributary KB4 – R. Voghchi	KB5 – R. Voghchi, near the tunnel KB8, KB9 – R. Voghchi, in the city KB10 – R. Voghchi, beyond the city	KB12 – R. Voghchi tributary, behind the hotel KB6 – stream from the colliery, near Kajaran's old TV tower KB7 – aqueduct from Darazami tailing repository KB11 – large stream from Voghchi tailing repository

3. Ion concentrations in the waters of R. Kaputan (KB2) tributary used for drinking meet the accepted standard.

4. All along River Voghchi extension ion concentrations in its waters show the following variations. <u>Cations:</u> mean Na^{+} concentrations in the city show 2.5 fold excess vs. the background (2.85 *mg/L*); mean K^{+} and Ca^{+} concentrations show 2-2.5 time excess vs. the background, and in the tributary (KB12) – 8.5 and 3 times, respectively; Mg^{2+} contents show 1.5-4 time excess vs. the background. In the city minimal concentrations (0.04 *mg/L*) of ammonium ions are common for points KB8, KB9, KB12; beyond the city (KB10) elevated concentrations are detected (0.46 *mg/L*).

Fig. 7. River Voghchi tributary – the Davachi (KB3).

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Anions: elevated concentrations are established for NO_2^- beyond the city (KB10, 2 backgrounds) and the tributary (KB12, 3 backgrounds). CO_3^{2-} (carbonate-ion) is established for point KB8, in the center of the city, its concentrations being insignificant (2.4 *mg/L*). Chlorine-ion concentrations are constant for all the points (35.5 *mg/L*), established is its 1.5 fold excess vs. the background. In the city, no excessive PO_4^{3-} contents vs. the background are established, beyond the city its excess vs. the background is established for 2 points: KB4 (2.5 fold) and KB10 (2 fold). NO_3^{2-} all along the river increases from 2.5 *mg/L* (KB5) to 4 *mg/L* (KB12); in the tributary (KB12) the contents are higher – 6.3 (6 fold excess vs. the background). A similar picture is observed for hydrocarbonate-ion (HCO_3^-) (*Fig. 6*). The contents of sulfate-ion all along the river are even and their mean 2 fold excess vs. the background is established.

Wholly, one may conclude that ecological state of River Voghchi is satisfactory but for point KB12 (the tributary) in which elevated ion contents are detected. Pollution of this tributary water is middle and may likely be associated with economic and household runoffs and active development of home-gardening throughout its watershed area.

5. Unlike the waters of River Voghchi, for those of aqueducts and especially of that flowing out from Darazami tailing repository high concentrations of practically all the ions are established (*Fig. 6*). Particularly high are the contents of sulfate-ion – 825*mg/L* (44 times higher vs. the background), NO_3^{2-} – (23 times higher vs. the background), and Mg^{2+} (29 times higher vs. the background).

6. The analysis of ion composition of spring waters except NO_3^{2-} and CO_3^{2-} show that peak contents of ions are established for "Esentuki" mineral water sample. In this water a 2 fold excess of sodium-ion vs. MAC is established. Sanitary-hygienic state of the water is not satisfactory (*Fig. 8*).

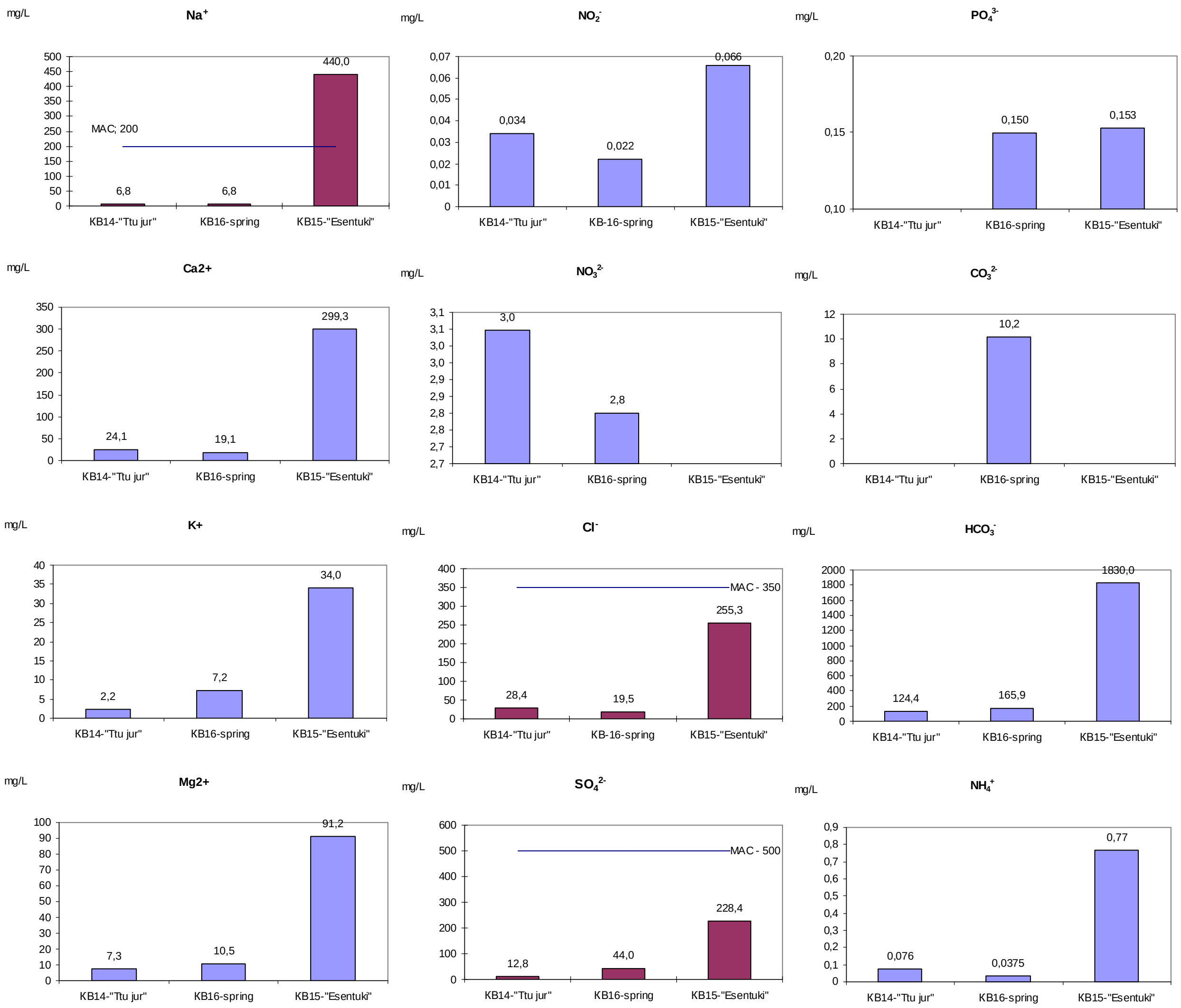

Fig. 8. Ion contents in the spring waters

In "Ttu jur" mineral water identified are relatively high contents of NO_2^- (0.034 *mg/L*) and NO_3^{2-} (3 *mg/L*), but wholly the state of the water is satisfactory (*Fig. 8*).

In the spring water (KB16) the ion contents are low. For the water elevated contents of carbonate-ion and PO_4^{2-} are common. The state of the water is satisfactory.

2.3. Heavy metal contents

Heavy metal contents in surface waters on Kajaran's territory were determined for 16 points (*Fig. 2*): in the waters of River Voghchi, its tributaries, and several springs (at Kajaran municipality suggestion). The obtained results are given in *Tab. 4*.

Table 4. Heavy metal contents in Kajaran's surface waters (*mkg/L*).

	Co	Ni	Cr	Cd	As	Ag	Mo	Hg	Cu	Zn	Mn	Pb
Background / Sampling points	-	2.95	0,016	0,011	0,41	0,001	0,101	-	1,096	39,0	24.2	-
Drinking water												
MAC *	100	100	50	1	50	50	250	0,5	1	1000	100	30
KB2 – the Kaputan (Kajarants) tributary	-	3,74	0,014	0,012	0,41	0,001	-	-	1,059	33,0	25,9	-
KB14 – mineral water "Ttu jur"	2,55	9,52	0,053	0,39	0,84	0,01	7,446	-	**12,77**	15,6	**493**	-
KB15 – mineral water "Esentuki"	4,28	8,634	0,018	-	**680,4**	-	**1619**	**23,36**	**4,0**	27,1	**269**	-
KB16 – the spring	0,36	0,43	0,25	0,048	0,92	0,005	3,68	**0,6**	**2,43**	1,0	44,0	0,07
Water for fish breeding and economic purposes												
MAC **	10	10	50	5	50	-	-	1	1	10	10	100
KB3 – the Davachi tributary	-	5,1	0,014	0,017	0,13	-	-	-	1,01	**39,75**	**31,2**	-
River Voghchi												
MAC ***	100	100	50	1	50	50	250	0,5	1000	1000	100	30
KB1 – the Kaputjugh tributary	-	2,11	0,019	0,01	-	-	0,101	-	1,133	45	22,5	-
KB4 – R. Voghchi	-	3,77	0,013	0,011	0,42	-	0,89	-	0,76	16,0	11,0	-
KB5 – R. Voghchi, near the tunnel	0,006	7,73	0,015	0,011	0,074	-	3,79	-	3,59	25,0	25,0	-
KB8 – R. Voghchi, in the city	0,015	1,98	0,014	0,009	0,633	-	156,6	-	4,11	25,0	60,0	-
KB9 – R. Voghchi, in the city	-	1,475	0,015	0,007	0,471	-	107,9	-	3,74	33,0	50,0	-
KB10 – R. Voghchi, beyond the city	0,08	3,72	0,015	0,01	0,33	-	85,5	-	5,17	29,0	62,5	-
KB12 – the Voghchi tributary, behind the hotel	-	1,9	0,013	0,006	2,08	0,001	65,05	0,53	1,08	22,5	45,0	-
Aqueducts												
MAC ***	100	100	50	1	50	50	250	0,5	1000	1000	100	30
KB6 – stream from the colliery, near old TV tower in Kajaran	-	2,47	0,013	0,014	2,31	0,018	**322,7**	**2,47**	9,26	37,5	26,0	-
KB7 – aqueduct from Darazami tailing repository	-	2,89	0,013	0,004	2,29	0,043	**288,7**	**5,12**	2,56	33,1	66,3	-
Near Voghchi tailing repository: KB11 – large stream	0,063	1,5	0,016	0,008	0,74	-	61,15	-	4,89	18	40	-
Near Voghchi tailing repository: 11A – small stream	0,009	1,22	0,013	0,006	0,17	-	100,5	-	1,83	27,2	66,2	-

Note: "-" – not detected; MAC by State Standard 2874-82 [1982] and by "List..." [1990].

2.3.1. *Drinking water*

One of Kajaran's drinking water sources is the Kajarants -River Voghchi tributary (KB2). No high concentrations of heavy metals were established (*Tab. 4*). The water of the Kaputan tributary meets sanitary-hygienic standards for water supply sources, should results of micro-biological tests be satisfactory.

2.3.2. *Springs*

At the suggestion of Kajaran municipality, sanitary-hygienic assessment was made for 3 mineral springs: “Ttu jur”, “Esentuki”, “spring KB16”. The investigations indicated a set of toxic elements in the waters.

1st grade hazard elements:

Arsenic (As) is identified only in “Esentuki” (*Fig. 9*). Its concentration (680.4 *mkg/L*) exceeds MAC (50 *mkg/L*) 13.6 times.

Mercury (Hg). Its high concentrations are established for “Esentuki” water. Its concentration (23.4 *mkg/L*) exceeds MAC (0.5 *mkg/L*) 46.7 times.

In the sample collected from the spring (KB16) Hg concentration (0.6 *mkg/L*) is slightly higher vs. MAC (1.2 times).

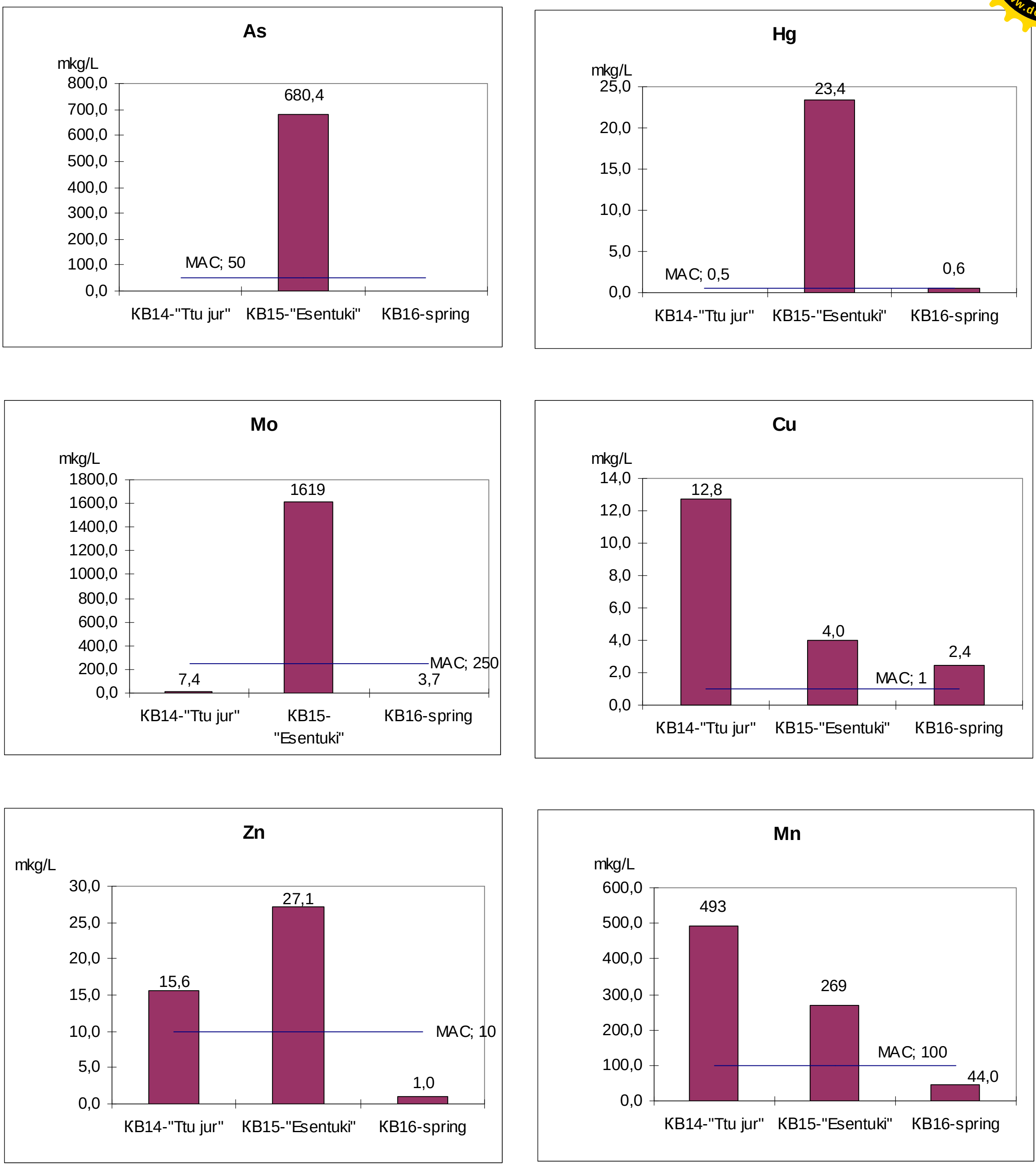

Fig. 9. The excess of heavy metal concentration vs. MAC in mineral springs.

Elements of 2nd class of hazard:

Copper (Cu) is established for all the samples. Its concentration in "Ttu jur", "Esentuki", Spring (KB-16) water samples exceeds MAC 12.8 - 4.0 – 2.4 times, respectively.

Detected are elevated concentrations of biophiles:

Molybdenum (Mo). Only in "Esentuki" water detected are concentrations (1619 *mkg/L*) that exceed MAC (250 *mkg/L*) 6.5 times.

Zinc (Zn). Insignificant excess vs. MAC (10 *mkg/L*) is established in the both springs: "Ttu jur" – 1.5 and "Esentuki" – 2.7 times.

Manganese (Mn). Its excess (100 *mkg/L*) vs. MAC are established for the both springs: "Ttu jur" – 4.9 and "Esentuki" 2.7 times.

Significant concentrations of toxic elements of 1st and 2nd class of hazard in mineral water "Esentuki" might be associated with their origination in the bounds of the ore field. The water cannot be used for drinking. Recommendation is made to close the spring.

Mainly, for water "Ttu jur" elevated concentrations of biophile elements (Cu, Zn, Mn) are common that are typical of the landscape. Small portions of the water are found safe for drinking.

The water from spring KB-16 is safe for drinking, should the results of micro-biological tests be satisfactory.

2.3.3. *The waters of River Voghchi, its tributaries and aqueducts.*

A sanitary-hygienic assessment of the waters of River Voghchi and its tributaries was made from positions of their appropriateness to economic, household, and fish breeding purposes.

Investigations of the Davachi tributary evidence that heavy metal contents except 2 biophiles: Zn and Mn (4 time excess vs. MAC) do not exceed MAC (*Tab. 4*). Wholly, the waters are satisfactory and may be used for fish breeding and economic purposes.

In River Voghchi waters heavy metal contents do not exceed MAC and may be used for economic and household purposes (*Tab. 4*).

Investigations of heavy metal contents in the stream flowing out from the colliery (near old TV tower, Kajaran, KB6) and aqueducts from Darazami (KB7) and Voghchi (KB11, KB11A) tailing repositories indicated the excess of Hg and Mo concentrations vs. MAC only in the stream from the colliery and aqueduct from Darazami tailing repository (*Fig. 10*). Peak contents of Hg (10.2 excess vs. MAC) are established for the waters of the aqueduct from Darazami tailing repository. Hg contents in the waters from the colliery show 5 fold excess vs. MAC.

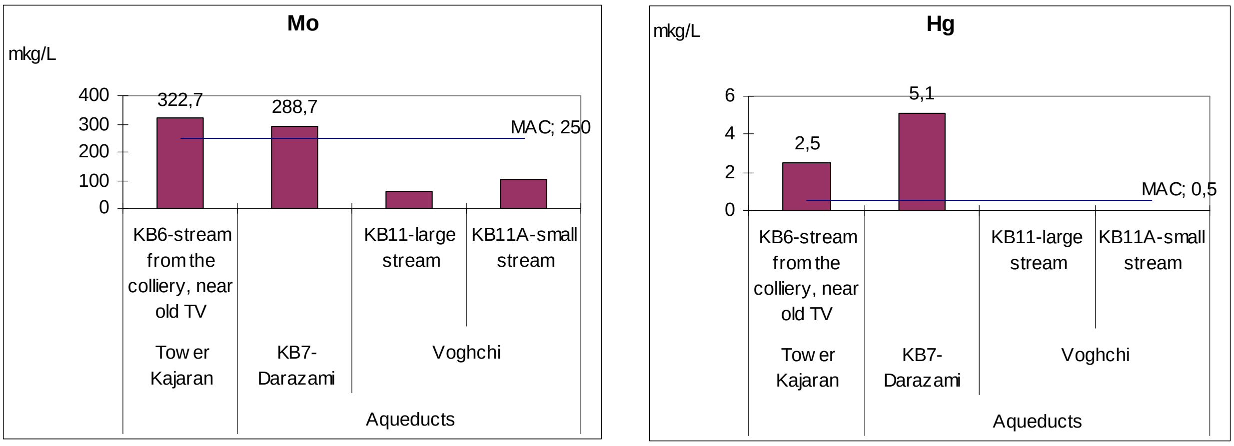

Fig. 10. Excessive concentrations of Hg and Mo vs. MAC in the waters of the stream and aqueducts from tailing repositories.

Excessive contents of Mo vs. MAC are insignificant (1.1-1.2 times), this being typical of local geochemical landscape.

High concentrations of Hg (element of the 1st class hazard) in the waters of the stream from the colliery and aqueduct from Darazami tailing repository evidence the danger of using these waters for economic and household purposes and in irrigation.

Thus, investigations of sanitary-hygienic state of Kajaran's surface waters show that

1) ***River Kaputan – the source of drinking water supply to Kajaran - fully meets the accepted standards,***
2) ***the state of River Davachi meets fish breeding and economic standards,***
3) ***by ion composition and heavy metal contents, the state of River Voghchi waters, except its tributary (KB12) behind the hotel, is satisfactory and may be used for economic and household purposes,***

4) ***due to high concentration of Hg and a number of ions established for the waters b[illegible] of the aqueduct from Darazami tailing repository (in Kajaran's suburbs) and the stream near old TV tower, the waters cannot be used either for economic purposes or in irrigation,***
5) ***of the studies waters, it is mineral water "Esentuki" that contains significant concentrations of toxic elements of 1st and 2nd class of hazard and thus cannot be used for drinking. It s strongly recommended that the spring should be closed.***

To get an exhaustive picture of sanitary-hygienic state of Kajaran's surface waters, monitoring studies are required for River Voghchi and its tributaries during basic hydrological phases (high water and low water).

Recommendation is made to assess the waters from all sources on Kajaran's territory paying special attention to aqueducts and streams around tailing repositories, where high contents of toxic elements (Hg, As) have been established.

Also, it is necessary to investigate River Voghchi bottom sediments, as they cumulate hazardous concentrations of toxic elements and thus may serve a potential source of supply of such elements, should redox potential of water environment sharply change.

3. SOIL POLLUTION

3.1. The assessment of Kajaran's territory pollution with heavy metals

3.1.2. *The analysis of heavy metal contents in soils*

Soil pollution levels are assessed as a result of collation of established contents with background concentrations. To calculate background concentrations, samples were collected from sites remote from the city. As data analysis show (*Tab. 5*), the leading role is given to Mo which background concentrations exceed lithosphere clarks (51 times), this being a specificity of bio-geochemical province enriched by molybdenum. In respect to clark, slightly elevated are background concentrations of Cu (3.7 times), Pb (2.6 times), Sn (2 times). Vs. MAC excessive contents are established for Mo (10.2 times), Ni (8.2 times), Co (2.6 times), Cu (1.7 times).

To determine a relative level of accumulation of elements, a geochemical series of the intensity of elements have been calculated. Positions of elements in the series are determined by the value of their mean contents excess vs. the background.

The analysis of mean contents of heavy metals in Kajaran's soils shows that in the series of elements Mo dominates:

$Mo_{29.8}$>$Cu_{5.1}$-$Pb_{2.2}$-$Co_{1.7}$-$Zn_{1.4}$-Mn,$V_{1.2}$-Ni,Sn,Ti_1-$Fe_{0,9}$-$Cr_{0,8}$ (summary intensity – 47,2).

Ecological risk is represented by elements with high contents vs. MAC. From positions of sanitary-hygienic characteristic of soils, the excessive contents of elements vs. MAC is considered, this however being problematic for bio-geochemical province regions to which Kajaran is attributed.

For spatial analysis of element concentration distribution on the city's territory, specialized mono-element geochemical schematic maps have been produced (Sc. 1 : 10000).

Table 5. The background and mean concentrations of heavy metals in Kajaran's soils (in *mg/kg*).

Heavy metals	Lithosphere clark [1]	MAC [2]	Town Kajaran (n=57)					
			Back-ground	Excess		C, *мг/кг* (вал.)	Excess	
	mg/kg (вал.)			Clarc	MAC		Background	MAC
Mo	1.0	5.0*	51.0	51.25	10.2	1524	29,8	304,9
Cu	46.0	100*	170	3.70	1.7	862	5,07	8,6
Pb	16.0	100*	42.0	2.65	0.42	91.0	2,16	0,9
Sn	2.5	50.0*	5.0	2.04	0.1	5.0	1,03	0,1
Zn	76.0	300*	70.0	0.92	0.23	95.0	1,40	0,3
Mn	770	1500	528	0.69	0.35	608	1,15	0,4
Ni	58.0	4.0	33.0	0.57	8.25	34.0	1,04	8,6
Cr	99.0	100*	48.0	0.45	0.48	39.0	0,80	0,4

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Co	23.0	5.0	13.0	0.56	2.6	22.0	1,70	4,4
V	110	100*	115	1.05	1.15	132	1,15	1,3
Ti	3200	-	3750	1.18	-	3619	1,0	-
Fe	43700	-	40500	0.93	-	37254	0,92	-

[1] According to A.P.Vinogradov [1962]; C – mean contents of heavy metals in Kajaran's soils;
[2] * According to A.Kloke [1980], Mn, Ni, Co – in "Ecology...." [1993].

3.1.2. ***Ecological and geochemical mapping of Kajaran's soils.***

3.1.2.1. *Mono-element geochemical schematic maps for heavy metals*.

Concentrations (C, %) and concentration coefficients (CC) of heavy metals in Kajaran's soil cover by different fields of concentrations, are given in *Tab. 6*.

Mono-element geochemical schematic maps are produced only for heavy metals dominating in Kajaran's soils. Their brief description is given below.

1. **Molybdenum** (*Fig. 11*) – a dominating element in the city's territory pollution. The background greatly exceeds (51 times) the clark in the lithosphere. On the city's territory the fields for 3 concentrations are contoured out. A field with peak values (>0.5%) is focused around the group of enterprises and spatially stretches out to collieries. The soils of the basic part of the city are attributed to the 2nd level of Mo concentrations 0.051-0.51%. The whole west suburb of the city is attributed to near-background level of concentrations (0.0051-0.051%). Spatial distribution of elevated concentrations of Mo is clearly associated with the group of enterprises and colliery.

2. **Copper** (*Fig. 12*). The background exceeds 3 times the clark in the lithosphere. On the city's territory, fields for 3 concentrations are contoured. Spatially, a field with peak values (>0.153%) is focused near the works chimney and is more developed westward from the group of enterprises (beyond the city). On the city's territory 2 basic fields have been identified: those of near-background (0.017-0.051%) and weak pollution (0.051-0.015%). The distribution of Co concentrations proves the lack of serious threat of pollution with this element.

3. **Lead** (*Fig. 13*). The background exceeds the clark in the lithosphere 2.6 times. On the city's territory 3 concentration fields are contoured. A field with peak level of concentration (>0.039%) is focused near the works chimney and in the center of the city. The first anomaly is associated with emissions to the atmosphere; the second one is traffic-induced. Around the group of enterprises and the colliery and in the residential center of the city located are weak intense fields (0.013-0.039%). In the east part of the city developed is a weak dispersed field with near-background indices (0.004-0.013%). Wholly, one may conclude that unlike other urbanized sites in Armenia no strong lead pollution of the city is detected.

4. **Cobalt** (*Fig. 14*). The background does not exceed the clark in the lithosphere. On the city's territory the fields of 2 concentration levels are singled out. The major part of the territory is occupied by a field with near-background concentrations (0.0013-0.0039%). Two local fields of the 2nd level (weak intensity, >0.0039%) are established near the chimney and in Darazami tailing repository. No high concentrations of cobalt are established.

Table 6. The background, concentrations (C, %) and concentration coefficients (CC) of heavy metals in Kajaran's soils.

Heavy metals	Background, %	Indices	CONCENTRATION FIELDS							
			< background		background – 3		3 - 9		9 - 27	
			C	CC	C	CC	C	CC	C	CC
Cu	0.017	min.	0,013	0.77	0,018	1,05	0,056	3,30	0,18	10,59
		max.	0,013	0,77	0,042	2,47	0,13	7,65	0,42	24,7
		mean	0,013	0,77	0,03	1,88	0,08	5,04	0,23	13,4
		N=	5		27		12		13	

Pb	0.0042	min.	0,001	0,24	0,0056	1,35	0,018	4,26	0,056	13,25
		max.	0,0042	0,99	0,013	3,07	0,032	7,58	0,1	23,67
		mean	0,0024	0,56	0,007	1,73	0,024	5,62	0,078	18,5
		N=	31		17		7		2	
Sn	0.0005	min.	0,00002	0,02	0,0006	1,09	0,0018	3,53	-	-
		max.	0,0005	0,98	0,0013	2,55	0,0018	3,53	-	-
		mean	0,0003	0,67	0,0007	1,39	0,0018	3,52	-	-
		N=	37		17		3		-	
Zn	0.007	min.	-	-	0,007	1	0,03	4,29	-	-
		max.	-	-	0,02	2,86	0,04	5,72	-	-
		mean	-		0,007	1,11	0,03	4,65	-	-
		N=	-		53		4		-	
Fe	4.05	min.	0,75	0,19	4,2	1,03	-	-	-	-
		max.	3,2	0,79	7,5	1,85	-	-	-	-
		mean	2,7	0,67	4,87	1,20	-	-	-	-
		N=	30		27		-		-	
Mn	0.053	min.	0,0042	0,079	0,056	1.06	-	-	-	-
		max.	0,042	0,79	0,13	2,46	-	-	-	-
		mean	0,03	0,58	0,08	1,48	-	-	-	-
		N=	21		36		-		-	
Ni	0.0033	min.	0,001	0,30	0,004	1,2	-	-	-	-
		max.	0,0032	0,97	0,006	1,6	-	-	-	-
		mean	0,003	0,83	0,005	1,3	-	-	-	-
		N=	36		21		-		-	
Cr	0.0048	min.	0,001	0,2	0,006	1,17	-	-	-	-
		max.	0,0048	1,0	0,01	2,08	-	-	-	-
		mean	0,0029	0,62	0,007	1,38	-	-	-	-
		N=	43		14		-		-	
Co	0.0013	min.	0,00042	0,32	0,0015	1,15	0,0042	3,23	-	-
		max.	0,0013	1	0,0032	2,46	0,0042	3,23	-	-
		mean	0,0009	0,68	0,0025	1,94	0,0042	3,23	-	-
		N=	14		40		3		-	
V	0.012	min.	0,0013	0,11	0,013	1,13	0,042	3,65	-	-
		max.	0,01	0,87	0,032	2,78	0,042	3,65	-	-
		mean	0,008	0,7	0,016	1,41	0,042	3,65	-	-
		N=	28		27		2		-	
Ti	0.38	min.	0,13	0,35	0,42	1,12	-	-	-	-
		max.	0,32	0,85	0,75	2	-	-	-	-
		mean	0,24	0,64	0,47	1,26	-	-	-	-
		N=	27		30		-		-	
Mo	0,0051	Indices	**CONCENTRATION FIELDS**							
			< background		**background – 10**		**10 -100**		**>100**	
			C	**CC**	**C**	**CC**	**C**	**CC**	**C**	**CC**
		min.	0,0032	0,625	0,0056	1,094	0,056	10,938	0,56	109,375
		max.	0,0042	0,82	0,042	8,203	0,400	78,125	3	585,9375
		mean	0,0037	0,73	0,023	4,387	0,102	19,799	1,212	236,71875
		N=	2		31		19		5	

Note: CC is calculated by the background.

5. **Zinc** (*Fig. 15*). The background does not exceed the clark in the lithosphere. On the city's territory identified are 2 levels of zinc dispersion fields in the soils: 1) with near-background concentrations (0.007-0.021%) that covers the major part of the city; 2) 3 local weak intense (>0.021%) fields near the works chimney, on the territory of the group of enterprises and in the center of the city.
6. **Tin** (*Fig. 16*). The background exceeds the clark 2 times. On the city's territory contoured are fields with 2 concentration levels: 1) with background concentrations (0.00051-0.00153%) that covers the west part of the city's territory and is spatially associated with the group of enterprises; 2) 2 local weak intense (>0.0015%) fields near the chimney and the suburbs near the group of enterprises.

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7. **Vanadium** (*Fig. 17*). The background approaches to the clark in the lithosphere. In residential part of the city dominant are low-background and background fields (0.0013-0.012%). Near-background (0.012-0.036%) fields are developed in the suburbs of the city. Identified are 2 local weak intense (>0.036%) concentration fields at the colliery exit and Darazami tailing repository.

8. **Nickel** (*Fig. 18*). The background does not exceed the clark in the lithosphere. On the city's territory identifies is only one field with near-background concentrations (>0.0036%) of nickel. The field is mainly associated to the territory of the group of enterprises.

The rest elements (Cr, Mn, Ti) practically do not form anomalous areas (*Fig. 19-21*). Their anomalies are weak developed and have near-background concentrations.

3.1.2.2. *Summary map of Kajaran's territory soil cover pollution with heavy metals.*

To assess complex pollution of Kajaran's territory soils with heavy metals, a schematic map of summary pollution of soils have been produced (*Fig. 22*). The methodic basis of the map is reflection of the value of summary index of concentration of elements. The index is calculated as a sum of element contents standardized by the background in the sample. Pollution level is assessed through a scale suggested by Yu. E. Sayet [1982].

On the city's territory singled out are 5 level pollution fields. The intense pollution field is focused in the area of the plant and colliery (summary index of concentration >128). Strong pollution field (64-128) surrounds the 1st field as a narrow strip. Similar not large field is focused in the center of the city. The leading role (90%) in formation of these fields belongs to molybdenum. A part of the central, south, and west portion of the city (towards the group of enterprises) is attributed to middle pollution level (32-64), the either part – to weak pollution class (16-32). Fields with high levels of element accumulation are mostly formed at the expense of molybdenum – a typomorphic element of bio-geochemical province. For this, the phenomenon of high concentrations of molybdenum cannot be regarded as "pollution".

In the vicinities of Darazami tailing repository a field is identified with near-background indices (8-16). This testifies to the fact that the tailing repository exerts no substantial impact upon the city in respect to heavy metal pollution.

Thus, geochemical survey of soil cover of Kajaran and its vicinities show that in pollution of the city molybdenum and partially copper dominate, but no intense pollution is detected allover the city. Fields with peak levels of heavy metals concentrations are focused on the territory of the group of enterprises, colliery, and westward, beyond residential part of the city. Elevated concentrations of molybdenum in Kajaran's soils is typical of biogeochemical province and should not be regarded as hazardous ecological situation. Wholly, pollution level of the city can be attributed to weak and partially middle pollution levels.

3.1.3. ***Sanitary-hygienic assessment of soil pollution with heavy metals.***

To provide sanitary-hygienic assessment of Kajaran's territory, mono-element schematic maps of heavy metals which contents exceeded MAC, were produced.

1. **Molybdenum** (*Fig. 23*). On the city's territory, 4 levels of MAC excess are established. The field with peak level (beyond MAC >30 times) is focused on the territory of the group of enterprises and colliery. Mean level (20-30 times excess vs. MAC) is associated with a territory both in industrial sites and partially towards the city center. Weak level of excess (10-20 times higher than MAC) is focused both in the center and south, east, north residential parts of the city covering Darazami tailing repository. Thus, the soils of the major part of the city contain concentrations of Mo that exceed MAC 10-20 times.

2. **Copper** (*Fig. 24*). On the city's territory identified are 4 level fields beyond MAC. The middle level fields (exceeding MAC >27 times) concentrations are presented by 2 local fields in west suburbs, beyond the city and within the area of the group of enterprises. Fields with weak level (9-27) are mainly associated with industrial sites, and in residential parts of the city they are focused in the south and east suburbs of the city. The rest major portion of soil cover contains concentrations of copper some 1-3 MAC. One should also note the fields where the concentrations are lower or higher MAC and particularly Darazami tailing repository site. From sanitary-hygienic positions copper pollution of the city is weak.
3. **Lead** (*Fig. 25*). On the territory of the city developed are fields with low lead excess (1-3 times) vs. MAC. Only near the plant chimney and in the center of city anomalies with 3-9 time excess s. MAC are identified. Wholly, lead pollution level is low.
4. **Nickel** (*Fig. 26*). In soils, 2 basic fields with very low (3-4 times vs. MAC) and low (6-14 times vs. MAC) levels are established. The low level is mostly developed on the territory of the group of enterprises and partially stretches out westward to residential parts of the city. For the rest part of the city and beyond it eastward very low pollution level is common.
5. **Cobalt** (*Fig. 27*). Mostly, on the city's territory a field is developed with low pollution level (3-14 vs. MAC). The fields with near-background (1-3) concentrations are represented by separate spots.

As the city is located in the limits of natural copper-molybdenum province, the obtained data on high molybdenum levels are not regarded as hazardous. Wholly, sanitary-hygienic state of Kajaran's soil cover is found satisfactory.

3.2. Investigation of gross -radioactivity of Kajaran's soils.

Investigations of gross -radioactivity of soils were carried on the territory of Kajaran for the first time. Totally, 54 soil samples were measured.

When assessing natural or man-made radiation anomalies, it is necessary to collate the obtained data with the regional background [Titaeva, 2000]. The analysis of the obtained data show that the lowest levels of gross -radioactivity in Kajaran are high vs. natural radiation background in Armenia. The background for the republic makes 500-600Bq/kg [Davtyan, Ananyan, 1963], whereas on Kajaran's territory minimal values are 736Bq/kg. As known, territories with high radiation level are associated with intrusions and deluvium sediments with Th-bearing minerals. [Titaeva, 2000]. As a significant portion of Kajaran's territory is composed by granite-metamorphic rocks (porphyro-granites and monzonites), so high natural radiation background is naturally determined.

The research results are reflected in the map (*Fig. 28*). When mapping, we used a pace 50 Bq/kg. 3 gradations have been obtained. The 1st field with near-background values (758-808 Bq/kg) is located on the east boundary of the city and beyond it, covering the area of Darazami tailing repository. The 2nd level field (808-858 Bq/kg) lies in the rest of the study area (including the city and the group of enterprises). In the west (behind location site of the group of enterprises) and in the north parts of the city 2 field with highest values of gross -radioactivity (858-889 Bq/kg) have been identified.

For more precise assessment of radioactivity of the territory, a detailed analysis of the activity of natural radionuclides ^{226}Ra, ^{232}Th,^{40}K in soils is required.

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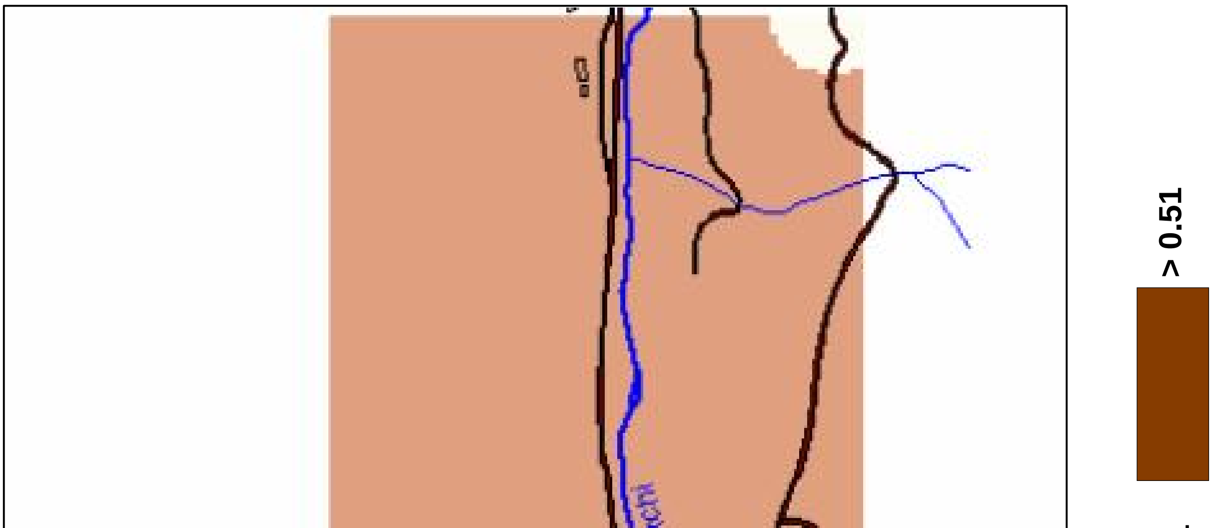

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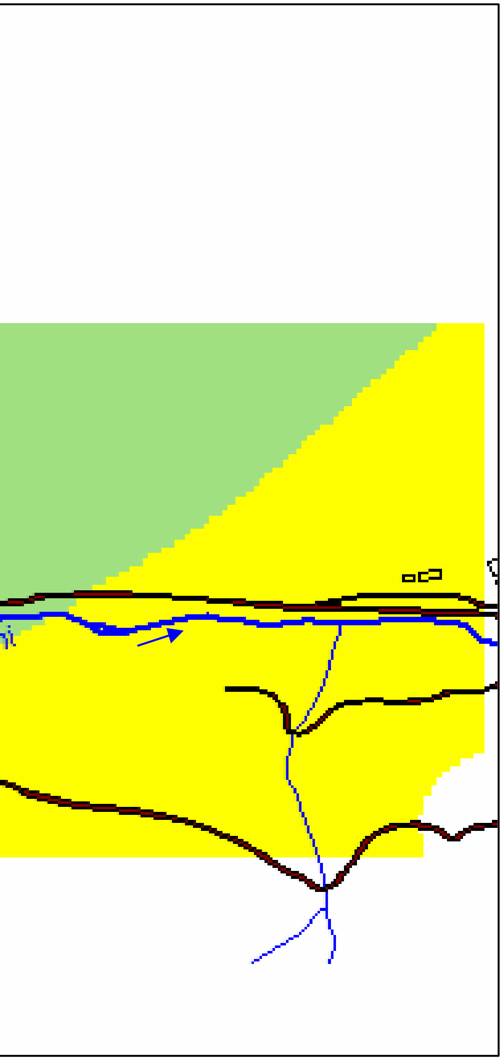

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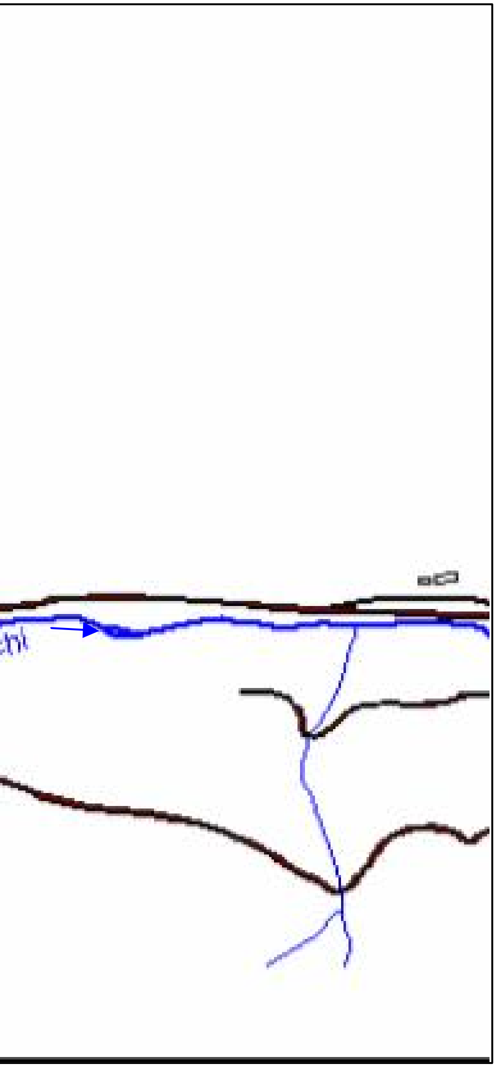

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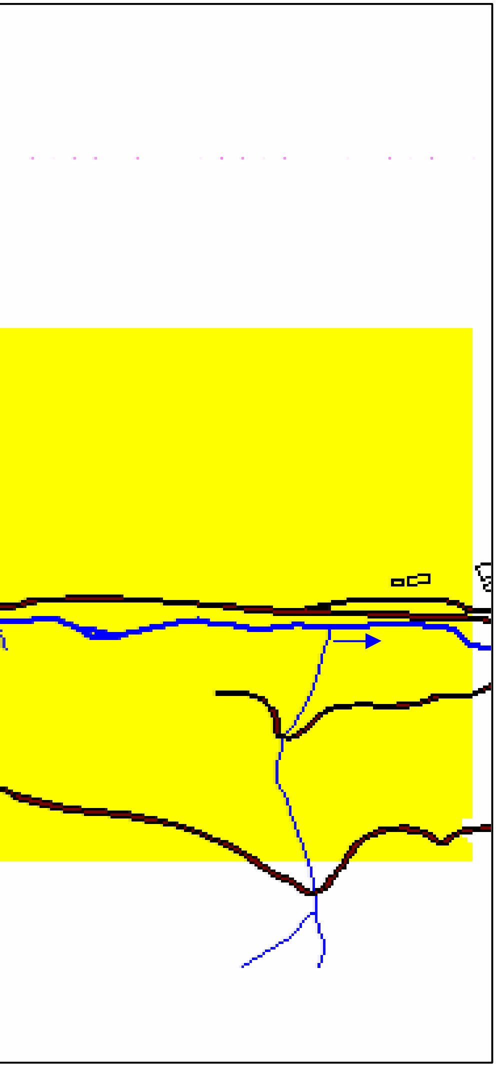

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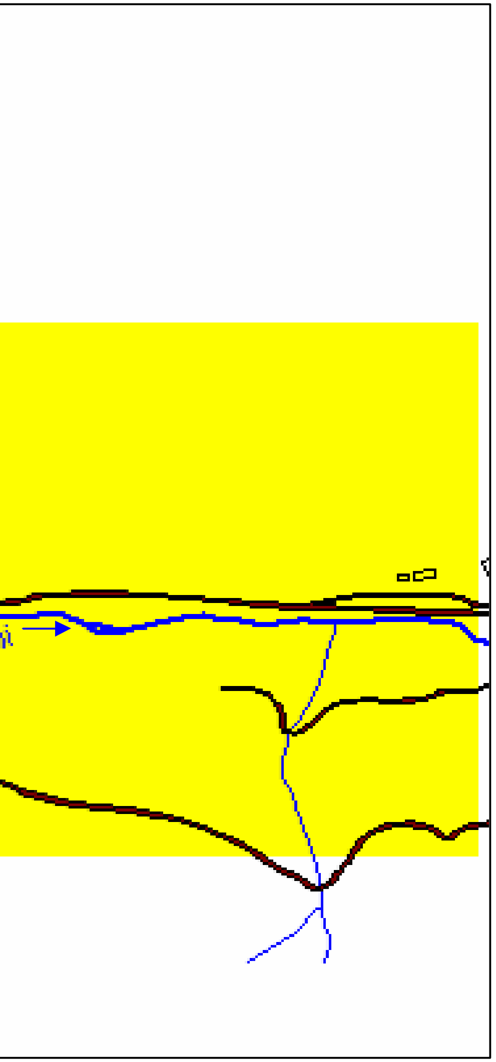

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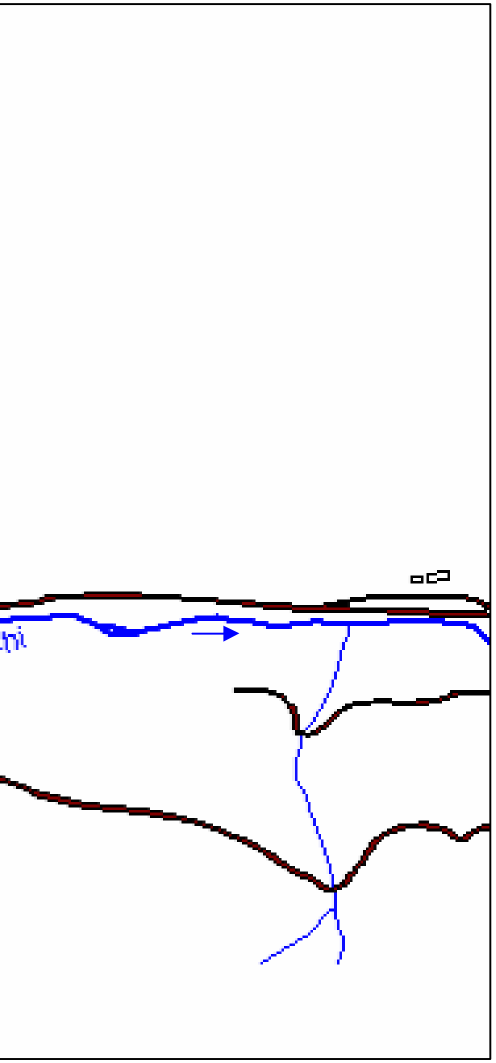

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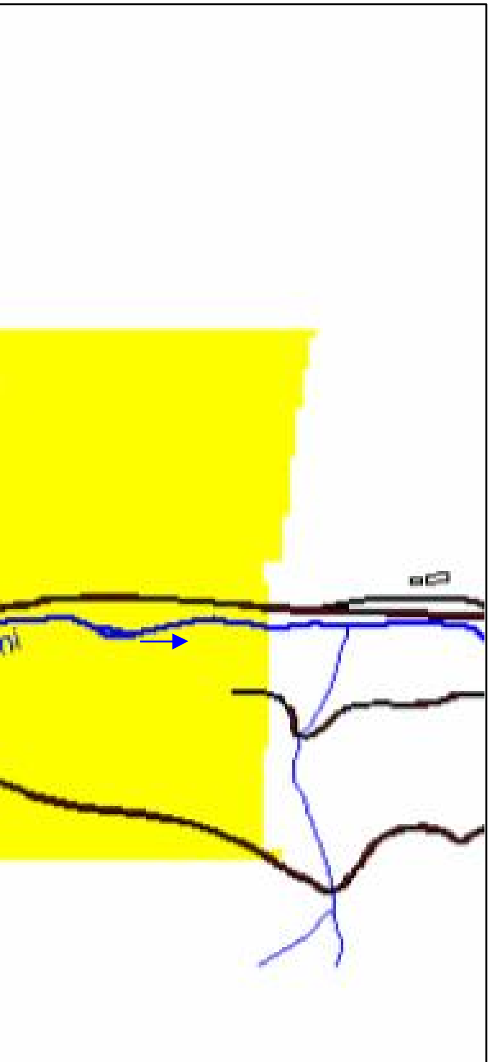

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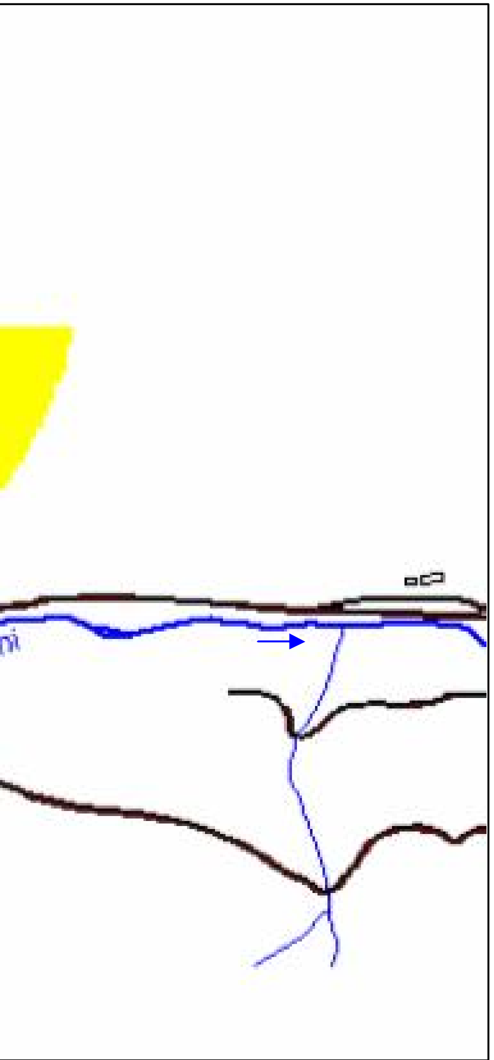

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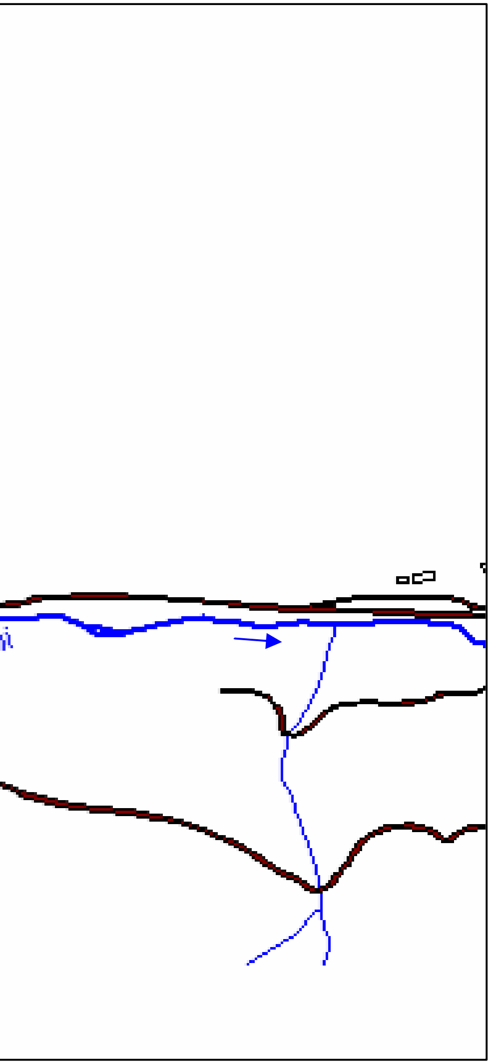

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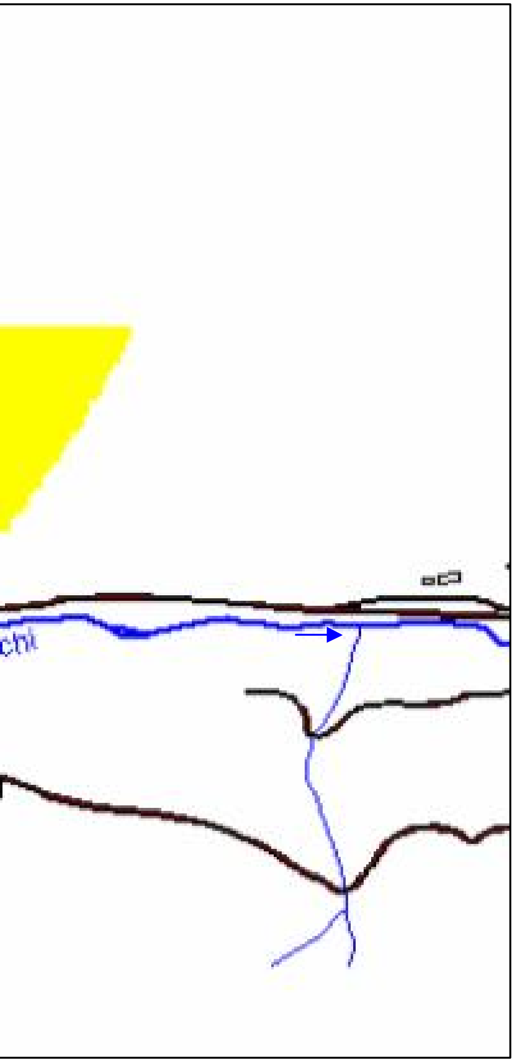

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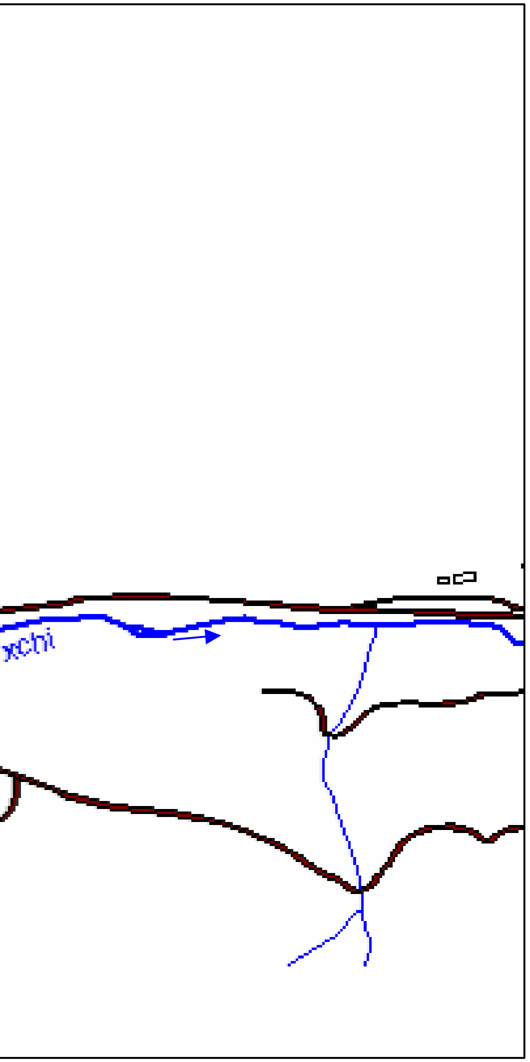

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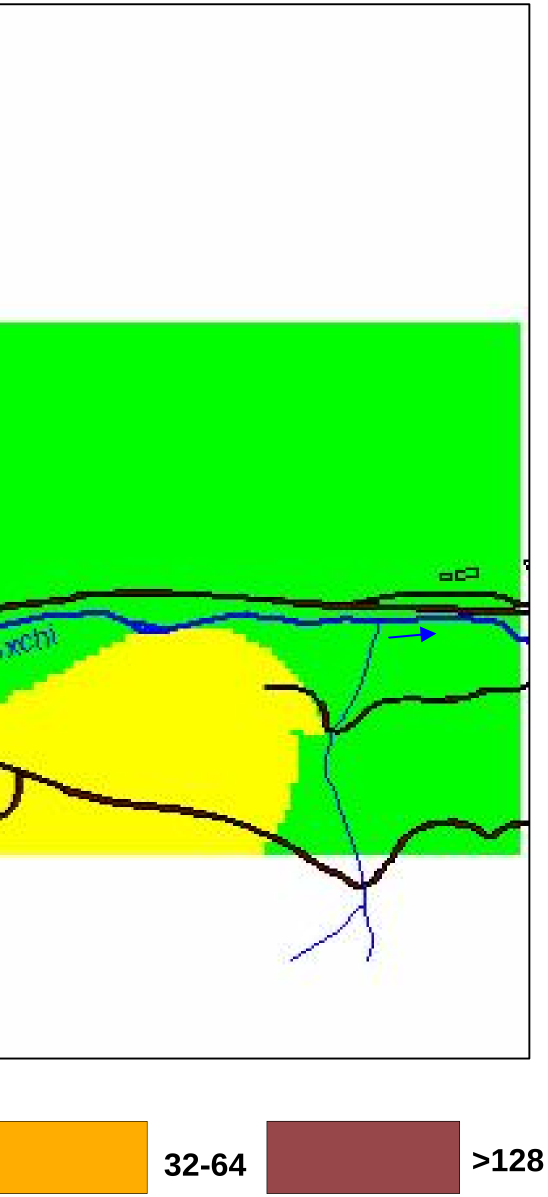
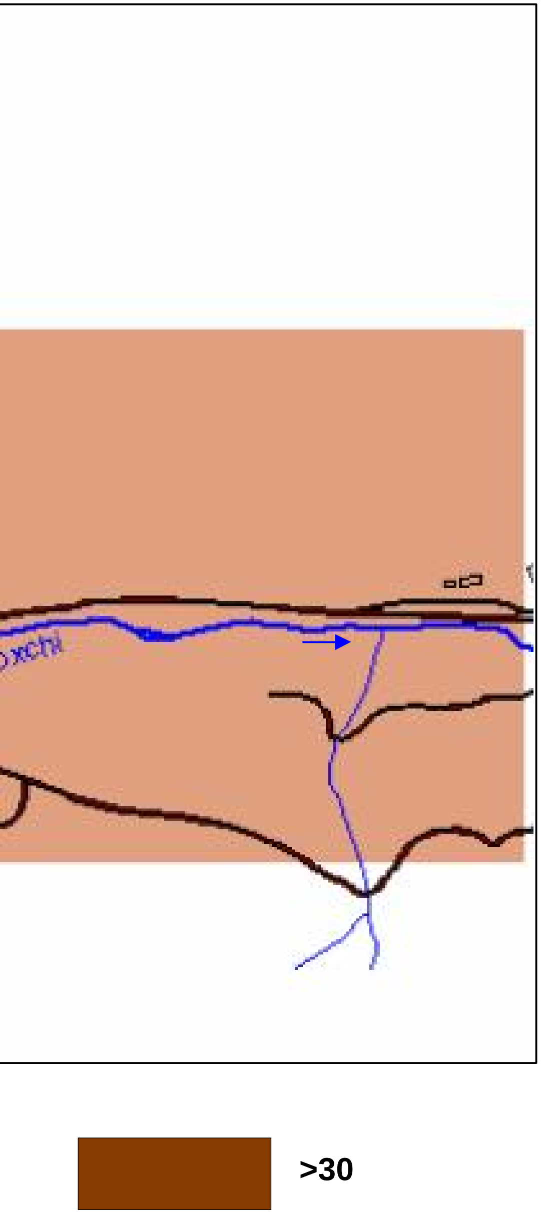


Kajaran's soils



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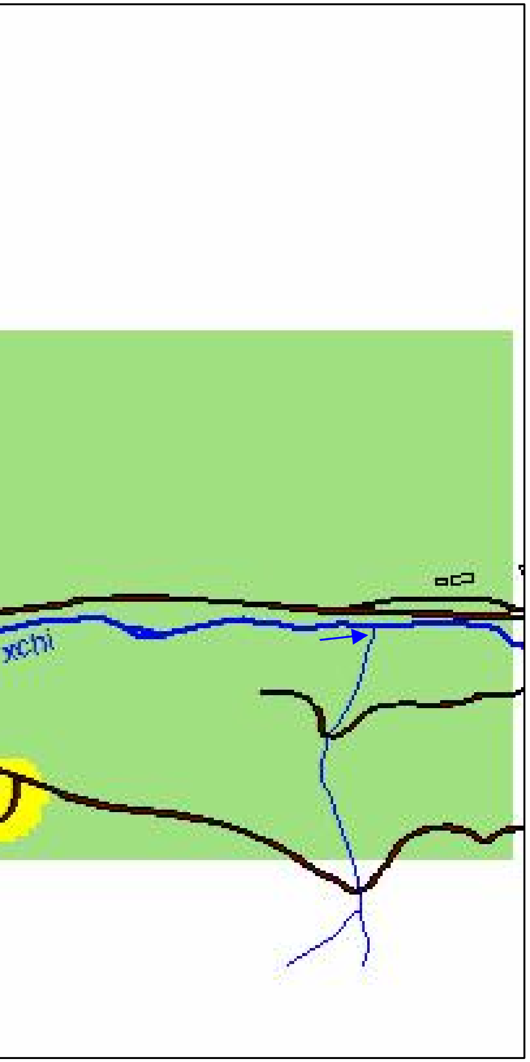

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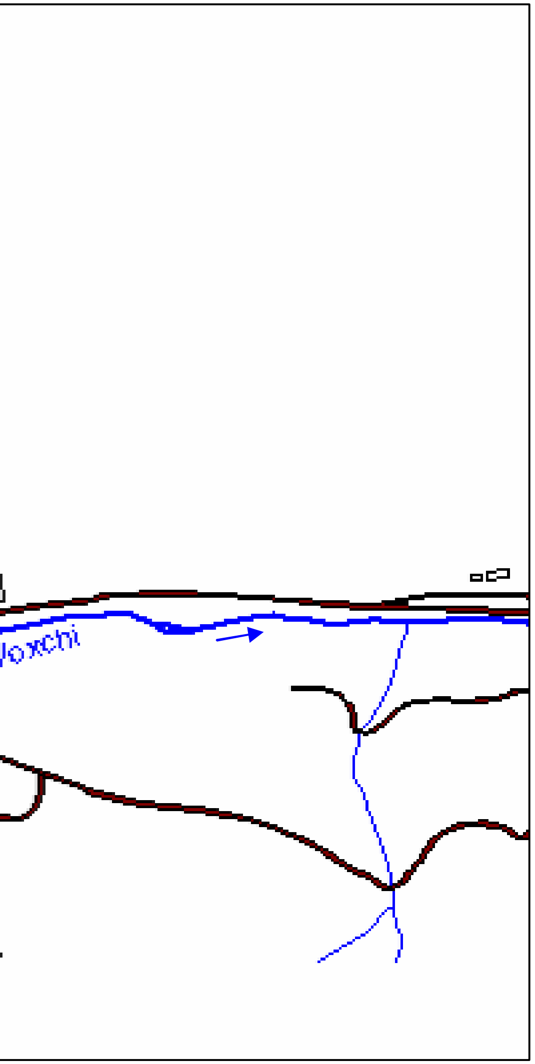

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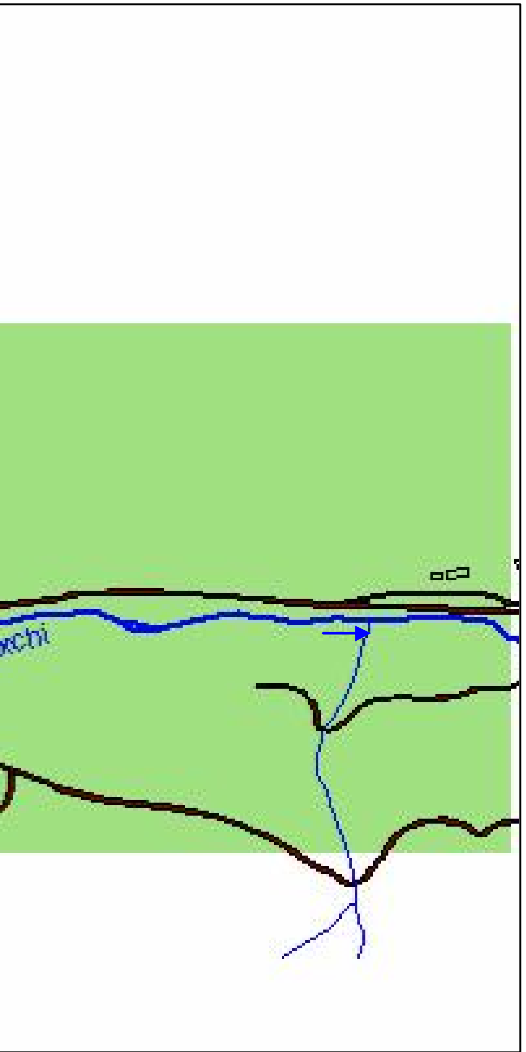

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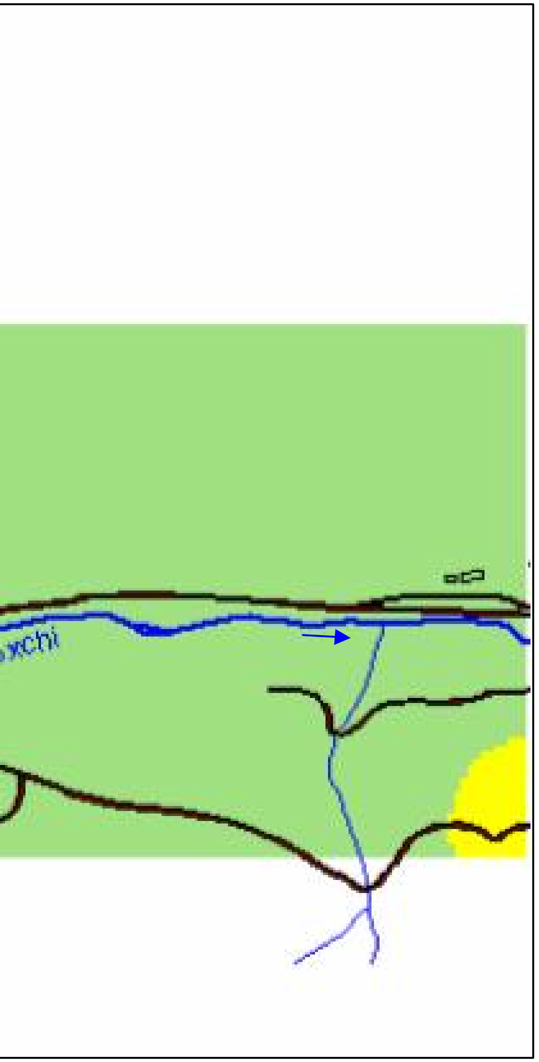
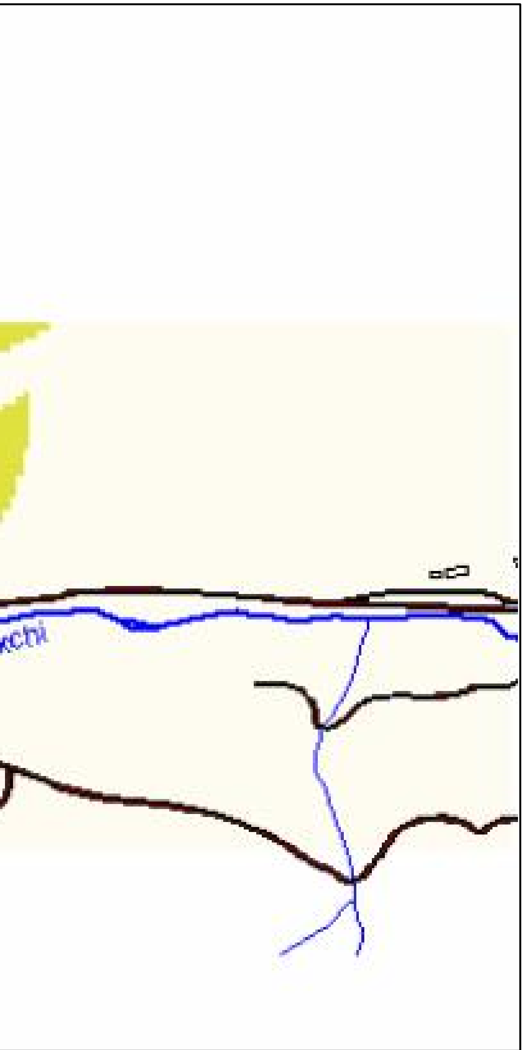


Kajaran’s soils



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4. POLLUTION OF PLANTS IN KAJARAN

4.1. Eco-toxicological assessment of agricultural crops

For eco-toxicological assessment of agricultural crops grown on Kajaran's territory we carried out pilot studies on heavy metal and total nitrogen (N_{total}) accumulation in basic species of vegetable and melon-field species on agricultural sites in the bounds of the city.

4.1.1. *Heavy metal accumulation*

The results of investigations of heavy metal accumulation in basic vegetable and melon-field species grown on the city's territory, are given in *Tab. 7.*

Table 7. Heavy metal contents (*mg/kg* of dry matter) in vegetable and melon-field species on Kajaran's territory.

Points	MAC * / Crops	Mo	Ni	Cr	Cu	Pb	Zn
	MAC *	2.0	0.5	0.2	5.0	0.5	10.0
K9-B	Potatoes	**17.31**	**1.73**	**0.7**	**12.98**	0.54	3.79
K12 -A		**9.14**	**0.91**	**0.7**	**16.87**	**0.7**	4.92
K30B		**164.4**	**1.64**	**0.69**	**8.91**	**0.69**	4.8
K12-B	Beans	**44.18**	**3.31**	**1.03**	**14.2**	**1.03**	5.52
K15 A		**61.04**	**1.42**	**0.82**	**10.9**	**1.09**	7.63
K30 A		**70.2**	**3.0**	**3.0**	**12.17**	**0.94**	6.55
K12-C2	Carrot	**6.5**	**0.87**	**0.65**	**8.66**	**0.87**	6.06
K9-A	Dill	**30.0**	**9.38**	**9.38**	**30.0**	**1.63**	8.75
K12-D		**61.6**	**6.16**	**8.25**	**26.4**	**1.10**	7.70
	MAC **	2.0	0.5	0.1	5.0	0.4	10.0
K12-E	Gooseberries	**17.66**	**1.77**	**0.55**	**9.94**	**0.72**	3.86

Note: MAC according to Dueck et al. [1984], – for vegetables, – for fruits.
Underlined are excessive values vs. MAC.

As seen, the contents of practically all the metals except Zn are excessive vs. MAC. By the sum of heavy metal concentration excess vs. MAC the crops make the following averaged accumulation series:

Dill – Cr-Mo-Ni>Cu-Pb>Zn (summary intensity 92.6);
Beans – Mo>Cr-Ni-Cu-Pb>Zn (summary intensity 47.6);
Potatoes – Mo>Cr-Ni-Cu-Pb>Zn (summary intensity 42.5);
Gooseberries – Mo-Cr-Ni-Cu-Pb>Zn (summary intensity 22);
Carrot – Mo,Cr-Cu,Pb,Ni>Zn (summary intensity 12.3).

As seen, the series are identical for all the crops except dill, and it is Mo – a biophile element, that mostly contributes to the intensity of summary accumulation of heavy metals.

For dill, it is Cr that holds the first position in the quantitative series of heavy metal accumulation. The subsequence of the rest elements is similar to that of other crops.

The lowest pollution level is established for gooseberries and carrot.

High contents of Mo are typical of the whole of Kajaran's ecosystem, whereas eco-toxicological state of the studied vegetable crops grown in the city may preliminary be attributed to middle level of pollution.

However for credible eco-toxicological assessment, the contents of toxic elements should be investigated. Additionally, we studied accumulation of elements of 1st grade of hazard (Hg, As, Cd) in crops grown in home gardens on the right bank of River Voghchi, where high concentrations of these elements are established in waters flowing out from the colliery (KB6) and Darazami tailing repository (KB7).

The obtained results show excessive concentrations of Hg only (*Fig. 29).* Especially high concentration is established for dill 0.8-1 *mg/kg* of dry matter (51.5 time excess vs. MAC). Agricultural lands (K9, K12) where high concentrations of Hg are established, are adjacent to Darazami tailing repository and thus surely experience its impacts.

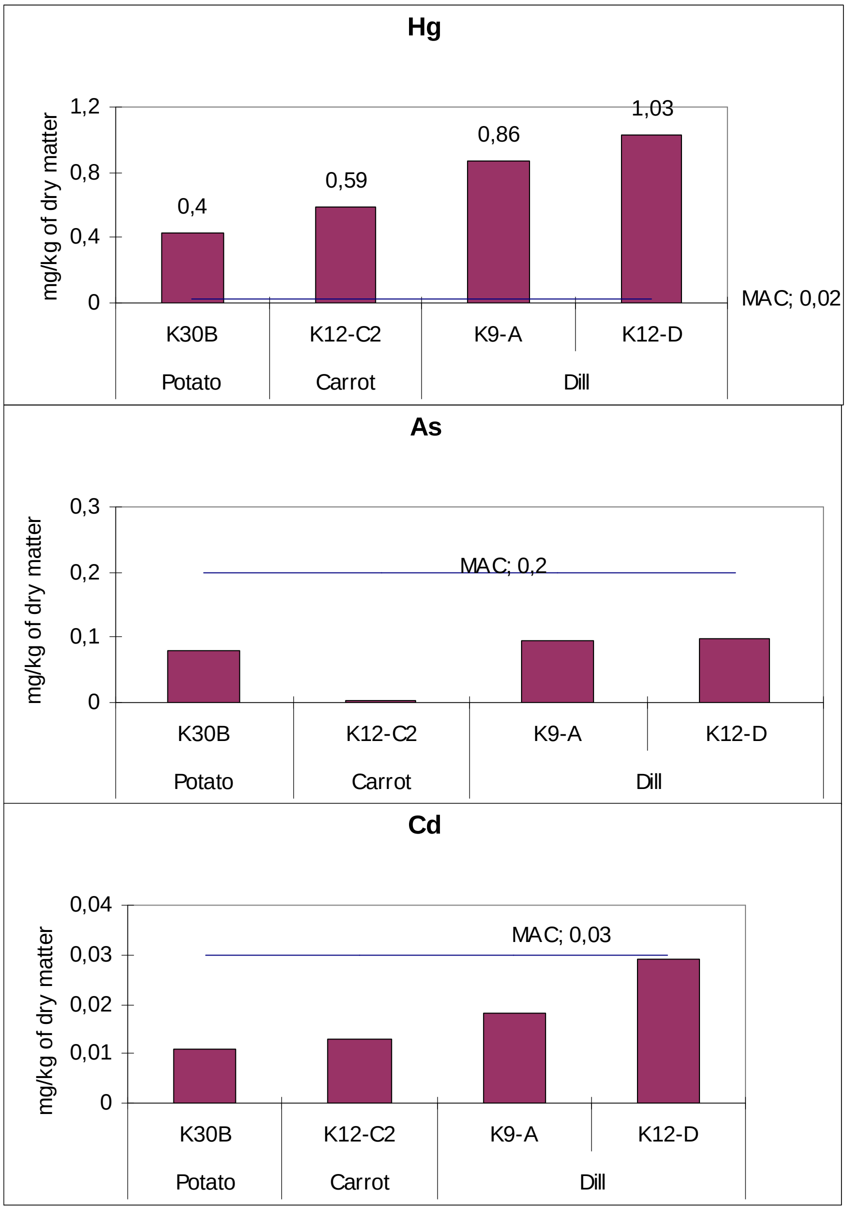

Fig. 29. The contents of toxic elements in vegetables grown on Kajaran's territory.

4.1.2. *The contents of N_{total} in vegetables grown on Kajaran's territory.*

The contents of N in agricultural crops were studied in connection with saltpetre-based explosions in Kajaran deposit colliery. During such explosions a huge dust cloud is formed, and the people are of the opinion that the dust holds large quantities of nitrogen that can accumulate in crops.

Nitrogen being a necessary plant-feeding agent is easily available from the ambient air and soil. Commonly, the contents of nitrous substances (0,5-2,0% of wet mass) in vegetables are less as compared with other plants. This results from larger amount of water in vegetables, except nitrogen catching species. For example, in legumes the content of N_{total} amounts to 5% of dry matter.

The contents of N_{total} in the studied vegetable species show no excess vs. MAC (*Fig.30*). As seen, relatively high concentration of N is established for bean (2,6%) and dill phytomass (1,7%). N contents are low in root crops, and no sharp difference is observed in separate vegetable species.

Supposedly, sulphur pollution of the study territory and respectively soil acidification inhibit exchange processes in plants and hamper nitrate accumulation in them. Simultaneously, acid medium in soils allows mobility of heavy metals, this making them easily available to plants. Mo and Fe are involved in nitrogen exchange process and their high concentration stimulate nitrification process (N rehabilitation) and thus do not allow nitrate accumulation in vegetables.

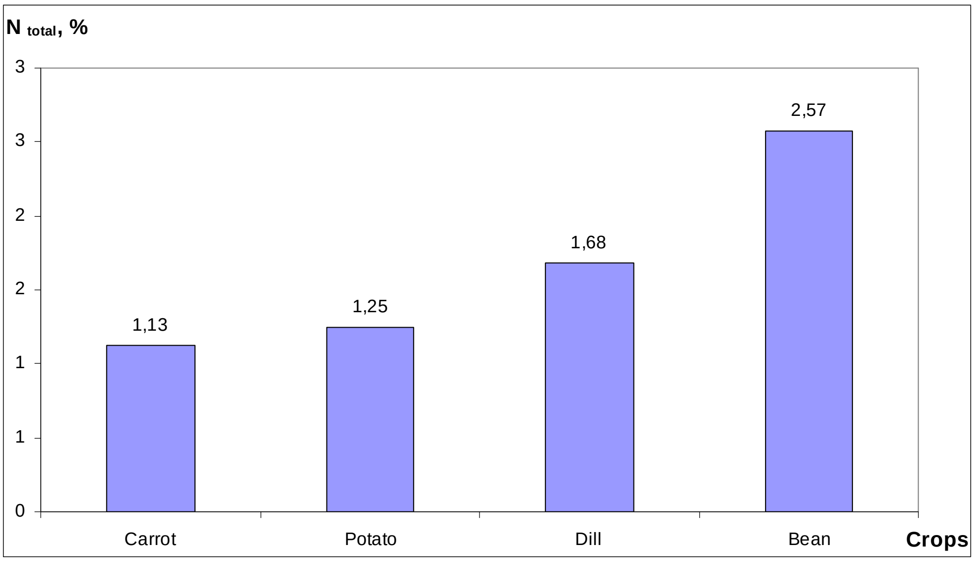

Fig. 30. Mean contents of N_{total} in vegetable and melon- field species on Kajaran's territory.

Possibly, sulphur and heavy metal pollution of the study territory negatively correlates to nitrogen exchange.

To fully make certain that vegetables on Kajaran's territory do not accumulate such toxicants as nitrates and nitrites harmful to the health of the people, a more detailed sanitary-hygienic assessment of the crops is required that should include the analysis of such biochemical indices as nitrogen forms (nitrates, nitrites) and the amount of amino-acids and proteins as well.

Thus, the outcomes of pilot eco-toxicological studies allow concluding that agricultural crops grown on Kajaran's territory accumulate a wide set of heavy metals in which Mo dominates. Dill accumulates highest concentrations of these elements including toxic Hg. It is recommended that dill should be excluded from the set of crops. The level of Hg accumulation in crops makes it necessary to carry out extended eco-toxicological studies covering agricultural lands on the right bank of River Voghchi.

For credible eco-toxicological assessment and functional zoning as well as for the development of an ecologically safe set of crops for Kajaran, detailed studies of all the agricultural lands are required.

4.2. The analysis of heavy metal contents in arboreous plants.

This direction of the research pursued studying metal-accumulation potential of basic arboreous species grown in the city so as to use them for further functional tree planting.

As a background accepted were the element contents beyond the city from where soil and arboreous plant samples were collected during the same time intervals.

Sampled and analyzed were basic tree species grown in the city: oak, maple, hornbeam, poplar, ash-tree.

The analysis of heavy metals contents in leaves of the study trees shows that Mo accumulation is leaves of oriental oak (*Quercus macranthera*) decreases with the remoteness from the works chimney (K34). Near the chimney the established concentration is 2637*mg/kg* (155 time higher background), down the chimney – 81 times, at some distance – 25 times (*Fig.31*).

No precise dependence is detected for accumulation of the rest elements. For further monitoring of Kajaran's environment pollution the oak is preferable.

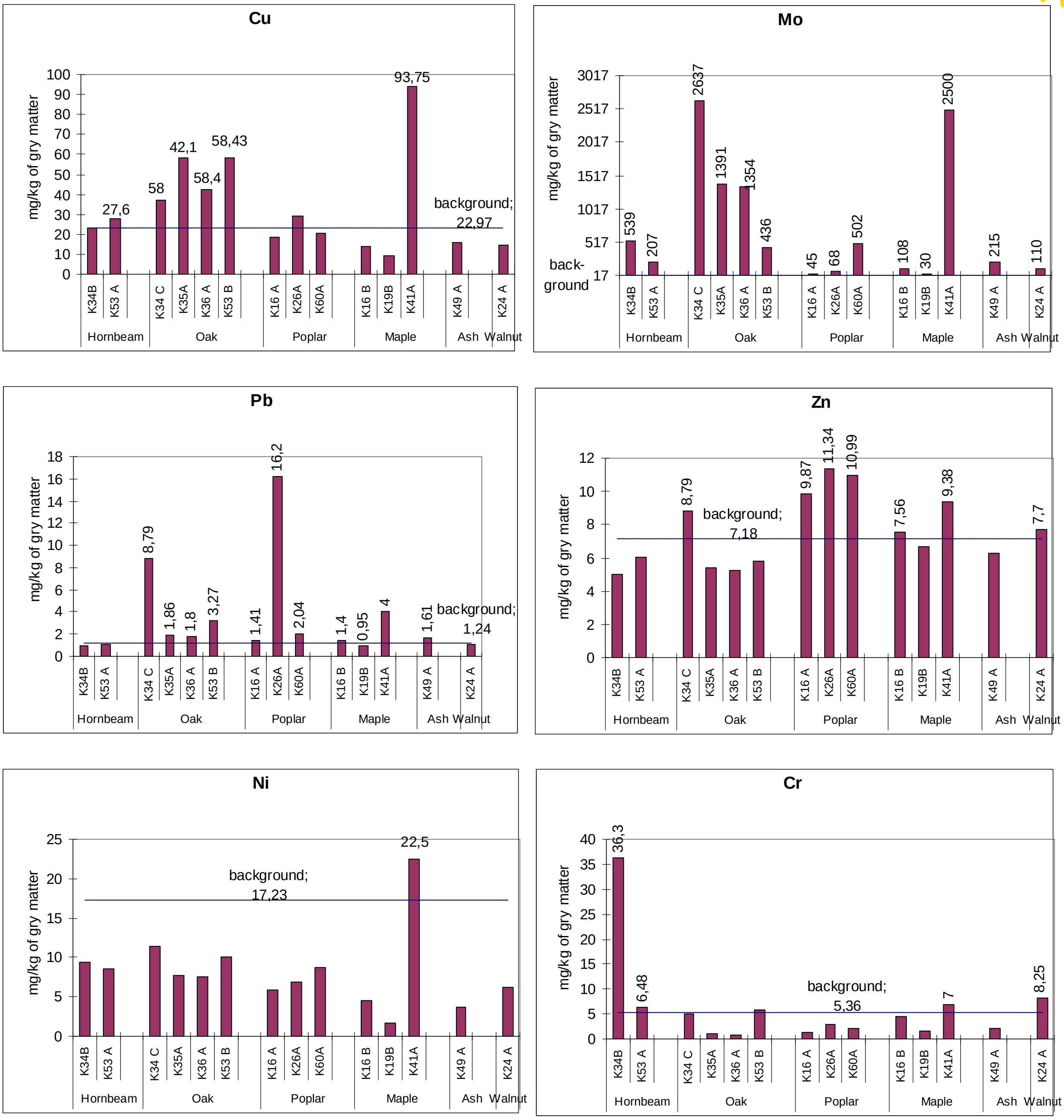

Fig. 31. Heavy metal contents (mg/kg of dry matter) in leaves of trees grown on Kajaran's territory.

Considering separate plant species in respect for Mo accumulation, maple should be singled out beside the oak. The maple accumulates concentrations (2500 *mg/kg*) 147 times higher vs. the background near the group of enterprises in residential part of the city (*Fig.31*). For the same point, elevated concentrations of copper (93.7 *mg/kg*), nickel (22.5 *mg/kg*), lead (4*mg/kg*), and zinc (9.4 *mg/kg*) are established. Rather high metal accumulation potential is typical of poplar, as well.

The noted peculiarities of trees should be considered while contouring functional sanitary-protection zones around the group of enterprises. Only combination of high metal-accumulation properties and long-term tolerance of plants to pollution may serve a prerequisite for creation of a reliable green barrier berween residential and industrial parts of the city.

5. THE ASSESSMENT OF SULPHUR AND NITROGEN IMPACTS UPON KAJARAN'S ECOSYSTEM

The impacts of acid emissions from the group of enterprises were studies due to the citizens' concern and data on environmental damage provided by a number of NGOs (*Figs. 32, 33*).

Fig. 32. Sulphureous anhydride emission from the works chimney.

Fig. 33. An explosion-induced dust cloud over the colliery.

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The impact of acid emissions (SO_x, NO_x) was assessed in two aspects: 1) soil cover acidification, 2) bioindication of sulphur and nitrogen pollution of ambient air.

5.1. The impact of sulphur emission upon physical and chemical indices of soil

To reveal the impact of SO_x emissions upon soil, pH index (logarithm of hydrogen ion concentrations) was measured in water extractions. As seen from *Fig. 34*, its values widely vary 2.17 to 8.25. A clear regularity is established in pH values distribution. Ultra-acid (2-3) and acid (3-6) soils are timed to the territory of the group of enterprises and Darazami tailing repository. The basic portion of soil cover on the city's territory is characterized by weak-acid (pH=6-7), neutral, and weak alkaline (pH=7-8) indices. As soils reflect long-term pollution processes, the established facts evidence local impacts of acid emissions upon the ecosystem.

To clarify the impact of the works-induced acid emissions upon the acidity of soils, additional measurements were made and a schematic map of sulfate ion contents distribution in Kajaran's soils, produced (*Fig. 35*). As seen, sulphur pollution source is the group of enterprises, and in soils around its chimney peak concentrations of sulfate ions are established (3.3-9.3%). The soils of residential parts of the city contain concentrations of sulfate ions 0.037-1.1%. In the eastern part of the city the contents of sulfate ions are low (0.04-0.12%) and are approaching to the accepted standard.

Thus, investigations of the impact of sulphur emissions upon physical and chemical indices of soil cover show that the impact of sulphur is local and covers only the territory of the group of enterprises and partially residential sector of the city. To get a more exhaustive picture, snow surveys are required.

5.2. Bioindication of the ambient air pollution with sulphur and nitrogen

At the request of Kajaran's municipality, to establish the impactof the works-induced acid emissions upon the city's ambient air pollution with regard for the use of ammoniac saltpetre while performing explosions in the colliery, we carried out pilot indication studies of total sulphur and nitrogen accumulation in leaves of basic arboreous plants grown on the city's territory. Plant tolerance by morphology was studied, as well.

5.2.1. *The analysis of sulphur accumulation in arboreous plants*

Bioindication of the impact of sulphur emissions upon Kajaran's environment is conducted based on studies of total sulphur accumulation in leaves of basic tree species. The results of measurements of total sulphur contents in tree leaves are given in *Fig. 36*.

As seen, peak levels of sulhur accumulation are established in leaves of the oak (*Quercus macranthera*, 1.3%), poplar (*Populus nigra*, 0.84%), and ash-tree (*Fraxinus excelsior*, 0.31%). Of the rest species typical is very weak sulphur accumulation approaching to the background (beyond eastern bounds of the city), and they get strongly damaged even in case of very low concentrations (0.08-0.09%) (*Fig. 37*) and loose their hygienic and decorative properties. Especially vulnerable are introduced species – American maple (*Acer negundo*) and indigenous species – hornbeam (*Carpinus betulus*). The leaves of the maple get fully burnt out, whereas the hornbeam gets mainly leaf-brimming injuries (particularly near the chimney, on the slope).

Beside oak, relatively tolerant are poplar and ash-tree, and we preliminary suggest their using in functional tree planting in residential part of the city.

Based on mean values of the contents of total sulphur in leaves of the studied trees (mostly of oak and poplar), a bioindication schematic map was produced showing the city's ambient air pollution with sulphur emissions (*Fig. 38*). As seen, the basic pollution source is focused around the emission source – the works chimney, where sulphur concentrations in leaves varies 0.44 to1.31%.

Fig. 34 **A schematic map of pH value distribution in Kajaran's soils**

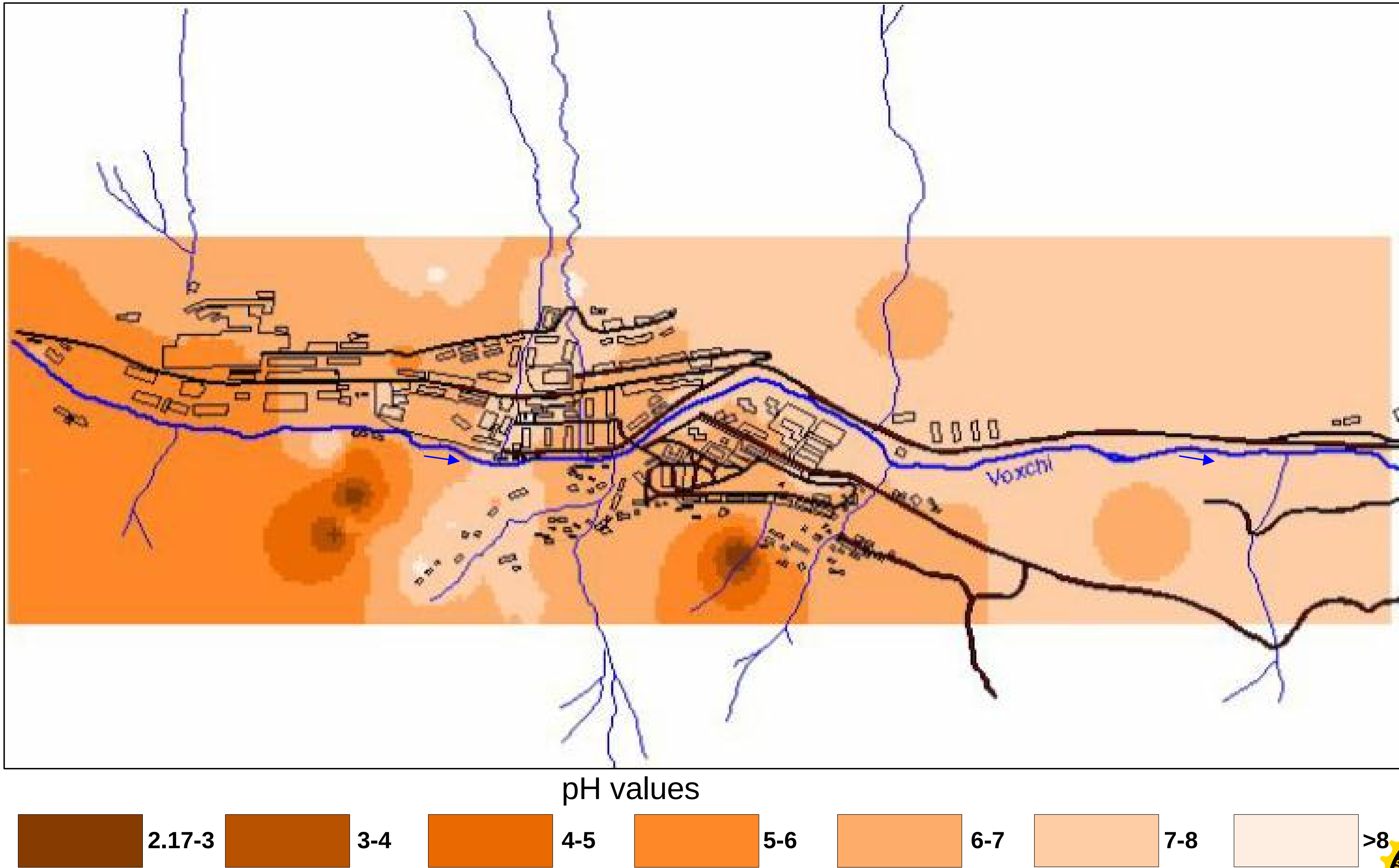
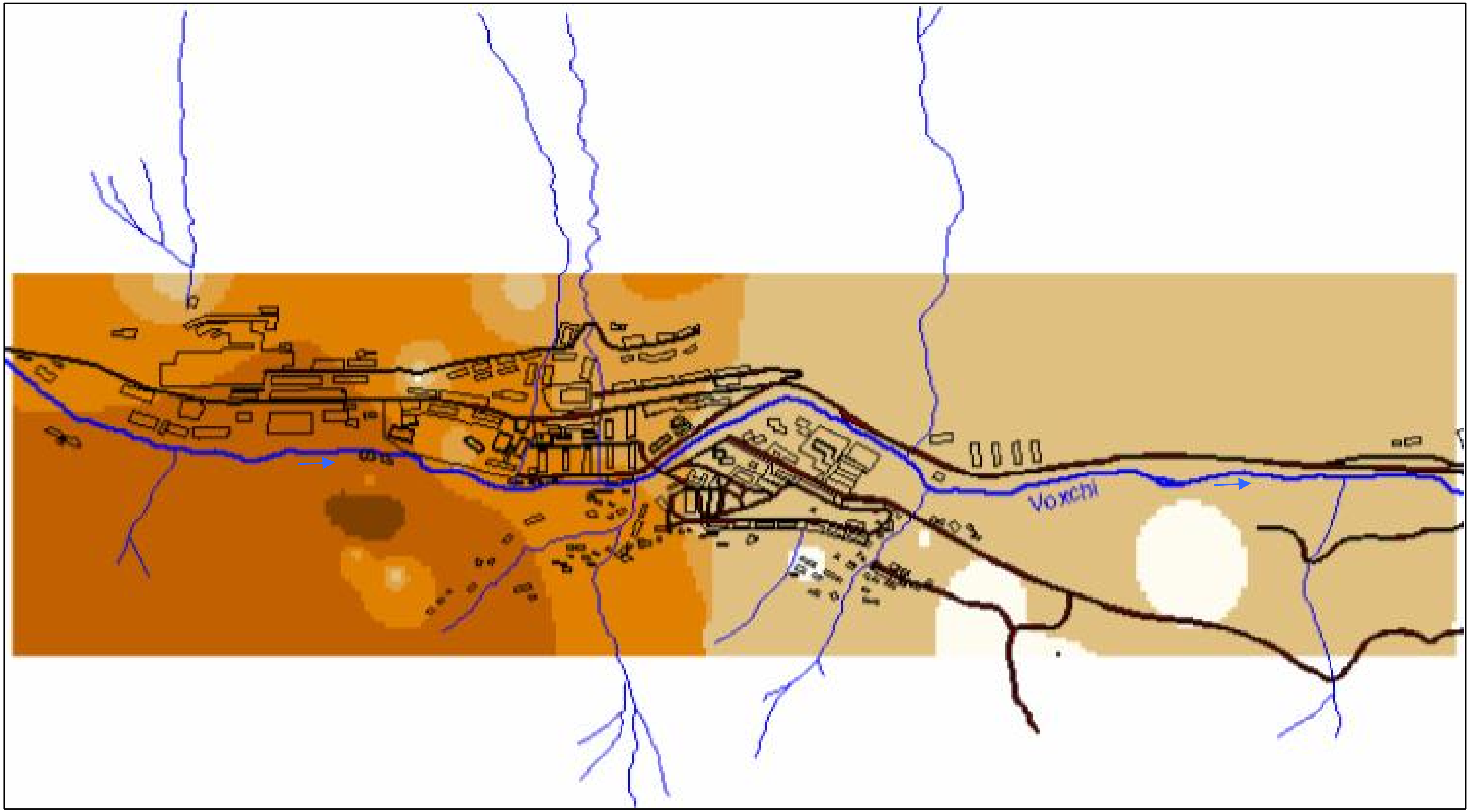


Fig. 35. **A schematic map of distribution of sulfate-ions contents in Kajaran's soils**



The contents of SO_4^{2-} in %

0.01-0.04 **0.04-0.12** **0.12-0.37** **0.37-1.11** **1.11-3.3** **3.3-9.3**

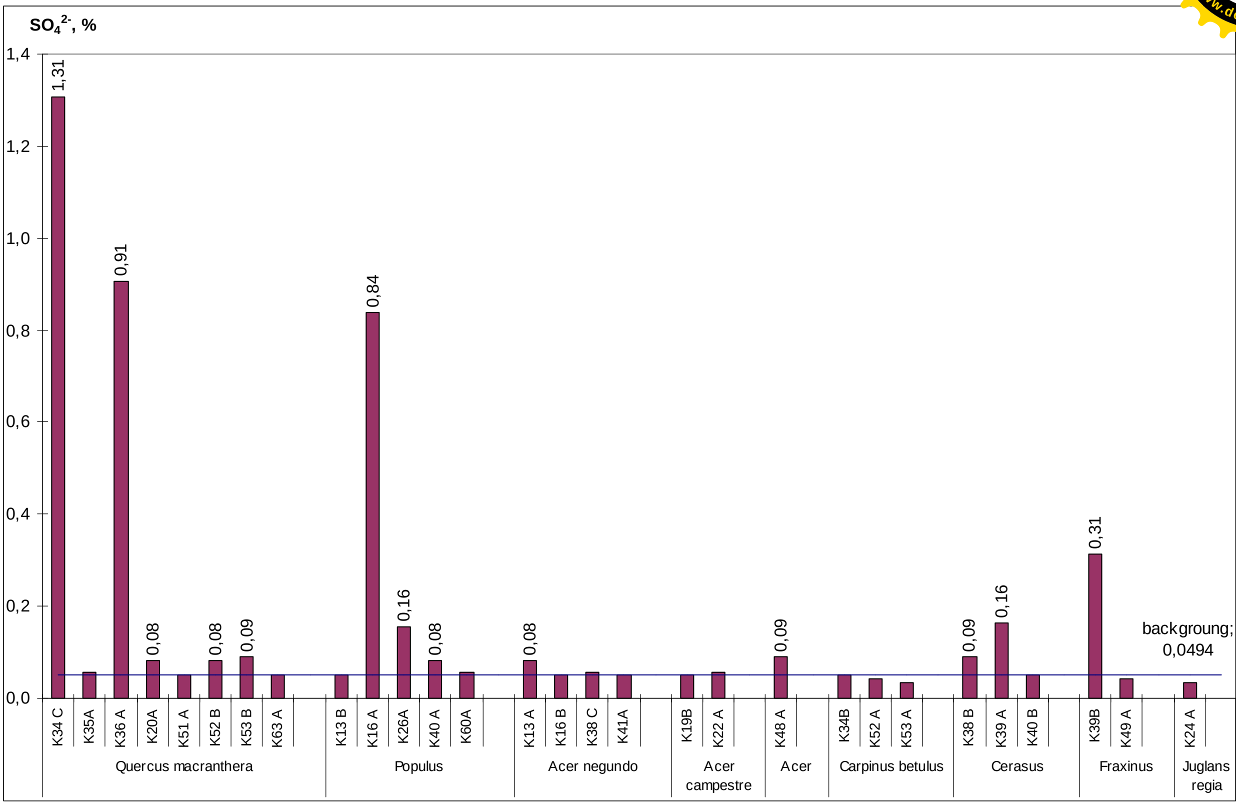


Fig. 36. The contents of total sulphur in leaves of trees grown on Kajaran's territory

Around the emission source toward the territory of the group of enterprises and in west part of the city a field with middle and low concentration of sulphur (0.15-0.44%) is located. A similar field stretches out from the eastern part of the city. As our investigations show, this results from the fact that during active operation time of the works (approximately from 9am to 9pm) the wind-rose shifts smoke-tongue westward, and only by the night time it turns by 180^0 eastward (toward the city). Moreover, as at night the wind is stronger, so the smoke tongue lands not in the center but on east bound of the city (Fig. 39).

Wholly, one may conclude that sulphur emissions are localized and no extended pollution of the city's ambient air is established.

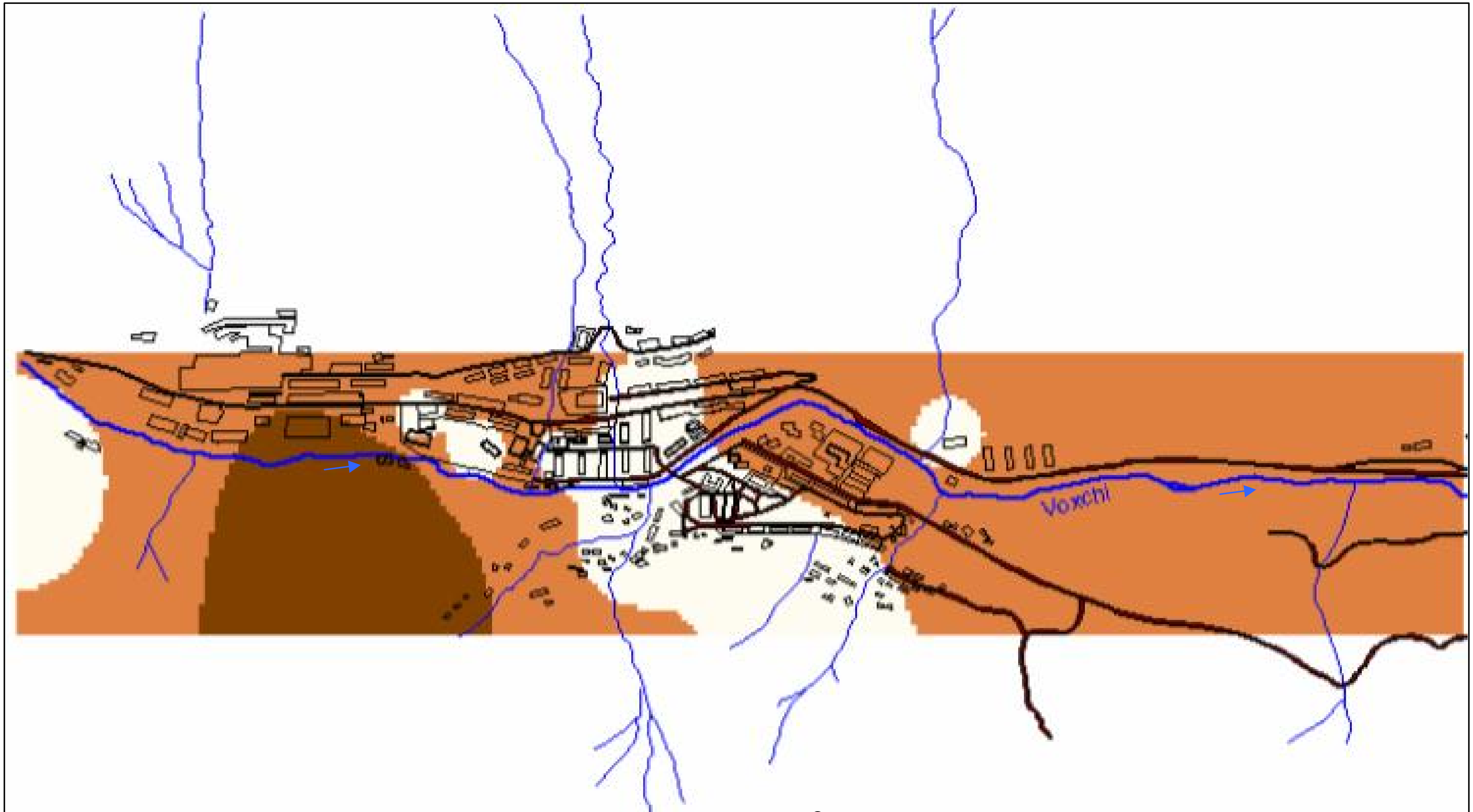
Acer negundo *Acer campestre*

Fig. 37a*.* Sulhur-induced injuries of tree leaves on Kajaran's territory.

Fig. 37b*.* Sulhur-induced injuries of tree leaves on Kajaran's territory.

Fig. 39. Sulphuric anhydride-induced injuries in leaves of trees exposed to the impact of the chimney (left: leaves of *Quercus macrathera*) and on the smoke-tongue landing site (right: leaves of *Bryonia alba*).

Fig. 38. **A schematic map of distribution of total sulphur contents in leaves of trees on Kajaran's territory**



The contents of SO_4^{2-} in %

0.049-0.15 **0.15-0.44** **0.44-1.31**

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5.2.2. *The contents of N_{total} in arboreous plants.*

Nitrogen – one of basic elements necessary for all living organisms, is a constituent of amino-acids, proteins and so on.

The increase in N concentrations to a certain extend allows activation of a number of very important metabolic processes. However its excessive concentrations in plants entail disturbances in metabolic processes.

Mean accepted contents of N in plants are 1.5-3% in dry matter.

Plants absorb nitric compounds mainly from the ambient air and are very sensitive to them due to autotrophic character of metabolism. High plants absorbing ammonium and nitric hydroxides from the air and assimilating them include N in nitric compounds in different organs (leaves, roots, stems etc.). The plants that absorb and intensively transform gaseous compounds of N and have large biomass, may be used in biological cleanup of the air.

We have investigated the contents of N_{total} in the leaves of the trees grown on Kajaran's territory. As established, mean concentrations of N_{total} in leaves of 7 basic tree species used in tree planting in the city and its vicinities are not excessive vs.MAC (*Fig. 40*).

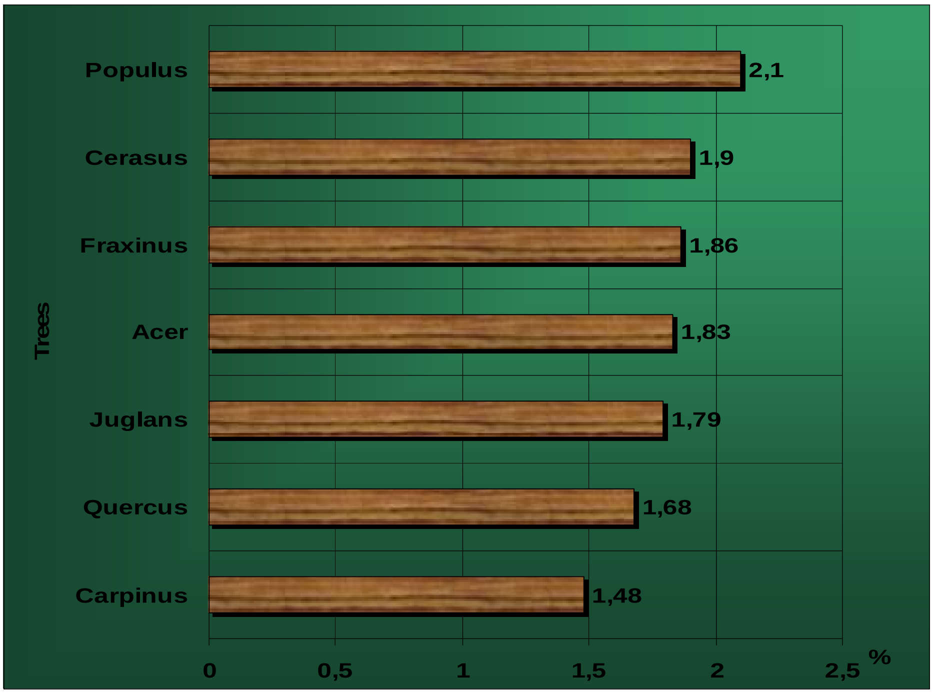

Fig. 40. Mean contents of N_{totla} (%) in leaves of trees grown in Kajaran.

No distinct regularities in N distribution is observed, and the relationships of concentrations and separate parts of the city is detected only at a level of mean values (*Fig. 40*). The contents of N_{total} increases toward the center of the city: the lowest concentrations – 1.4-1.6%, peak – 2.0-2.7% in dry matter.

Of all the study plant species particular interesting are maple, poplar, and oak that are widely spread allover the territory. As seen from Fig. 41, it is the maple and poplar leaves that accumulate highest concentrations of N (2.7 and 2.5%, respectively).

As known, the level of plants tolerance to gases correlates to high level of accumulation of N_{total} in leaves. Simultaneously the increase in total contents of N is an active protection-adaptation response aimed to metabolisation of accumulated toxicants and improvement of tolerance under unfavorable conditions [Sergeychik, 1994]. In this respect, maple, poplar and oak may be tolerant species in tree planting. However, of trees that experience stresses disturbance of natural balance of feeding elements is typical. Our studies allowed revealing strong sulphur – induced injuries in the leaves of maple exposed to the impact of the group of enterprises.

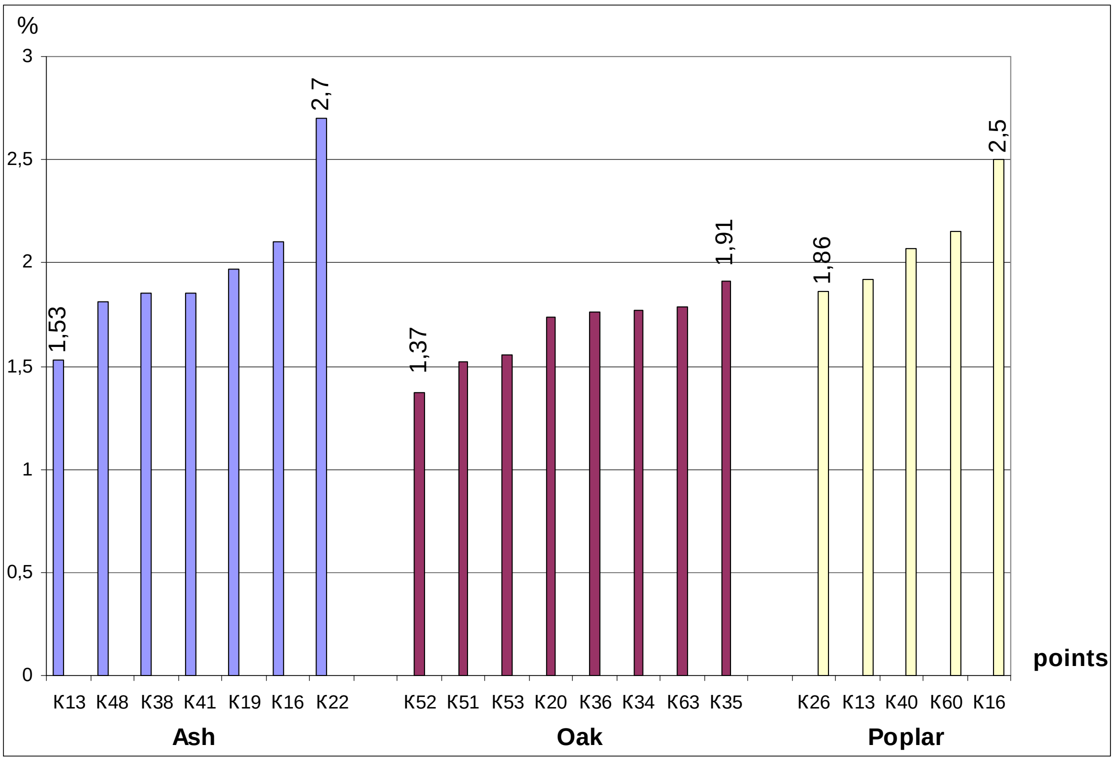

Fig. 41. Concentrations of N_{total} in leaves of basic tree species grown on Kajaran's territory.

The stated facts testify to the necessity of detailed biochemical studies (and nitric compound forms in particular) so as to identify the most effective and tolerant set of species to be used in functional tree planting on Kajaran's territory.

Thus, bioindication studies showed no excessive contents of N_{total} in tree leaves, and, therefore, no nitrogen pollution is detected on the city's territory.

5.3. Approaches to functional tree planting on Kajaran's territory.

As our investigations indicated that the species composition of dendroflora is scarce in the city. Mainly, it is represented by species widely used in tree planting throughout the republic (*Acer negundo, A. campestre, Populus nigra, Fraxinus excelsior*), and only on northern slopes – by indigenous species (*Quercus macrnthera, Carpinus betulus*). This and there in the city, *Juglans regia, Robinia pseudoacacia,* etc. are met with.

However, only the oak, ash-tree and poplar are relatively tolerant to pollution with acid emissions. For this, to develop a functional tree planting plan for residential part of the city it is suggested using the noted species, including elm as it, too, is relatively tolerant to acid emissions. All this may be put into being through additional studies and development of a set of tolerant and decorative species.

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6. ECOLOGICAL ASSESSMENT OF TAILING REPOSITORIES

During Soviet era, the tailing repositories of Kajaran group of enterprises were covered by re-cultivation soil layer. However, re-cultivation actions are far from being efficient when recovering soil and vegetation cover, and often may even cause long-term ecological damage. Storing mining production-induced waste creates new sources of secondary pollution. For recent decades, the surface of the tailing repositories got eroded due to wind and water erosion. This results in active migration of heavy metals that are contained in tailing repository stuffs and thus actively pollute the components of the ecosystem (soils, waters, plants).

Following the project task, we assessed pollution of the sites of the 3 tailing repositories of the group of enterprises (Darazami, Pkhrut, Voghchi) located in the canyons of River Voghchi tributaries.

6.1. Heavy metals in soils and grounds and slimes of tailing repositories

Heavy metal contents in soils and grounds and slimes of the tailing repositories were studied from sanitary-hygienic positions.

1. ***Darazsami tailing*** repository with capacity of some 3mln m^3 is located on River Voghchi right-bank tributary, near Darazami village and covers an area of some 20 hectares. Territorially, the tailing repository is adjacent to the suburbs of Kajaran.

   Soil and plant sampling points are shown in *Fig. 42*.

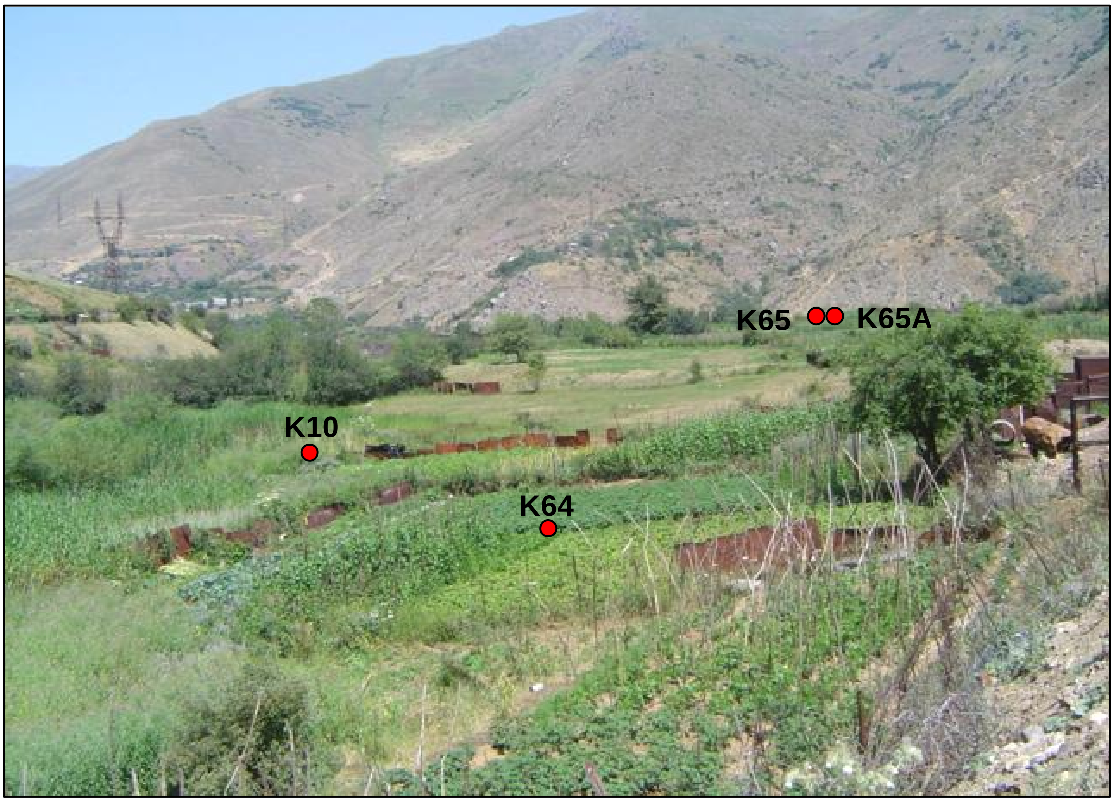

Fig. 42. Soil and plant sampling points on Darazami tailing repository site.

According to data obtained (*Tab. 8*), for Darazami tailing repository soils and grounds high contents of Mo, Cu, Ni, Co, V are common. Peak excessive values vs. MAC are typical of Mo (36 times), Co (8.4 times), and Ni (8 times). No excessive contents for the rest of elements are established.

For exhaustive eco-toxicological characteristic of the tailing repositories, additional analyses were performed for availability of elements of the 1st grade of hazard (Hg, As, Cd) in re-cultivation soil and ground layer (*Fig. 43*).

Table 8. Excessive concentrations of heavy metals vs. MAC (*mg/kg*) in soils and grounds of Darazami tailing repository.

Heavy metals	MAC [1]	n=4		
		min.	max.	mean
Mo	5.0*	**11.2**	**36.0**	**22.5**
Cu	100*	**1.3**	**4.2**	**2.4**
Pb	100*	0.1	0.2	0.2
Sn	50.0*	0.08	0.08	0.08
Zn	300*	0.2	0.2	0.2
Mn	1500	0.09	0.3	0.2
Ni	4.0	**6.0**	**8.0**	**7.0**
Cr	100*	0.1	0.4	0.3
Co	5.0	**3.6**	**8.4**	**6.3**
V	100*	1.0	**2.4**	**1.7**

[1]* MAC according to A. Kloke [1980], – Mn, Ni, Co – по “Ecology…” [1993]. Underlined are excessive values vs. MAC.

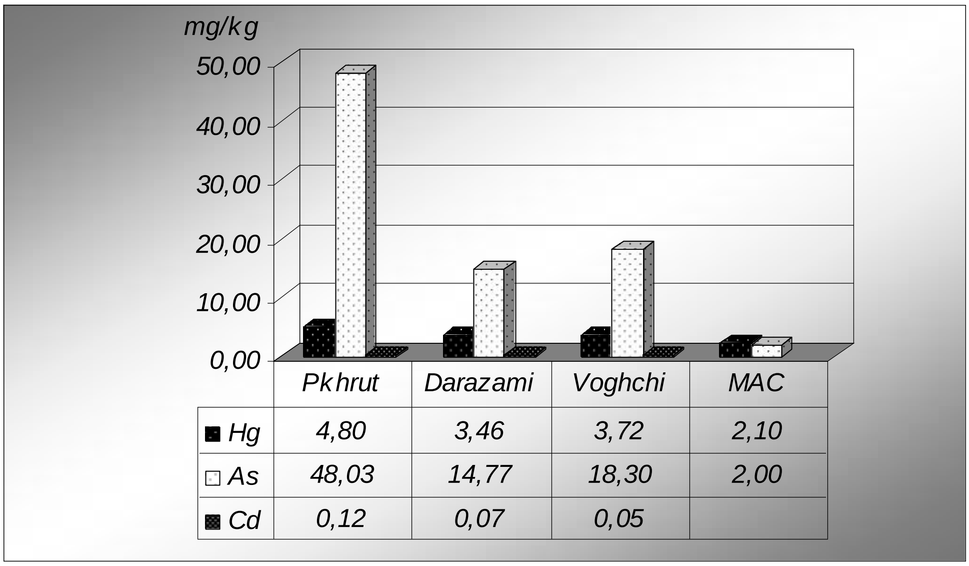

Fig. 43. The contents of elements of the 1st grade of hazard in the soils and grounds of the tailing repositories.

The investigations allowed identifying all the studied toxic metals in soils and grounds of Darazami tailing repository. Hg concentration in Darazami is 1.6 times high vs. the rest tailing repositories. This results in presence of mercury in the waters of aqueduct.

Also, established are harmful concentrations of arsenic (7 fold excess vs.MAC). Our studies showed (*Tab. 4*) insignificant contents of arsenic (2.3 *mkg/L*) in the waters of aqueduct vs. MAC (50 *mkg/L*). Likely, arsenic is mainly bound and weak mobile. To prove this, additional investigations are required.

In soils and grounds of the tailing repository, cadmium has been identified, as well.

We also investigated heavy metal distribution by separate sectors of the tailing repository (*Fig. 44*). As seen from *Fig. 45*, Mo contents are 2 times excessive on the eroded slope in the area of Darazami tailing repository, in upper 15*cm* – thick soil layer (soils and grounds), vs. tailing stuffs. On this layer Mo concentrations are 36 times excessive vs.MAC, at a depth 50 *cm* – 15 times.

Cu concentration increases with depth 240 to 420 *mg/kg*. Cu concentrations on these sectors exceed MAC 2.4 to 4.2 times, respectively. Similar situation is established for Co concentrations: with depth it increases from 18 to 42 *mg/kg*.

Ni, V, Cr by-sector distribution is even and makes 24, 180, 10 *mg/kg*, respectively. Excessive are Ni and V concentrations, by 6 and 1.8 times, respectively.

Fig. 44. By-sector sampling in Darazami tailing repository.

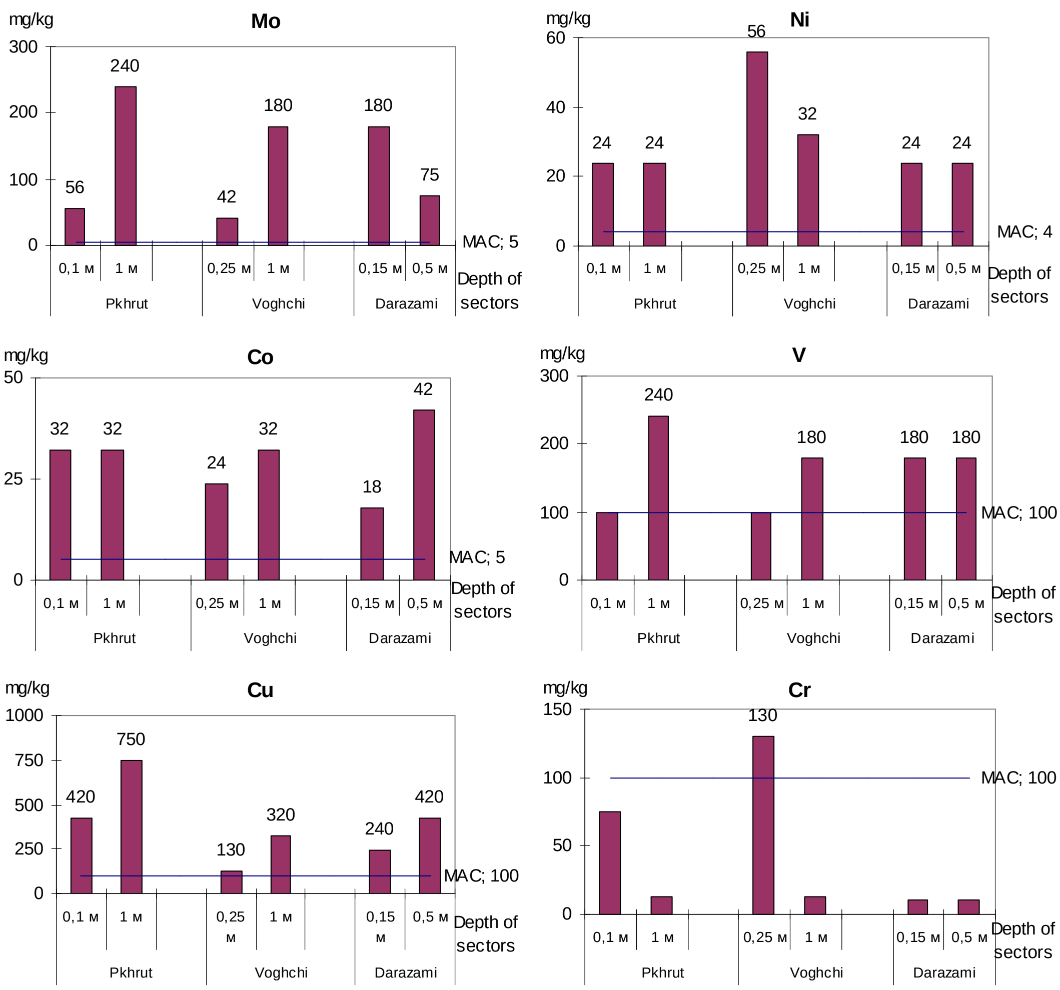

Fig. 45. Heavy metals contents by sectors of the tailing repositories.

2. ***Pkhrut tailing repository***. Territorially the tailing repository is located beyond Kajaran c[illegible] near Darazami, on the right bank of River Voghchi, near Pkhrut village. Its area is 35 hectares, capacity-some 3.2 mln m^3.

Soil and plant sampling points are shown in *Fig. 46*.

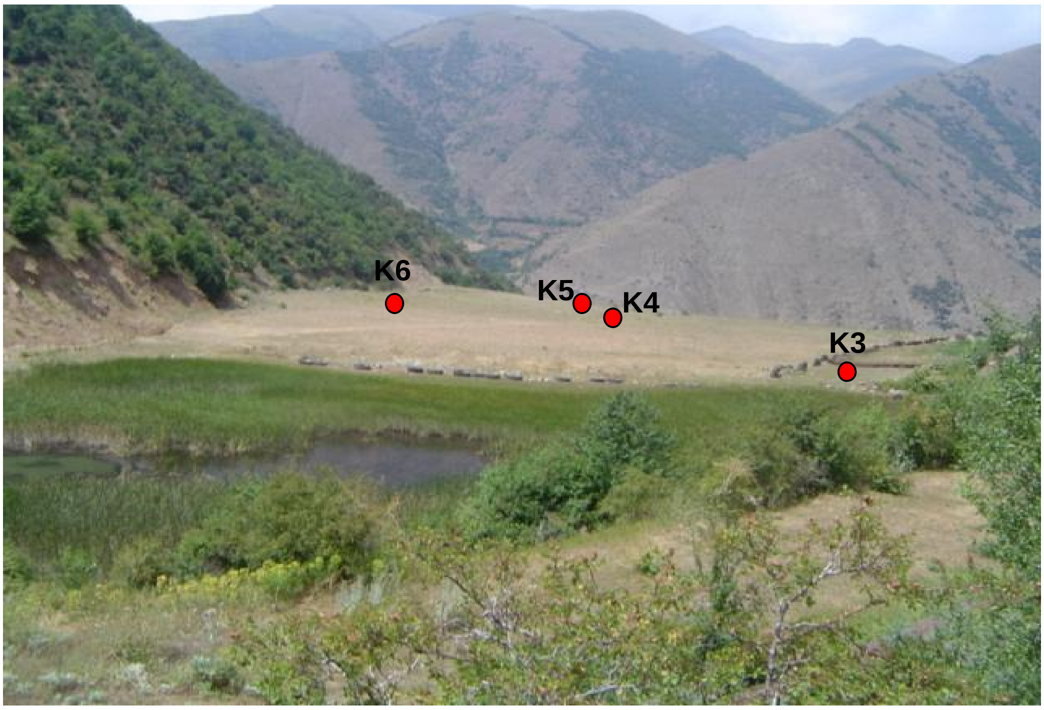

Fig. 46. Soil and plant sampling points on Pkhrut tailing repository.

Table 9 gives calculations of excessive contents of metals in soils and grounds of the tailing repository. As seen, high contents are established for Mo, Cu, V only. Maximal excess of MAC is 48, 7.5, 6.4 times, respectively, this being high vs.soils and grounds of the rest tailing repositories. No excessive contents for rest elements are established.

Table 9. MAC (*mg/kg*) exceeding concentrations of heavy metals in soils and grounds of Pkhrut tailing repository.

Heavy metals	MAC [1]	n=4		
		min.	max.	mean
Mo	5.0*	**11.2**	**48.0**	**21.4**
Cu	100*	**2.4**	**7.5**	**4.6**
Pb	100*	0.1	0.6	0.2
Sn	50.0*	0.05	0.06	0.06
Zn	300*	0.2	0.2	0.2
Mn	1500	0.4	0.5	0.4
Ni	4.0	0.001	0.008	0.005
Cr	100*	0.1	0.7	0.5
Co	5.0	0.002	0.003	0.003
V	100*	**4.8**	**6.4**	**6.0**

[1]* MAC according to A. Kloke [1980], – Mn, Ni, Co – по “Ecology…” [1993].
Underlined are excessive values vs. MAC.

The analysis of contents of elements of 1st grade of hazard (Hg, As, Cd) on re-cultivation soil and ground layer (*Fig. 43*) of Pkhrut tailing repository vs. the rest tailing repositories show the highest contents of Hg (4.8 *mg/kg*; 2.3. time excess vs. MAC), As (48.03 *mg/kg*; 24 time excess vs. MAC), Cd (0.12 *mg/kg*). Such a situation is to be considered hazardous, as all these elements despite compound forms, really threaten all the components of the ecosystem.

Additional investigations were carried out for heavy metal distribution by vertical sector of the tailing repository (*Fig. 47*).

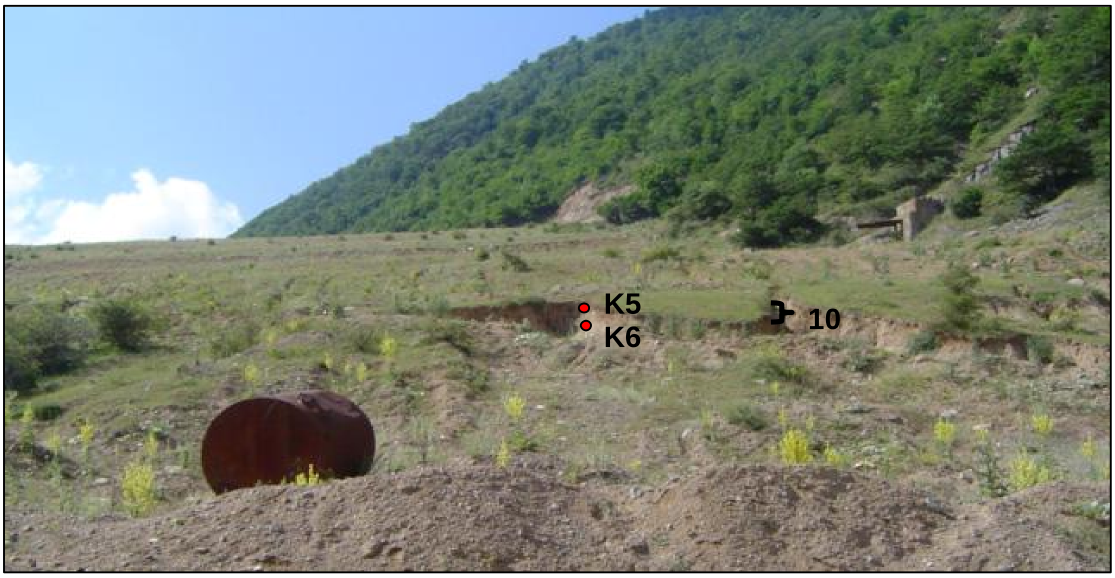

Fig. 47. By-sector sampling in Pkhrut tailing repository

The investigations showed (*Fig. 45*) that on the tailing repository, Mo concentration increases by 4 times with the depth (56 to 240 *mg/kg*). All the concentrations show 10 to 48 time excess vs. MAC.

The same is true for Cu (420 to 750 *mg/kg*). Co concentration on these layers is 4.2 and 7.5 time excessive, respectively.

Co and Ni concentrations are homogenous for all the layers and show six-fold excess vs. MAC respectively.

V concentration in upper sectors of the tailing repository do not exceed MAC. It increases at a depth 1*m* exceeding MAC 2.4 times.

Cr contents in soil and grounds are high vs. slime, however no high (MAC exceeding) concentrations are established.

3. ***Voghchi tailing repository*** located in River Voghchi canyon is the biggest tailing repository by its area (70 hectares) and slime capacity (some 30 mln m^3).

Soil and plant sampling points are shown in *Fig. 48*.

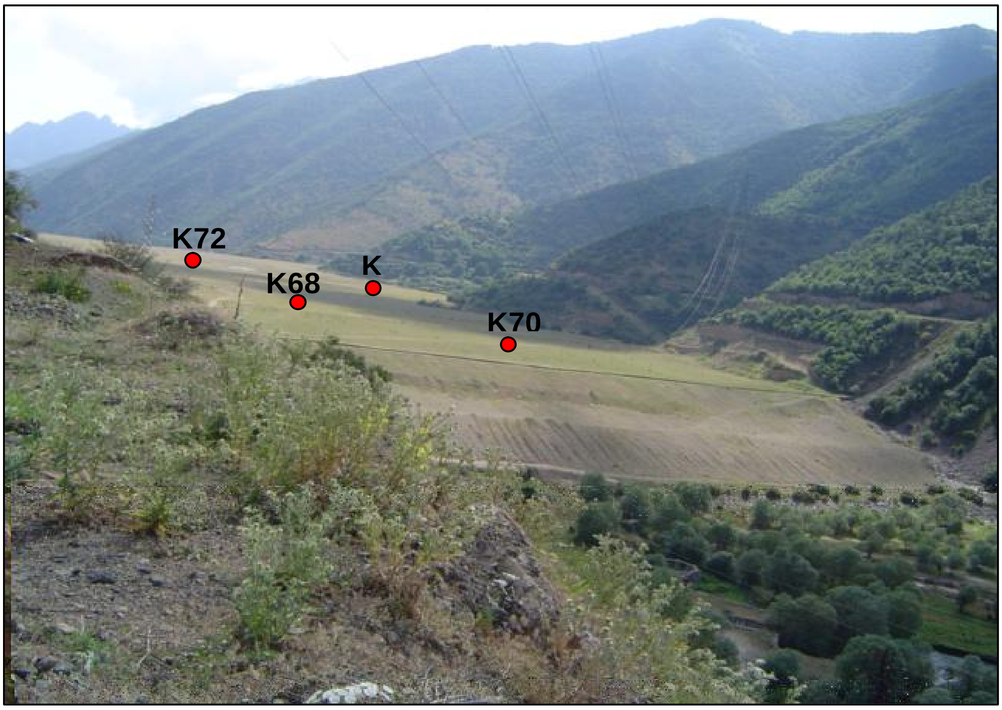

Fig. 48. Soil and plant sampling points on Voghchi tailing repository

According to *Tab. 10*, like Darazami, for soils and grounds of Voghchi tailing repository high indices for Mo, Cu, Ni, Co, V are common, the most significant of them being by the first elements. Unlike Darazami, peak values of Ni are twofold (14 times) excessive vs. MAC.

Table 10. MAC (*mg/kg*) exceeding concentrations of heavy metals in soils and grounds of Voghchi tailing repository.

Heavy metals	MAC [1]	n=5		
		min.	max.	mean
Mo	5.0*	**8.4**	**36.0**	**19.8**
Cu	100*	**1.3**	**5.6**	**3.4**
Pb	100*	0.2	0.6	0.3
Sn	50.0*	0.08	0.08	0.08
Zn	300*	0.6	0.2	0.2
Mn	1500	0.09	0.5	0.3
Ni	4.0	**4.5**	**14.0**	**8.6**
Cr	100*	0.1	1.3	0.5
Co	5.0	**2.0**	**8.4**	**5.6**
V	100*	**1.0**	**1.8**	**1.5**

[1]* MAC according to A. Kloke [1980], – Mn, Ni, Co – по “Ecology…” [1993].
Underlined are excessive values vs. MAC.

Additional analyses for toxic elements on re-cultivation soil and ground layer (25 *cm*, *Fig. 43*) indicated high concentrations of mercury and arsenic (vs. MAC 1.7 and 9 times, respectively) and the traces of cadmium (0.05 *mg/kg*) as well.

Studying heavy metals distribution by separate sectors of the tailing repository (*Figs. 45, 49*) indicated that Mo, Cu, Co, V concentrations show inclination to the increase with depth.

For Ni and Cr high concentrations are common in all the sectors. On re-cultivation layer (0,25*m*) the contents of these elements are 1.5 and 10 times higher than in slimes. This possibly occurs at the expense of higher contents of organic matter on re-cultivation layer, as during Soviet era the territory of Voghchi tailing repository was sown with nitrogen-catching herbs [Golbraycht, Kataryan, 1980], that actively accumulate nickel and chromium. Today, our observations show that on the tailing repository site *Lotus* and *Festuca* are widely spread in which high contents of Ni and Cr are established.

Fig. 49. By-sector sampling on Voghchi tailing repository site.

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Thus, the established high concentrations of high toxic elements in the tailing repository stuff demand the development of cleanup actions and special approaches to the use of the territories for economic purposes.

6.2. Eco-toxicological assessment of pollution of agricultural crops grown on tailing repository sites.

6.2.1. *Heavy metal accumulation in vegetables and herbs.*

Vegetable and melon–field species

Tab. 11 generalizes the research results on heavy metals accumulation in vegetable and melon-field species grown on the territories of the 3 tailing repositories.

Table 11. The contents of heavy metals (*mg/kg* of dry matter) in vegetable and melon-field species grown on tailing repositories sites.

Points	Crops / MAC*		Cu 5.0	Mo 2.0	Pb 0.4	Zn 10	Ni 0.5	Cr 0.1	Accumulation series	Sum of excess vs. MAC
Darazami tailing repository										
K-10	Potato		11.8	6.5	0.7	4.6	2.1	0.6	Cr-Ni-Mo-Cu-Pb	17.8
	Bean		19.4	60.5	1.4	7.6	4.5	1.4	Mo-Cr>Ni-Cu-Pb	60.7
	Beet		28.0	11.4	0.9	6.1	2.8	0.9	Cr-Mo-Ni-Cu-Pb	27.8
	Onion	onion	22.5	29.6	0.7	4.9	3.9	0.9	Mo>Cr-Ni-Cu-Pb	38.2
		green mass	26.6	62.2	1.5	10.4	3.5	6.2	Cr-Mo>Ni-Cu-Pb	109.4
K11	Potato		14.9	20.0	0.6	4.4	2.6	0.6	Mo-Cr-Ni-Cu-Pb	25.9
	Garlic		7.4	9.9	0.3	2.2	0.7	0.3	Mo-Cr-Ni-Cu>Pb	11.8
K-64	Potato		19.8	26.0	1.1	4.3	1.5	0.6	Mo-Cr-Cu-Ni-Pb	28.9
	Bean		14.6	194.2	0.8	5.7	1.9	0.8	Mo>Cr-Ni-Cu-Pb	114.0
	Dill		38.1	89.3	2.1	8.3	3.8	2.9	Mo>Cr-Ni-Cu-Pb	93.8
K-65	Potato		16.4	9.2	0.7	3.6	2.2	1.2	Cr-Mo-Ni-Cu-Pb	26.2
	Bean		22.0	158.6	1.2	8.5	3.9	1.2	Mo-Cr>Ni-Cu-Pb	106.8
Voghchi tailing repository										
K-70	Potato		15.3	47.8	0.6	4.5	0.8	0.5	Mo>Cr-Cu-Pb-Ni	35.0
	Bean		15.6	113.0	0.9	6.1	0.9	0.6	Mo>Cr-Cu-Pb-Ni	70.0
	Beet		17.8	13.3	0.6	3.9	0.7	0.4	Mo-Cr-Cu-Pb-Ni	17.2
	Carrot		12.0	16.0	0.7	4.7	2.1	0.7	Mo-Cr-Ni-Cu-Pb	23.0
	Dill		27.4	85.5	1.2	8.0	4.8	4.8	Cr-Mo>Ni-Cu-Pb	108.5
Pkhrut tailing repository										
K-1	Potato		25.5	7.9	0.6	4.2	1.1	2.5	Cr>Cu-Mo-Ni-Pb	38.2
K-2	Dill		60.5	108.0	1.9	10.1	3.5	1.9	Mo-Cr-Cu>Ni-Pb	96.4

Note: according to Dueck et al. [1984]. Underlined are excessive values vs. MAC.

The data analysis shows that concentrations of heavy metals except Zn are excessive vs.MAC in all the studied species. Let's consider the contents of heavy metals in different species.

Darazami tailing repository. The most polluted are green vegetative organs of vegetables and first of all dill (*Anethum graveolens*), bean (*Phaseolus vulgare*), and green portion of onion (*Allium cepa*). Such a regularity is common for all the studied tailing repositories.

In dill the index of the sum of heavy metals concentration excess vs. MAC is the highest and makes 93.8. It is Mo that greatly contributes to summary pollution (accumulation series Mo>Cr-Ni-Cu-Pb). It is recommended that dill should not be cultivated on the tailing repository sites.

In bean, too, high indices of heavy metal accumulation are establishhhed. In differe parts of Darazami tailing repository the sum of heavy metal accumulation is different. The highest indices of summary accumulation are established in upper (114, K64) and lower (106.8, K65) sectors of the tailing repository, nearby the aqueduct.

For K10 this index is about twice as little (60.7). Despite such difference, the accumulation series is identical for all the points: Mo-Cr.Ni-Cu-Pb. Intense accumulation of Mo in bean is conditioned by high level of nitrogenification, Mo being involved in this process. Provided that high contents of Mo as an element typical of Kajaran is not considered, then pollution level of bean in point K10 may be attributed to middle grade, over the more no excess vs. MAC has been established in respect to toxic elements (*Fig. 50*).

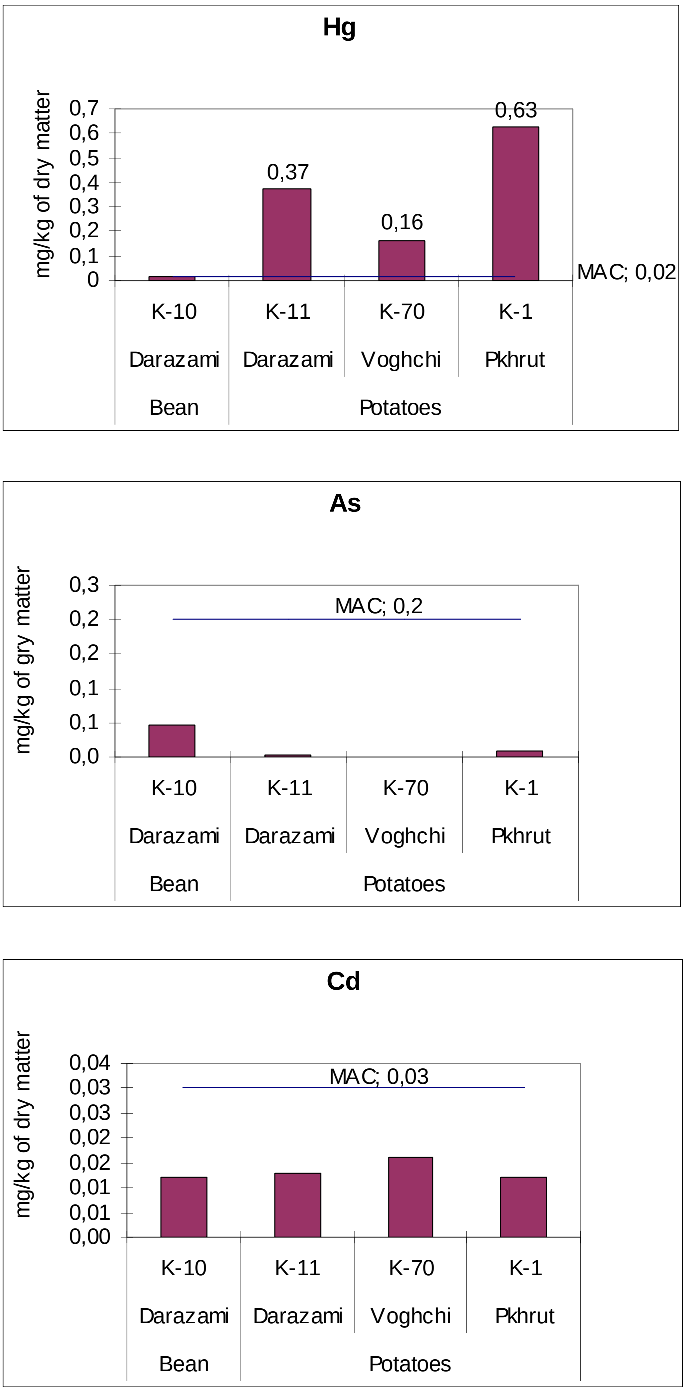

Fig. 50. The contents of toxic elements in vegetables grown on tailing repository sites

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An interesting situation is observed for different organs of onion. As seen from the data (*Tab. 11*), in green mass the level of summary accumulation of elements (109.4) approaches to dill and bean, leading elements being Cr and Mo (accumulation series Cr-Mo>Ni-Cu-Pb). However for onion the summary accumulation index is about thrice as little (38.2) and in accumulation series (Mo>Cr-Ni-Cu-Pb) Mo dominates and thus pollution level of onion is low. Thus, only onion can be used.

For garlic (*Allium sativum*) the index of summary accumulation of elements (11.8) is even lower, which accumulation series (Mo-Cr-Ni-Cu>Pb) is fully identical to that for onion. Eco-toxicological state of garlic is satisfactory with regard for the considered elements. However for final recommendation for garlic growing on Darazami tailing repository, additional studies are required.

On the tailing repository site we studied 3 species of root-crops: potato (*Solanum tuberosum*), beet (*Beta vulgaris*), and carrot (*Daucus carota*). As our investigations indicate, of all root crops grown on the study site potato is dominant, and thus beside basic elements (*Tab. 11*) we also studied the contents of toxic metals in it (*Fig. 50*).

The analysis of potato grown on Darazami tailing repository site shows that in different parts of the tailing repository except K10 the sum of MAC excesses is middle and varies 25.9 to 28.9. For K10 this index in lower 1.5 times (17.8) due to low concentrations of Mo. However, potato pollution level cannot be attributed to low grade, as for K11 (on the boundary between Kajaran and Darazami) in roots high concentrations of mercury are established (18.5 time excess vs. MAC), and ecological situation may be considered dangerous. Though beet root pollution level is also middle (sum of excess-27.8), anyway additional investigations of contents of toxic elements in it are required.

Pkhrut tailing repository. The highest pollution level is established for dill, which index of the sum of heavy metal concentration excess vs. MAC is 96.4. Basic share to summary pollution falls to Mo, Cr, Cu (Mo-Cr-Cu>Ni-Pb). Recommendation is made to fully exclude cultivation of dill on tailing repository sites.

Especially harmful turned out to be potato, in which high contents of mercury (31.5 time excess vs. MAC) are established (*Fig. 50*). Such a state should be regarded as that of emergency.

It is recommended that agricultural activities should be forbidden on the tailing repository site.

Voghchi tailing repository. Investigations of agricultural crops on Voghchi tailing repository site allowed singling out dill and bean as the most polluted crops. For dill the index of the sum of heavy metal concentration excess vs. MAC is 108.5. In summary pollution Mo and Cr dominate (accumulation series Cr-Mo>Ni-Cu-Pb). Recommendation is made to exclude dill from diet.

The level of accumulation of the sum of elements (70) in bean can also be attributed to middle pollution due to Mo (accumulation series Mo>Cr-Cu-Pb-Ni).

Studying potato allowed establishing high contents of mercury (8 time excess vs.MAC) in its roots.

The contents of elements in beet are 1.5 times lower (17.2) than in carrot (23).

Thus, eco-toxicological investigations of agricultural crops grown on the tailing repository sites showed that

1) *green vegetative organs (dill, bean, onion) accumulate high concentrations of typomorphic elements, and their dietary use is found inadvisable;*
2) *the contents of metals in onion are low; after they have been thoroughly tested for the contents of toxic elements, they may be used in diet;*
3) *the contents of heavy metals in roots is on middle level;*
4) *in the roots of potato grown on the 3 tailing repository sites , established are high concentrations of mercury, and thus they must be completely excluded from diet.*

To provide more exhaustive and comprehensive assessment of the tailing repository sites, recommendation is made to conduct extended monitoring of vegetarian and animal (dairy and meat food) farming produce.

Fodder grasses

Investigations of fodder grasses are conditioned by the fact that the tailing repository sites and mostly Voghchi are used as pastures, too. The herd from Lernadzor village (some 250 heads of horned cattle) systematically grazes on this territory (*Fig. 51*).

Fig. 51. Herd of cows on Voghchi (left) and Pkhru (right) tailing repository sites

Investigations were carried out of heavy metal accumulation in separate grass and grass stuff species consumed by horned cattle.

On Darazami tailing repository measurements of heavy metal contents in clover (*Trifolium*) indicated high concentrations of Mo (131 time excess vs. MAC), Cr (22 time excess vs. MAC), Ni (6.3 time excess vs. MAC) (*Tab. 12*). Moreover, high contents of mercury, too, are established (28.8 time excess vs. MAC) (*Fig. 52*). Thus, the fodder may serve the source, through which mercury and other heavy metals may enter human organism via food chain.

Table 12. Concentrations (*mg/kg* of gry matter) of heavy metals in grasses on the tailing repository sites

Points	Grasses / MAC*	Cu 30.0	Mo 2.0	Pb 5.0	Zn 50	Ni 3.0	Cr 0.5
Darazami							
K-64	*Trifolium*	35.0	**262.8**	1.9	10.2	**19.0**	**10.9**
Voghchi							
K-8	Grass stuffs	**44.5**	**106.0**	2.5	7.9	**7.9**	**7.9**
K-71	*Festuca*	13.3	**42.8**	1.3	7.1	**57.1**	**57.1**
	Hypericum	15.5	**36.3**	0.8	4.5	**4.9**	**6.5**
	Lotus	27.4	**273.6**	1.5	8.0	**20.5**	**36.5**
	Cichorium	16.0	**21.4**	0.9	6.2	2.8	**3.7**
Pkhrut							
K66 A	Grass stuffs	**41.9**	**31.4**	1.3	9.2	**13.1**	**7.3**
K67 A	*Artemisia. Euphorbia*	**38.4**	**67.2**	2.0	9.0	**28.8**	**9.0**

Note: MAC according State Standard №123-41281-87. 15.07.1987.

In grass stuffs and separate grass species on Voghchi tailing repository, established are high contents of Mo (especially in Lotus – 137 excess vs. MAC), Ni, Cr, Hg (9.6 time excess vs. MAC), this, too, excluding grazing.

In the grasses on Pkhrut tailing repository high concentrations of elements (Mo, Ni, and Cr) are established, too.

The research outcomes evidence the necessity of controlling the fodder for cattle and dairy and meat produce quality monitoring.

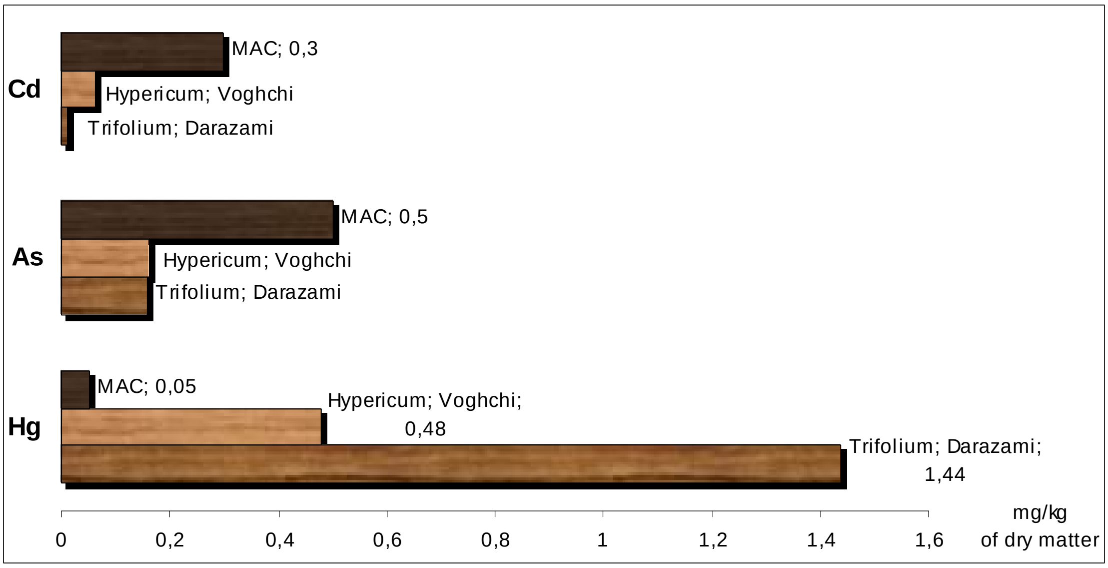

Fig. 52. The contents of toxic elements in grasses on the tailing repository sites

6.2.2. *The contents of N_{total} in vegetable species and grass stuffs on tailing repository sites.*

We studied the contents of N_{total} in vegetable species and grass stuffs grown on the tailing repository sites. The outcomes show (*Fig. 53*) sharp variations in the contents of N_{total} for separate crops. Especially clear are such variations for dill: peak concentrations (2.2%) are established on Pkhrut tailing repository. Nitrogen concentrations in potato, too, are high (1.5%) vs. the rest 2 tailing repository sites.

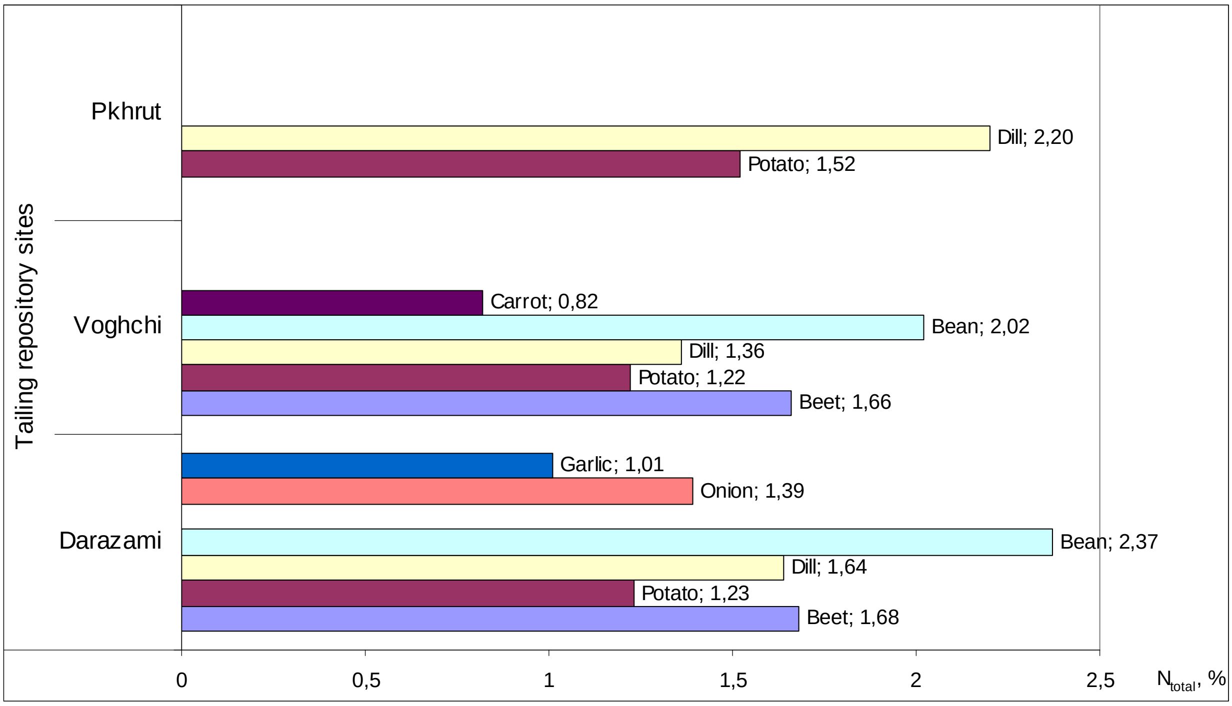

Fig. 53. The contents of N_{total} in vegetable and melon-field crops on tailing repository sites.

On Voghchi tailing repository site, vegetable species make the following series by the increase in concentration on N_{total} carrot (0.8%) – potato (1.2%) – dill (1.4%) – beet (1.7%) – bean (2%).

On Darazami tailing repository site, vegetable species make the following series by a increase in concentration on N_{total}: garlic (1%) – potato (1.2%) – onion (1.4%) – dill, beet (1.7%) – bean (2.4%).

Investigations of the contents of N_{total} in grass stuffs on the tailing repository sites indicated no sharp difference between them, whereas there was a difference in nitrogen accumulation in separate species of fodder crops found in the composition of grass stuffs (*Fig. 54*. The analysis of separate grasses on Voghchi tailing repository site showed that wholly the level of accumulation of N_{total} was low (0.7-1.7%). Peak indices are established for dominating species with large biomass – chicory (1.7.) and nitrogen-catcher - birds-foot trefoil (1.6%).

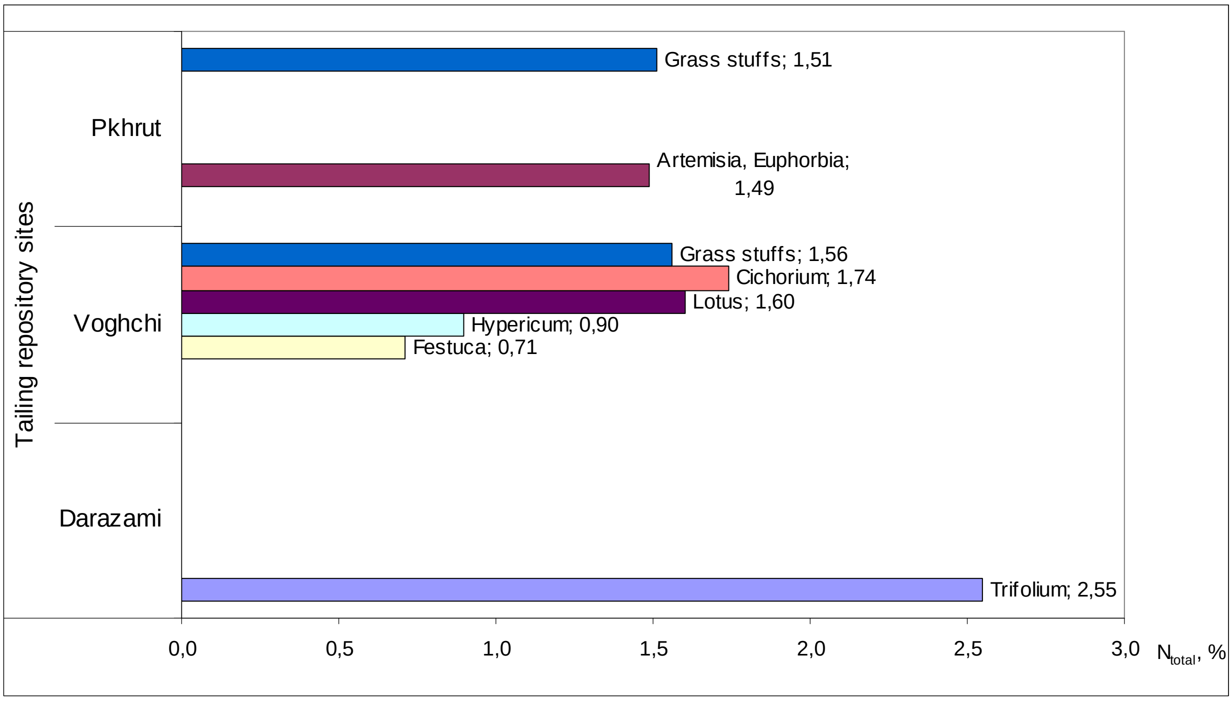

Fig. 54. The contents of N_{total} in grass stuffs on tailing repository sites.

Unlike plants grown on Pkhrut and Voghchi tailing repository sites, clover (also a nitrogen-catcher) on the territory of Darazami is characterized by highest indices of nitrogen accumulation (2.5%). This index is important from positions of saturation of fodder grasses with proteins for cattle.

Wholly, one may conclude that all the established concentrations of nitrogen in vegetables and grasses show in-MAC variations.

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7. CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

- **Studies of sanitary-hygienic state of Kajaran's surface waters showed that**

Ø *the source for water supply to the city (River Kaputan) meets the standards;*

Ø *the state of River Davachi meets fish-breeding and economic standards;*

Ø *the state of River Voghchi by ion composition and heavy metal contents is satisfactory and may be used for economic and household purposes, except the tributary (KB12) behind the hotel;*

Ø *in waters of the aqueduct of Darazami tailing repository and in the stream from the colliery near old TV tower established are high concentrations of a number of ions and mercury; the water should not be used either for economic purposes or in irrigation of adjacent agricultural lands;*

Ø *no substantial impact of the composition of aqueducts and ore waters upon River Voghchi pollution has been established;*

Ø *mineral water "Esentuki" contains significant concentrations of toxic elements of 1st and 2nd grade of hazard (Hg, As, and Cu, respectively); the water should not be used for drinking. Recommendation is made to close the spring.*

- **Geochemical survey of soil cover of Kajaran and its vicinities showed that**

Ø *a dominating role in pollution of the city is given to Mo and partially to Cu, however no intense pollution of the whole of the city's territory is observed;*

Ø *fields with peak levels of heavy metal concentrations are focused on the territory of the group of enterprises, colliery and behind residential part of the city;*

Ø *elevated concentrations of Mo in Kajaran's soils are typical of biogeochemical province and should not be regarded as a harmful ecological situation;*

Ø *pollution of the city is attributed to low and partially middle level.*

- **Sanitary-hygienic assessment of soil cover of Kajaran and its vicinities showed that the state of soils approaches to standards.**

- **Established is high local radiation background of soil cover (758 Bq/kg). On the city's territory, fields of 3 levels of gross -radiaoctivity are contoured out.**

- **Bioindication studies of pollution of ambient air of Kajaran with sulphur and nitrogen emissions showed that**

Ø *sulphur emissions are localized, and no extensive sulphur pollution is observed in the city;*

Ø *the contents of N_{total} in the leaves of trees do not exceed standards and, respectively, no nitrogen pollution is established on the city's territory.*

- **In the tailing repository materials established are high concentrations of high toxic elements (Hg, As, Cd).**

- **Eco-toxicological studies of agricultural crops and fodder grasses on the tailing repository sites indicate high concentrations of heavy metals and mercury in them.**

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RECOMMENDATIONS

- **To get an exhaustive picture of sanitary-hygienic state of Kajaran's surface waters recommendation is made to**
  - ü *conduct monitoring studies of waters of River Voghchi and its tributaries during basic hydrological phases (high water, low water);*
  - ü *assess water from all the springs on Kajaran's territory, emphasizing aqueducts and streams around the tailing repositories, where high contents of toxic elements (Hg, As) are established;*
  - ü *assess River Voghchi bottom sediment, as (as the gained the experience indicates) they accumulate explosive concentrations of toxic elements and may serve potential source for these elements during sharp changes in redox potential of water environment.*

- **For more precise assessment of radioactivity of Kajaran's territory, a detailed analysis of the value of specific radioactivity of naturally occurring radionuclides ^{226}Ra, ^{232}Th, ^{40}K in soils is required.**

- **For clear contouring out the zones of the works-induced emissions impact upon Kajaran's ambient air, investigation of snow cover is required.**

- **The establishment of high concentrations of heavy metals and mercury in vegetables and herbs on the tailing repository sites demands ecological risk assessment for local populace. For this, detailed eco-toxicological studies of vegetarian (vegetables and melon-field species) and animal (dairy and meat products) for the contents of toxic elements, are required.**

- **The establishment of high concentrations of toxic elements in the tailing repository materials demands development of actions for detoxification and special approaches when involving the territories in economic activities. Detailed investigations of tailing repositories aimed to their re-cultivation through the technology for creating anti-filtration barrier underpinned by the principle of binding active phases of toxic elements, are necessary. For these purposes it is possible to apply local natural cheap raw-stuff.**

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