THE NATIONAL ACADEMY OF SCIENCES OF RA

CENTER FOR ECOLOGICAL-NOOSPHERE STUDIES

ASSESSING ENVIRONMENTAL IMPACT OF TAILING STORAGE SITES FROM MINING AND DRESSING PRODUCTION AND ACTIVITIES OF THE KAPAN COPPER ENTERPRISE ON THE TERRITORY OF KAPAN TOWN (SYUNIK MARZ)

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THE CENTER FOR ECOLOGICAL-NOOSPHERE STUDIES

«Approved»
Director of the Center for Ecological-Noosphere Studies NAS RA
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THE PROJECT REPORT

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

Principal investigator
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CONTENTS

1. INTRODUCTION

This research «Assessing environmental impact of tailing storage sites from mining and dressing production and activies of the Kapan copper enterprise on the territory of Kapan town (Syunik Marz)» has been performed based on the Agreement with the Organization for Security and Cooperation in Europe Office in Yerevan. The project was developed at the request of Municipality of Kapan.

The assessment of environmental status is one of basic components while elaborating plans of social-economic development of territories. Such assessment is underpinned by data on territory pollution with heavy metals.

This problem is especially topical for Syunik marz (province) situated in the southern portion of the Republic, as in Kapan a powerful copper mining and dressing plant has been operating since 1846.

The remoteness of Syunik marz from the country's capital is a significant economic lag, resulting in a very high level of unemployment and active migration of the people. For this the OSCE Office in Yerevan supported elaboration of a research on the prospects of Syunik marz socio-economic development, this project fully complies with funding and recommendations of ENVSEC report and map, where the respective district has been identified as environmental hotspot. Environmental protection initiatives in the cross boarder district of Syunik marz are of special importance for environment-related safety and security.

After the USSR collapse, environmental control and monitoring services in Armenia operated insufficiently, and for recent 15 years no data on environmental pollution with heavy metals and the extension of impact zones of the noted mining and dressing plant were obtained.

The project goal was to assess environmental status of the territory of the city of Kapan with an emphasis on the impact of the tailing repository and today's operation of the Kapan copper plant in respect to soil, water and plant pollution.

In the frame of the project technical tasks

- Digital topographic and city plan maps were developed,
- The level of heavy metal pollution of soils, water, and plants on Kapan's territory and adjacent areas was assessed,
- Sanitary-hygienic assessment of crops was performed, peculiarities of heavy metal accumulation in different vegetable species indicated,
- Schematic maps of territory's pollution with heavy metals were produced,
- A set of recommendations for local governing bodies to mitigate the risk of the impact of environmental pollution with heavy metals upon the populace was developed.

The research was performed by: **project supervisor -** Dr. sci. *A. K. Saghatelyan,* **principal investigator** – Dr. *S. H. Arevshatyan,* **senior Investigators -** Dr. *S. A. Arakelyan, PhD student L. V. Sahakyan,* **investigators** – Dr. *T. L. Tadevosyan, O. A. Belyaeva,* **consultant -** *V. Sh. Martirosyan,* **lab assistants -** *G. S. Nersisyan, A. V. Kharatyan, A. G. Sakoyan,* **interpreter -** *A. N. Beyleryan,* **drivers -** *K. G. Babayan, G. G. Sahakyan*

The research was performed between August and December, 2007.

1.1. A brief description of the territory of the city of Kapan

The city of Kapan (former Kafan, Madan) is the administrative center of Syunik Marz and one of basic industrial cities of the Republic of Armenia.

The city is situated in the southeastern part of the country (*Fig.1*) within the bounds of Kapan ore region – between lower streams of Rivers Voghchi and Norashenik. Spatially the city associates with a same-name hollow of River Voghchi middle stream basin at some 700*m a.s.l.* [9-11].

Fig. 1. *A map of disposition of the city of Kapan*

Geological structure involves thick fractured volcanogenic and volcanogenic-sedimentary formations of Jurassic Age and subordinate intrusive and sub-volcanic rocks on which mountain-forest, steppe and mountain-brown dry-steppe soils are developed [10-11].

The climate is moderately warm, with mild winter and hot summer. Mean annual temperature is +12-14^{0}C. Mean annual amount of precipitation is 500-600 *mm* [11].

The city's territory is characterized by a well- defined relief and is limited by a mountain-steppe natural-landscape belt [11].

The region has long been well known for its abundant copper and polymetallic deposits with vein- and stockwork-type mineralization [9].

Historically, Kapan was the miners' city, and as a symbol a monument to miners was erected there (*Fig.2*). The Kapan deposit has been developed since 1846 [9].

The Kapan mining plant is a city-constituting enterprise. Presently, a basic share holder is Dundee Precious Metal Company which possesses of 80% of shares of former owner Deno Gold Mining Company and performs works on the Shahumian polymetallic and the Kapan copper- pyrite deposits.

Fig. 2. *A monument to miners*

1. 2. Research materials and methods

Soil samples were collected from the city’s territory following a topographic plan (Sc. 1:10000) applying GPS (for getting precise geographical coordinates of sampling points). Total amount of sampling points was 147 (*Fig. 3*).

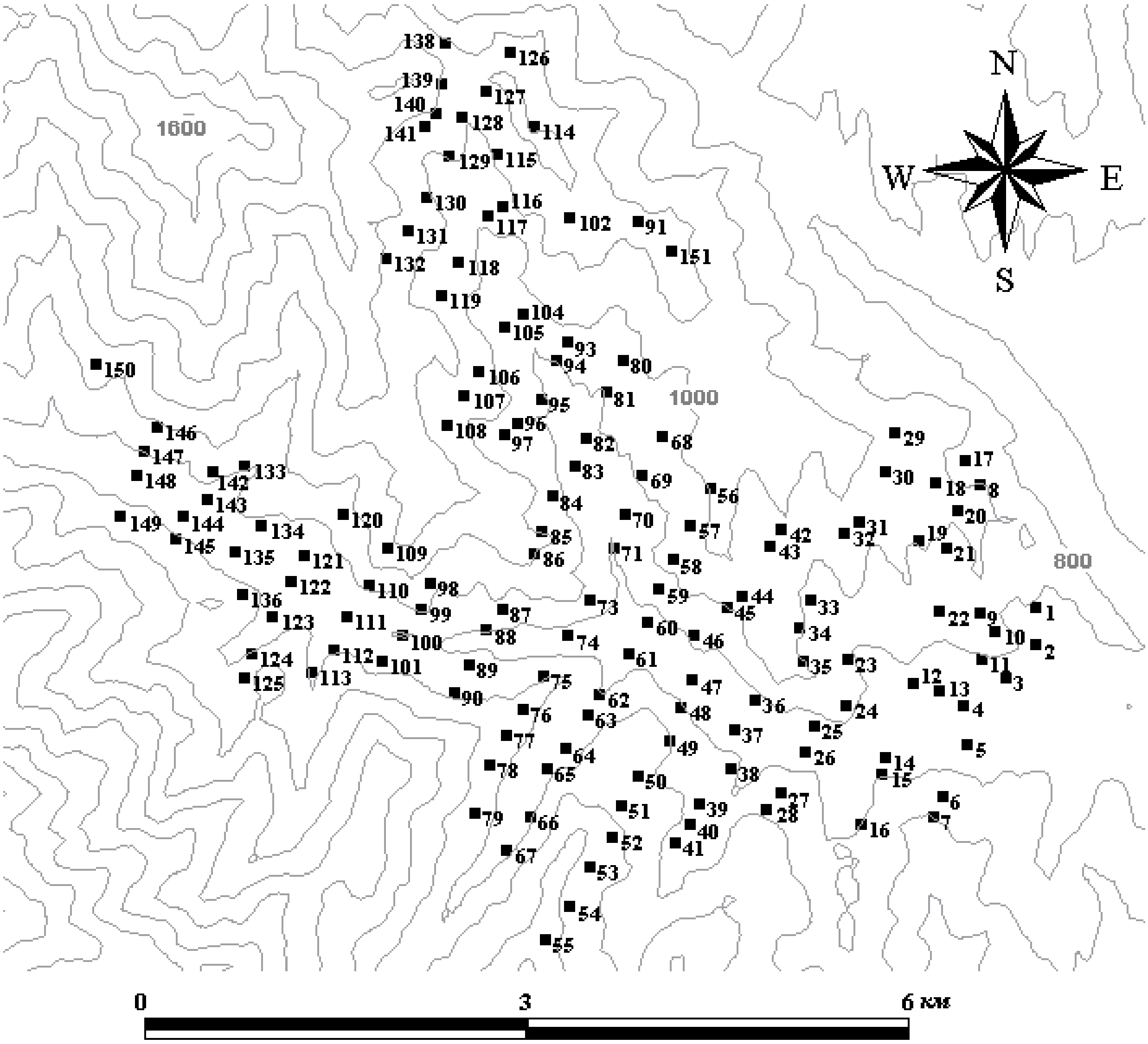


Fig. 3. *A schematic map of soil sampling sites.*

Water samples were collected from the main streams of the left bank of River Voghchi and from several industrial streams.Total amount of sampling points was 12 (*Fig. 4*).

The soil, water, vegetation samples were collected (*Fig. 5*) and processed through methods developed in IMGRE and the V. V. Dokuchaev Soil Institute [4-5].

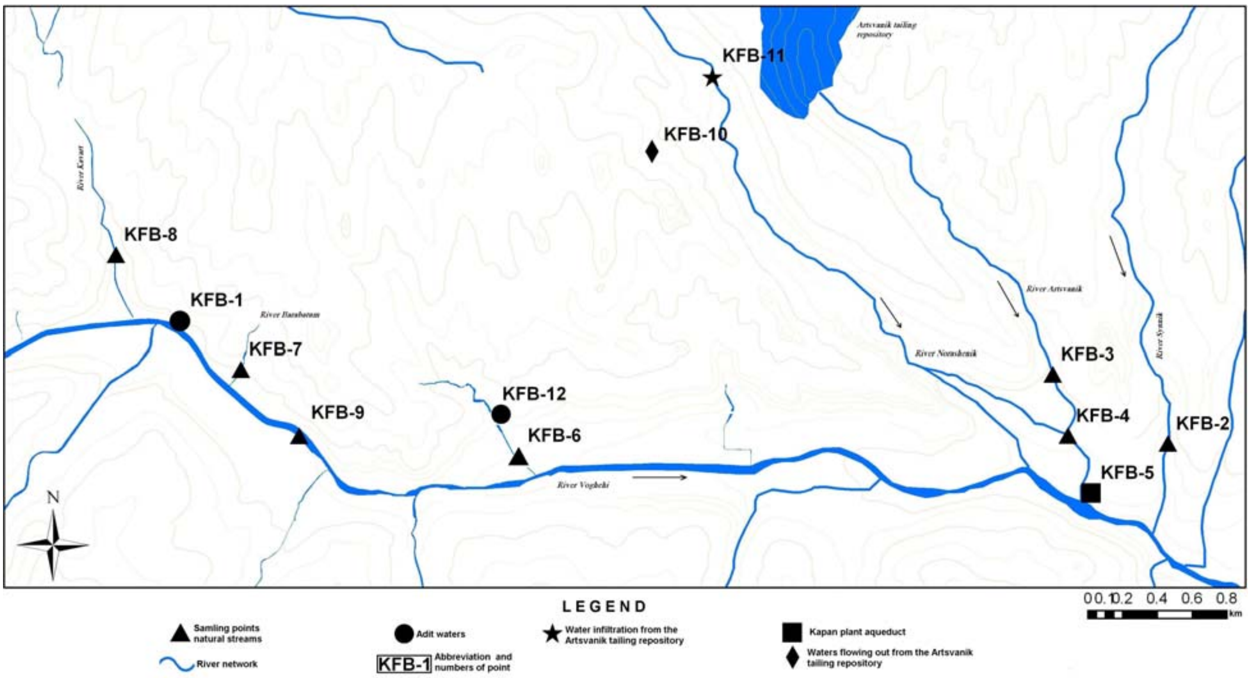


Fig. 4. *A schematic map of water sampling points.*
Sampling points:

KFB-1 – Mine waters from adit, opposite the supermarket, city of Kapan
KFB-2 – River Syunik
KFB-3 – River Artsvanik, Syunik vil.
KFB-4 –Rivers Artsvanik and Norashenik confluence site,near the airport
KFB-5 – The Kapan plant aqueduct, near Norashenik vil.
KFB-6 – Canyon stream, near gas station
KFB-7 – River Barabatum, Barabatum canyon
KFB-8 – River Kavart, near the school
KFB-9 – River Voghkhi, city of Kapan
KFB-10 – Aqueduct from Artsvanik tailing repository
KFB-11 – Infiltration waters from under Artsvanik tailing repository dam
KFB-12 – Mine waters from the adit, near administrative building of the plant

Fig. 5. A s*ample collection procedure*

For eco-toxicological studies, soil and vegetable- and melon-field and fruit samples were collected from private farms in River Barabatum canyon and in the village of Syunik as well as from a farm located in River Norashenik alluvial plain (near the former milk factory).

Under field conditions, in-situ measurements were done for basic physical and chemical indices of water (T, pH, mineralization, salinity, dissolved oxygen, conductivity) on a Horriba U-10 multi-analyzer. Synchronously, water discharge was measured applying AquaCalc 5000.

The collected soil, water, plant samples were analyzed in the laboratory of CENS NAS RA (*Tab. 1*).

Table 1. *The scope of analyses of separate environmental components*

Parametrs / Environ-mental components	pH	Eh	T^0C	Salinity	Electro-conduc-tivity	Minerali-zation	Turbi-dity	Dis-charge	Ions	Heavy metals, element/ analysis
Waters	9	9	9	9	9	9	9	9	96	143
Soil	–	–	–	–	–	–	–	–	–	1729
Plants	–	–	–	–	–	–	–	–	–	561

Heavy metal contents were determined by atomic-absorption (Perkin Elmer 800) and quantity spectral (СТЭ-1) methods; ionic composition was determined through the accepted methods, too, [1] following ISO international standards (ISO 9964-3, ISO 9964-3 ISO 6058, 6059, ISO 9297).

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) [2, 3, 8, 12].

For cartographic reflection of sampling points and results of further material processing, digital maps of the territory were produced on a topographic basis (sc. 1 : 10000).

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 software ArcView 3.2a. While collating mono-element schematic maps, a 3-fold grade scale was used.

1.2.1. Cartographic works

Cartographic works were performed by the following stages:

- Collection and processing of available data (satellite images, geodesic maps, etc.),
- Development of necessary digital layers and compilation of relevant databases,
- Decipherment of satellite images and specification of cartographic data.

The maps were produced on a topographic basis applying GIS technologies (a licensed software ArcView 3.2a).

The topographic maps were registered in the system of geographic coordinates Pulkovo 1942, and then digitized; afterwards relevant databases were compiled. Developed were digital layers for settlements, roads, river network, hypsometric levels of relief (*Fig.6*).

The maps were produced through remote sensing methods of data processing, too.

To assure the accuracy of cartographic works, panchromatic and multi-spectral satellite images Spot and Landsat TM with a 4 and 28 *m* resolution, respectively, were used. The latter was registered in the system of coordinates Pulkovo 1942 on the basis of coordinate network point with previously registered topographic maps (Fig.7).

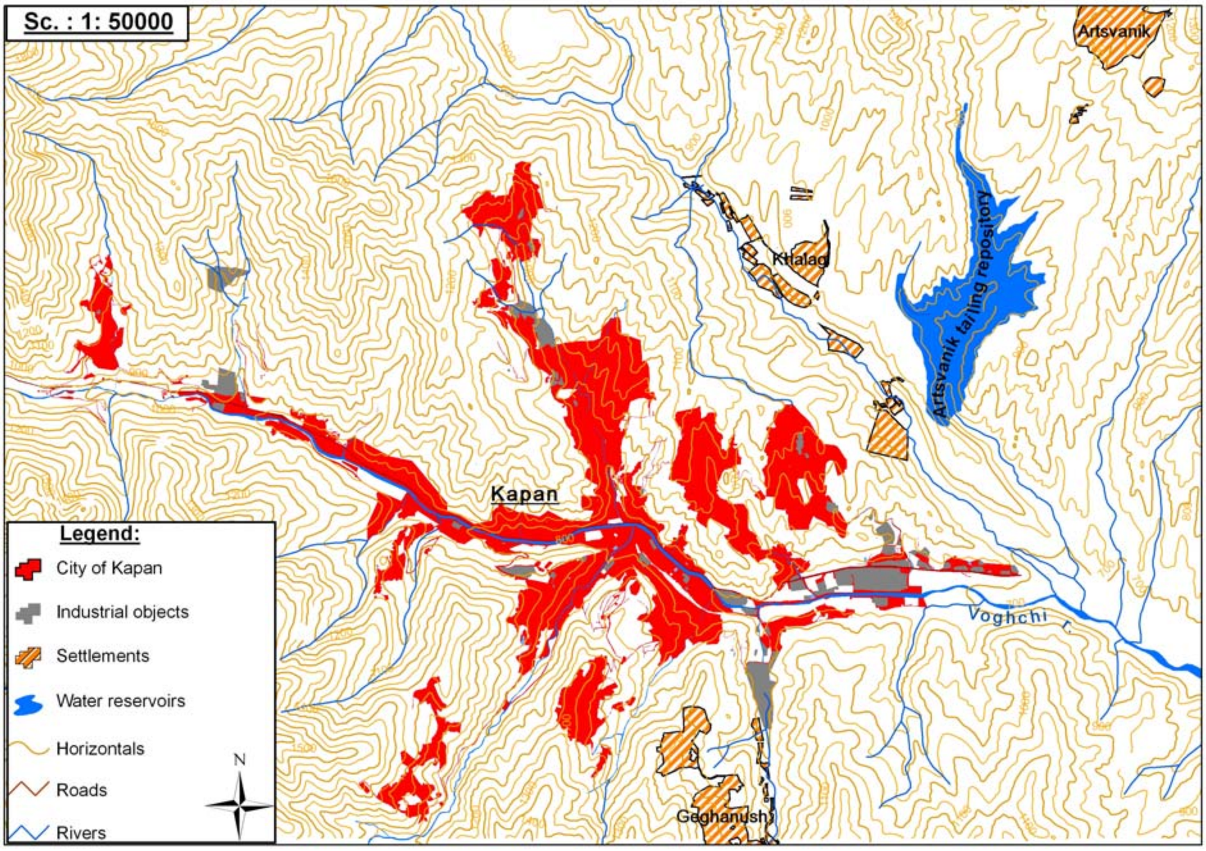


Fig. 6. *A digital map of the city of Kapan*

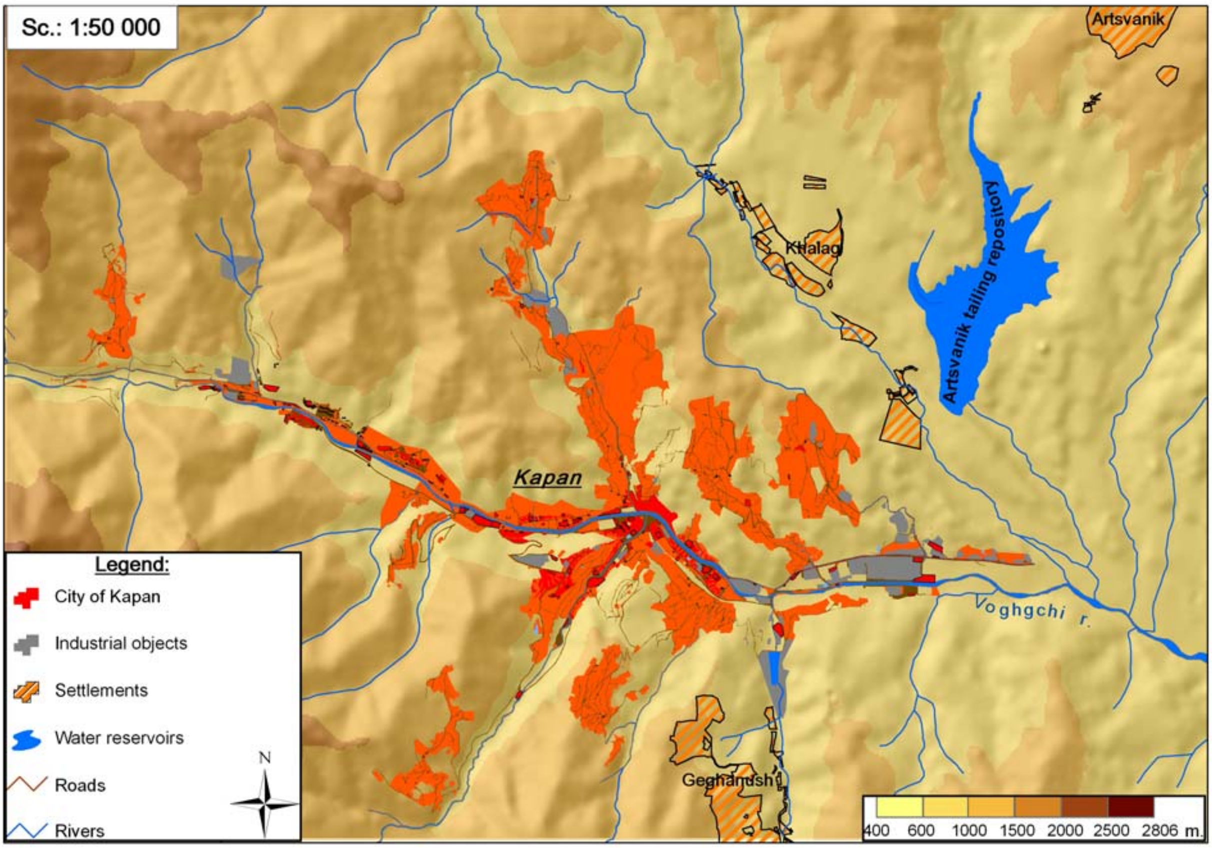
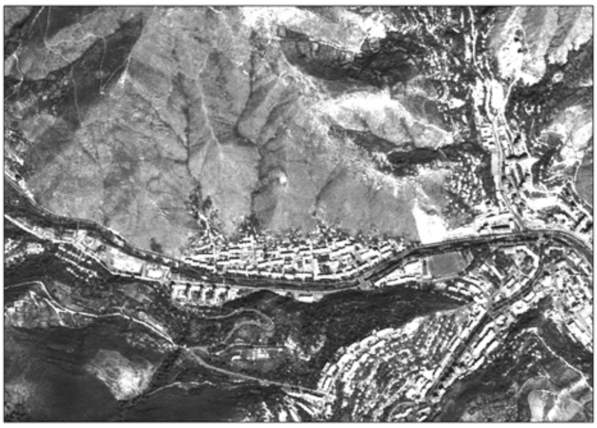


Fig.7. *A spatial image of Kapan*



Spot image (4 m.)

Landsat ETM (28 m)

Fig. 8. *Satellite images 3Spot and Landsat ETM*

The satellite maps were deciphered and processed using Image Analyst sub-program.

Through spectral processing of a satellite image Landsat ETM (*Fig. 8*), automatic classification of the image was performed, and as a result plots of hydrothermally changed rocks (*Fig. 9*) and old dumps were defined on Kapan's territory (*Fig. 10*).

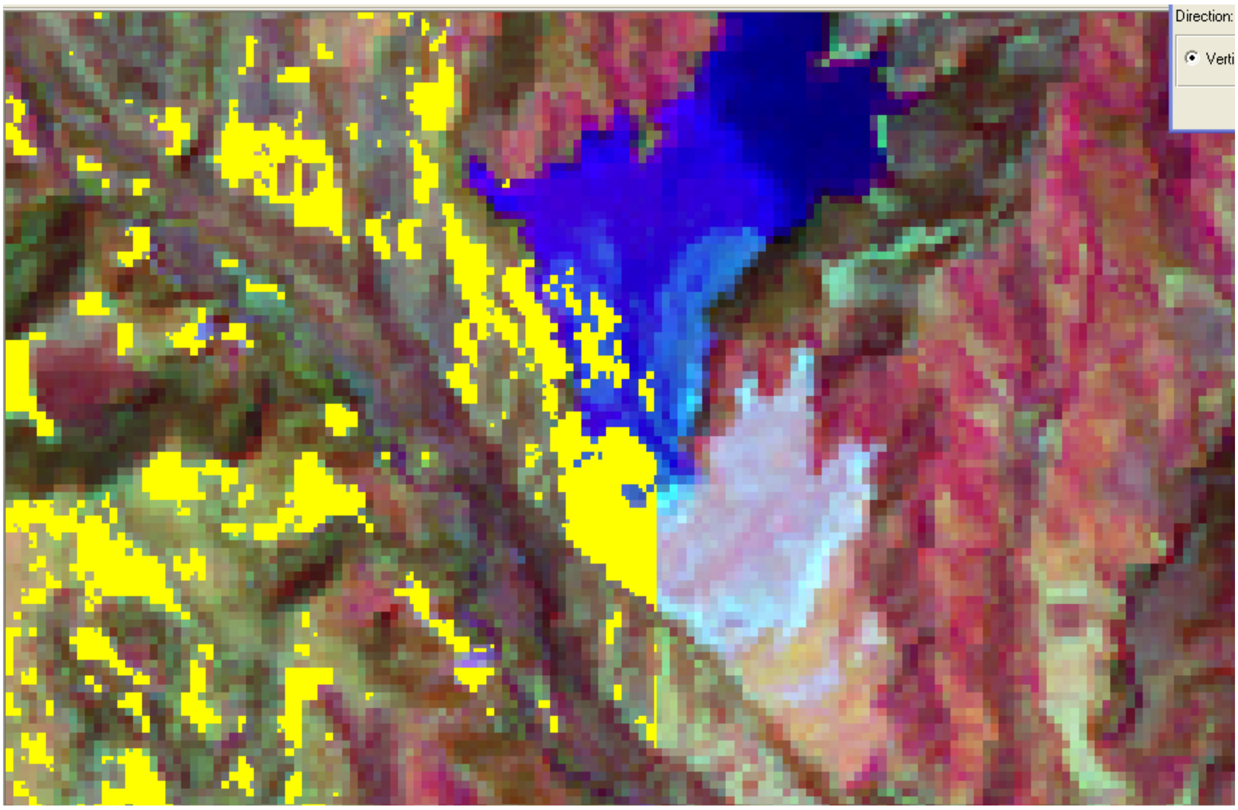


Fig. 9. *Plots of hydrothermally changed rocks and old adit dumps on Kapan's territory (by satellite image decipherment data).*

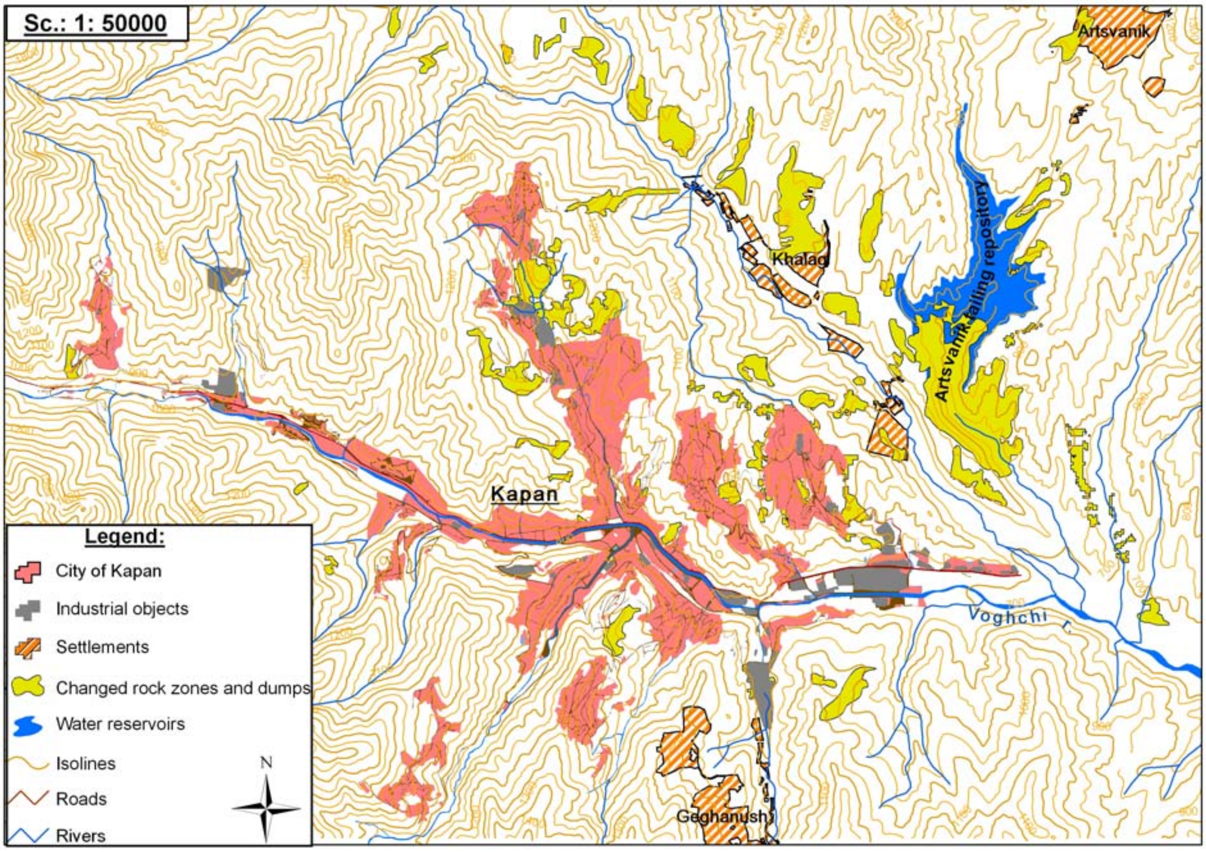


Fig. 10. *A map of disposition of old dumps and changed rock zones on the territory of Kapan and adjacent sites.*

Using high resolution image data (Spot image 4m) the layers obtained when digitizing topographic maps, were renewed and specified.

All the information obtained through GPS as the work advanced was associated to the digital map.

2. THE ASSESSMENT OF SURFACE WATER POLLUTION LEVEL

The assessment of surface water pollution levels is essential from both sanitary-hygienic and ecological positions. Activation of most chemical elements and particularly of heavy metals in water environment rapidly brings to pollution of environmental components (soils, plants, etc.), and as a result heavy metals enter the human organism via trophic chains.

Water samples were collected from natural and industrial streams from total 12 points allover the studied site (the city of Kapan and adjacent areas) on early September under conditions of dry season (*Fig. 4*).

Under field and lab conditions the collected samples were measured for a wide spectrum of physical and chemical indices, some ions and heavy metals.

2.1. Physical and chemical indices of water

Table 2 gives measurement data on basic physical and chemical indices of surface waters for Kapan and adjacent areas.

Table 2. *Physical and chemical water indices*

	Indices	**pH Standards**** *6,5-9,5* **(EU)**, *6,5-8,5* **(WHO)**, *6,0-9,0* **(MAC)**	**Electro conductivity,** *mS/cm*	**Turbidity,** *NTU*	**T^0C**	**Salinity** *%*	**Eh** (redox potential)	**Q** (water discharge) L/sec.
Sampling points *		***River Voghchi tributaries***						
	KFB-2	7,83	0,72	> 999***	19	0,03	220	8,2
	KFB-3	8,47	0,38	98	20	0,01	200	7,1
	KFB-4	7,96	0,43	652	21	0,01	210	695
	KFB-7	7,42	1,54	46	23	0,10	220	0,3
	KFB-8	6,36	0,67	128	20	0,02	180	51
	KFB-9	7,68	0,48	36	15,2	0,01	220	1840
		Mine waters from adit and industrial stream waters						
	KFB-1	5,30	1,8	60	14	0,10	280	1,4
	KFB-5	11,37	2,86	326	21	0,17	120	14,5
	KFB-6	4,42	1,74	248	20	0,11	320	120

Note: *Sampling points are given in Legend to *Fig.4;* **Standards: EU – by Directive 98/83/EC, WHO - by Guidelines for water,1999, MAC – by [7]; *** Over sensitivity limits of the instrument.

One of essential indicators of the state of waters is ***pH value***, which predetermines both the intensity of migration and phases of most chemical elements. Data from *Tab. 2* evidence that pH for all the studied natural streams varied in a range (6.36-8.47) of standards accepted for the NIS and EU territories (6.0-9.5). pH for mine waters from adit and industrial stream waters did not meet standards. The mine waters (KFB-1, the tunnel) and those from KFB-6 were characterized as acid: pH was 5.3 and 4.42, respectively, whereas the waters from the Kapan plant aqueduct were of alkaline reaction: pH=11.37.

By ***electroconductivity*** indices, natural waters and mine and industrial stream sharply differed, too. This index for natural waters varied 0.43 to 0.72 *mS/cm*, except River Barabatum waters (KFB-7) which electroconductivity was 1.54 *mS/cm*. Apparently, this could be linked to high level of electrolythic ion dissociation and associated high salinity level. ***Salinity*** index for these waters was 0.1%, whereas for the rest waters the index decreased varying 0.01 to 0.03%.

Unlike natural waters, mine waters from adit and industrial stream waters had a high electroconductivity (1.74-2.86 *mS/cm*) and salinity (0.10-0.17%) indices. Maximal index values were specific of the waters of the Kapan plant aqueduct (2,86 *mS/cm*; 0,17%).

For all the studied streams**,** ***turbidity*** index depending predominantly on the presence of suspended silty fractions varied in a wide range 36->999 NTU. The minimal turbidity index 36 NTU was indicated for River Voghchi (KFB-9), and the maximal >999 – for River Syunik waters. A relatively high turbidity index 652 *NTU* was indicated for the waters of Rivers Norashenik and Artsvanik confluence site (KFB-4), and a relatively low turbidity index - for River Artsvanik waters before the confluence - 98 *NTU*. The observed some sevenfold increase in turbidity is explained by transfer of silty fractions from riverbank soils of agricultural lands and from ore zones through which River Norashenik runs.

For the studied period, the **temperature balance** of the studied surface waters varied 14-23^{0}C. The temperature regime of the basic part of the streams varied 19-21^{0}C. Low temperature indices were indicated for mine waters flowing out from the adit (KFB-1) – 14^{0}C, and for River Voghchi – 15,2^{0}C; maximal index 23^{0}C – for shallow (0.3 *L/sec*) River Barabatum (KFB-7). The temperature regime of the studied streams is essential in respect to formation of thermodynamic geochemical barriers on the stream confluence bounds at which toxic volatile elements (Hg, Se etc.) could possibly precipitate.

Our research indicated that ***redox potential*** (Eh) of natural and mine waters varied 180-220 and 120-320, respectively. High Eh values in the waters evidenced the presence of impressive amounts of substances with varying valency.

By ***water discharge*** (Q) except River Voghchi (Q=1840 *L/sec.*) maximal volumes were common to Rivers Norashenik and Artsvanik conflux (695 *L/sec.*) and River Kavart (51 *L/sec.*)

2.2. Ionic composition of waters

The obtained measurement data on quality and quantity indices for basic ions in the studied waters are given in *Tab. 3.*

Consistent with the ionic composition equation (*Tab.3*), the studied natural waters are attributed predominantly to sulfate-hydrocarbonate-calcium-magnesium, fragmentary – to hydrocarbonate-chloride-calcium-magnesium and sodium classes.

***Table 3.** Ionic composition of waters*

	Standards *	Cations (mg/L)					Anions (mg/L)							Total mineralization	Total hardness, mg-eqv/L
		Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_2^-	NO_3^-	PO_4^{3-}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}		
	EU / WHO	–	–	–	–	–	–	*50*	–	–	–	*250*	250	–	–
	MAC	200	–	100	50	1,5		45				350	500	1000	10
Samling points **	***River Voghchi basin tributaries***														
	KFB-2	5,6	5,6	54,4	41,3	n/d	0,2	10,7	2,0	21,6	322,0	106,4	82,3	652,0	3,1
		$\frac{HCO_3^- 59\ Cl^- 20\ SO_4^{2-} 15\ CO_3^{2-} 4\ NO_3^- 2}{Ca^{2+} 51\ Mg^{2+} 39\ Na^+ 5\ K^+ 5}$													
	KFB-3	44,6	17,5	74,2	43,8	n/d	0,09	3,5	1,3	12,0	170,8	106,4	243,6	717,7	3,7
		$\frac{SO_4^{2-} 45\ HCO_3^- 32\ Cl^- 20\ CO_3^{2-} 2\ NO_3^- 1}{Ca^{2+} 41\ Na^+ 25\ Mg^{2+} 24\ K^+ 10}$													
	KFB-4	110	18,8	56,1	17,0	n/d	0,3	6,9	0,9	12,0	129,3	92,2	288,1	731,6	2,1
		$\frac{SO_4^{2-} 55\ HCO_3^- 25\ Cl^- 17\ CO_3^{2-} 2\ NO_3^- 1}{Na^+ 55\ Ca^{2+} 28\ K^+ 9\ Mg^{2+} 8}$													
	KFB-7	116	24,0	**106,2**	**52,3**	**5,2**	9,7	**76,3**	0,8	н/о	324,5	241,1	332,9	**1289,4**	4,8
		$\frac{SO_4^{2-} 34\ HCO_3^- 33\ Cl^- 25\ NO_3^- 8}{Na^+ 38\ Ca^{2+} 35\ Mg^{2+} 17\ K^+ 8\ NH_4^+ 2}$													
	KFB-8	32,0	2,9	**154,3**	**105,8**	**2,3**	0,04	0,8	1,6	н/о	68,3	113,5	**722,2**	**1203,6**	8,2
		$\frac{SO_4^{2-} 80\ Cl^- 13\ HCO_3^- 7}{Ca^{2+} 52\ Mg^{2+} 36\ Na+11\ K^+ 1}$													
	Waters from adit and industrial stream waters														
	KFB-1	5,3	3,4	**246,5**	**106,8**	n/d	n/d	7,0	0,7	н/о	24,4	141,8	**979,4**	**1515,4**	**10,5**
		$\frac{SO_4^{2-} 85\ Cl^- 12\ HCO_3^- 2\ NO_3^- 1}{Ca^{2+} 68\ Mg^{2+} 30\ Na^+ 2}$													
	KFB-5	33,1	16,5	**316,6**	n/d	**10,7**	0,8	**47,1**	0,5	494,0	112,1	212,8	378,6	**1622,7**	7,9
		$\frac{CO_3^{2-} 40\ SO_4^{2-} 30\ Cl^- 17\ HCO_3^- 9\ NO_3^- 4}{Ca^{2+} 84\ Na^+ 9\ K^+ 4\ NH_4^+ 3}$													
	KFB-6	26,0	2,9	**168,3**	**162,9**	**3,3**	0,04	5,6	0,4	n/d	24,4	141,8	**961,7**	**1497,3**	**10,9**
		$\frac{SO_4^{2-} 85\ Cl^- 13\ HCO_3^- 2}{Ca^{2+} 46\ Mg^{2+} 45\ Na^+ 7\ NH_4^+ 1\ K^+ 1}$													

Note: "n/d" – not detected; "-" – no data; * Standards: EU – by Directive 98/83/EC, WHO – by Guidelines for water, 1999, MAC – by [7]; ** Sampling points are given in Legend to *Fig.4*

Industrial waters are attributed to sulfate-chloride-calcium-magnesium (KFB-1, KFB-6) and carbonate-sulfate-calcium classes (KFB-5).

A dominating role of sulfate-ion in all the studied waters is explained by its high concentration in component rocks and in the material of numerous dumps as well.

pH dependant phases of weak acids and separate trace elements in river waters noticeably impact their assimilability to different biological objects.

Cations

Sodium ion belongs to elements which predetermine river water irrigation properties; its high contents lead to soil salinization. Na was detected in all the studied waters. Its maximal concentrations were indicated in the waters of River Barabatum (KFB-7, 116 *mg/L*) and Rivers Norashenik and Artsvanik conflux (KFB-4, 110 *mg/L*), whereas Na concentration was min. twofold lower in River Artsvanik waters before confluence (KFB-3, 44,6 *mg/L*). For the rest waters, Na concentration varied 5.3-33.1 *mg/L*. Wholly, no excesses vs. standard (200 *mg/L*) were observed (*Fig. 11*). In ionic composition of the studied rivers sodium ion played a secondary role.

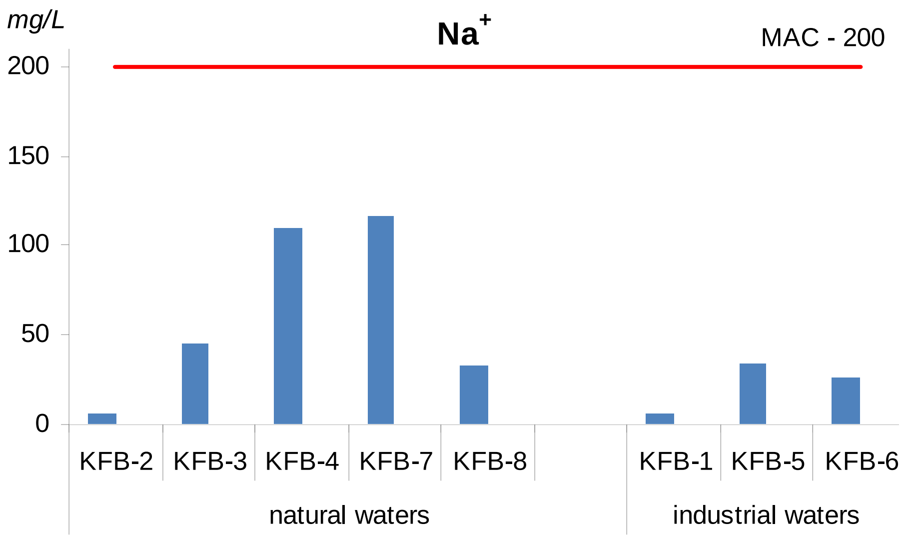


Fig. 11. *Na contents in surface waters*

Calcium ion is very active in natural waters due to carbonate and sulfate solubility barriers in fresh water and brine where calcium is bound to chlorine and due to good solubility of calcium chlorides its solubility barrier practically disappears. A sorption barrier for calcium is characterized by high absorption energy. Calcium is intensively absorbed by negatively charged rock colloids. Calcium ion belongs to positively aquated ions.

Calcium dominated cations in the studied rivers. Wholly its contents varied 54.4-316.6 *mg/L*, MAC standard being 100 *mg/L*. Practically, Ca concentrations were not excessive vs. MAC in the waters of natural streams except those of Rivers Barabatum and Kavart in which Ca concentrations were slightly (1-1.5 times) excessive vs. MAC. Unlike natural waters, Ca contents in industrial waters were 1.7-3 times excessive vs. MAC. The last index was indicated for the waters of the Kapan plant aqueduct. High concentrations of Ca in industrial waters are reflected on total water hardness (*see Tab.3, Fig.12).*

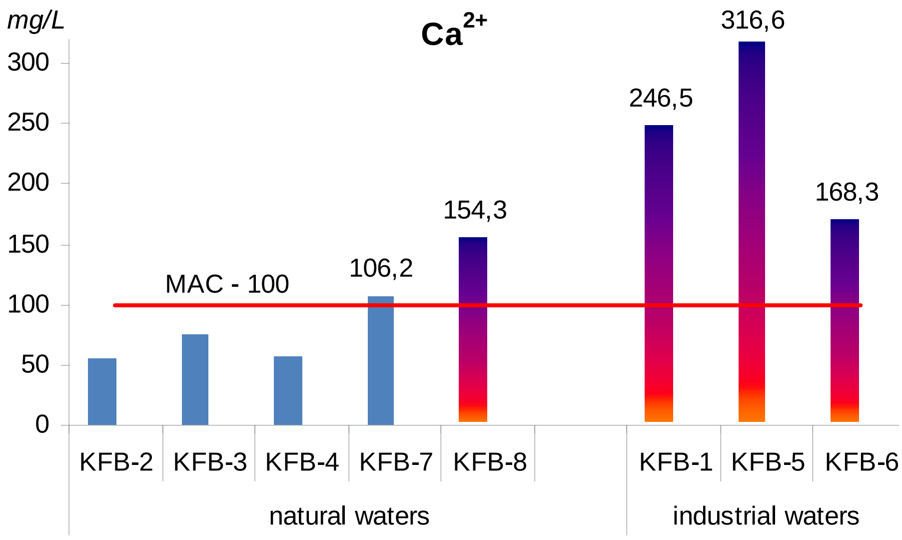


Fig. 12. *Ca contents in surface waters.*

The solubility of **magnesium** salts is higher than that of calcium salts. However in natural waters it plays a secondary role as a sorption barrier prevents free migration of magnesium as a result of high assimilation energy. Like Ca, high contents of Mg ions in natural waters increase water hardness. According to the accepted classification, by hardness level the waters are classified as soft (max. 2 *mg-eqv/L*), hard (2-10 *mg-eqv/L*) and highly hard (>10 *mg-eqv/L*). The waters of the studied streams were classified as hard and very hard (*Fig. 13*). Using these waters even in irrigation is unadvisable as they hamper the growth of vegetables and particularly leguminous species due to formation of insoluble compounds of pectines and Ca and Mg ions.

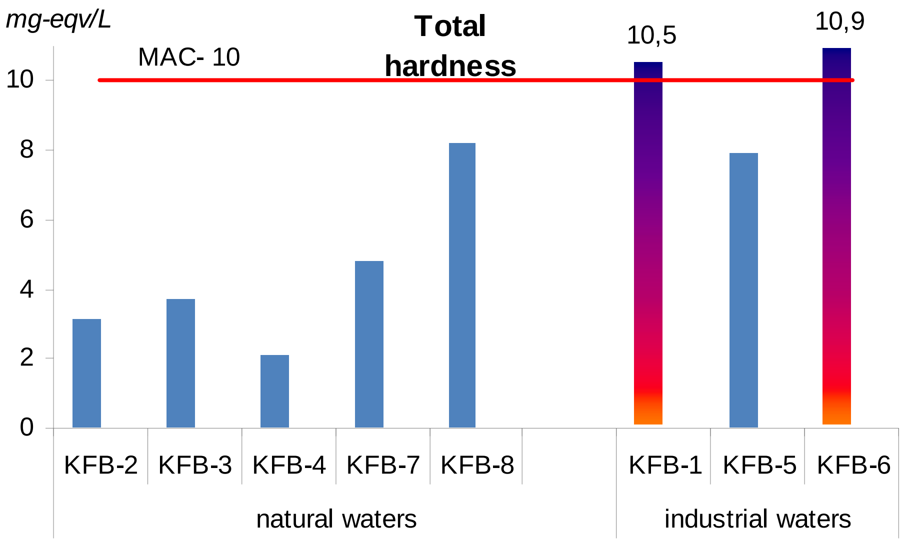


Fig. 13. *Total hardness of surface waters*

In the studied natural and industrial waters, Mg contents varied 17-105.8 and 106.8-162.9 *mg/L* respectively (Fig. 14). Except River Kavart, in the rest natural waters Mg does not play any noticeable role in formation of total water hardness, substantially contributing in this respect to industrial waters (up to 6.7 *mg-eqv/L*).

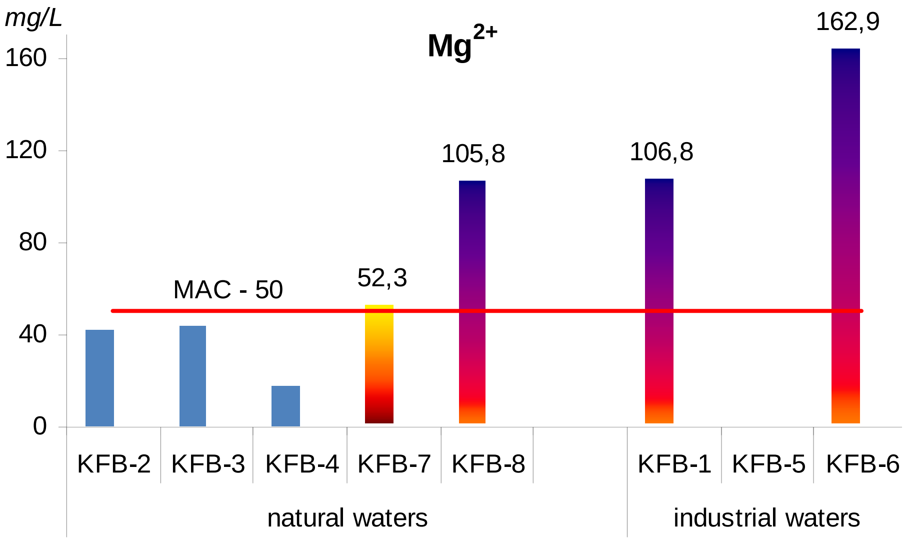


Fig. 14. *Mg contents in surface waters*

As seen from *Fig.14*, insignificant excesses of Mg vs. MAC were indicated for River Kavart (twofold) and for industrial streams (2-3 times).

Potassium ion is attributed to biologically essential and valuable elements. Potassium was detected in all the studied waters, its concentration varying 2.9-24 *mg/L*. Minimal contents were indicated for mine waters, and maximal - for River Barabatum (24 *mg/L*) and Rivers Norashenik and Artsvanik conflux (18.8 *mg/L*) (*Fig.15*).

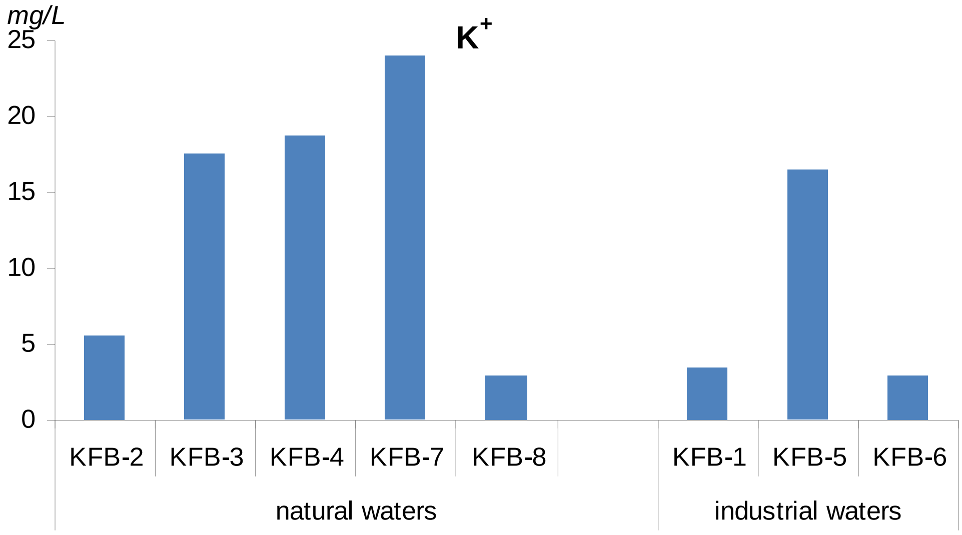


Fig. 15. *K contents in surface waters*

In natural waters nitrogen compounds represented by **ammonium ion** (NH_4^+) were detected only for Rivers Barabatum and Kavart: 5.2 and 2.3 *mg/L*, which overstepped MAC by 3.5 and 1.5 times, respectively. In industrial waters concentrations were a little bit higher. Ammonium ion was detected in the waters of the Kapan plant aqueduct (10.7 *mg/L*) and a KFB-6 stream (3.3 *mg/L*) which concentrations overstepped MAC by 7.1 and 2.2 times, respectively (*Fig. 16*).

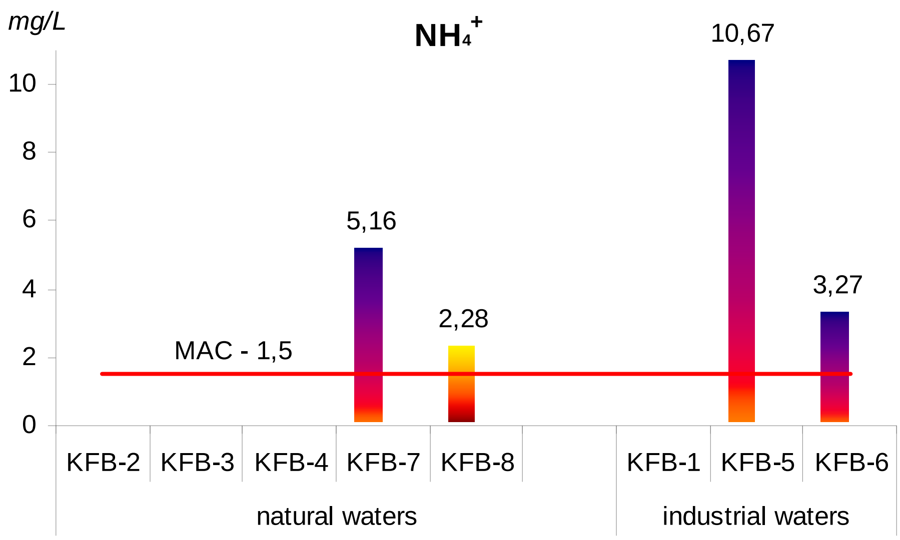


Fig. 16. *NH_4^+ contents in surface waters*

Anions

Carbonate- and hydrocarbonate ions are positively aquated ones that heighten structural pressure of solution due to which they actively migrate in natural waters. Their migration is predetermined by the presence of solubility barriers.

Carbonate-ion was detected in the waters of 3 of 5 studied natural streams on River Voghchi left bank area. Maximal concentrations of CO_3^{2-} were established for River Syunik waters - 21.6 *mg/L*; for Rivers Norashenik and Artsvanik waters it reached 12 *mg/L* at the most. As for industrial waters, CO_3^{2-} was detected only in the waters of the Kapan plant aqueduct, its concentration was rather high – 494 *mg/L* and made ¼ part of total mineralization thus predetermining a carbonate character of the waters (*Fig.17*).

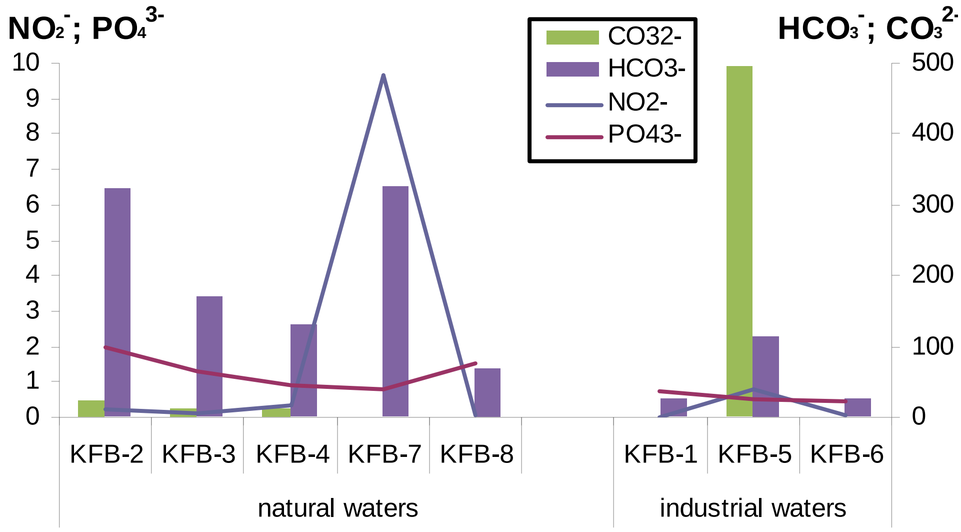


Fig. 17. *CO_3^{2-}, HCO_3^-, NO_2^-, PO_4^{3-} contents in surface waters*

The contents ***of hydrocarbonate ions*** in natural waters with the exception of River Kavart (68.3 *mg/L*) were relatively high: 129.3-324.5 *mg/L*. Maximal concentrations were detected for the waters of Rivers Syunik (322 *mg/L*) and Barabatum (324.5 *mg/L*), this making ½ and ¼ part of total mineraliztion of those waters, respectively. In industrial waters HCO_3^- concentrations were considerably lower than in natural waters: 24.4 (KFB-1, KFB-6) and 112.1 *mg/L* (KFB-5) (*Fig.17*).

Chlorine-ion (Cl^-) freely migrates in natural waters due to the absence of solubility barrier and finally forms well-soluble salts (NaCl, $MgCl_2$, $CaCl_2$). Chlorine belongs to negatively aquated ions due to which it destroys the water structure and lowers the structure pressure of solution. Chlorine-ions have no biological barriers as plants and microorganisms do not absorb them. Cl^- migrates in natural waters in form of free ion in different concentrations. The studied waters contained varying concentrations of Cl^-: from 92.2 to 241.1 *mg/L*. Neither noticeable differences nor excess vs. standards (250-350 *mg/L*) was observed between its contents in natural and industrial waters (*Tab.3, Fig.18*).

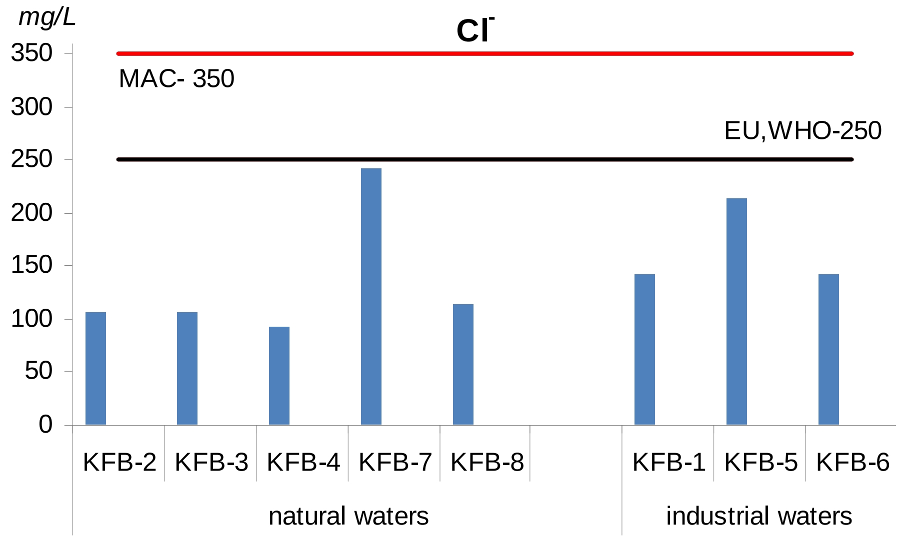


Fig.18. *Chlorine contents in surface waters.*

Sulfate-ion (SO_4^{2-}) belongs to positively aquated ions that heighten the structural pressure of solution, this predetermining its intense migration. In 75% of the studied waters sulfate-ion played a dominating role in formation of qualitative and quantitative ionic composition. In natural waters its contents widely varied 82.3 to 722.2 *mg/L* (*Fig.19*). The latter was indicated for the waters of River Kavart which crosses the territory of a copper-pyrite deposit, and thus the determined concentration (a slight excess vs. the standards – 250 and 500 *mg/L*) was quite natural to the region.

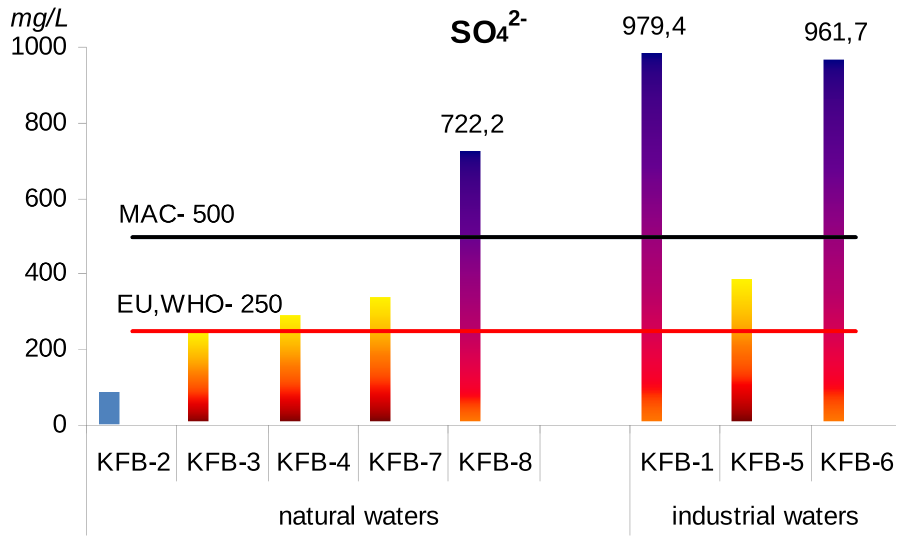


Fig.19. *Sulfate contents in surface waters.*

More noticeable concentrations of SO_4^{2-} were detected in mine waters (KFB-1, *Fig.20*) and a KFB-6 stream: 979.4 and 961.7 *mg/L*, respectively, which exceeded the accepted standards by 2 to 4 times. These waters belong to highly sulfate category, where a dominating role (max. 65%) in ionic composition is given to sulfate-ion.

Fig. 20. *Waters flowing out from the adit opposite the supermarket (KFB-1).*

The rest anions (NO_2^-, NO_3^-, PO_4^{3-}) play a secondary part in the waters of the studied streams. $\mathbf{NO_2^-}$ concentrations in natural waters with the exception of River Barabatum (9.7 *mg/L*) varied 0.04-0.3 *mg/L*; in indusrial waters $\mathbf{NO_2^-}$ concentrations were rather low (0.04-0.8 *mg/L*) (*Fig. 17*).

$\mathbf{NO_3^-}$ concentrations in natural waters widely varied from 0.8 to 76.3 *mg/L*. The latter exceeded the standards by 1.5 times and was established for River Barabatum waters only. In industrial waters $\mathbf{NO_3^-}$ concentrations (5.6-47.1 *mg/L*) did not practically exceed the standards (*Fig.21*).

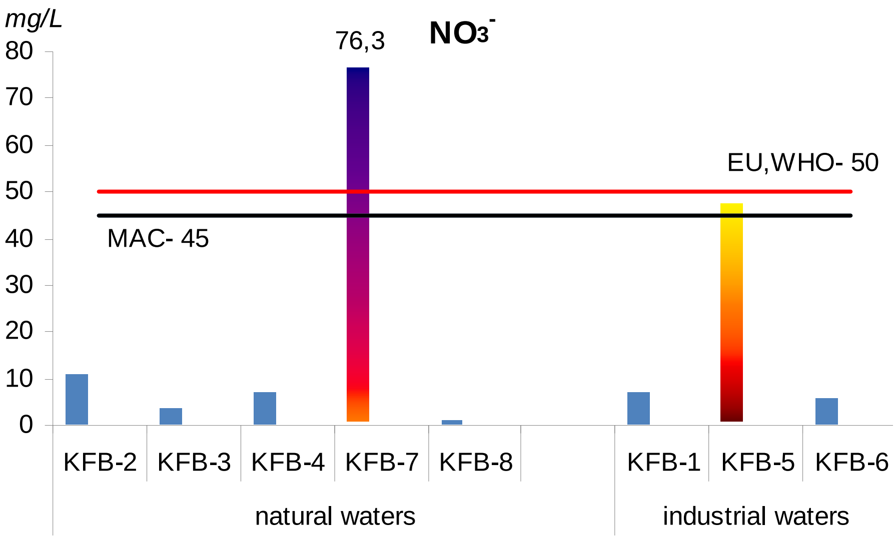


Fig. 21. *NO_3^- contents in surface waters.*

$\mathbf{PO_4^{3-}}$ ion in all the waters showed limited variations 0.4-2 *mg/L* (*Fig.17*).

2. 3. The contents of heavy metals

The obtained data on heavy metals in the waters by separate points are given in *Table 4*.

2.3.1. *Heavy metal contents in the waters of River Voghchi left bank tributaries.*

As seen from *Tab.4*, the contents of all the measured metals in the waters of natural streams in River Voghchi left bank area did not practically reach the accepted standards. Relatively high concentrations of 3 site-specific ore elements: Cd, Cu and Zn- were detected solely in the waters of River Kavart.

Cd contents varied in a wide range: 0.01-0.85 *mkg/L*. Peak concentrations were typical of the waters of Rivers Artsvanik and Norashenik confluence site – 0.85 *mkg/L*, which constitutes 85% of MAC, except the waters of River Kavart in which Cd concentrations were 5.52 *mkg/L* and exceeded both EU and MAC standards - 5 and 1 *mkg/L*, respectively.

Cu contents, too, widely varied in river water: 0.008-1.7 *mg/L*. A maximal index (1.7 *mg/L*) was observed in River Kavart waters. However such concentration was not excessive vs. EU (2 *mg/L*) and RF (1 *mg/L*, MAC) standards.

Zn concentrations in river waters varied 0.06-14.02 *mg/L*. The latter was established only for River Kavart waters: the concentration was 2.8 times excessive vs. MAC.

Table 4. *Heavy metal contents in the studied waters*

Index		As	Cd	Co	Cr	Hg	Mo	Ni	Pb	Se	Cu	Zn
		mkg/L									*mg/L*	
MAC	*EU**	*10*	*5*	*–*	*50*	*1*	*–*	*20*	*10*	*10*	*2*	*–*
	*MAC***	*50*	*1*	*100*		*0,5*	*250*	*100*	*30*		*1*	*5*
River Voghchi tributaries												
Sampling points***	**KFB-2**	1,73	0,01	1,21	2,28	0,04	18,16	1,41	0,40	1,60	0,12	0,07
	KFB-3	0,86	0,01	0,19	0,97	0,02	170,00	0,79	0,54	0,42	0,02	0,06
	KFB-4	0,83	0,85	0,72	1,45	0,02	137,90	1,12	1,82	0,38	0,05	1,15
	KFB-7	0,39	0,20	1,68	0,91	0,10	6,55	1,01	0,02	0,38	0,66	0,12
	KFB-8	0,30	**5,52**	20,00	0,52	0,03	3,21	3,85	0,19	0,90	**1,70**	**14,02**
	KFB-9	1,08	0,42	0,88	0,38	n/d	6,40	1,91	n/d	–	0,0077	0,11
	Waters from adit and industrial stream waters											
	KFB-1	3,42	**8,75**	17,13	2,28	0,09	5,18	3,18	0,19	2,28	**3,80**	**9,83**
	KFB-5	0,47	n/d	0,18	1,45	0,01	21,39	5,53	3,01	0,53	0,01	0,06
	KFB-12	**13,44**	**16,30**	46,74	4,16	0,03	13,37	15,36	0,28	1,41	**20,20**	**10,88**
	KFB-6	4,46	**10,62**	40,10	2,13	0,05	10,91	8,96	0,68	1,77	**15,18**	**6,75**
	KFB-10	0,70	0,02	0,81	0,80	**3,31**	8,27	0,33	0,05	0,06	0,10	0,75
	KFB-11	0,15	0,01	0,27	0,70	0,03	87,65	0,70	0,12	0,32	0,02	0,06

Note: “n/d” – not detected; “-” – no data; Standards: * EU – by Directive 98/83/EC, **MAC – by [7];
***Sampling points are given in Legend to *Fig.4*

The rest 9 measured elements were not excessive vs. MAC.

As contents in river water varied 0.30-1.73 *mkg/L*, considering that EU and MAC is 10 and 50 *mkg/L*, respectively. Maximal concentrations were detected in Rivers Syunik and Voghchi waters (1.73 and 1.08 *mkg/L*, respectively).

Co concentrations varied in a wide range 0.19-20 *mkg/L*, and did not reach MAC (100 *mkg/L*). The maximal concentration 20 *mkg/L* was indicated for River Kavart.

Cr concentrations varied in a range 0.38-2.28 *mkg/L*, the standard being 50 *mkg/L*. Maximal concentrations were detected in the waters of River Syunik (2.28 *mkg/L*) and Rivers Artsvanik and Norashenik conflux (1.45 *mkg/L*).

Hg concentrations were rather low and varied 0.02-0.1 *mkg/L*, whereas EU and MAC standards are 1 and 0.5 *mkg/L*, respectively. Maximal concentration of Hg (0.1 *mkg/L*) was indicated for River Barabatum waters.

Mo concentrations varied in a very wide range 6.4-170 *mkg/L*, MAC being 250 *mkg/L*. Maximal concentration (170 *mkg/L*) was detected in River Artsvanik (KFB-3) waters, which flows out from the same-name tailing repository. When flowing into River Norashenik, Mo concentration lowered a little reaching 137.9 *mkg/L*.

Ni contents showed rather limited variations 0.79-3.85 *mkg/L*, the standard being 20 (EU) and 100 *mkg/L* (MAC). Maximal concentration 3.85 *mkg/L* was observed in River Kavart waters.

Pb contents, too, were very low 0.19-1.82 *mkg/L*, whereas the standards are 10 (EU) and 30 *mkg/L* (MAC). Maximal concentration 1.82 *mkg/L* was indicated for river waters behind Rivers Artsvanik and Norashenik confluence site. This can be explained by the fact that River Norashenik runs in the zone of the Shahumian polymetallic deposit.

Se concentration limits were 0.38-1.6 *mkg/L*, the standard being 10 *mkg/L*. Maximal concentrations were detected in Rivers Kavart (0.9 *mkg/L*) and Syunik (1.6 *mkg/L*).

2. 3. 2. *Heavy metal contents in mine waters from adits and industrial streams.*

Unlike natural stream waters, mine waters from the adit and industrial stream waters were high in a number of toxic (Cd, As, Hg) and ore (Cu, Zn,) elements (*Tab.4*). Let's focus on per-element water composition.

Cd concentrations in the studied waters varied 0.01-16.3 *mkg/L*. High concentrations of Cd were indicated for mine waters from the adit (KFB-1) – 8.75 *mkg/L*, which overstepped all the accepted standards: EU – 5 *mkg/L*, MAC - 1 *mkg/L*. Maximal harmful concentration of Cd

Fig. 22. *A confluence site of technical waters and canyon stream, nearby adiminstrative building of the plant* (KFB-12)

was detected in waters flowing out from the adit (KFB-12, *Fig. 22*) – 16.3 *mkg/L*. Cd concentration lowered by 1.6 times (10.6 *mkg/L*) after the inflow to the canyon stream (KFB-6), however it still remained harmful (*Fig. 23*).

Like Cd, **As** concentrations, too, were high in point KFB-12 – 13.44 *mkg/L* (a 1.3 time excess vs. EU standards). After confluence of mine waters and the canyon stream, As concentrations showed a threefold decrease (4,46 *mkg/L*). Wholly, no harmful concentrations were indicated for the rest sampling points (*Fig. 23*).

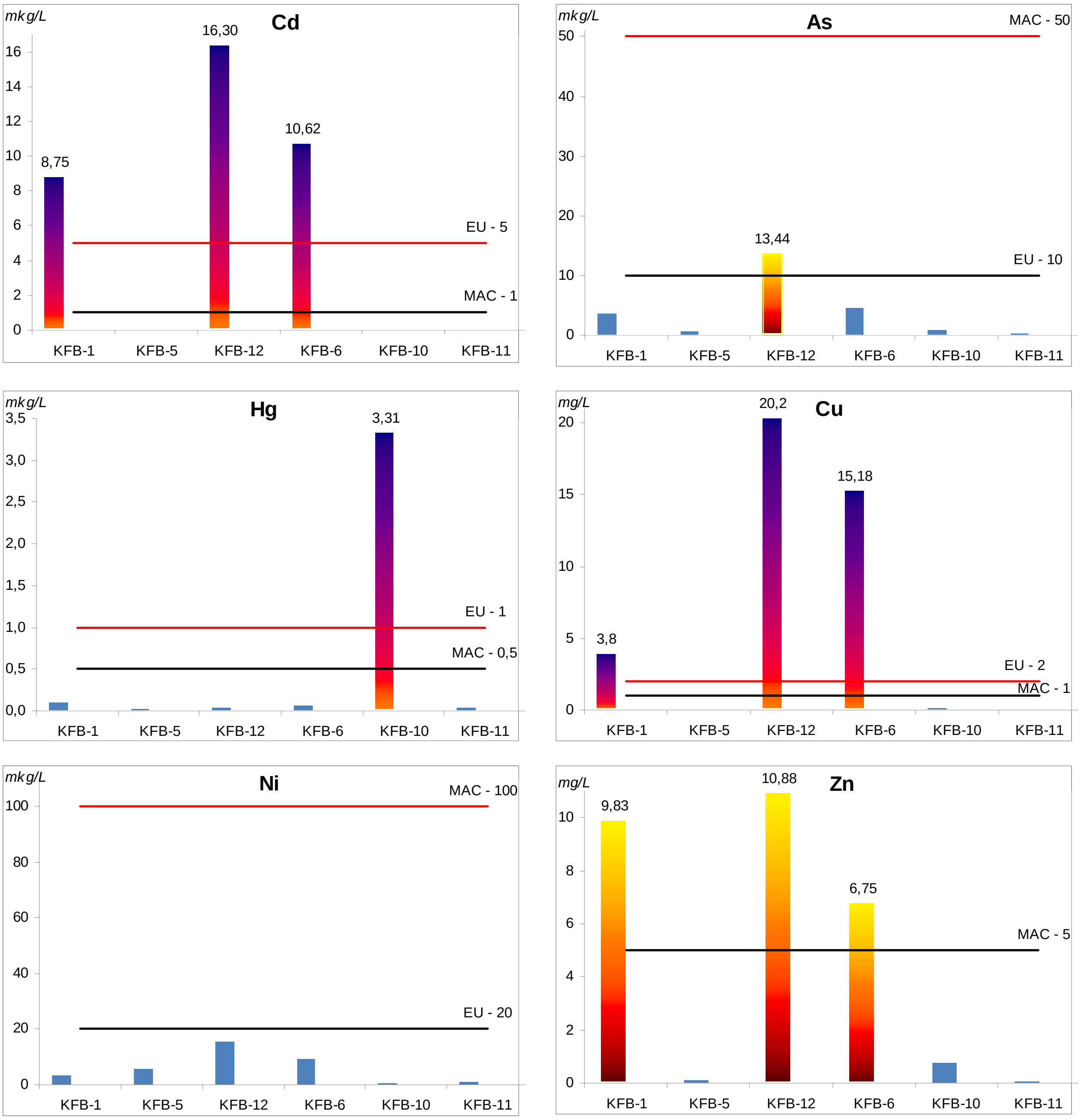


Fig. 23. *Heavy metal concentrations in the waters from the adit and the aqueduct*

Our research indicated that **Hg** concentrations were low and varied in a range 0.01-0.09 *mkg/L*. Maximal concentration (0.09 *mkg/L*) was detected in mine waters (KFB-1), except the Artsvanik tailing repository aqueduct waters (KFB-10) used for irrigation of agricultural land of Syunik and the farm (*Fig. 24*). Hg concentration was 3.31 *mkg/L* which is 6.6 and 3.3 times excessive vs. MAC and EU standards (0.5 and 1 *mkg/L*, respectively). The situation is alarming and it is obvious that the farm produce intended both for individual use and for commercial needs would contain dramatic concentrations of this super toxic element.

Fig. 24. *Waters flowing out from the Artsvanik tailing repository (KFB-10)*

The studied waters were high in Cu and Zn – site-specific ore elements. As seen from *Fig*. 23**,** similarly to Cd and As, high concentrations of Cu and Zn were detected in the same points.

Cu was 3.8-20.2 and 1.6-10 time excessive vs. MAC and EU standards, respectively, and Zn showed a 1.3-2 time excess vs. MAC. Maximal values were indicated for the KFB-12 waters. After confluence with the canyon stream the concentration of the both elements decreased due to dissolution, but remained harmful (*Fig. 23*).

No MAC-overstepping concentrations of the rest measured elements were detected. MAC- approaching concentrations were established only for Ni (15.36 *mkg/L*) in KFB-12, this making 77% of EU standard (20 *mkg/L*).

The detected concentration limits for the rest elements were as follows:

Co- 0.18-46.74 *mkg/L* (MAC – 100 *mkg/L*); max.concentrations were observed in the waters from 3 points: KFB-1- 17.13 *mkg/L*, KFB-12 – 46.74 *mkg/L*, KFB-6 – 40.1 *mkg/L*;

Cr- 0.7-4.16 *mkg/L* (MAC – 50 *mkg/L*); max.concentrations were observed in the waters of the same 3 points: KFB-1 – 2.28 *mkg/L*, KFB-12 – 4.16 *mkg/L*, KFB-6 – 2.13 *mkg/L*.

Mo- 5.18-87.65 *mkg/L* (MAC – 250 *mkg/L*); max. concentrations were established for the plant aqueduct waters (KFB-5) – 21.39 *mkg/L* and infiltration waters from under the Artsvanik tailing repository dam (KFB-11, *Fig.25*) - 87.65 *mkg/L*.

Pb- 0.05-3.01 *mkg/L* (MAC and EU standard – 30 and 10 *mkg/L*, respectively); max. concentration was detected in the plant aqueduct waters (KFB-5) – 3 *mkg/L*.

Se – 0.06-2.28 *mkg/L* (MAC – 10 *mkg/L*); max. concentrations were established for the waters flowing out from adits: KFB-1 – 2.28 *mkg/L*, KFB-12 – 1.41 *mkg/L*, KFB-6 – 1.77 *mkg/L*.

Fig.25. *Water infiltration from the Artsvanik tailing repository (KFB-11)*

2.3.3. Heavy metal transfer by streams

Additionally we calculated volumes of elements transferred by separate streams. The outcomes are given in *Tab.5.*

Table 5. The volumes of element transfer by separate streams.

Points*	Water discharge, *L/sec*	Volumes of element transfer										
		As	**Cd**	**Co**	**Cr**	**Hg**	**Mo**	**Ni**	**Pb**	**Se**	**Cu**	**Zn**
		g/day									*kg/day*	
KFB-8	51	1,3	24,3	88,1	2,3	0,13	14,14	17,0	0,84	3,97	7,49	61,78
KFB-1	1,4	0,4	1,06	2,07	0,3	0,01	0,63	0,38	0,02	0,28	0,46	1,19
KFB-7	0,3	0,01	0,01	0,04	0,02	-	0,17	0,03	-	0,01	0,02	-
KFB-9	1840	171,1	66,0	140,2	60,3	-	1016,8	303,3	-	-	1,23	17,49
KFB-6	120	46,24	110,1	415,76	22,08	0,52	113,1	92,9	7,05	18,35	157,4	69,98
KFB-3	7,1	0,53	0,01	0,12	0,60	0,01	104,28	0,48	0,33	0,26	0,01	0,03
KFB-4	695	49,84	51,04	43,23	87,07	1,2	8280,6	67,25	109,3	22,8	3,0	69,06
KFB-5	14,5	0,59	-	0,23	1,82	0,01	26,80	6,93	3,8	0,7	0,01	0,08
KFB-2	8,2	1,23	0,01	0,86	1,62	0,03	12,87	1,00	0,28	1,13	0,08	0,05

Note: Calculations of per-element transfer volumes were underpinned by stream water discharge data and the outcomes of chemical analyses given in *Tab.3,** Abbreviation for points is provided in Attachment to *Tab.3,* "-" – no data.

The data from *Tab. 5* prove that for the whole studied period maximal water discharge was established for River Voghchi – 1840 *L/sec,* followed decreasingly by Rivers Norashenik and Artsvanik conflux – 695 *L/sec*, a major portion of water volume – 99% falling on River

Norashenik, and by a conflux KFB -6 -120 *L/sec* and River Kavart - 51 *L/sec*.

Judging by the first block of data from *Tab.4,* where the observation points are given as far as the waters inflow to River Voghchi, maximal volume of water to River Voghchi (KFB-9) was transferred by River Kavart (max.2.8%). Total share of the rest 2 studied tributaries (KFB-1, KFB-7) made as much as 0.09% of overall water volume throughout studied section of River Voghchi (KFB-9). According to calculation data (KFB-8, 1, 7, 9), maximal transferred volumes of the element sum fell on River Voghchi. By transferred volumes the elements make up the following ranked series (*kg/day*):

$$Zn_{(17,5)} > Cu_{(1,2)} – Mo_{(1)} > Ni_{(0,3)} – Co_{(0,14)} – As_{(0,17)} > Cd,Cr_{(0,06)}$$

(in brackets, the element transfer volumes are given)

As seen from the series, the leading position is held by Zn, which – by transfer volumes- is by an order ahead of elements such as Cu and Mo. Consistent with data from *Tab.4* maximal volume of Zn was transferred by River Kavart – 61.78 *kg/day*, and incomparably small - from the adit (KFB-1)- 1.19 *kg/day*. Difference between the volumes of transfer is some 3.5 times. Presumably, this could be explained by the fact that after River Kavart emptied into River Voghchi some 2 *km* upstream an intense dissolution occurred adding Zn sedimentation under observed neutralization of waters: pH values increased from 6.36 to 7.68. A similar picture was observed for Cu, too. By the rest elements (Cd, Co, Cr, Ni) a relative increase in concentration was indicated (*Fig.26*).

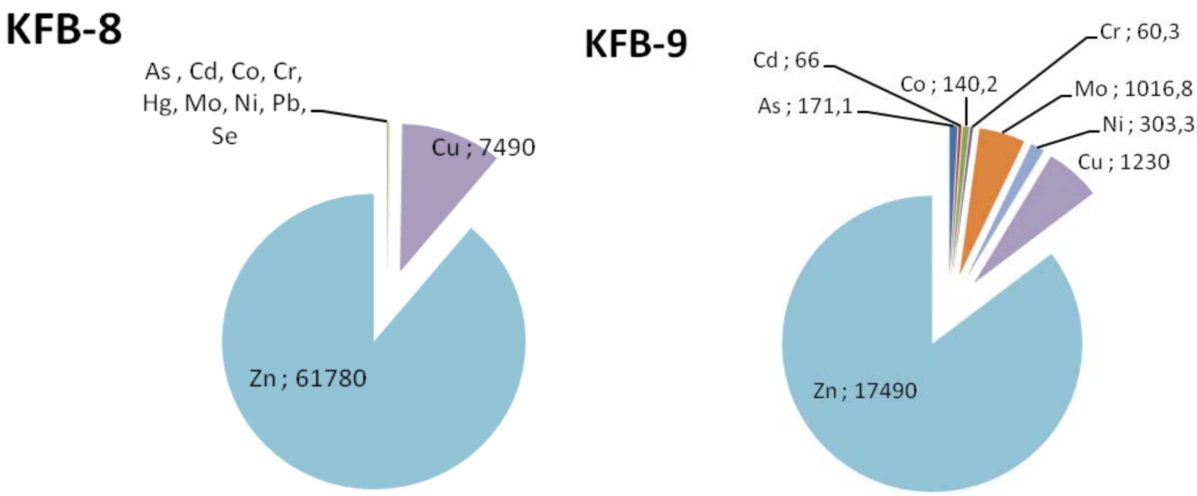


Fig. 26. *Relations between the volumes of element tranfer by Rivers Kavart (KFB-8) and Voghchi (KFB-9) streams, g/day*

Though available in tributary waters (KFB-8,1,7), some elements (Hg, Pb, Se) were not detected at all in River Voghchi waters. Basic reasons were too small volumes of these element transfer by the noted tributary waters (in the range 0.00013-0.004 *kg/day*); active dissolution by River Voghchi waters, possible sedimentation of elements. The last phenomenon can occur in the presence of a number of geochemical barriers (thermodynamic, redox, etc.) on the stream confluence line as results of a drastic change in some physical and chemical indices of waters (see *Tab. 2*). So one should expect that the sites of the inflow of tibutaries to River Voghchi bottom sediments would accumulate substantial volumes of heavy metals, especially in the case of River Kavart inflow as the river crosses the territory of ore field.

As noted above, of the rest studied streams, maximal water discharge index fell on confluxes KFB-6 and KFB-4 (Rivers Norashenik and Artsvanik). The both streams are characterized by large volumes of metal transfer. By the volumes of transfer by these streams heavy metals make up the following series (*kg/day*):

KFB-6: $Cu_{(157)} > Zn_{(70)} >> Co_{(0,4)}–Mo,Cd_{(0,1)} > Ni_{(0,09)}–As_{(0,04)}–Cr,Se_{(0,02)} > Pb_{(0,007)} – Hg_{(0,0005)}$;
KFB-4: $Zn_{(69)} > Mo_{(8)}–Cu_{(3)} > Pb_{(0,1)} > Cr_{(0,09)}–Ni_{(0,07)}–Cd,As_{(0,05)}–Co_{(0,04)} > Se_{(0,02)} > Hg_{(0,001)}$.

As seen from the series, the character of qualitative and quantitative compositions of element transfer by the streams is quite different. In point KFB-6 the leading position was held by Cu and Zn that had maximal volumes of transfer: 157 and 70 *kg/day*, respectively.

In KFB-4 the volume of Zn transfer was similar to the previous stream, however the transfer of the rest elements had different volume characteristics. One should emphasize the size of Mo transfer volume: some 8 *kg/day*.

2.4. Irrigation properties of waters

The quality of river water used in irrigation of agricultural land was assessed with regard for a number of indices: water mineralization level, Stebler’s irrigation index and so on [14].

The most effective is the assessment of irrigation water appropriateness by mineralization level through the following scale:

1) **good waters:** total mineralization - max. 400 *mg/L*,
2) **satisfactory waters:** total mineraliztion ≤ 1000 *mg/L*,
3) **harmful waters:** total mineralization varies 1000-3000 *mg/L*,
4) **waters bringing to soil salinization:** total mineralization - 4000>*mg/L*.

However, besides the sum of dissolved salts, one should also consider a number of ecologically important indices and particularly the contents of separate ions and heavy metals. *Tab. 6* contains basic characteristics of the studied waters used in irrigation.

Table 6. Water appropriateness to irrigation by basic indices

Points	Excess vs. MAC										**Sum of excesses >1**
	1000 *mg/L* by total minerali zation	**by ions**					**by heavy metals**				
		Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cd	Cu	Zn	Hg	
Waters satisfactory for irrigation purposes											
KFB-2	0,6	0,5	0,8	n/d	0,2	0,1	0,01	0,12	0,01	0,08	–
KFB-3	0,7	0,7	0,9	n/d	0,07	0,5	0,01	0,02	0,01	0,04	–
KFB-4	0,7	0,5	0,3	n/d	0,1	0,6	0,8	0,05	0,23	0,04	–
Waters harmful for irrigation purposes											
KFB-7	1,3	1	1	3,4	1,5	0,7	0,2	0,66	0,02	0,2	8,2
KFB-8	1,2	1,5	2,1	1,5	0,01	1,4	5,5	1,7	2,8	0,06	17,7
KFB-6	1,5	1,7	3,2	2,2	0,1	1,9	10,6	15,2	1,3	0,1	37,6
KFB-10	–	–	–	–	–	–	0,02	0,1	0,15	6,6	6,6

Consistent with the given classification and with regard for the contents of harmful concentrations of ions (*Tab.3*) and heavy metals (*Tab.4*), the studied waters were attributed to 2 basic groups: satisfactory and harmful. No “good” waters.

1.Waters satisfactory for irrigation purposes

This group includes the waters from 3 streams: River Syunik (KFB-2), River Artsvanik (KFB-3) and Rivers Norashenik and Artsvanik conflux (KFB-4). For all the waters the measured indices (total mineralization, ion and heavy metal contents) met the accepted standards.

2.Waters harmful for irrigation purposes

This group includes waters of Rivers Barabatum (KFB-7) and Kavart (KFB-8) as well as those from the studied man-made sources (KFB-6, 10). For these waters, indicated were high mineralization indices (1203-1622 *mg/L*), excessive ions (Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}) and excessive heavy metals (Cd, Cu, Zn).

For River Barabatum waters, pollution was induced by ions and high mineralization (M), about half a pressure falling on biogenic pollution – ammonium ion (42%, *Fig. 27*). The sum of excesses vs. MAC was 8.2.

For the waters of River Kavart, beside pollution by the sum of ions, a considerable share belonged to ore elements dominated by Cd (31%, *Fig.27*). The sum of excesses vs. MAC was 17.7.

Pollution of KFB-6 stream waters was of a complex character, too. The leading position was held by heavy metals: Cu - 40%, Cd-28% (*Fig.27*). The sum of excesses vs. MAC was 37.6.

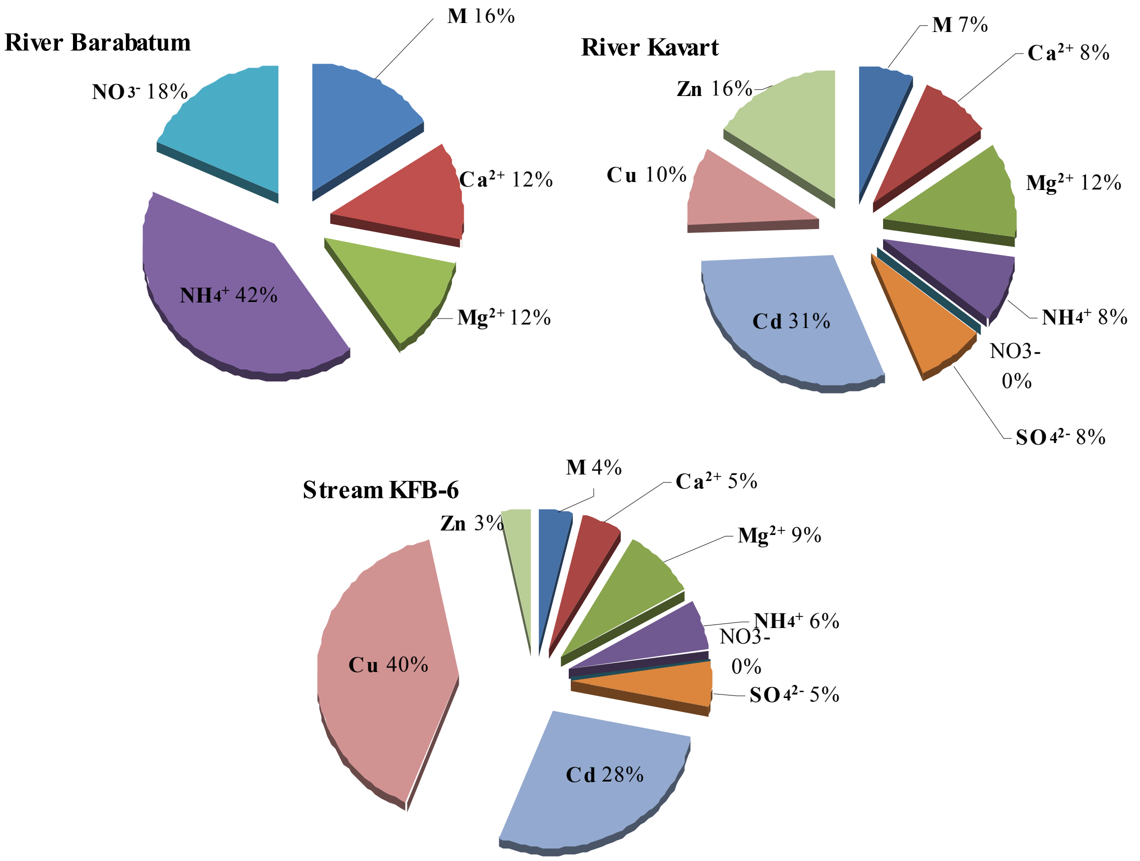


Fig. 27. *The share of separate pollutants by separate streams*

One should pay special attention and emphasize a danger of the tailing repository aqueduct (KFB10) containing critical concentrations of mercury.

It should be noted that these waters should not be used in irrigation of agricultural land as high level and poly-element character of pollution is a serious factor of ecological risk to the ecosystem.

CONCLUSIONS

- By basic physical and chemical parameters (pH, electroconductivity, salinity) mine waters did not meet the accepted standards.
- The waters of the rivers crossing the agricultural lands (Rivers Syunik and Norashenik) were characterized by high turbidity index.
- The leading role in ionic composition of the studied waters was given to calcium and sulfate, which maximal concentrations were indicated in mine waters.
- Due to high concentrations of Ca and Mg the waters were attributed to the category of hard and very hard ones.
- Mine waters from adits and industrial waters from the aqueduct were high in toxic (Cd, As, Hg) and mine (Cu, Zn) elements.
- Vs. MAC, no excessive heavy metals were detected in the studied rivers except River Kavart with excessive Cd, Cu and Zn.
- By mineralizaton level and standards for ion and heavy metal contents, Rivers Syunik, Artsvanik waters and Rivers Norashenik and Artsvanik conflux were characterized as satisfactory for irrigation purposes.
- The waters of River Barabatum were harmful for irrigation purposes due to high mineralization indices and excessive ions (Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-). The waters of River Artsvanik and the stream KFB-6 were also harmful due to high mineralization indices and excessive ions (Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}) and excessive heavy metals (Cd, Cu, and Zn). Especially hazardous were the Artsvanik aqueduct waters due to critical concentrations of Hg.
- The mixing of mine waters with surface streams leads to the increase in concentration of a number of compounds and heavy metals in the waters of River Voghchi left-bank tributaries. Though the concentrations of chemical elements did not reach MAC, but one should not ignore a real ecological risk factor due to their high coefficients of cummulation in biological environments.
- The volumes of metal transfer by separate streams were calculated. The largest volumes were those of Rivers Norashenik and Artsvanik conflux.

3. SOIL POLLUTION

3.1. The assessment of heavy metal pollution of the territory of the city of Kapan

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

Soil pollution level was assessed through collation of actual and background contents of heavy metals. To calculate the background contents, a plot was selected in southeastern part of the city where the soils are developed on unchanged andesite porphyrites.

Data analysis indicated (*Tab.7*) that vs. the lithosphere clark the background contents were 8.8 times excessive for Mo, 5.5 – for Cd, 4.5 – for As, 4.3 – for Pb, 3.2 – for Zn, 2.7 - for Cu. Vs. lithosphere clark the background concentrations of Ni and Sn were also slightly excessive – by 1.5 and 1.1 times respectively. By the background excess vs. MAC, detected were excessive contents of As (3.8) and insignificant excesses of Mo and Ni (1.76 and 1.74, respectively) and of Cu (1.24 times).

Table 7. *Lithosphere clark, MAC and the background contents of heavy metals in Kapan's soils.*

Elements	**Lithosphere clark** [1]	**MAC**[2]	Kapan (n=147)					
			background	Excess vs.		*C, mg/kg* **(sum.)**	*C* excess vs.	
	mg/kg **(sum.)**			**Clark**	**MAC**		**background**	**MAC**
Cu	46.0	100*	124	2.7	1.24	410	3.3	4.1
Pb	16.0	100*	68	4.3	0.68	237	3.5	2.4
Mo	1.0	5.0*	8.8	8.8	1.76	9.7	1.1	1.9
Sn	2.5	50.0*	2.8	1.1	0.056	4	1.4	0.08
Zn	76.0	300*	245	3.2	0.82	231	0.9	0.77
Ni	58.0	50.0***	87	1.5	1.74	124	1.4	2.5
Cr	99.0	100*	60	0.6	0.6	85	1.4	0.85
As	1.7	2**	7.6	4.5	3.8	8	1.1	4.0
Cd	0.2	2	1.1	5.5	0.55	2	1.8	1

Note: ***C*** *- mean contents of heavy metals in Kapan's soils;* [1] *According to A.P.Vinogradov [1962];* [2] *to [3],* ** *-to [15],* *** *- [12]*

The outcomes of the analysis of heavy metal contents in Kapan's soils (*Fig. 28*) distinctly indicated excessive Pb and Cu vs. the background. To determine a relative element accumulation level, a geochemical series of the intensity of the elements was calculated. The position of the element in the series was determined by the value of its mean contents excess vs. the background.

A series by mean contents: **Pb** $_{(3.5)}$-**Cu** $_{(3.3)}$–**Cd** $_{(1.8)}$–**Ni, Sn, Cr**$_{(1.4)}$–**As, Mo** $_{(1.1)}$– **Zn** $_{(0.9)}$
(summary intensity = 15.9).

As seen from the series, the first position is given to Pb showing a 3.5 time excess vs. the background; similar excess vs. the background (3.3 times) is established for Cu which holds the second ordinal position.

A series made up by maximal concentration coefficient values is more intense; however by dominating elements (Pb, Cu) the series is qualitatively bound to the previous one:

A series by maximal contents: Pb $_{(73..5)}$–**Cu** $_{(60.5)}$–**Zn** $_{(6.1)}$–**Sn** $_{(5.4)}$–**Ni** $_{(5.2)}$–**Mo** $_{(4.6)}$–**Cr** $_{(4.2)}$ – **Cd** $_{(4.0)}$ – **As** $_{(1.7)}$
(summary intensity = 165.2).

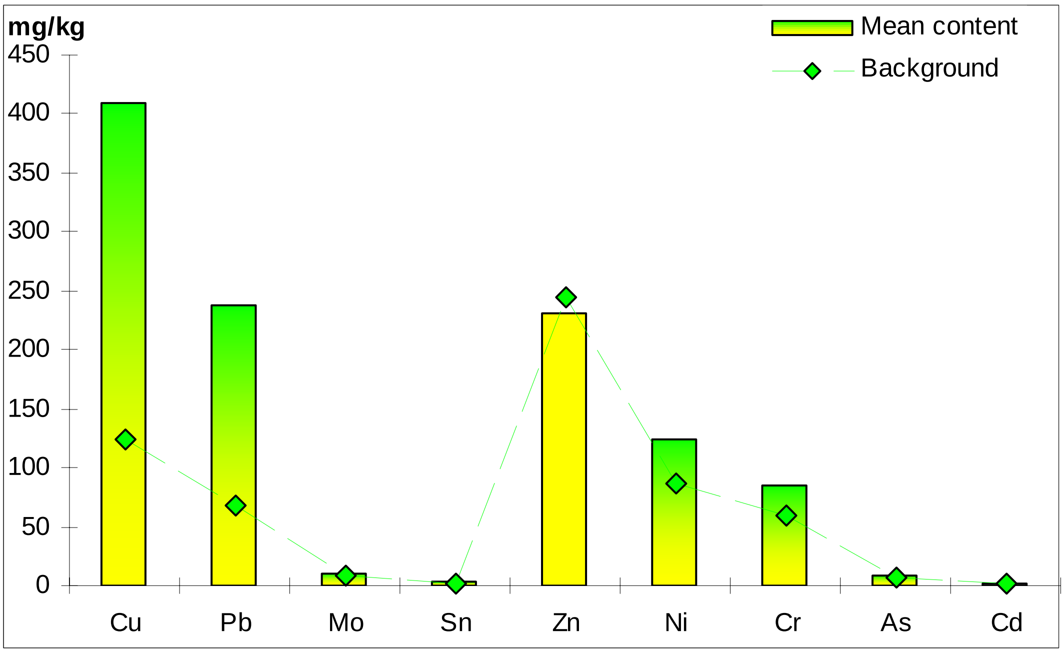


Fig. 28. *The background and mean concentrations (mg/kg) of heavy metals in Kapan's soils.*

Ecological risk is seen in elements with high contents vs. the background. From positions of sanitary and hygienic characteristics of soils, MAC-overstepping contents are also taken into consideration.

In this respect (*Fig. 29*), one should stress Cu and As in Kapan's soils, which mean contents were 4.1 and 4.0- times excessive vs. MAC, respectively. Mean contents of Ni, Pb, and Mo were 2.5, 2.4 and 1.94 times excessive, too. A more detailed sanitary and hygienic characteristic of Kapan's soils is discussed in Chapter 3..2.

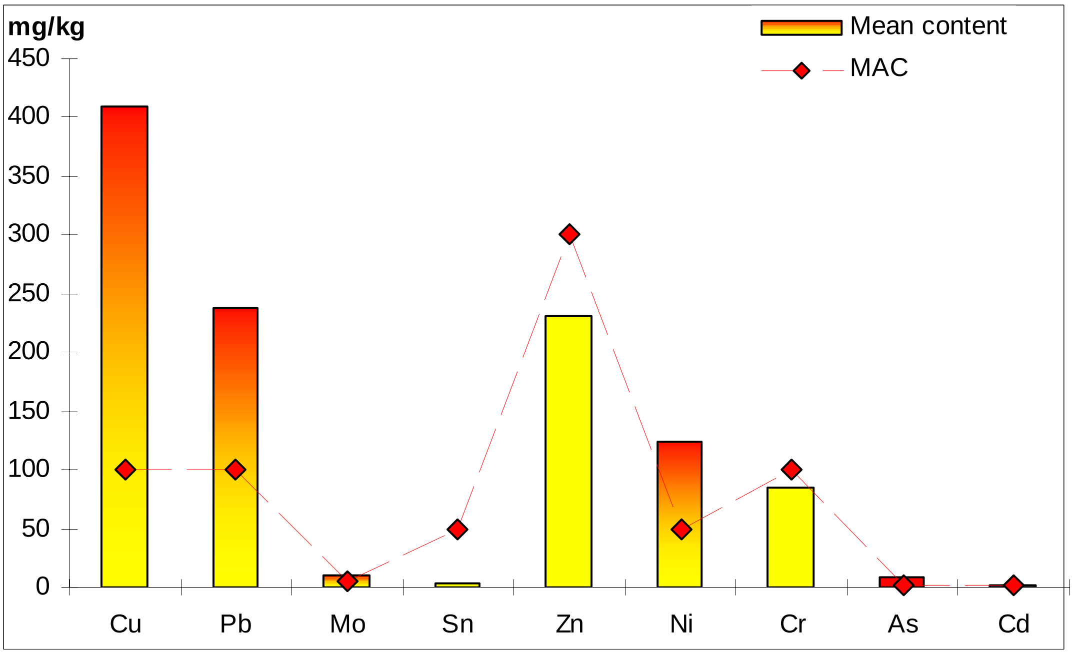


Fig. 29. *MAC and mean concentrations (mg/kg) of heavy metals in Kapan's soils.*

To analyze spatial distribution of element concentrations on the city's territory, specialized mono-element geochemical schematic maps were produced.

3.1.2. Ecological and geochemical mapping of the soils of the city of Kapan

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

Heavy metal concentrations (C, %) and concentration coefficients (*CC*) on Kapan's soils cover by separate fields are given in *Tab. 8.*

Table 8. *The background, concentrations (C, %) and concentration coefficients (CC) of heavy metals in Kapan's soils.*

Elements	background %	Indices	FIELDS OF CONCENTRATIONS							
			< background		background – 3		3 - 9		9 – 27	
			C	CC	C	CC	C	CC	C	CC
Cu	0.0124	min.	0.009	0.73	0.015	1.21	0.040	3.23	0.250	20.16
		max.	0.012	0.97	0.035	2.82	0.070	5.65	0.750	60.48
		mean	0.011	0.87	0.025	1.99	0.048	3.90	0.500	40.32
		N=	24		85		34		4	
Pb	0.0068	min.	0.0035	0.51	0.007	1.03	0.025	3.68	0.075	11.03
		max.	0.0065	0.96	0.020	2.94	0.045	6.62	0.500	73.53
		mean	0.0054	0.79	0.009	1.39	0.031	4.54	0.281	41.28
		N=	27		99		14		7	
Mo	0.00088	min.	0.0004	0.45	0.0009	1.02	0.0030	3.41	-	-
		max.	0.0008	0.91	0.0025	2.84	0.0040	4.55	-	-
		mean	0.0007	0.81	0.0011	1.30	0.0032	3.64	-	-
		N=	84		58		5		-	
Zn	0.0245	min.	0.008	0.33	0.025	1.02			-	-
		max.	0.020	0.82	0.070	2.86	0.150	6.12	-	-
		mean	0.017	0.68	0.033	1.35			-	-
		N=	103		42		2		-	
Sn	0.00028	min.	0.00008	0.27	0.0003	1.07	0.0009	3.21	-	-
		max.	0.00025	0.89	0.0007	2.50	0.0015	5.36	-	-
		mean	0.00017	0.61	0.0004	1.42	0.0011	3.84	-	-
		N=	28		115		4		-	
Ni	0.0087	min.	0.005	0.57	0.009	1.03	0.028	3.22	-	-
		max.	0.008	0.92	0.025	2.87	0.045	5.17	-	-
		mean	0.007	0.83	0.014	1.62	0.034	3.88	-	-
		N=	48		95		4		-	
Cr	0.006	min.	0.0008	0.13	0.006	1.00	0.020	3.33	-	-
		max.	0.0050	0.83	0.016	2.67	0.025	4.17	-	-
		mean	0.0044	0.73	0.009	1.47	0.023	3.89	-	-
		N=	20		124		3		-	
Cd	0.0001	min.	0.00005	0.50	0.00015	1.50			-	-
		max.	0.00008	0.75	0.00030	3.00	0.0004	4.0	-	-
		mean	0.00007	0.74	0.00019	1.92			-	-
		N=	29		116		2		-	
As	0.00076	min.	0.00050	0.66	0.0010	1.32	-	-	-	-
		max.			0.0013	1.71	-	-	-	-
		mean			0.0011	1.38	-	-	-	-
		N=	59		88		-		-	

Note: *Concentration coefficients (CC) were calculated by the background.*

The mono-element geochemical schematic maps were produced solely for heavy metals dominant for Kapan's soils. Brief description is given below.

Lead (*Fig. 30*) – a dominating element to the city's soils pollution. The background is 4.3 high vs. lithosphere clark. On the city's territory fields of 5 concentration levels were contoured out.

The fields (5^{th}) with maximal values (>0.1836%) have a point morphostructure and are localized along River Voghchi left- (northern part of the city, in the vicinities of Kavart settlement) and right banks (southern part of the city) as well as in central part of the city. The fields of 4^{th} and 3^{rd} Pb concentration level (respectively 0.0612-0.1836% and 0.0204-0.0612%) surround the 5^{th} concentration level field and spatially stretch out predominantly toward industrial objects of the city (the north), and - in central part of the city - towards garages and roads. The soils of the basic part of the city's territory are attributed to the 2^{nd} concentration level (0.0068-0.0204%), where a 1-3 fold excess vs. the background was observed. The city's territory comprises sites with low-background contents of Pb (<0.0068%) as well – predominantly, sharply local fields localized throughout the city's area.

<u>Copper</u> (*Fig. 31*) – The second essential element in the city soil pollution. The background is 2.7 and 1.24 times excessive vs. the lithosphere clark and MAC, respectively. On the city's territory fields of 5 concentration levels were contoured out. Spatially, the fields (5^{th}) with maximal values (>0.3348%) are localized along River Voghchi left bank (northern part of the city, in the vicinities of Kavart settlement) as well as in central part of the city. The field has a point morphostructure and spatially stretches out toward the outcrops of intensively and hydrothermally changed rocks. The fields of 4^{th} (0.1116-0.3348%) concentration level belt that of 5^{th} concentration level and are found in central part of the city, too, on a confluence site of the Kavart and Vachaganchet tributaries and River Voghchi. A relatively wide distribution is common for fields of the 3^{rd} concentration level (0.0372-0.1116%) spreading tape-like from the north and northeast parts of the city to its center. Several point and oval fields are discretely located throughout the city's area. The soils of the basic part of the city's territory belong to the fields of the 2^{nd} concentration level (0.0124-0.0372%), where a 1-3 fold excess vs. the background was indicated. The city's territory comprises sites with low-background (<0.0124%) contents of Cu, manifested mainly by a few point fields scattered throughout the city.

<u>Nickel</u> (*Fig. 32*). The background is 1.5 and 1.74 times excessive vs. the lithosphere clark and MAC, respectively. Only 3 nickel concentration fields were identified on the city's territory. The fields of the 3^{rd} concentration level (0.0261-0.0783%) are located in the north of the city (River Voghchi left bank, in the vicinity of Kavart settlement) and are characterized by point morphostructure. A field of the 2^{nd} level of Ni concentration (0.0087-0.0261%) is more widely developed in space, compassing practically the entire territory of the city. Eastern and western parts of the city are covered by fields with low-background contents of Ni (<0.0087%).

<u>Tin</u> (*Fig. 33*). The background is 1.1 times excessive vs. lithosphere clark. On the city's territory fields of 3 concentration levels were contoured out. Fields of the 3^{rd} concentration level (0.00084-0.00252%) are localized in northern (left bank of River Voghchi, in the vicinities of Kavart settlement) and central parts of the city in form of small anomalies with point morphostructure. Fields of the 2^{nd} level of tin concentration (0.00028-0.00084%) are developed more widely in space, compassing practically the whole territory of the city. The city's territory comprises also parts with low-background tin contents (<0.00028%); in most

Fig. 30. ***A Geochemical Schematic Map Of Lead Contents In The Kapan Soils.***

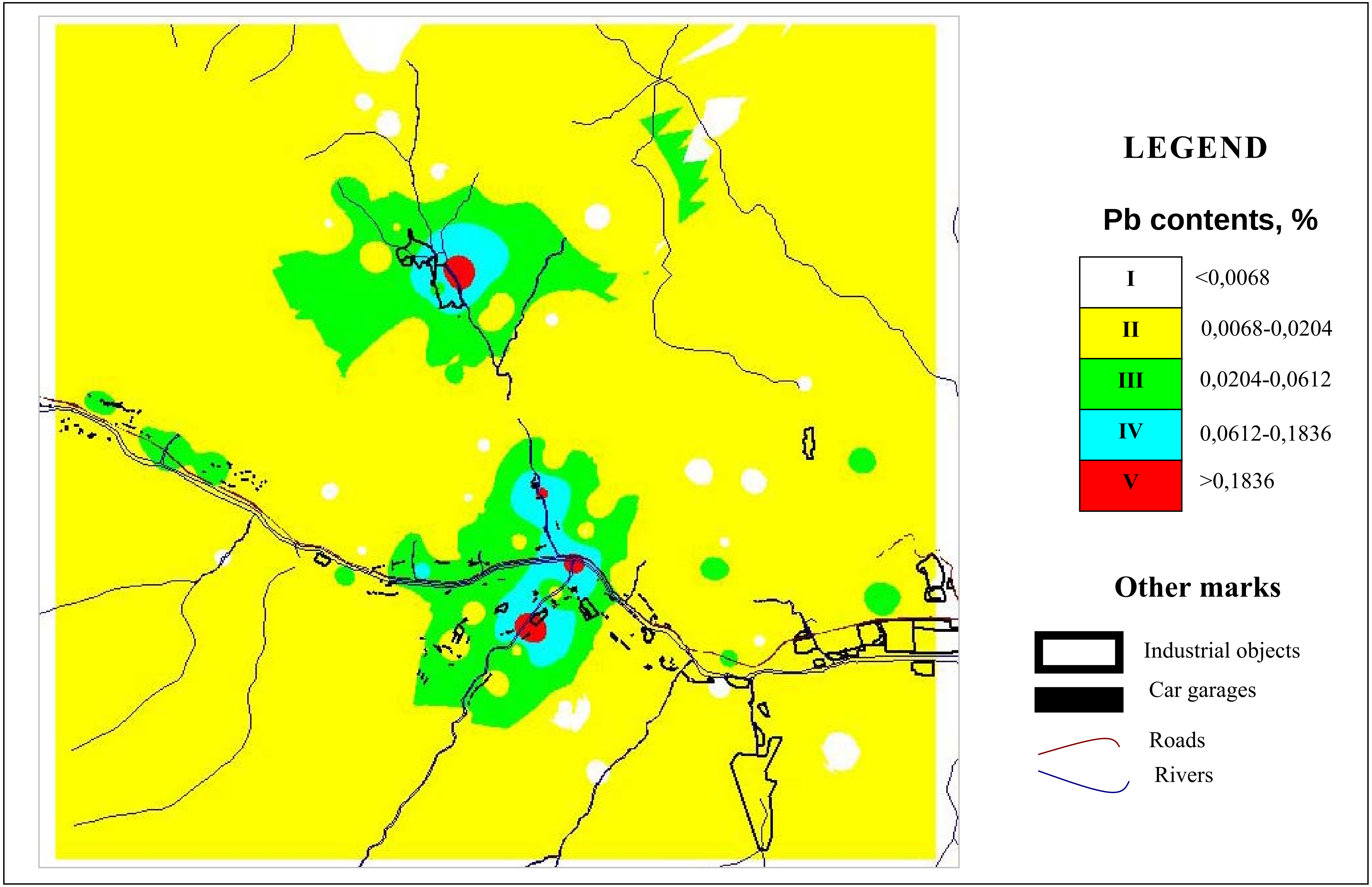


Fig. 31. ***A Geochemical Schematic Map Of Copper Contents In The Kapan Soils.***

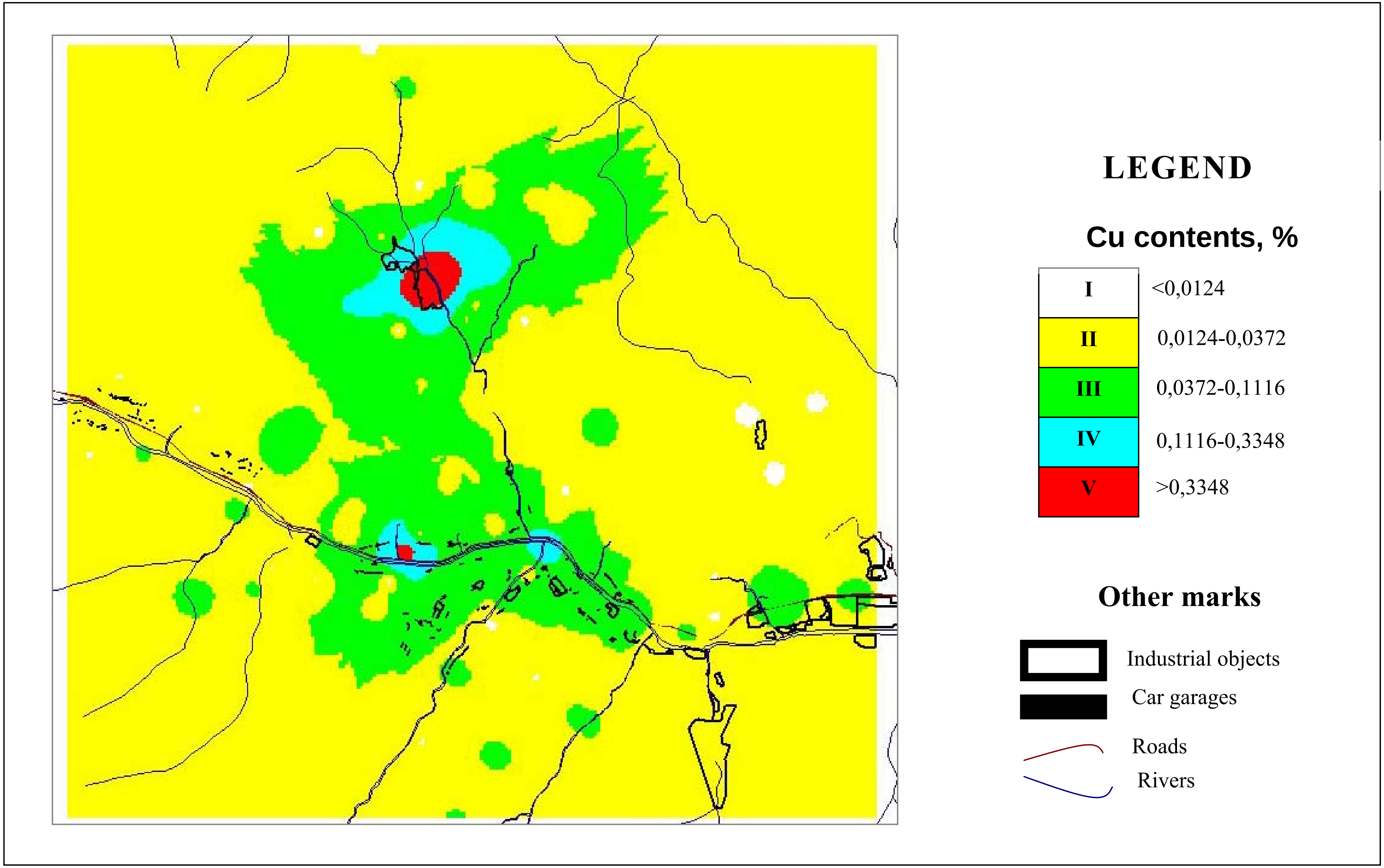


Fig. 32. ***A Geochemical Schematic Map Of Nickel Contents In The Kapan Soils.***

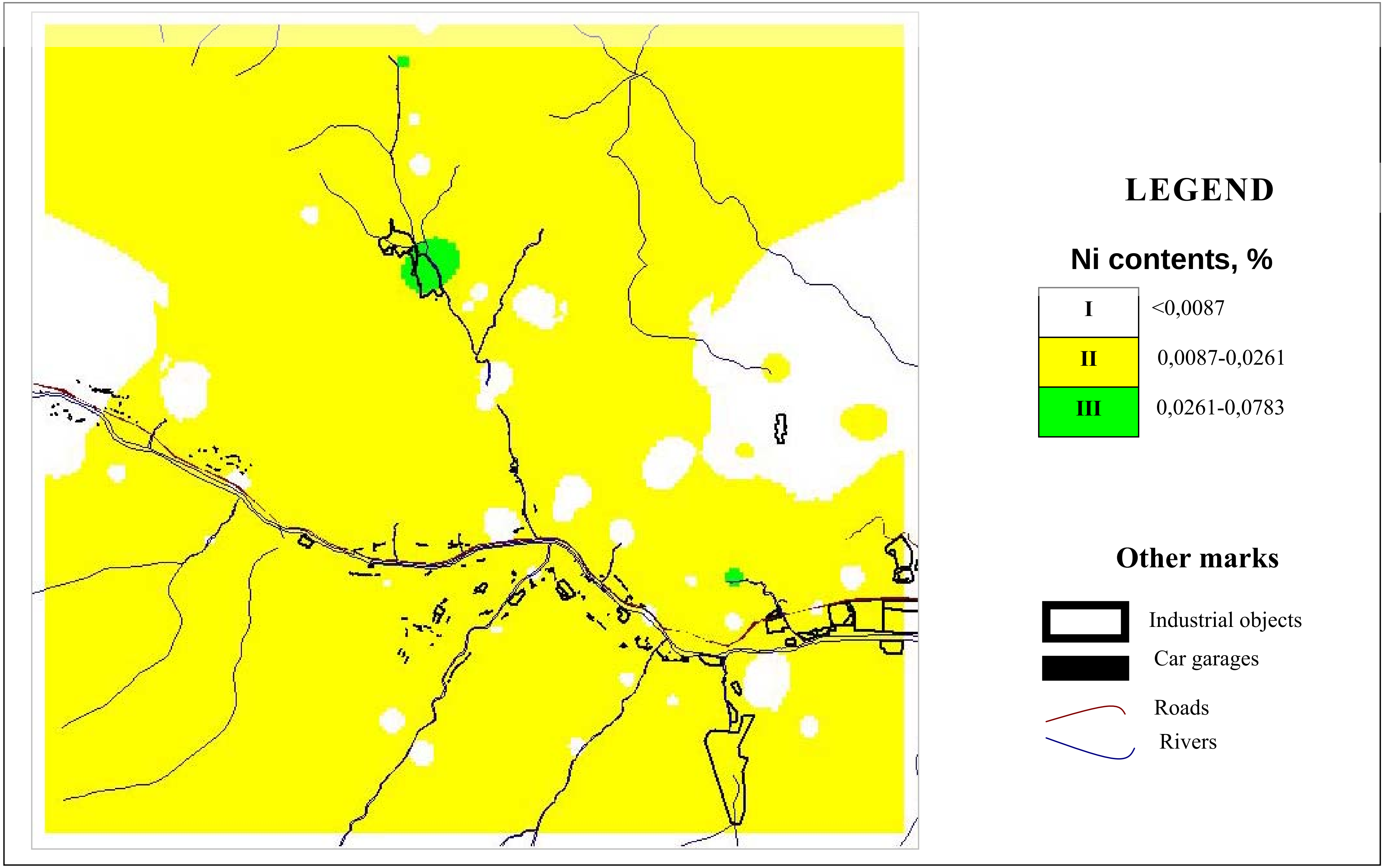


Fig. 33. ***A Geochemical Schematic Map Of Tin Contents In The Kapan Soils.***

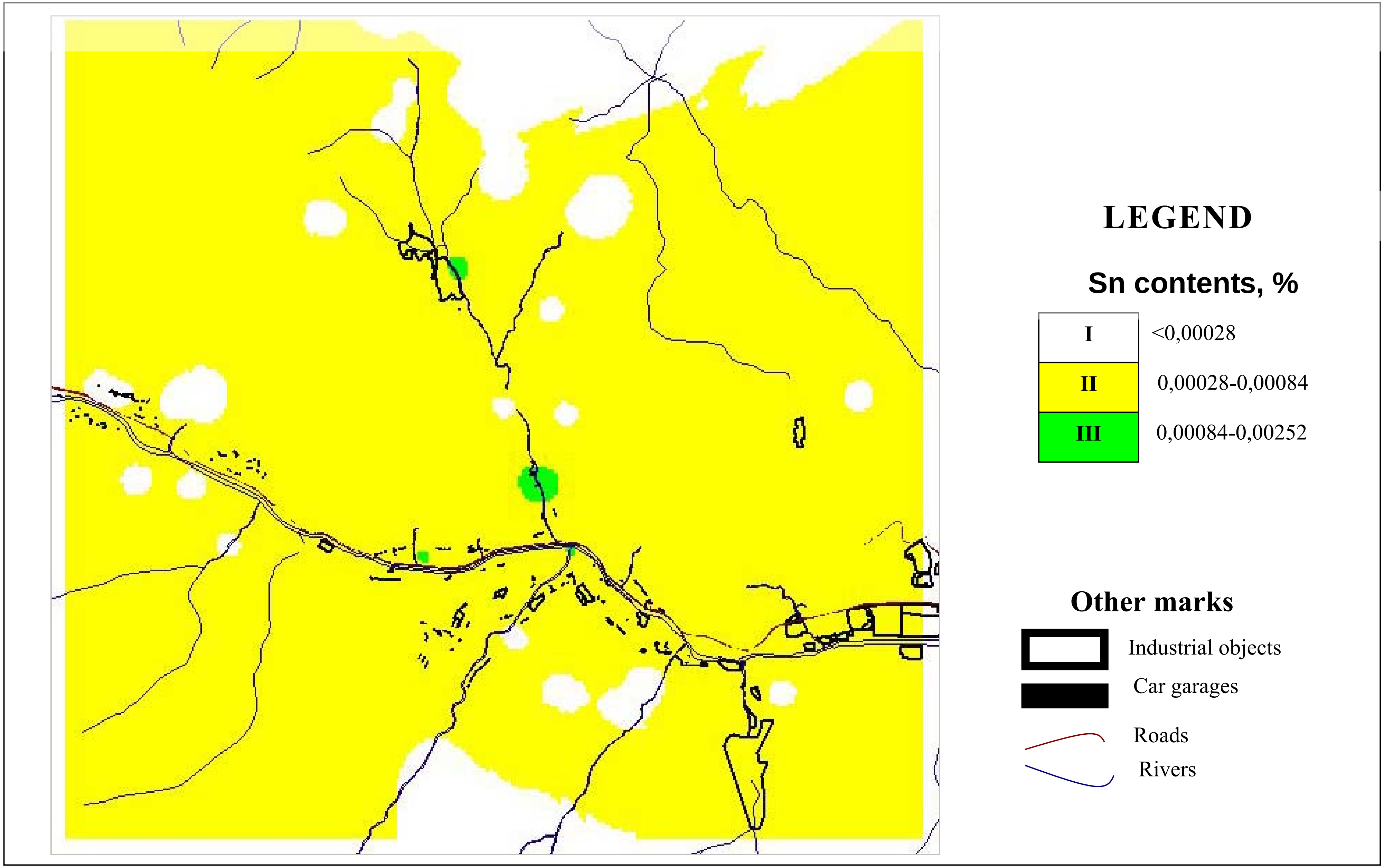


Fig. 34. ***A Geochemical Schematic Map Of Chromium Contents In The Kapan Soils.***

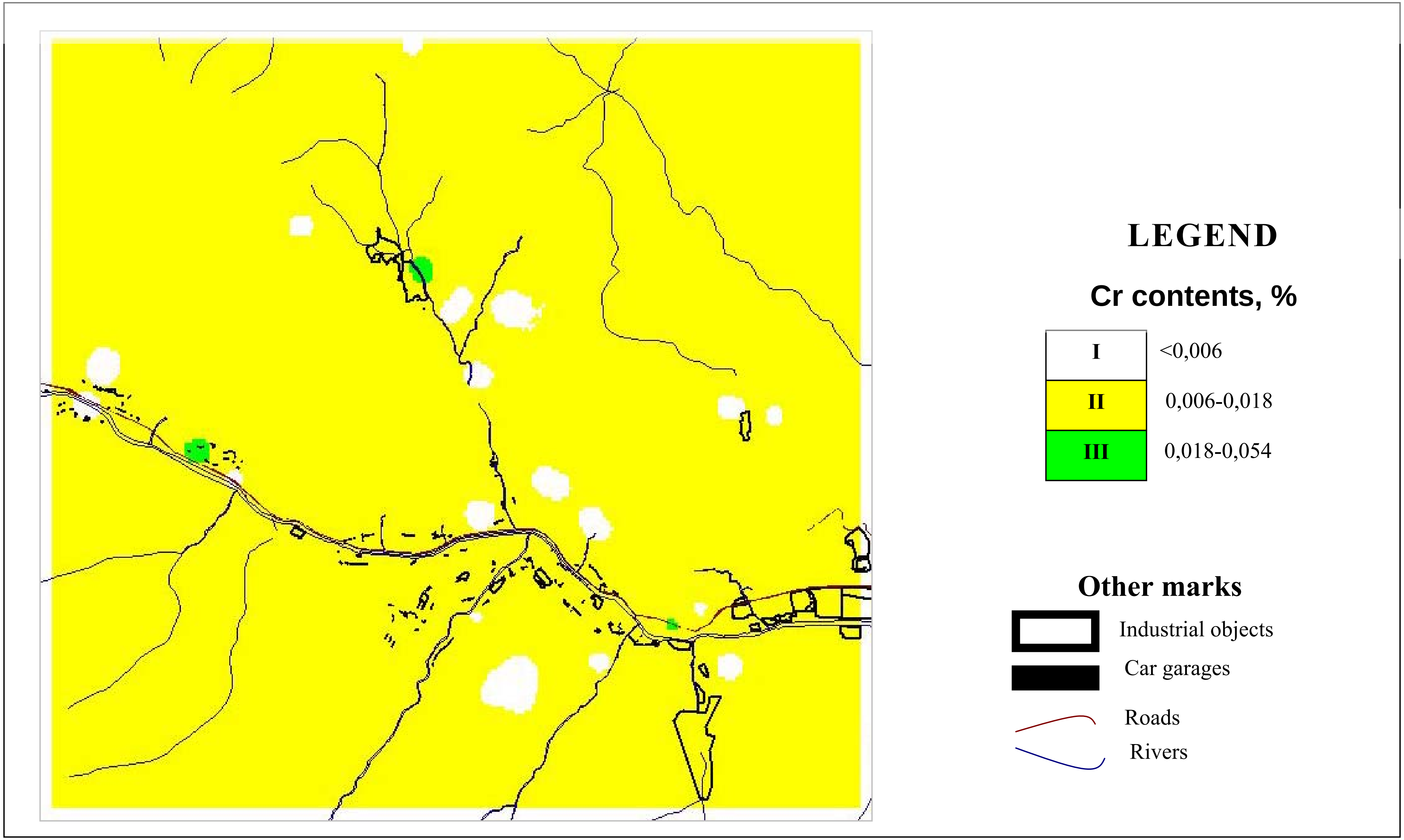


Fig. 35. ***A Geochemical Schematic Map Of Molybdenum Contents In The Kapan Soils.***

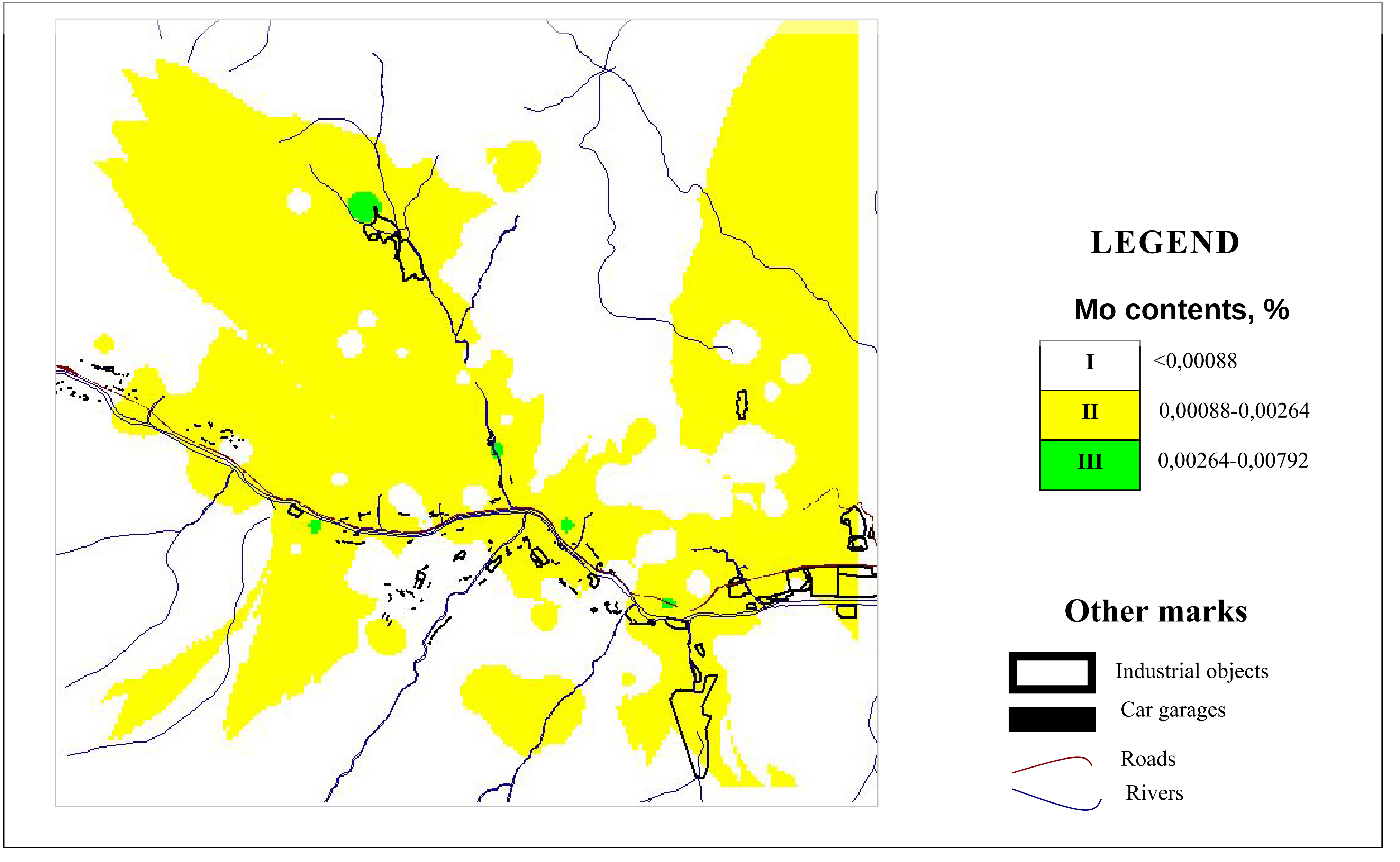
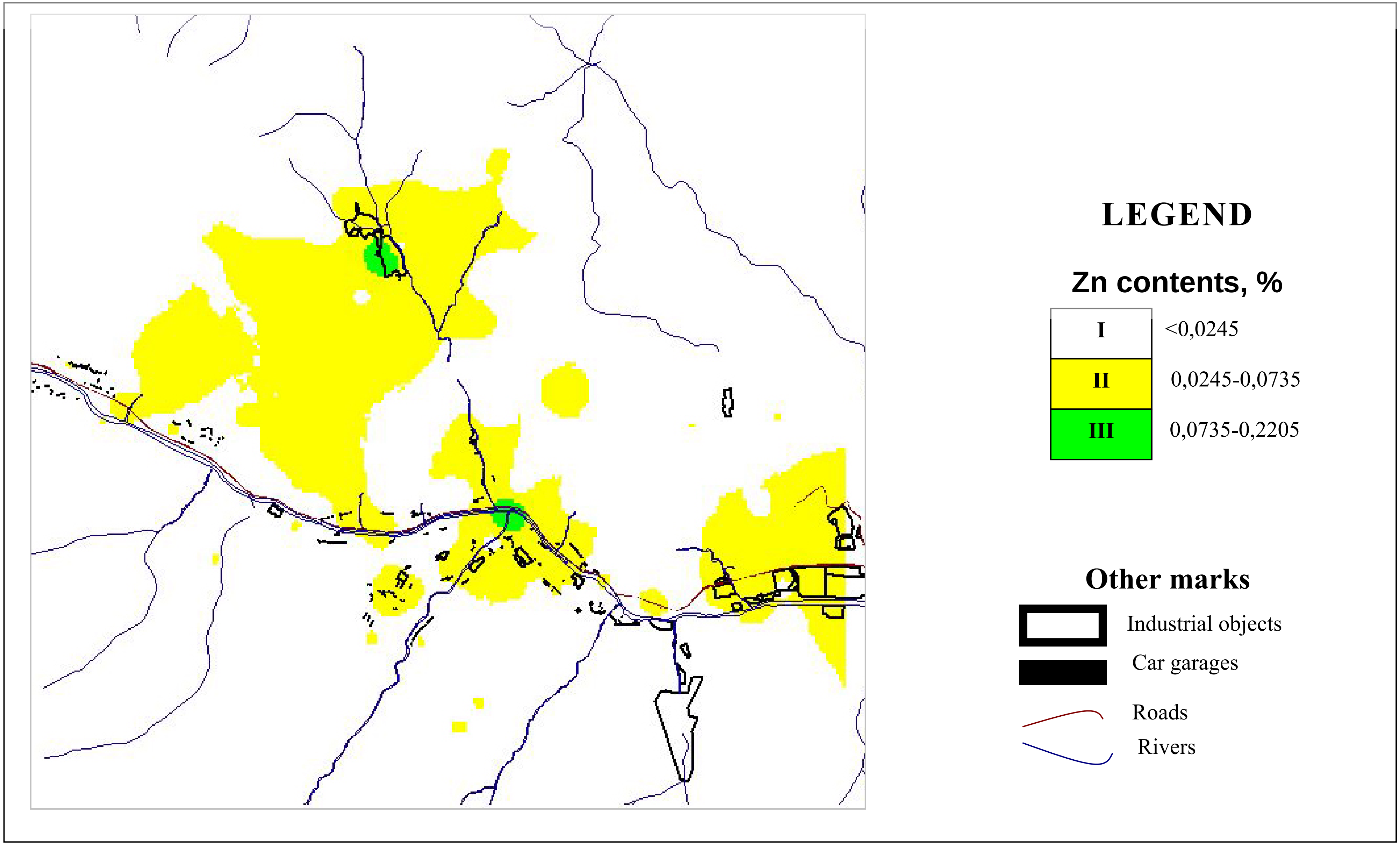


Fig. 36. ***A Geochemical Schematic Map Of Zinc Contents In The Kapan Soils.***



cases, they are discretely spread all across the city and its northern and southern suburbs as well.

Chromium (*Fig. 34*). The background is not high vs. lithosphere clark. On the city's territory fields of 3 concentration levels were contoured out. Fields of the 3rd concentration level (0.018-0.054%) are localized in northern (left bank of River Voghchi, in the vicinities of Kavart settlement) and western (nearby the garages) parts of the city in form of small anomalies with point morphostructure. Spatially a field of the 2nd level of Cr concentration (0.006-0018%) is developed more widely compassing practically the whole territory of the city. The city's territory comprises also parts with low-background Cr contents (<0.006%) discretely spread allover the city.

6. **Molybdenum** (*Fig. 35*). The background is 8.8 and 1.76 times excessive vs. lithosphere clark and MAC, respectively. On the city's territory fields of 3 concentration levels were contoured out. The fields of the 3rd concentration level (0.00264-0.00792%) are localized in the north (left bank of River Voghchi, in the vicinities of Kavart settlement) part of the city in form of small anomalies with point morphostructure. Spatially a field of the 2nd level of Mo concentration (0.00088-0.00264%) is developed more widely predominantly in the north and east of the city. The city's territory comprises also parts with low-background Cr contents (<0.00088%); in most cases they are discretely spread allover the city.

Zinc (*Fig. 36*). The background is 3.2 times excessive vs. lithosphere clark; no excesses vs. MAC were indicated. No large Zn anomalies were revealed on the city's territory. The fields of the 2nd (0.0735-0.2205%) and 3rd (0.0245-0.0735%) concentration level are localized in northern, central and eastern parts of the city. Practically the entire territory of the city is covered by low-background fields (1st<0.0245%).

The elements of the Ia and I category of danger such as Cd and As are considered from sanitary and hygienic positions below.

3.1.2.2. *A summary map of Kapan's soil cover pollution by heavy metals.*

To complexly assess heavy metal pollution of the territory of Kapan, a schematic map of summary pollution of soils by heavy metals was produced (*Fig. 37*). A methodic basis of the map is reflection of the value of summary concentration index (SCI) of elements. Such an index is calculated as a sum of the background-standardized contents of elements in the sample. Pollution level is assessed through a scale suggested by [6]. Tab. 9 gives both geochemical series calculated through mean contents of metals by separate fields and mean excesses of elements of Ia, I, II and III category of danger vs. MAC within a separate field. As seen from the *Tab. 9*, in the limits of different fields quality and quantity differences are indicated. In geochemical series of 1st, 2nd and 4th pollution level Cu holds the first position; however only in the 2nd pollution level fields Cu holds the second and Pb - the first ordinal positions. Within the field, mean excessive contents vs. MAC adding the category of danger of elements serve as an essential index. All the studied pollution fields contained elements of the I category of toxicity: As (a 3.8-6.6 time excess vs. MAC) and Ni (a 3.2-9.0 time excess vs. MAC); fields of 2nd, 3rd, 4th pollution level contained Cr (1.1-2.5) and Pb (a 2.0-35.0 time excess vs. MAC). In the fields of all pollution levels the contents of Cu - an element of II-III category of danger - were 2.4-75.0 time excessive vs. MAC. In the limits of the 3rd pollution level field Zn contents showed a 2.5 time excess vs. MAC. Excessive contents of Mo – an element of the III category of danger – were indicated, as well.

Table 9. *The Kapan soil pollution level and danger assessment scale.*

Zc* value	Pollution level, degree of danger	THE SOILS OF KAPAN		
		Mean geochemical series	**Zc**	**Mean excessive contents of elements of Ia, I, II, III category of danger** vs. MAC**
1st-16>	**Low**	$Cu_{(1,9)}-Cd_{(1,5)}-Ni;Cr;Pb_{(1,3)}-Sn_{(1,2)}-As_{(1,0)}-Mo_{(0,9)}-Zn_{(0,8)}$	11.2	Excess vs. MAC: **I** (**As**-3.8, **Ni**-2.2), **II-III** (**Cu**-2,4), **III** (**Mo**-1,6 times)
2nd-16-32	**Medium, moderately dangerous**	$Cu_{(3,8)}-Pb_{(2,9)}-Cd_{(2,3)}-Ni_{(2,0)}-Cr;Mo_{(1,9)}-Sn_{(1,7)}-As_{(1,4)}-Zn_{(1,1)}$	18.9	Excess vs. MAC: **I** (**As**-5.3, **Cr**-1.1, **Ni**-3.4, **Pb**-2.0), **II-III** (**Cu**-4.7), **III** (**Mo**-3.3 times)
3rd-32-128	**High, dangerous**	$Pb_{(34,8)}-Cu_{(16,5)}-Zn_{(3,2)}-Cd;Sn_{(2,9)}-Ni_{(2,2)}-Cr_{(1,9)}-Mo_{(1,7)}-As_{(1,6)}$	67.4	Excess vs. MAC: **I** (**As**-5.9, **Cr**-1.1, **Ni**-3.9, **Pb**-23.6), **II-III** (**Cu**-20.4, **Zn**-2,5), **III** (**Mo**-2.9 times)
4th->128	**Very high, extremely dangerous**	$Cu_{(60,5)}-Pb_{(51,5)}-Ni_{(5,2)}-Cr_{(4,2)}-Sn_{(3,6)}-Cd_{(2,5)}-As_{(1,7)}-Mo_{(1,5)}-Zn_{(0,8)}$	131.4	Excess vs. MAC: **I** (**As**-6.5, **Cr**-2.5, **Ni**-9.0, **Pb**-35.0), **II-III** (**Cu**-75.0), **III** (**Mo** в 2.6 times)

Note: * Zc – a summary pollution index; ** - category of ecological threat: Ia-super toxic, I – high toxic, II-III – toxic [13].

To analyze spatial distribution of SCI (Zc) values allover the city's territory, a specialized geochemical schematic map was produced (*Fig. 37*).

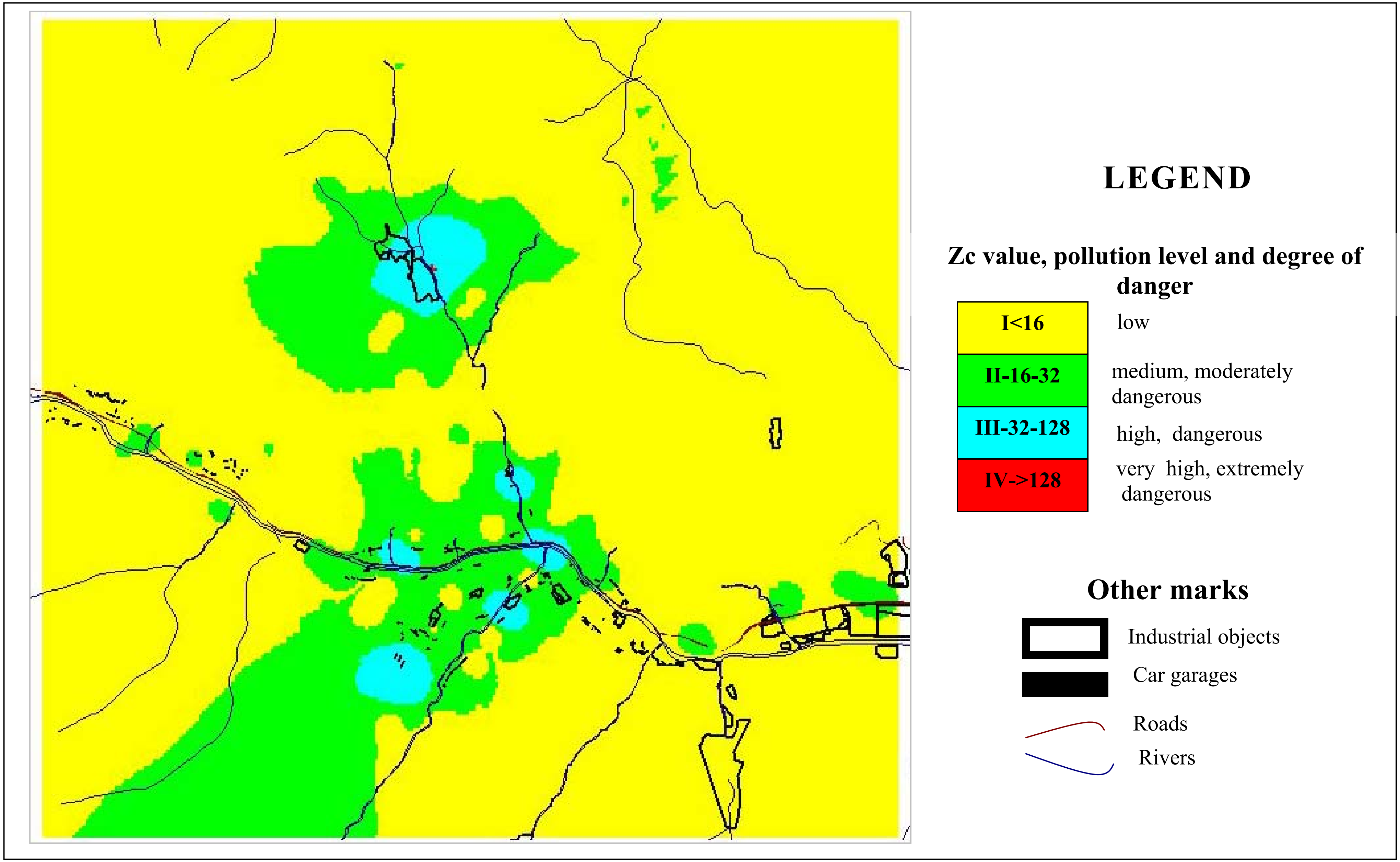
On the city territory, pollution fields of 4 levels were contoured out. A point intense pollution field is localized in northern industrial part of the city, on River Voghchi left bank (SCI>128). Copper and lead are dominant in formation of this field.

Fields with high pollution level (SCI-32-128) are focused on northern and central populated and industrial parts of the city and have a point morphostructure. Lead and copper are dominant in formation of this field.

Mainly, fields with medium pollution level (SCI-16-32) surround the previously noted fields and have isometric form. Separate point fields were identified in western and eastern parts of the city, too.

The rest part of the city is covered by a low pollution level field (SCI<16).

Fig. 37. ***A Schematic Map Of Summary Pollution Of Kapan's Soils With Heavy Metals.***



Thus, geochemical survey for the soil cover of the city of Kapan indicated that the city pollution was dominated by copper and lead. However no intense pollution of the whole territory of the city was observed. Fields with maximal level of heavy metal concentration were localized in northern and central parts of the city. Wholly, the level of the territory pollution can be attributed to low and partially to medium pollution.

3. 2. Sanitary and hygienic assessment of soil pollution with heavy metals

To provide sanitary and hygienic assessment of Kapan's soils, produced were mono-element schematic maps of heavy metals excessive vs. MAC.

1. **Copper** (*Fig. 38*). On the city's territory fields of 5 levels of excess vs. MAC were indicated. Fields 5th – with maximal excesses vs. MAC (>27 times) are represented by 2 local fields in left- and right-bank sections of the city. Fields 4th with a 9-27 time excess vs. MAC predominantly contour fields of the 5th level. Mainly, the noted fields are associated with industrial part of the city, and practically the whole territory of a populated part is covered by fields of the 3rd level with a 3-9 fold excess vs. MAC. The rest part of soil cover was 1-3 times excessive in Co vs. MAC. Fields with near - MAC or lower contents were also identified.

2. **Lead** (*Fig. 39*). On the city's territory fields of 5 levels of excesses vs. MAC were indicated. Fields 5th – with maximal excesses (>27 times) vs. MAC are represented by 3 local fields in left- and right-bank sections of the city. Fields 4th and 3rd with a respective 9-27 and 3-9 time excess vs. MAC predominantly surround fields of the 5th level. Mainly, the noted fields are associated with industrial part of the city and the garages. Pb contents for the rest part of soil cover did not reach MAC or showed near-MAC variations..

3. **Arsenic** (*Fig. 40*). Two fields: 3rd level (a 3-9 time excess vs. MAC) and 2nd - (a 1-3 time excess vs. MAC) were identified on the city's territory. The basic part of the city is covered by a 3rd - level fields. Mostly, the fields of 2nd level have a point morphostructure and are scattered allover the city territory. Relatively large anomalies are found in peripheral part of the city.

4. **Nickel** (*Fig. 41*). On the city's territory 2 fields- 3rd (a 3-9 time excess vs. MAC) and 2nd (a 1-3 time excess vs. MAC) were identified. The 3rd level fields are discretely distributed in both populated and industrial parts of the city and on southern and northeastern periphery. The basic part of the territory is covered by the 2nd level fields.

5. **Molybdenum** (*Fig.42*). On the city's territory 2 fields- 3rd (a 3-9 time excess vs. MAC) and 2nd (a 1-3 time excess vs. MAC) were identified. The 3rd -level fields are characterized by point morphostructure and are located mainly in left-bank section of the city. The basic part of the city is covered by a 2nd level field.

Fig. 38. ***Sanitary And Hygienic Schematic Map Of Copper Contents In The Soils Of Kapan***

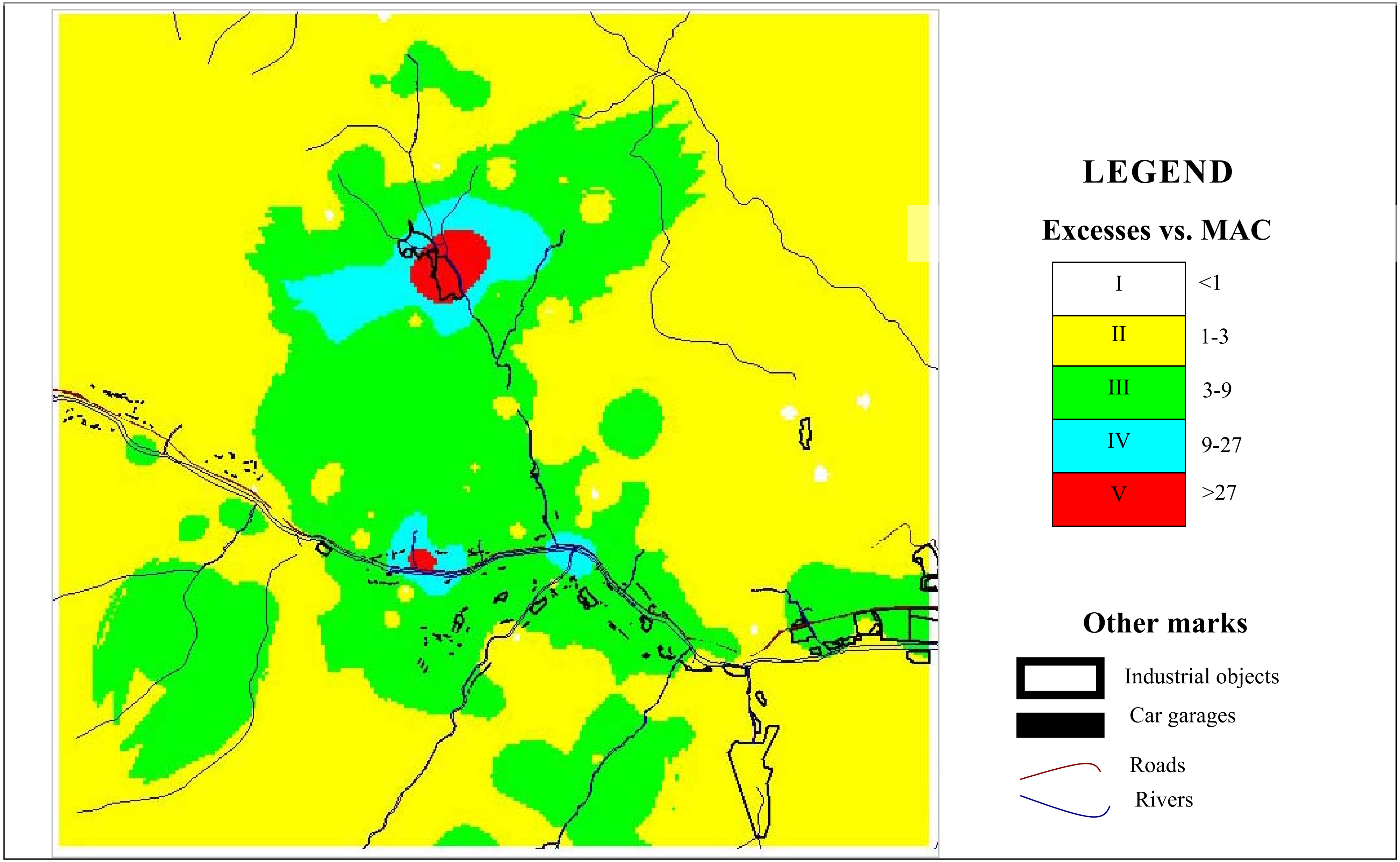


Fig. 39. ***Sanitary And Hygienic Schematic Map Of Lead Contents In The Soils Of Kapan***

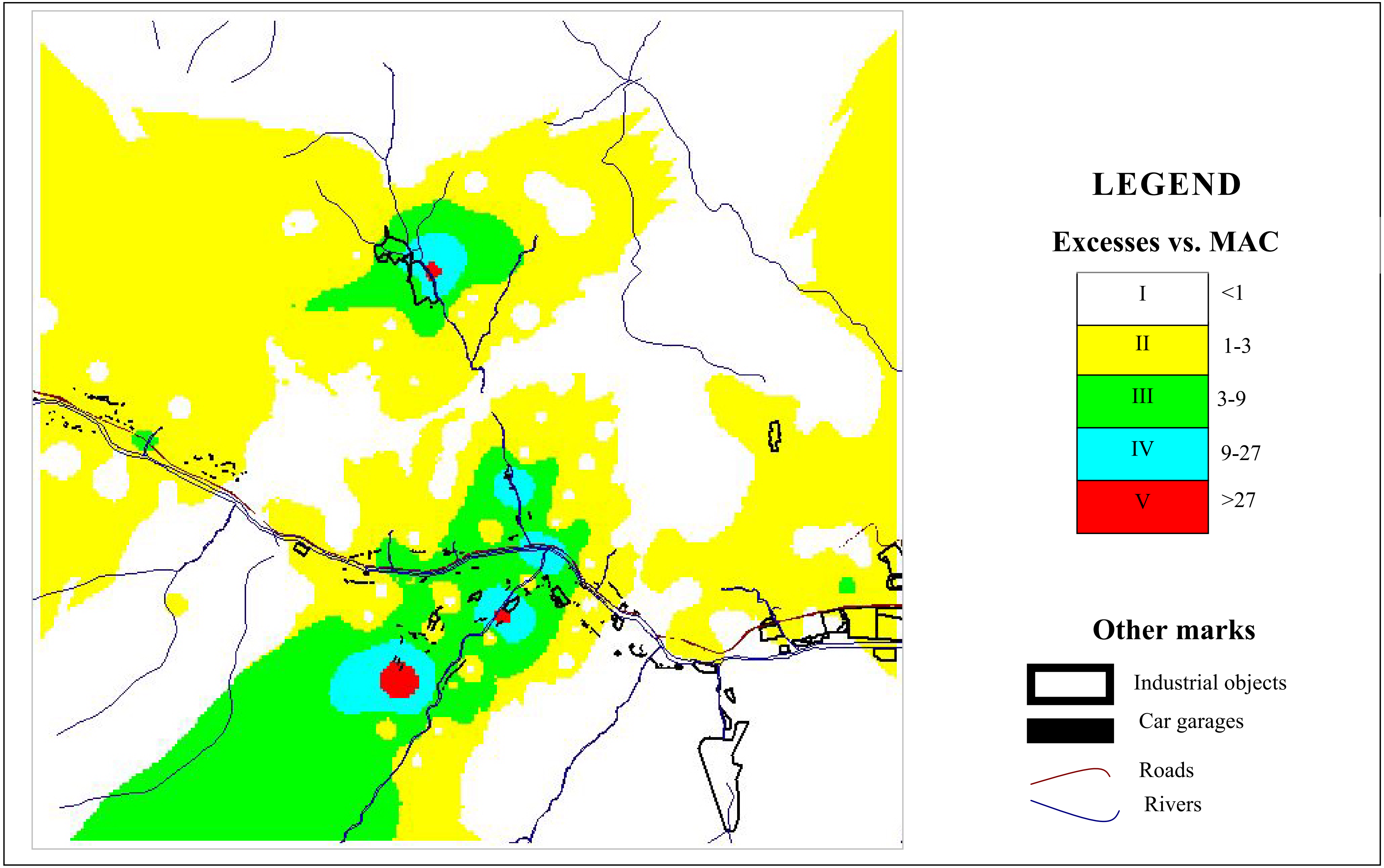


Fig. 40. ***Sanitary And Hygienic Schematic Map Of Arsenic Contents In The Soils Of Kapan***

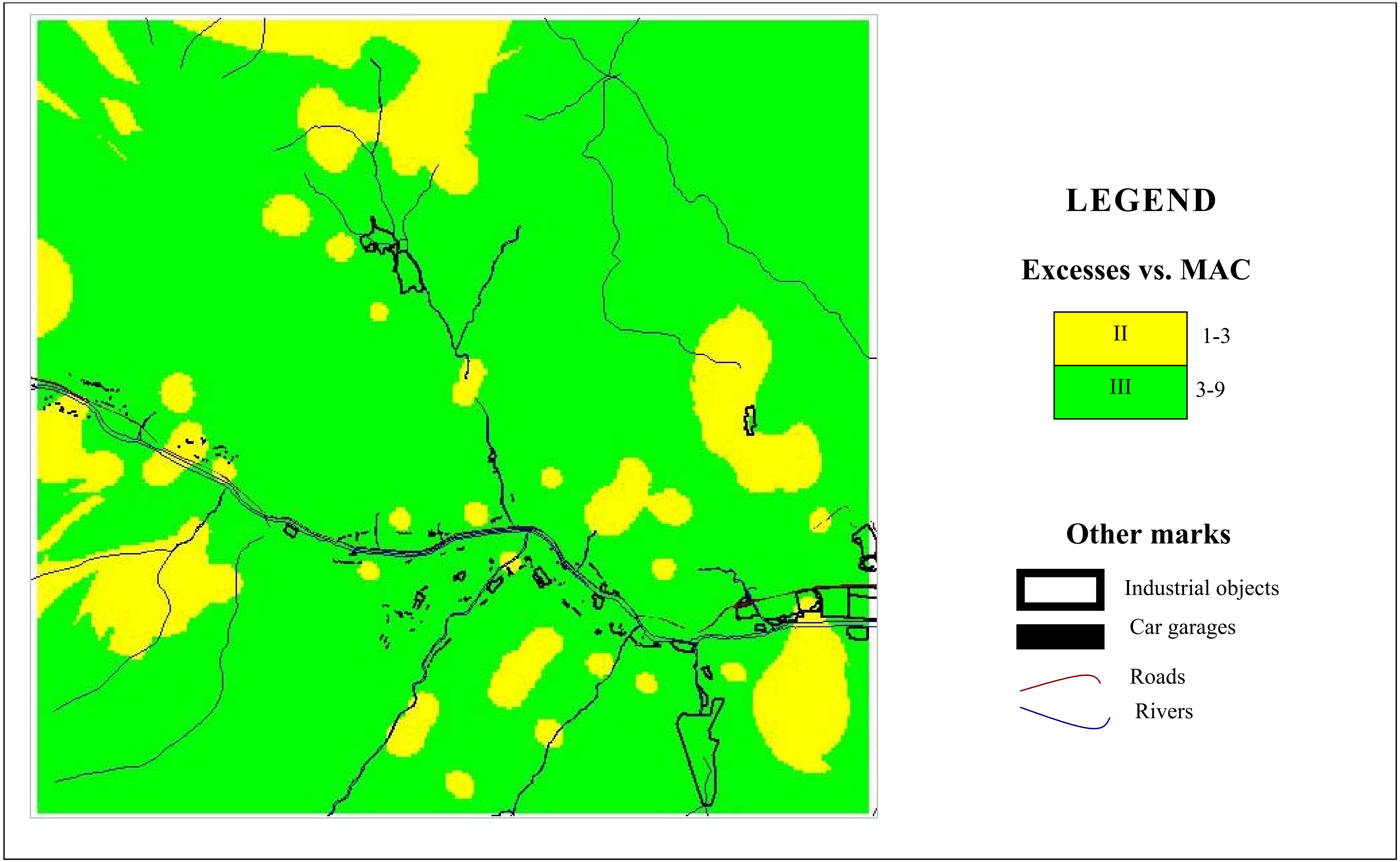


Fig. 41. ***Sanitary And Hygienic Schematic Map Of Nickel Contents In The Soils Of Kapan***

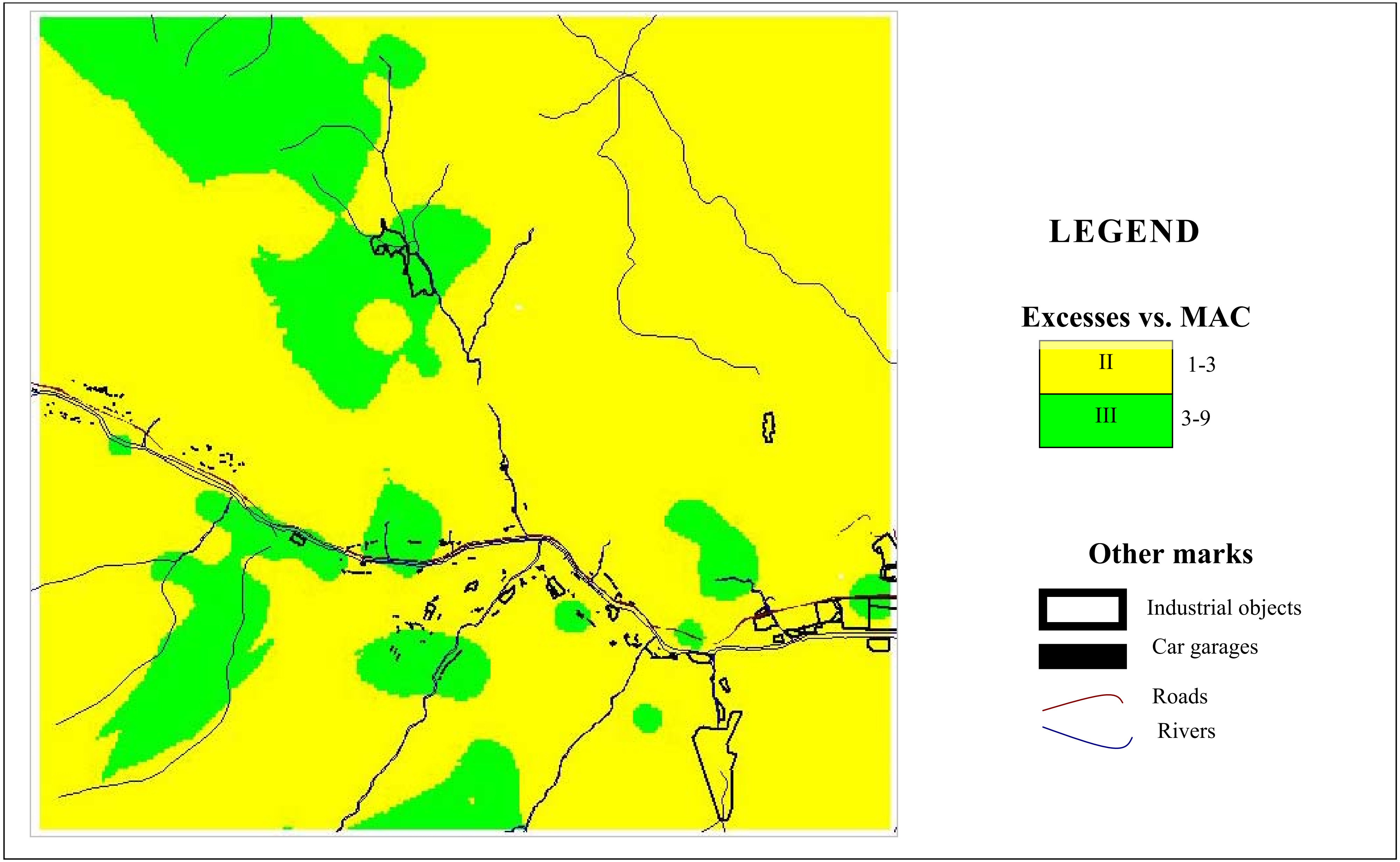


Fig. 42. ***Sanitary And Hygienic Schematic Map Of Molybdenum Contents In The Soils Of Kapan***

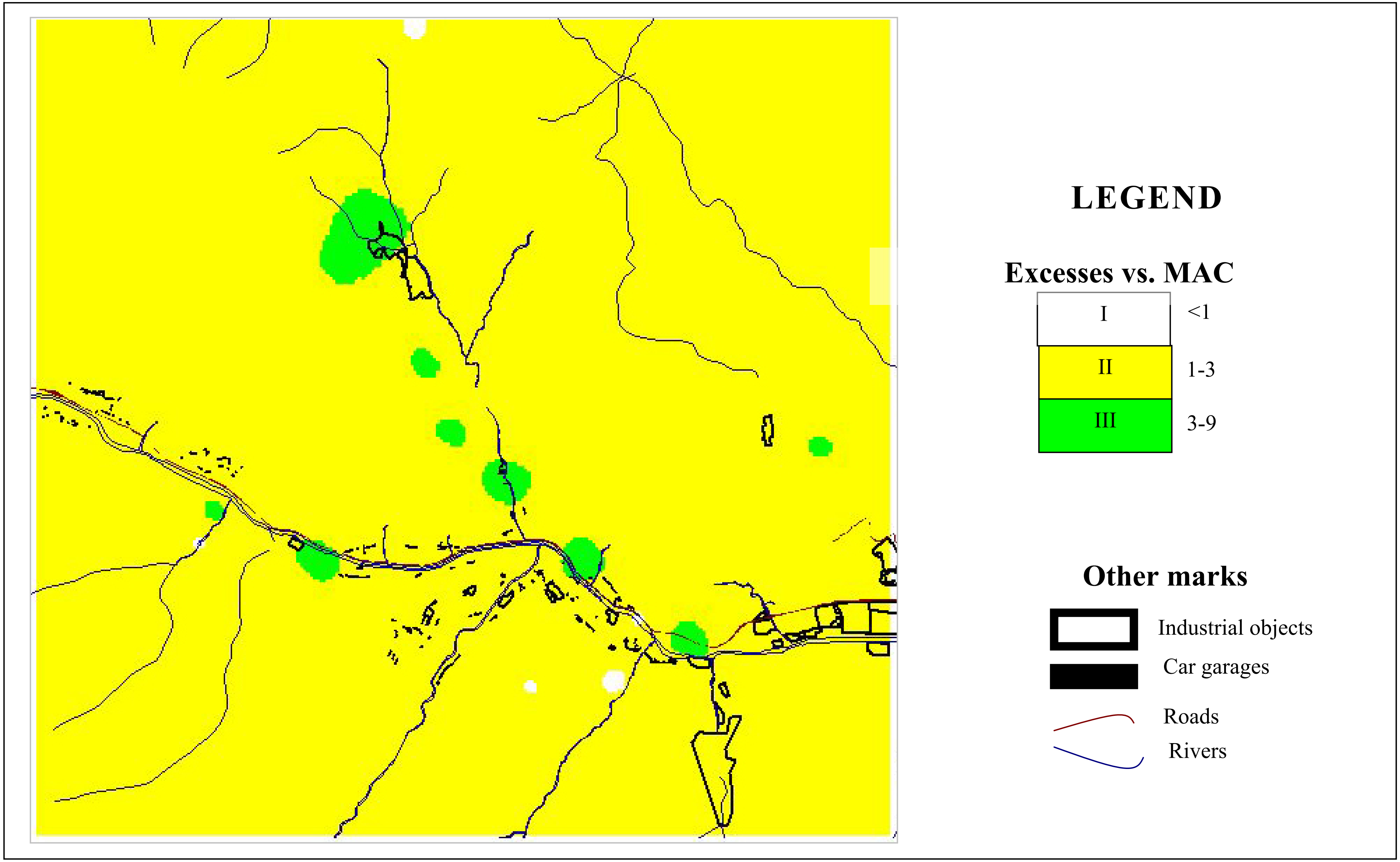


Fig. 43. ***Sanitary And Hygienic Schematic Map Of Zinc Contents In The Soils Of Kapan***

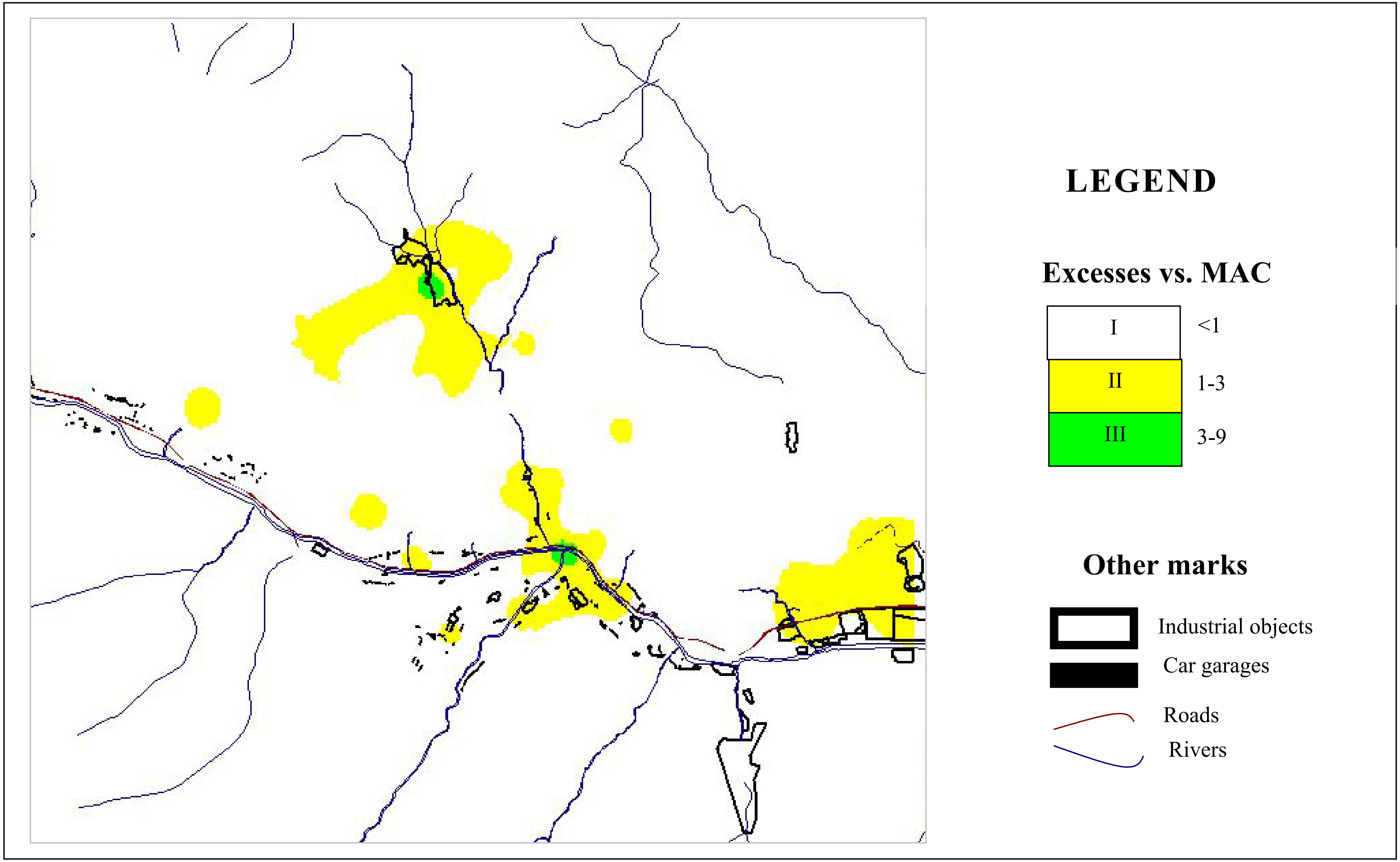


Fig. 44. ***Sanitary And Hygienic Schematic Map Of Chromium Contents In The Soils Of Kapan***

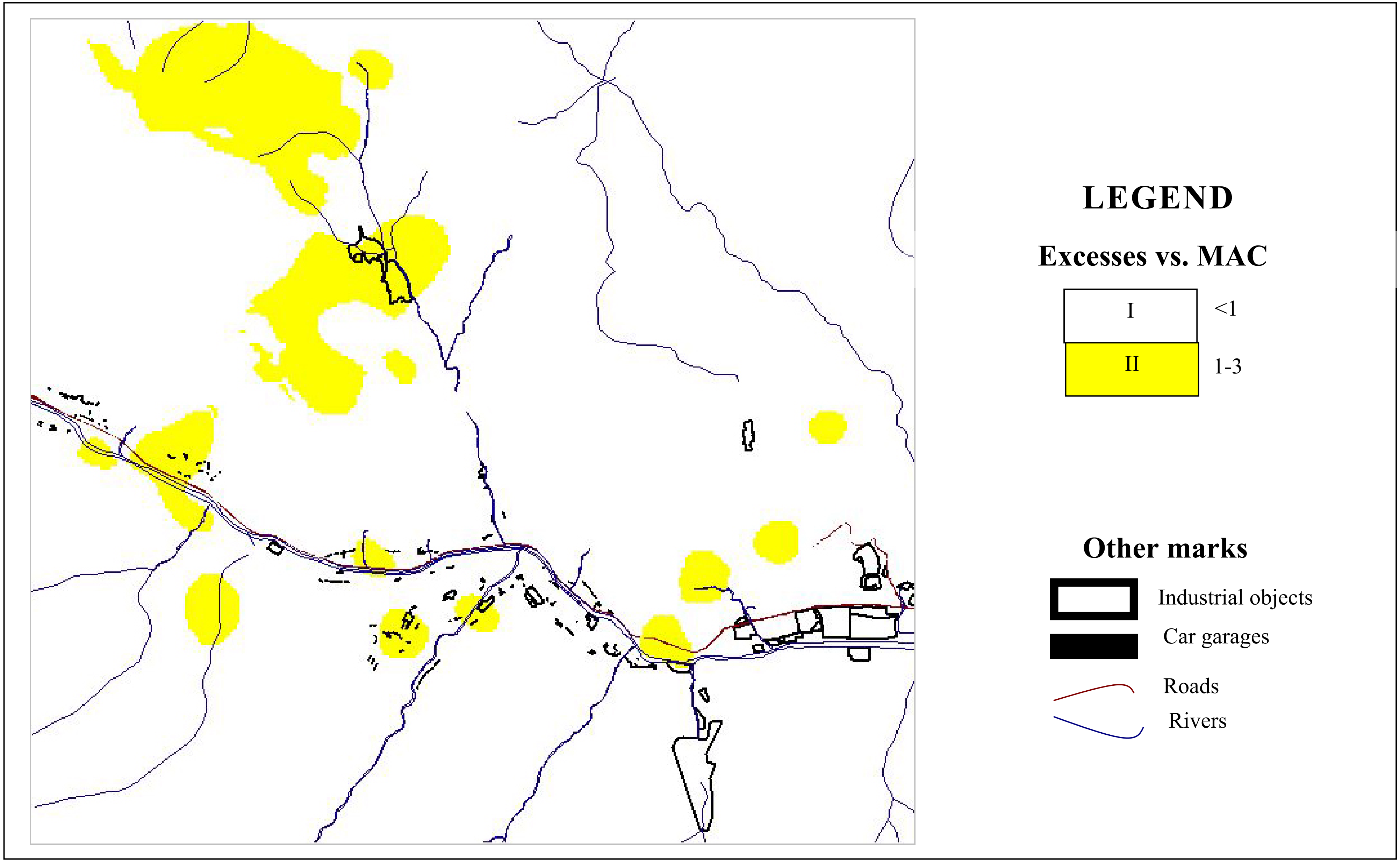
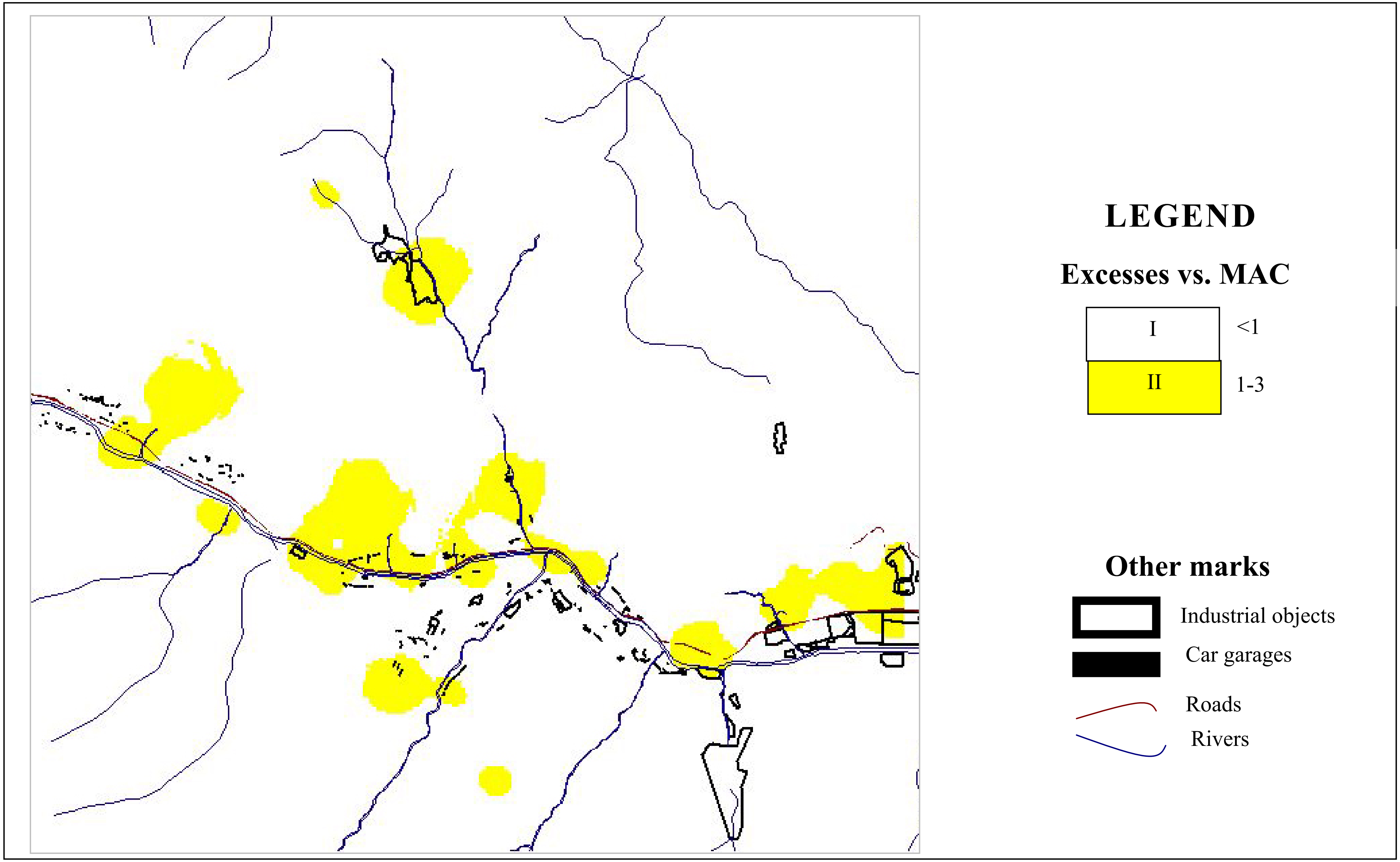


Fig. 45. ***Sanitary And Hygienic Schematic Map Of Cadmium Contents In The Soils Of Kapan***



6. **Zinc** (*Fig.43*). On the city's territory two fields were identified: a 3rd level field (a 3-9 time excess vs. MAC) and a 2nd level - (a 1-3 time excess vs. MAC). The fields have local distribution and are mainly associated with industrial objects. Wholly, no excessive contents were indicated in the soils of the basic part of the city.
7. **Chromium** (*Fig.44*). On the city's territory the 2nd level (a 1-3 time excess vs. MAC) fields were identified. The fields have discrete distribution. Relatively large anomalies are mainly associated with industrial objects. Wholly, no excessive contents were indicated in the soils of the basic part of the city.
8. **Cadmium** (*Fig.45*). On the city's territory a 2nd level (a 1-3 time excess vs. MAC) fields were identified. The fields are discretely distributed both in populated and industrial parts of the city. Wholly, no excessive contents were indicated in the soils of the basic part of the city.

Thus, a sanitary-hygienic assessment of pollution of Kapan's soils with heavy metals proved noticeable MAC overstepping contents of elements of both I and II-III category of toxicity. By sanitary-hygienic indices special attention should be given to the entire left-bank part of the city and particularly to areas associated with industrial objects and in some cases – to sites associated with the garages.

3. 3. Heavy metal transfer to the territory of the city of Kapan by mudflows.

An independent task managed in the frame of the project was a pilot study of heavy metal transfer to Kapan’s territory by mudflows. After rain huge volumes of soil-ground formed on numerous dumps are washed out down the slopes. The dried material of washed-out soil-grounds is then dispersed by the wind and enters the human organism in form of inhaled dust. A special risk group is children and teen-agers as they spend t most part of the day on local sites of the territory.

To assess heavy metal transfer by mudflows, mud samples were collected after rain from 3 key points on Kapan’s territory. The analysis data are given in *Tab. 10*.

Table 10. *Heavy metal contents in mudflow samples collected from Kapan’s territory*

Points \ MAC[1]	Cu 100*	Mo 5*	Ni 50***	Cr 100*	Pb 100*	Sn 50*	Zn 300*	As 2**	Cd 2	Hg 2,1	Se 1,5
A plot near the Consumer Service Center (KF-154)	**550 (5,5)**	**25 (5)**	**80 (1,6)**	70	**100 (1)**	4,0	250	1,7	0,21	0,04	0,36
A.Avetisian Street (KF-155)	**500 (5)**	**30 (6)**	**90 (1,8)**	80	70	3,0	200	1,8	0,17	0,02	0,4
The city market (KF-156)	**350 (3,5)**	**9 (1,8)**	**70 (1,4)**	50	60	1,5	200	5 (2,5)	0,35	0,11	0,46

Note: [1]According to [3], **-to [15], *** - to [12]; in brackets, excesses vs. MAC are given.

The obtained data evidenced that the mudflow-transferred mud material contained substantial concentrations of ore elements. As seen from *Tab. 10,* element composition of mudflow material was different for separate part of the city.

A qualitative and quantitative composition of polluting elements in mudflow material from 2 points (KF-154, KF-155) was similar (*Fig.46*), basic portion of pollution falling on ore elements (Cu, Mo, Ni).

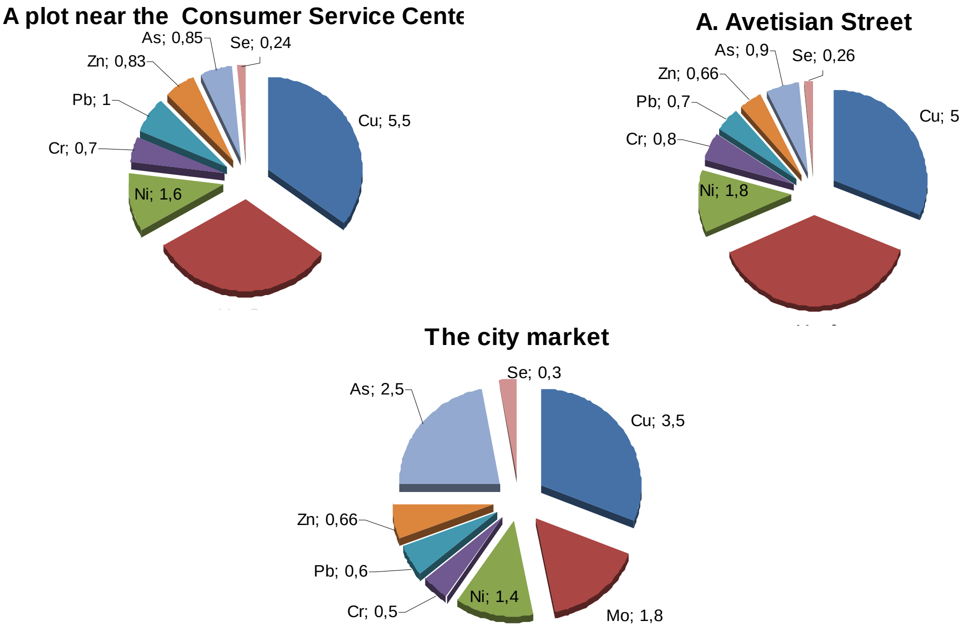


Fig.46. *Chemical element transfer by mudflow material to territories of separate plots in Kapan (the elements are provided with indices of MAC excess).*

For the surroundings of the Consumer Service Center (KF-154) the composition of mudflow-transferred heavy metals was as follows: Cu (5.5 MAC) – Mo (5 MAC) – Ni (1.6 MAC) – Pb (1 MAC), adding elements which contents made decimals of MAC: As and Zn (0.8 MAC), Cr (0.7 MAC), and Se (0.2 MAC).

For A. Avetisian Street (KF-155), too, a basic spectrum of transferred pollutants was seen in ore elements which concentrations were excessive vs. MAC: Mo (6 MAC) – Cu (5 MAC) – Ni (1,8 MAC). The share of the rest elements made decimals of MAC: As (0.9 MAC), Cr (0.8 MAC), Pb and Zn (0.7 MAC), Se (0.26 MAC).

Though the determined concentrations of secondary polluting elements (As, Zn, Pb, Cr, Se) were not excessive vs. MAC, however one could not exclude that as result of accumulation they could induce toxic effects. In this respect, As is specially hazardous.

By the quality, the spectrum of chemical elements transferred by mudflow material to the territory of the city market (KF-156) differed from the previous 2 points (*Fig. 46.*)

The concentrations of ore elements were noticeably lower than MAC: Cu (3.5) – As (2.5) – Mo (1.8) – Ni (1.4). However noteworthy were relatively high concentrations of a toxic element As - 2.5 time excessive vs. MAC. This represents a serious risk factor to the populace, adding Cd and specially contrasting contents of Hg. As seen from *Fig. 47*, by the contents of a super toxic element Hg – a 3-5 time excess vs. MAC KF-156 sharply differed from the previous points.

Thus, the studies indicated that

- substantial concentrations of ore elements (Cu, Mo, Ni) were taken with mudflows to the city's territory,
- on the city market territory, toxic elements were dominated by As (2.5 time excessive vs. MAC).

Implementation of engineering and technical actions pursuing prevention of the inflow of rain- induced mud to the city will contribute to reduction of the level of pollution of the city by heavy metals.

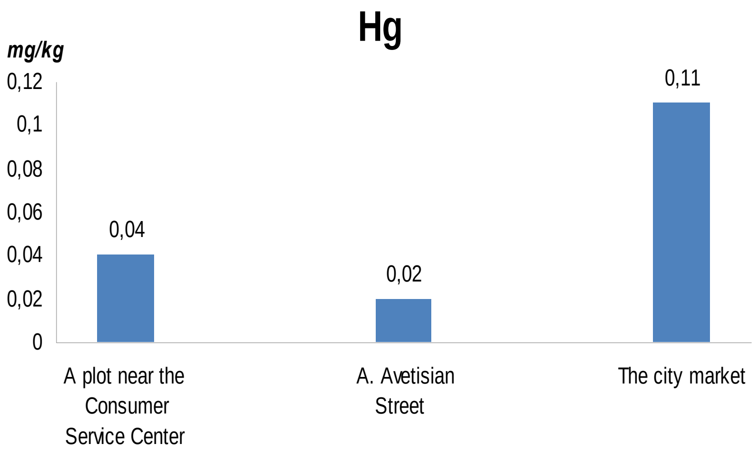


Fig. 47. *Hg contents in mudflow material on separate plots in Kapan*

3.4. Heavy metal contents in soils eroded by the Artsvanik tailing repository infiltration waters.

In the frame of the project an additional research was performed on heavy metal contents in soils eroded by the Artsvanik tailing repository infiltration waters. The essence of such research was justified by a potential threat of chemical element transport from the tailing repository and further accumulation in the soils of River Norashenik alluvial plain. Speciel attention was given to a group of highly toxic elements.

Soil samples were collected in River Norashenik alluvial plain from the tailing repository slopes – a site of active outlet of infiltration waters considered in Chapter 2.

The analysis data (*Tab.11*) proved relatively high concentrations of the 3 ore elements: Cu (4.5)- Mo (2.6) – Ni (1.8 times vs. MAC) in the studied slope soils. The rest elements were no excessive vs. MAC.

Table 11. *Heavy metal contents in soils from under the Artsvanik tailing repository dam.*

MAC[1] / Point	Cu	Mo	Ni	Cr	Pb	Sn	Zn	As	Cd	Hg	Se
	100*	**5***	**50*****	**100***	**100***	**50***	**300***	**2****	**2**	**2,1**	**1,5**
KF-157	**450 (4,5)**	**13 (2,6)**	**90 (1,8)**	80	80	4,0	200	0,8	0,10	0,02	0,04

Note: [1]*According to [3], **-to [15], *** - to [12]; in brackets, excesses vs. MAC are given.*

Thus, the studies indicated that pollution of slope soils eroded by the Artsvanik tailing repository infiltration waters was dominated solely by ore elements.

4. ECO-TOXICOLOGICAL ASSESSMENT OF AGRICULTURAL SOILS AND BASIC CROPS

In the frame of the project, pilot eco-toxicological studies were carried out on heavy metal accumulation in soils and in a basic assortment of agricultural crops. The research covered agricultural lands within the bounds of Kapan (the Barabatum canyon), 5 private plots in the village of Syunik and 1 farm (River Norashenik alluvial plain, nearby the former milk factory). Wholly, 24 vegetable, melon field, cereal (corn), oil-bearing (sunflower) species adding spicy herbs and fruits were studied.

4.1. The assessment of agricultural soils pollution with heavy metals

Heavy metal contents were studied on Syunik's agricultural lands, in a farm in River Norashenik canyon and on a re-cultivated soil layer allover Tejadin site. The obtained outcomes are given in *Tab.12.*

Table 12. *Heavy metal contents in soils of agricultural lands and in soil-ground of a re-cultivated soil layer on Tejadin and its vicinities.*

	Cu	Mo	Ni	Cr	Pb	Sn	Zn	As	Cd	Hg	Se	Sum of excesses
MAC[1]	100*	5*	50***	100*	100*	50*	300*	2**	2	2,1	1,5	
Syunik village (KF-159)	**600 (6)**	**20 (4)**	**120 (2,4)**	70	70	3,0	250	1,2	0,29	0,06	0,8	12,4
A farm (KF-152)	**250 (2,5)**	**13 (2,6)**	**350 (7)**	**200 (2)**	70	3,0	100	1,3	0,2	0,04	0,78	14,1
Tezhadin site (KF-158)	**200 (2)**	**10 (2)**	**70 (1,4)**	50	60	4,0	200	1,9	0,05	0,04	0,57	5,4

Note: [1]*MAC * according to [3], ** to [15], ***[12]; in brackets, excesses vs. MAC are given.*

Data from *Tab.12* prove that the studied agricultural land soils contained substantial concentrations of Cu, Mo, Ni - several times excessive vs. MAC.

The sums of excesses vs. MAC were close for the soils of the both agricultural lands (14.1 and 12,4), however they differed by qualitative and quantitative composition of chemical elements.

Vs. MAC, the soils of private farms in ***Syunik vil***. were excessive in Cu (6), Mo (4), Ni (2.4 times). The concentrations of the rest elements made decimal shares of MAC: Zn (0.8 MAC), Cr and Pb (0.7 MAC), As (0.61 MAC), Se (0.5 MAC).

Cd and Hg concentrations were higher than in the farm soils (*Tab.12*), this should be evident in their concentration in agricultural crops. Cd sources are bedding parent rocks, whereas Hg source is irrigating water. As noted in Chapter on Water, the waters of the aqueduct flowing out from the Artsvanik tailing repository were high in Hg (>6 vs. MAC).

Vs. MAC, ***the farm*** soils were maximally excessive in Ni (7), Mo (2.6), Cu (2.5) and Cr (2 times). One should expect that crops growing on those soils would contain the noted elements.

The concentrations of the rest elements made decimal shares of MAC. Maximal values were indicated for Pb (0.7 MAC), As (0.65 MAC), Se (0.5 MAC), and Zn (0.3 MAC). No Cd and Hg excesses were indicated. However the presence of insignificant concentrations of these toxic elements in soils can lead to their transfer to agricultural crops.

Additionally we studied soil-grounds of a re-cultivated layer on Tejadin site and its vicinities (*Fig.48*). As seen from *Tab.12*, the sum of metal excesses vs. MAC was not high on soil-grounds, however the indicated considerable concentrations of As – 1.9 *mg/kg* practically reached MAC (2 *mg/kg*). One should give special attention to this fact when utilizing such soils in agriculture.

Fig. 48. *A soil-ground layer on Tejadin territory.*

Thus, the studies enabled us to conclude that

1) *The soils of agricultural lands of the village of Syunik and a farm on River Norashenik alluvial plain are polluted with a scope of heavy metals (Ni, Mo, Cu, Cr); the contents of toxic elements (Hg, Cd) in the soils of Syunik were higher than in farm soils;*
2) *The soil-grounds in Tejadin and its vicinities are high in As, and this fact should not be ignored while cultivating the soils for agricultural purposes.*

4.2. The assessment of agricultural crop pollution

4.2.1. The contents of ore elements (Cu, Mo, Ni, Cr, Pb, Sn, Zn) in crops

The research outcomes on ore element accumulation in agricultural crops are given in *Tab.13*.

Table 13. *The contents of ore elements in agricultural crops*

Abbreviation for farms	Group	MAC * (mg/kg raw matter) / Agricultural crops	Sn	Cu	Mo	Ni	Cr	Pb	Zn	Accumulation intensity	Accumulation series
		MAC	200	10	2	0,5	0,2 [1], 0,1 [2]	0,5 0,4	10		
The Barabatum canyon (KF-1)											
	Vegetables	Egg-plant	0,05	1,4	0,4	0,8 (1,6)	0,5 (2,7)	0,5 (1)	5,4	4,4	Cr–Ni–Pb
	Vegetables	Beans	0,08	8		2,7 (5,3)	1,9 (9,3)	1,87 (3,7)	8	18,4	
	Herbs	Basil	0,1	6	0,6	1,9 (3,8)	1,4 (7)	1,9 (3,8)	7,2	14,9	Cr–Ni,Pb
Private farms in Syunik vil.											
KF-2	*Vegetable and melon-field species*	egg-plant	0,02	6,4	0,7	1,3 (2,6)	0,96 (4,8)	1 (2)	8	9,3	Cr– Ni–Pb
KF-3			0,03	5	0,3	0,9 (1,8)	0,8 (4)	0,8 (1,6)	3,9	7,3	
KF-5			0,06	4,8	0,9	1,2 (2,3)	0,96 (4,8)	1,1 (2,3)	6,7	9,4	Cr–Ni,Pb
KF-6			0,02	5,5	1	1,5 (3,1)	1,3 (6,6)		5,5	11,9	Cr–Ni–Pb
KF-2		Beans	0,16	20 (2)	4 (2)	3,6 (7,2)	2,8 (14)	3,2 (6,4)	22 (2,2)	33,8	Cr>Ni–Pb–Zn–Cu,Mo
KF-3			0,06	4	0,5	1,4 (2,8)	1 (5)	1,2 (2,4)	6	10,2	Cr–Ni–Pb
KF-5			0,02	8,2	0,8	1,9 (3,7)	1,4 (7)	1,4 (3)	7	13,5	
KF-6			0,02	7	0,5		1,6 (8)	1,2 (2,3)		14,2	
KF-2		Tomatoes	0,03	4,4		0,8 (1,5)	0,8 (4)	0,7 (1,3)	3,3	6,7	
KF-3			0,03	3,3	0,2	0,7 (1,3)	0,6 (3)	0,5 (1)	2,7	5,2	
KF-5			0,02	1,25		0,4	0,4 (2)	0,4	2	1,8	Cr
KF-6			0,06	2,5	0,8	1,5 (3)	1,3 (6,3)	1,7 (2,5)	4,2	11,8	Cr–Ni–Pb
KF-2		Pepper	0,06	7		1,4 (2,8)	1,2 (6)	1,4 (3)	7	11,6	Cr–Ni,Pb
KF-3			0,08	6,6	0,9	1,3 (2,6)	1 (5)	1,6 (3,2)	7,9	11,1	Cr–Pb–Ni
KF-6			0,1	10,2 (1)	1,2	2,4 (4,8)	1,7 (8,3)	2,4 (4,8)	12 (1,2)	19,2	Cr–Ni,Pb–Zn–Cu
KF-5		Cucumber	0,01	6,1	0,5	0,9 (2)	0,7 (3,4)	0,7 (1,4)	5,4	6,7	Cr–Ni–Pb
KF-6			0,05	8,1	0,5	1,9 (3)	1,4 (7)	1,1 (2,2)	4,5	12,6	
KF-3		marrow	0,03	3,5	0,6	0,8 (1,7)	0,7 (3,5)	0,8 (1,7)	4,2	6,9	Cr–Ni,Pb
		beet roots	0,008	1,6	0,2	0,6 (1)	0,6 (3)	0,4	2	3,9	Cr–Ni
KF-6			0,04	5	0,7	2 (4)	1,6 (8)	1,2 (2,4)	6	14,4	Cr–Ni–Pb
		Cabbage	0,03	1,3	0,5	0,4	0,45 (2,3)	0,5 (1)	3,2	3,3	Cr–Pb
	Corn		0,2	15 (1,5)	9 (4,5)	4,8 (9,6)	3,6 (18)	3,6 (7,2)	15 (3)	43,8	Cr>Ni–Pb–Mo–Zn–Cu
KF-5	*Herbs*	Dill	0,08	5,8	0,6	1,9 (4)	1,4 (7)	1,4 (2,7)	6,8	13,4	Cr–Ni–Pb
KF-6			0,07	6,6	1	3,3 (6,6)	4,4 (22)	1,3 (2,6)	7,7	31,2	Cr>Ni–Pb
KF-2		Basil	0,08	9,1	7,8 (3,9)	2,1 (4)	18,2 (91)	1,8 (3,6)	9,1	103	Cr>Ni–Mo–Pb
KF-3			0,02	2,8	0,3	0,7 (1,4)	0,6 (3)	0,5 (1)	2,4	5,8	Cr–Ni–Pb
KF-6			0,01	1,3	0,1			0,7 (1,4)	4,2	5,6	Cr–Ni,Pb
		Parsley	0,03	6,8	1,5	2,4 (4,8)	2,4 (12)	1,7 (3,4)	9,6 (1)	20,1	Cr>Ni–Pb–Zn
		Celery	0,13	11	1,9 (1)	3,5 (7)	3 (15)	3,1 (6,2)	15,4 (1,5)	31,2	Cr>Ni–Pb–Zn–Cu,Mo
KF-3	*Fruits*	Pears	0,04	6,3	0,3	0,8 (1,7)	0,7 (7)	0,8 (2)	3,5	10,8	Cr–Pb–Ni
KF-6			0,03	8,5	1,7	2,4 (4,8)	2 (20)	1,7 (4,3)	13,6 (1,4)	30,8	Cr>Ni–Pb–Zn
		Quince	0,04	5,6	0,5	1,1 (2)	1,3 (13)	0,8 (2)	4,2	16,9	Cr>Ni–Pb
		Apples	0,007	0,84	0,2	0,5 (1)	0,6 (6)	0,3	1,7	5,6	Cr–Ni
		Cornel	0,2	1,5	0,1		0,5 (5)	0,4 (1)	1,8	6,9	Cr–Ni,Pb
KF-4		Prunus spinosa	0,03	2	0,3	0,8 (1,6)	0,6 (6)	0,6 (1,5)	3	9,6	Cr–Ni–Pb
KF-5		Plump	0,02	1,2	0,2	0,5 (1)	0,3 (3)	0,4 (1)	2,4	3,2	Cr–Ni,Pb
KF-6		Prunus divaricata	0,04	3	0,2	0,6 (1,2)	0,4 (4)	0,6 (1,5)	3	6,9	Cr–Pb–Ni

Table 13 (continuation).

A farm (near a milk factory, KF-7)										
Vegetable- and melon-field species	egg-plant	0,07	**12 (1,2)**	1,1	**1,4 (3)**	**1,7 (8,4)**	**1,7 (3,4)**	8,4	15,8	Cr–Pb–Ni–Cu
	Beans	0,12	**16,5 (1,6)**	**7,5 (3,7)**	**4,5 (9)**	**2,4 (12)**	**2,4 (4,8)**	**15 (1,5)**	32,7	Cr>Ni–Pb–Mo–Cu–Zn
	Pepper	0,08	**14,3 (1,4)**	1,6	**2,1 (4,2)**	**1,3 (6,5)**	**1,8 (3,6)**	7,8	15,7	Cr–Ni–Pb–Cu
	Tomatoes	0,04	5,8	0,5	**1 (2)**	**0,8 (4)**	**0,9 (1,8)**	3,9	7,8	Cr–Ni–Pb
	Marrow	0,03	**14,4 (1,4)**	**2,2 (1)**	**2,2 (4,5)**	**1,3 (6,4)**	**2,2 (4,5)**	**9,6 (1)**	17,9	Cr–Ni,Pb–Cu–Mo–Zn
	beet roots	0,06	9	**8 (4)**	**1,4 (2,8)**	**1,2 (6)**	**1,4 (2,8)**	5	15,6	Cr–Mo–Ni,Pb
	Cabbage	0,05	7,6	**2,5 (1,3)**		**0,8 (4)**	**1,2 (2,4)**	5,9	10,6	Cr–Ni–Pb–Mo
	Potatoes	0,04	7,2	1,1	**1,1 (2,2)**		**0,8 (1,7)**	4,2	8,0	Cr–Ni–Pb
	bulb onion	0,03	4,9	0,7	**0,8 (1,5)**	**0,4 (2)**	**0,9 (1,8)**	4,4	5,5	Cr–Pb–Ni
	Watermelon	0,008	1,7	0,2	**0,5 (1)**	**0,4 (4)**	0,3	1,7	4	Cr–Ni
Herbs: basil		0,1	**9,8 (1)**	1	**2,5 (5)**	**1,96 (9,8)**	**2,5 (5)**	**9,8 (1)**	19,9	Cr–Ni,Pb–Cu,Zn
Oil-bearing: sunflower		0,04	**22 (2,2)**	1,6	**6 (12)**	**4 (20)**	**2,4 (4,8)**	**24 (2,4)**	41,4	Cr–Ni>Pb–Zn–Cu
Cereals: corn		0,1	16,7	1,5	**3,3 (6,7)**	**2,7 (13,3)**	**2,7 (5,3)**	8,3	27,0	Cr>Ni–Pb–Cu

Note: **MAC according to [2]: [1] for vegetables, herbs, cereal and oil-bearing species, [2] – for fruits; in brackets excesses vs. MAC are given; concentrations making decimal share of MAC are underlined.*

According to data from *Tab.13*, pollution of all the studied agricultural crops independent of the land was dominated by Cr, Ni and Pb. Basically, Cu, Mo and Zn concentrations showed in- MAC variations. Sn concentrations were noticeably low vs. MAC.

Let's consider sanitary and hygienic characteristics of agricultural crops by separate sites.

RIVER BARABATUM CANYON

On this site 2 vegetable and 1 herb species were studied. As seen from *Tab.13*, all the 3 species were polluted by Cr, Ni and Pb.

By accumulation intensity coefficient, the lowest pollution level was indicated for **egg-plants** (*Solanum melongena*): intensity – 4.4. A basic share in summary pollution fell on Cr (61%). Ni was 1.6 times excessive vs. MAC; Pb did not exceed MAC (*Fig. 49*). Mo and Zn concentrations made 20 and 50% of MAC, respectively. Sn and Cu concentrations were tens times low vs. MAC.

Maximal summary pollution was indicated for green bean pods (Phaseolus vulgaris) – 18,4; 50% of pollution fell on Cr, and 20% - on Ni.

Summary pollution (14.9 MAC) of above-ground mass of ***basil*** (*Ocimum basilicum*) was also dominated by Cr (46.9%). Ni and Pb shares were similar – 26.5% each.

Domination of ore element (Cr, Ni, Pb) over pollution of the studied crops steps from the fact that cultivated plots of land are located just on numerous adit dumps (*Fig. 50*).

Wholly, the assessment of sanitary and hygienic state of the studied crops grown on private plots in River Barabatum canyon enabled us to establish crop pollution; the lowest level of heavy metal accumulation was indicated for egg-plants.

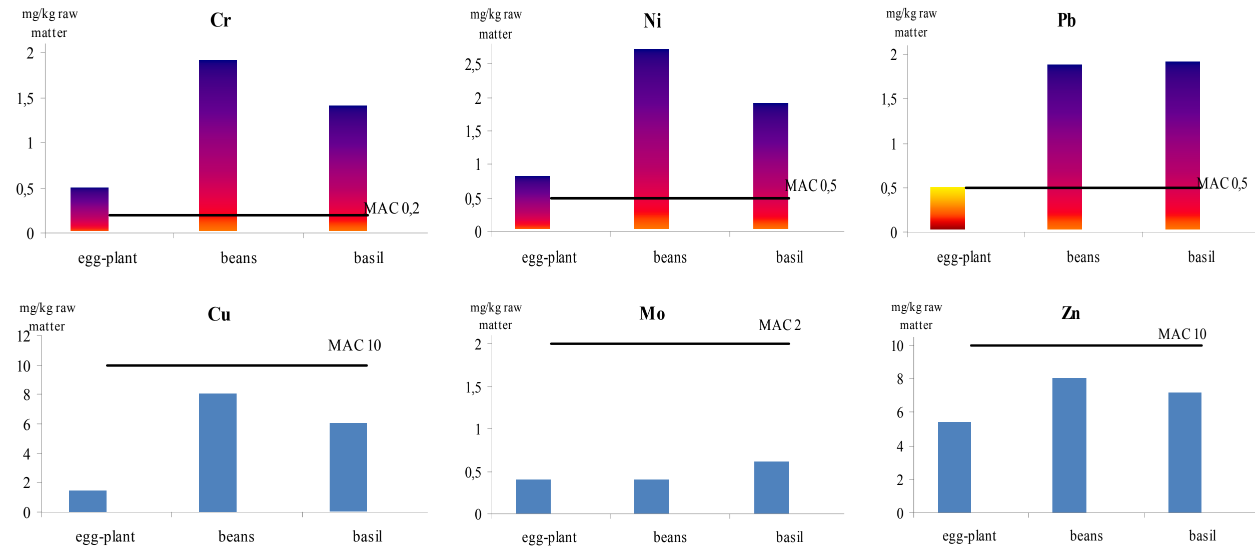


Fig. 49. *Heavy metal contents in vegetables grown in River Barabatum canyon*

Fig. 50. *Cultivated plots on dumps in River Barabatum canyon.*

PRIVATE FARMS IN THE VILLAGE OF SYUNIK

On Syunik's territory, studied was a wide scope of agricultural crops gathered from 5 private farms (KF-2-6).

Let's consider the contents of toxic elements by separate groups of crops.

Vegetable- and melon-field crops were represented by 8 vegetable species (*egg-plant, beans, tomato, pepper, cucumber, marrow, beet root, cabbage,),* corn, and 4 herb species (*dill, basil, parsley, celery).*

By mean accumulation intensity coefficients the studied species made up the following regressive series:

beans$_{(17.9)}$>pepper$_{(13.9)}$>cucumber$_{(9.6)}$>egg-plant$_{(9.5)}$>
beet root$_{(9.2)}$>marrow$_{(6.9)}$>tomato$_{(6.4)}$>cabbage$_{(3.3)}$

As seen from the series, maximal values are typical of beans and pepper (*Fig. 51, 52*) and minimal – of cabbage. Pollution of basic assortment of crops was dominated only by 3 ore elements (Cr, Ni, Pb), whereas Cu, Zn and Mo, too, added to summary pollution of beans and pepper (on separate plots).

Maximal values of the intensity of summary accumulation of heavy metals (33.8) were indicated for ***beans*** (*Fig. 51, 52*). Cr accumulation coefficients for beans varied 5-14, Ni – 2.8-7.2, Pb-2.3-6.4, Zn-0.6-2.2, Cu-0.4-2, Mo – 0.2-2 vs. MAC. ***Such level of pollution with heavy metal makes the crop hazardous for dietary needs.***

Fig. 51. *Private agricultural land in Syunik and its vicinities: pepper and bean beds*

Summary pollution indices for ***pepper*** (*Capsicum annuum*) – the second species by pollution level - varied 11.1-19.2 vs. MAC. A dominating role was given to Cr, Ni, Pb, however on plot KF-6 Zn and Cu insignificantly added to pollution. Wholly, the species did not meet the standards.

For ***cucumber*** (*Cucumis sativus*)***, egg-plants, tomatoes*** (*Lycopersicon esculentum*) ***and beet roots*** (*Beta vulgaris*) indicated were mean indices of heavy metal accumulation intensity: 6.7-12.6, 7.3-11.9, 1.8-11.8, 3.9-14.4, respectively.

Maximal values for the noted species like those for pepper were detected on plot KF-6. The indicated pollutants were Cr, Ni, and Pb only.

Lowest pollution intensity indices were established for ***marrow*** (*Cucurbita pepo*) and ***cabbage*** (*Brassica oleracea*)**.**

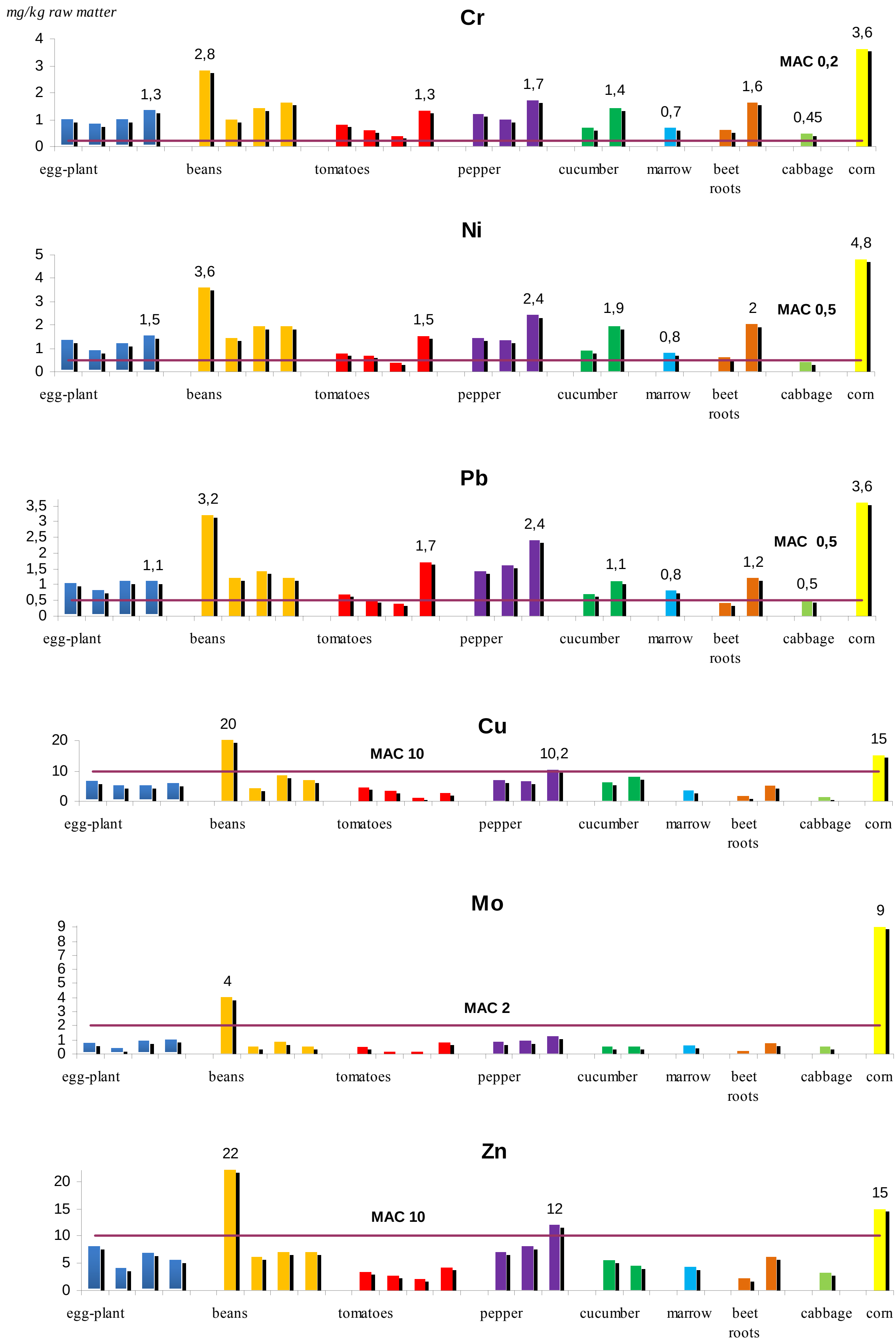


Fig. 52. *The contents of heavy metals in vegetable- and melon-field crops grown on agricultural land of the village of Syunik.*

As a cereal species, we studied ***corn grains*** (*Zea mays*). Unlike vegetable- and melon-field crops, pollution level for this one was higher: summary index of excesses vs. MAC was 43.8. All the measured elements except Sn are involved in accumulation series: Cr>Ni-Pb-Mo-Zn-Cu. Cr was an order ahead of the rest elements and showed a 18- time excess vs. MAC. ***This crop is hazardous for dietary needs.***

Herbs gathered from private plots in Syunik included dill (*Anethum graveolens*), basil (*Ocimum basilicum*), parsley (*Petroselinum crispum*) and celery (*Apium graveolens*). As indicated by the analysis data (*Tab.13*) the studied herbs were characterized by high coefficients of heavy metal accumulation. By mean accumulation intensity indices they make up the following regressive series:

basil $_{(38)}$ – *celery* $_{(31)}$ – *dill* $_{(22)}$ – *parsley* $_{(20)}$

Pollution-dominating elements for all the studied herbs were Cr, Ni, Pb. Maximal indices were established for Cr; in basil it reached 91 vs. MAC. Accumulation of elements in herbs by separate plots was varying (*Fig. 53*).

Wholly, one can conclude that the studied herbs are hazardous for dietary needs.

Fruits included 7 species: *pears* (*Pyrus sp.*), *quince* (*Cydonia oblonga*), *apples* (*Malus sp.*), *cornel* (*Cornus mas*), plump species *Prunus spinosa*, *Prunus domestica*, *Prunus divaricata*. By summary accumulation coefficient the studied species made up the following series:

pears $_{(21)}$ – *quince* $_{(17)}$ > *Prunus spinosa* $_{(9.6)}$ – *cornel, Prunus divaricata* $_{(7)}$ – *apples* $_{(5.6)}$ – *Prunus divaricata* $_{(3.2)}$

As seen from the series, maximal indices of summary accumulation are typical of species with hardest consistence: pears and quince. Heavy metal and particularly Cr accumulation in them is by an order higher compared with juicy species (*Fig. 54*).

Pollution of all the studied species was dominated by Cr, Ni and Pb.

Agricultural crops growing on the territory of ***a farm*** on River Norashenik alluvial plain were also polluted with heavy metals dominated by Cr, Ni and Pb. We studied 10 vegetable- and melon-field species (egg-plants, beans, pepper, tomatoes, marrow, beet roots, cabbage, potatoes, bulb onion, watermelon), 1 – herb (basil), oil-bearing (sunflower) and cereal (corn) species (*Fig.55*).

By summary accumulation level the studied vegetable- and melon-field species made up the following series:

beans $_{(33)}$ – *marrow* $_{(18)}$ – *pepper, egg-plant* $_{(16)}$ – *beet root* $_{(15.6)}$ – *cabbage* $_{(10.6)}$ > *potatoes, tomatoes* $_{(8)}$ – *bulb onion* $_{(5.5)}$

As seen from the series, a tenfold accumulation level group includes 6 crops, and maximal indices were specific of beans only (33). Like for beans from Syunik, pollution level for the farm beans was high. The lowest indices were indicated for potato (*Solanum tuberosum*) and tomato (8) and bulb onion (*Allium cepa*) - (5.5).

Like that from Syunik, the farm basil had a high accumulation level. Inclusion of this herb in diet is undesirable.

Sunflower seeds (*Helianthus annus*) were characterized by high pollution level – 41.4. Beside Cr, Ni and Pb (89%), biophile elements (Zn and Cu) also added to pollution (11%). Using this crop in diet is hazardous.

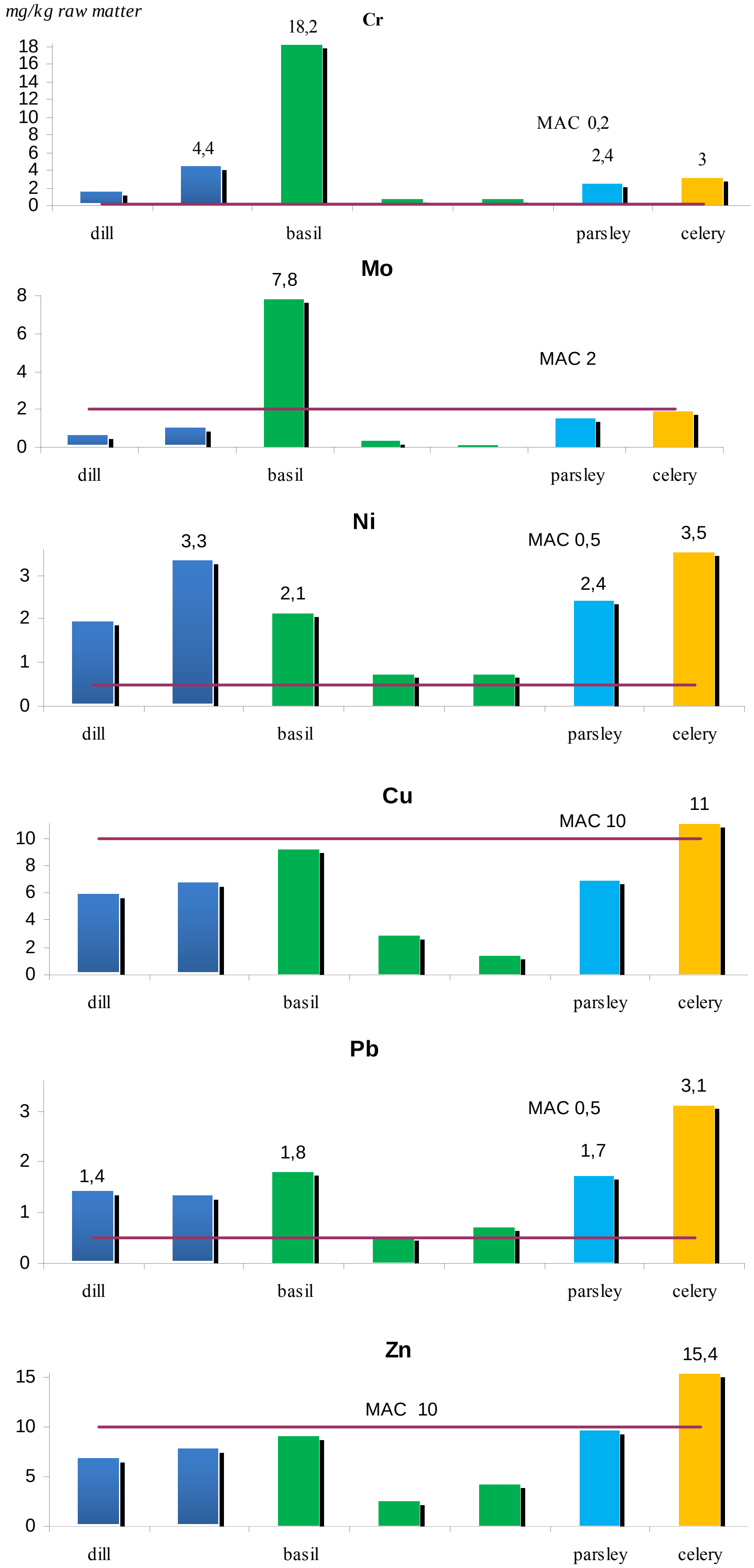


Fig. 53. *Heavy metal contents in herbs grown on agricultural land of the village of Syunik.*

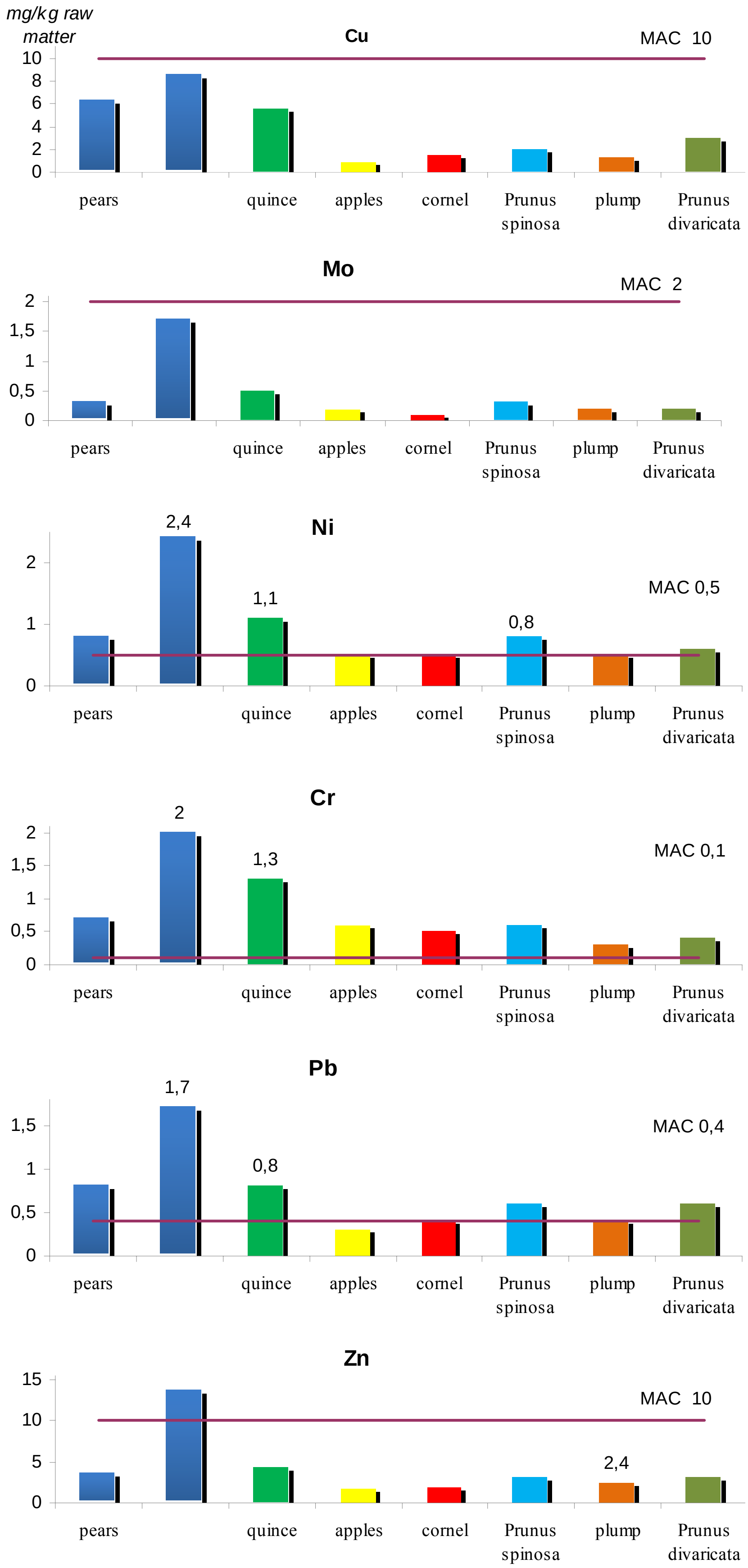
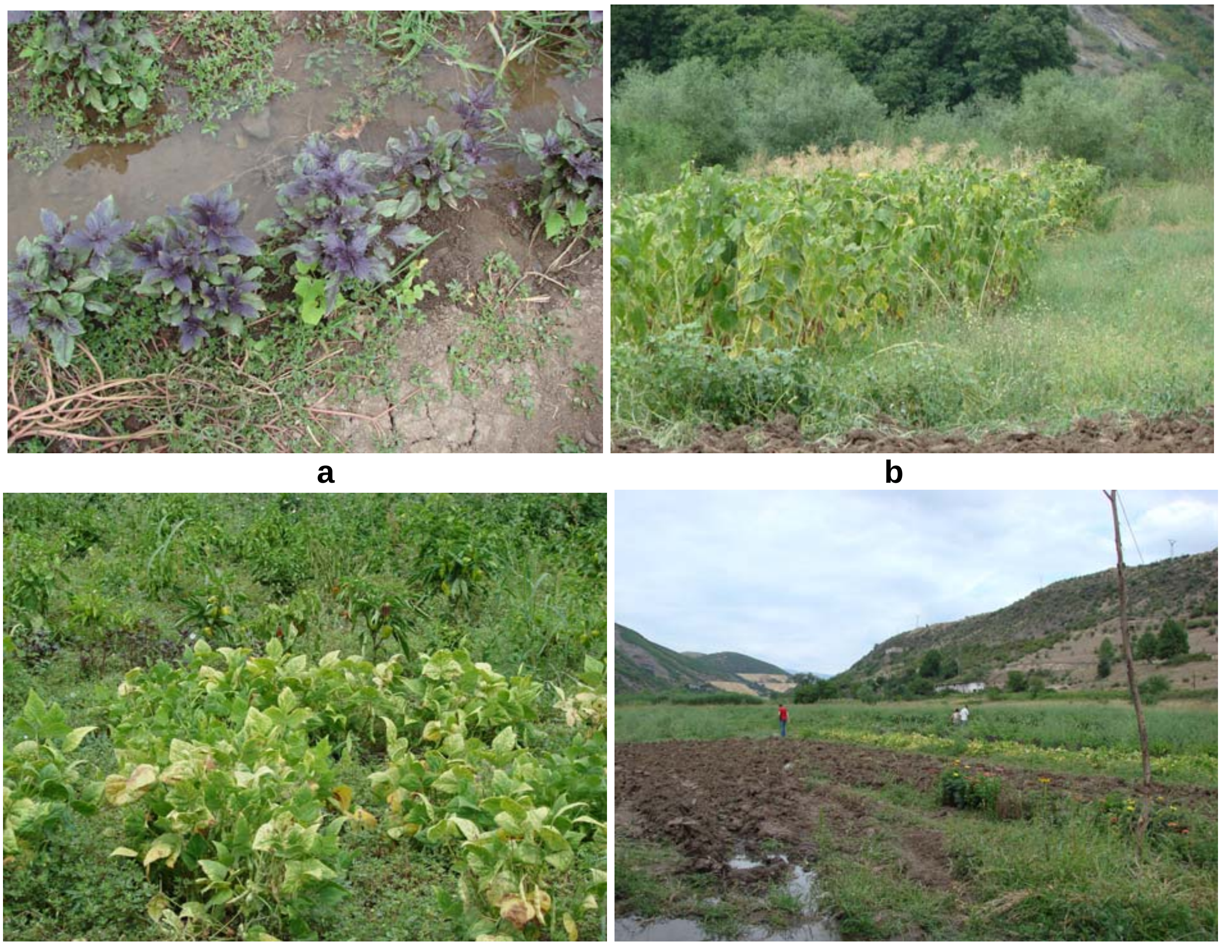


Fig. 54. *The contents of heavy metals in fruits grown of agricultural land of the village of Syunik*

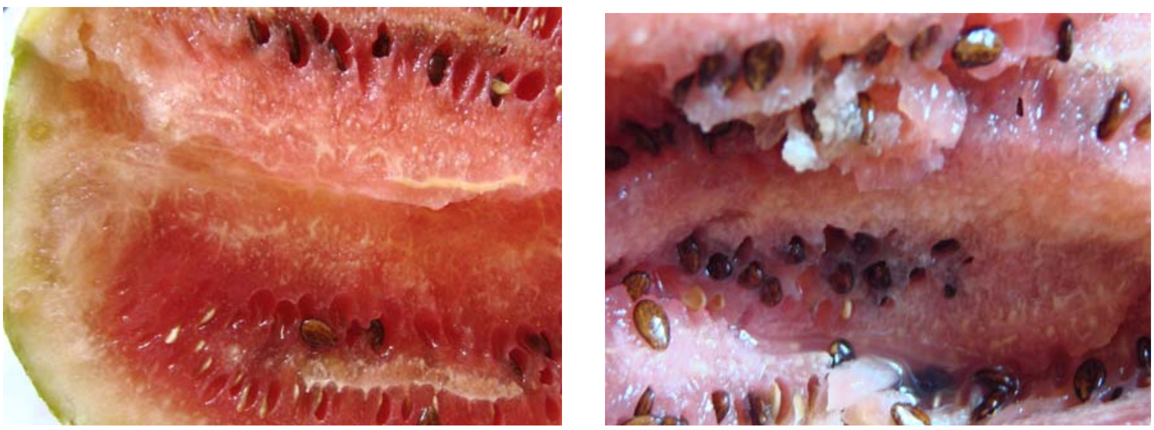


a b c d

__Fig. 55__. A farm: a) basil, b) sunflower plantation, c) beans, d) ploughed fields

Wholly, the contents of accumulated heavy metals in corn grains from the farm were twofold lower than in those from Syunik, however pollution level remained high – 27.

A minimally polluted crop growing in the farm was watermelon (*Citrulus lanatus*), which biomass accumulated only Cr (4 MAC). Ni (1) and Pb (0.7) accumulation did not exceed MAC. The rest elements were substantially lower than MAC. Despite a relatively low pollution level, visual observations indicated that the crop was unsuitable for use due to its sluggish consistency and cancer formations (*Fig. 56*). Presumably, this could be linked to irrigation water and agrochemical properties of soils.



а б

***Fig. 56.** Watermelon section: a) general view, b) cancer formations*

Thus, eco-toxicological studies of vegetable- and melon-fields and fruit species growing on private plots in the village of Syunik and in the farm indicated that

1) *Pollution of vegetable- and melon-field and fruit species was dominated by Cr, Ni and Pb.*
2) *Using beans, pepper, corn and sunflower is hazardous for dietary needs.*
3) *The most polluted were species with hard consistency (pears, quince).*

4.2.2. The contents of highly toxic elements (As, Cd, Hg, Se) in agricultural crops

The obtained research data on highly toxic element accumulation in the studied agricultural crops are given in *Tab.14*. Let's consider eco-toxicological state of farm produce by separate territories.

RIVER BARABATUM CANYON

As seen from *Tab. 14*, the contents of toxic elements (As, Cd, Hg, Se) in vegetables and basil from private farms located in the Barabatum canyon were not excessive vs. standards.

Maximal contents of ***As*** were detected in basil – 0.0048 *mg/kg* raw mass, whereas its concentrations in egg-plants were 4 times lower (0.0012 *mg/kg* raw mass).

Very low concentrations of ***Cd*** and ***Hg*** were detected in egg-plants only – 0.0002 and 0.001 *mg/kg* raw mass, respectively.

Se was detected in all the 3 studied species, maximal contents were established for basil. No excesses vs. MAC.

Wholly, one can conclude that by the contents of highly toxic elements the studied crops meet sanitary and hygienic requirements but with regard for the contents of ore elements (*Tab.13*) the crops were indicated as polluted.

PRIVATE FARMS OF SYUNIK VILLAGE

On the territory of the village of Syunik, studied were agricultural crops from 5 private farms (KF-2-6). The contents of toxic elements were measured in 9 vegetable-and melon-field species (egg-plant, beans, pepper, tomato, cucumber, marrow, beet, cabbage), corn grains, 4 herb species (dill, basil, parsley, celery), and in 7 fruit species (pear, quince, apple, cornel, 3 plump species).

Let's consider the contents of toxic elements by separate groups of crops.

Vegetable- and melon-field crops

For ***egg-plants***, ***As*** was detected in 3 samples only. Its concentrations varied 0.0012-0.0082 *mg/kg* raw mass. No excesses vs. MAC (0.2 *mg/kg* raw mass).

Cd was detected in all the samples, its concentrations varied in a very limited range (0.0001-0.0004 *mg/kg* raw mass) and was hundred times low vs. MAC (*mg/kg* raw mass).

Hg, too, was detected in all the samples; its concentrations varied 0.0003-0.01 *mg/kg* raw mass. Basically, the concentration was manifold lower than MAC, however in crops from KF-3 it reached (0.01) half a MAC (0.02 *mg/kg* raw mass), this representing a risk factor, indeed.

Se concentrations showed no variations (0.001-0.002 *mg/kg* raw mass) and did not reach MAC.

Table 14. *The contents of toxic elements in agricultural crops*

		MAC * *(mg/kg raw mass)*	**As**	**Cd**	**Hg**	**Se**
Abbreviation for farms		**Agricultural crops**	0,2	0,03	Vegetables, herbs oil-bearing– 0,02; fruits – 0,01; cereals – 0,03	0,5
The Barabatum canyon (KF-1)						
	Vegetables	egg-plant	0,0024	0,0004	0,002	0,002
	Vegetables	beans	n/d	n/d	n/d	0,003
	Herbs	basil	0,0096	n/d	n/d	0,048
Private farms in Syunik vil.						
KF-2	***Vegetable and melon-field species***	egg-plant	0,016	0,0002	0,002	0,002
KF-3		egg-plant	0,0024	0,0006	**0,02** (*1*)**	0,004
KF-5		egg-plant	0,0074	0,0008	0,0006	0,002
KF-6		egg-plant	n/d	0,0004	0,002	0,002
KF-2		beans	n/d	n/d	0,0007	0,03
KF-3		beans	n/d	n/d	**0,03** (*1,7*)	0,03
KF-5		beans	0,005	n/d	0,0013	0,01
KF-6		beans	0,0007	n/d	n/d	0,013
KF-2		tomatoes	n/d	0,0001	0,003	0,001
KF-3		tomatoes	n/d	0,0002	0,003	0,001
KF-5		tomatoes	0,0023	0,0003	0,001	0,002
KF-6		tomatoes	n/d	0,0001	n/d	0,003
KF-2		pepper	n/d	n/d	0,008	0,005
KF-3		pepper	n/d	0,0002	**0,028** (*1,4*)	0,001
KF-6		pepper	n/d	0,0002	n/d	0,002
KF-5		cucumber	0,0152	0,0001	0,0012	0,01
KF-6		cucumber	0,0015	0,0001	0,0065	0,002
KF-3		marrow	n/d	n/d	**0,45** (*22,5*)	0,005
KF-3		beet roots	n/d	0,0002	**0,63** (*31,3*)	0,0004
KF-6		beet roots	n/d	n/d	**0,12** (*6*)	0,002
KF-6		cabbage	n/d	0,0001	**0,021** (*1,1*)	0,01
KF-6	Corn		0,0017	0,0007	n/d	0,003
KF-5	***Herbs***	dill	0,007	n/d	0,002	0,01
KF-6		dill	0,007	0,0008	**0,02** (*1*)	0,02
KF-2		basil	n/d	n/d	**0,18** (*9*)	0,06
KF-3		basil	0,0004	0,0002	**0,28** (*14*)	0,04
KF-6		basil	0,0014	n/d	0,004	0,08
KF-6		parsley	0,0092	0,0002	0,002	0,04
KF-6		celery	0,014	0,0034	0,0006	0,06
KF-3	***Fruits***	pears	0,004	n/d	**0,06** (*6*)	0,004
KF-6		pears	0,02	0,005	**0,056** (*5,6*)	n/d
KF-6		quince	n/d	0,0002	0,002	n/d
KF-6		apples	0,0003	n/d	n/d	0,001
KF-6		cornel	n/d	0,0001	0,004	0,001
KF-4		Prunus spinosa	0,001	0,0001	0,002	n/d
KF-5		plump	n/d	n/d	n/d	0,001
KF-6		Prunus divaricata	n/d	0,001	0,001	n/d

Table 14 (continuation)

		As	Cd	Hg	Se
MAC * (*mg/kg raw mass*) **Agricultural crops**		0,2	0,03	Vegetables, herbs oil-bearing– 0,02; fruits – 0,01; cereals – 0,03	0,5
A farm (near a milk factory, KF-7)					
Vegetable- and melon-field species	egg-plant	0,006	0,0028	0,0008	0,002
	beans	n/d	n/d	0,003	0,007
	pepper	0,0076	0,0028	0,0008	0,002
	tomatoes	0,002	0,001	n/d	0,001
	marrow	0,0042	0,002	0,001	0,002
	beet roots	0,0026	0,0008	0,0004	0,002
	cabbage	0,026	0,001	n/d	0,005
	potatoes	n/d	0,001	0,003	n/d
	bulb onion	0,002	0,001	0,0004	0,003
	watermelon	0,0007	n/d	n/d	0,0013
Herbs: basil		0,02	0,002	0,0006	0,06
Oil-bearing: sunflower		0,004	**0,048 (*1,6*)**	0,003	0,01
Cereals: corn		0,004	0,0003	0,0013	0,001

Note: *"n/d" – not detected; *MAC – according to [2]; ** in brackets: excesses vs. MAC: underlined: concentrations making decimal shares of MAC*

Green bean pods gathered from the same plots as egg-plants accumulated ***As, Hg, Se***; no ***Cd*** was detected.

As was indicated in 2 samples only; its concentrations varied 0.0002-0.0015 *mg/kg*, MAC being 0.2 *mg/kg* raw mass.

Hg contents in beans, like egg-plants, were low 0.0003-0.01 *mg/kg* raw mass. The latter made 0.5 MAC and was also indicated for point KF-3 .

Se concentrations were higher than in egg-plants and varied 0.003-0.01 *mg/kg* raw mass. No excesses vs. MAC were indicated.

Tomatoes accumulated predominantly ***Cd, Hg*** and ***Se***. ***As*** was identified only in a sample from KF-5; its concentration was 0.0023 *mg/kg* raw mass, this being 100 times lower than MAC. ***Cd*** concentrations showed no variations (0.0001-0.0003 *mg/kg* raw mass) and did not reach MAC. ***Hg*** was detected in a range 0.001-0.003, this making 15% of MAC. Se contents were low 0,001-0,003 *mg/kg raw mass.*

Pepper accumulated ***Cd, Hg*** and ***Se***. ***Cd*** and ***Se*** concentrations were practically stable, whereas ***Hg*** varied 0.004-0.014 *mg/kg* raw mass, this making 20 and 70% of MAC and representing a risk factor.

Cucumber. ***As*** contents varied 0.0015-0.015 *mg/kg* raw mass, which was higher than in other vegetable species and noticeably lower than MAC. ***Cd*** contents – 0.0001 *mg/kg* raw mass. ***Hg*** (30% of MAC) was detected in point KF-6. ***Se*** contents varied 0.002-0.01 *mg/kg* raw mass.

Marrow specimens were gathered in point KF-3. They accumulated ***Hg*** and ***Se***. For marrow, the highest ***Hg*** values were established. Concentration was 0.45 *mg/kg* raw mass, this overstepping MAC by 22.5 times (*Fig. 57*). **Using this species for dietary needs is extremely hazardous.**

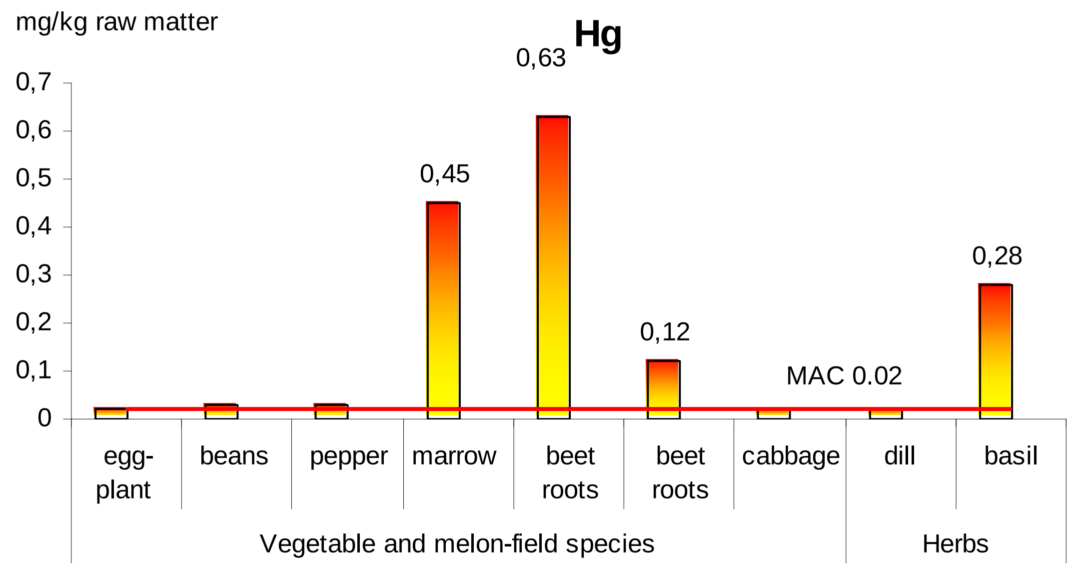


Fig. 57. *MAC-overstepping contents of Hg in vegetable- and melon-field species and herbs (Syunik vil.).*

Beet roots and ***cabbage*** showed similar inclinations in respect to highly toxic elements; in their biomass high concentrations of ***Hg*** were indicated. Here one should stress beet roots from KF-3, where Hg concentrations reached 15.6 MAC. In cabbage, Hg excesses made 1.1 MAC (*Fig. 57*). Though vegetation period is approximately the same for the both species, however the observed 15-fold difference in Hg accumulation is conditioned by functional difference of commercial organs. Beet roots accumulate Hg directly from soil, whereas Hg enters the cabbage through xylem strands of the cord. Besides, these crops substantially differ by water capacity: the cabbage contains much more water than beet roots. **Using the both species for dietary needs is hazardous.**

The contents of toxic elements in ***corn grains*** was tens times lower than MAC, however taking into account high levels of accumulation of other heavy metals (total 43.8 MAC, see *Tab.14*) **the use of this species for dietary needs is hazardous.**

Of all the studied ***herbs***, the highest ***Hg*** accumulation indices were indicated for dill and basil. Maximal indices were established for basil (9-14 MAC) from points KF-2 and 3. Hg contents in parsley and celery biomass were tens times lower than MAC.

Noteworthy is the fact of ***Se*** accumulation in herbs. In all the studied agricultural species growing in the village of Syunik. Se accumulation levels varied 0.0004-0.03 *mg/kg* raw mass, whereas its contents in herbs were 0.01-0.08 *mg/kg* raw mass, this reaching 16% of MAC. Especially high concentrations were indicated in basil (max.0.08) and celery (0.06 *mg/kg* raw mass) biomass.

The level of pollution of herbs by toxic elements and heavy metals is high and thus using them in diet is hazardous.

Eco-toxicological studies of ***fruits*** from private farms of the village of Syunik. indicated that like ore elements (Cr, Ni, Pb), substantial accumulation of ***Hg*** was detected in fruits with hard consistency and pears in particular in which Hg was 6 times excessive vs. MAC. In quince, cornel, Prunus spinosa and P. divaricata Hg contents reached up to 20-40% of MAC. Taking into account a poly-element character of pollution of the noted species, using them in diet is hazardous.

No Hg was detected in plumps. Taking into account low level of pollution by ore elements, the plums are found safe for dietary needs.

FARM

Eco-toxicological studies of agricultural crops growing on the territory of the farm indicated that in basic assortment of vegetable- and melon-field species the levels of highly toxic element accumulation did not reach MAC, except sunflower in which seeds the detected ***Cd*** concentration was 0.048 *mg/kg* raw weight, this being 1.6 time excessive vs. MAC (0.03), and the detected insignificant concentrations of ***Hg*** made 0.003 *mg/kg* raw weight. Similar level of ***Hg*** concentration was established for beans and potato (0.15 MAC). For the rest crops the contents of the elements were either low or were not detected at all.

Thus, the performed pilot eco-toxicological studies enabled us to conclude that

1) *the soils of the village of Syunik and the farm are polluted by a number of heavy metals (Ni, Mo, Cu,Cr); soil-ground of Tejadin site contains As.*
2) *Agricultural crop pollution is dominated by Cr, Ni and Pb.*
3) *Agricultural crops growing on the land of the village of Syunik accumulate Hg besides ore elements, which make them hazardous for dietary need..*

Taking into consideration high levels of heavy metals and Hg accumulation in agricultural crops of the village of Syunik, further research and monitoring of farm produce (milk, meat, etc.) is needed for all agricultural lands for detailed eco-toxicological assessment and functional zonation as well as for the development of ecologically safe assortment of agricultural crops.

5. CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

The obtained research outcomes on surface waters of the city of Kapan and adjacents sites indicated that

- By basic physical and chemical indices (pH, electrocionductivity, salinity) ore waters discharged into river network did not meet the accepted standards;
- The waters of Rivers Syunik and Norashenik that cross agricultural lands were characterized by high turbidity indices;
- Ionic composition of the studied waters was dominated by calcium and sulfate which maximal concentrations were determined in ore waters;
- Due to high contents of Ca and Mg, the waters were attributed to those of hard and very hard categories;
- Mine waters from adits and industrial waters contained high concentrations of toxic (Cd, As, Hg) and ore elements (Cu, Zn);
- Heavy metal contents in natural waters were not excessive vs. MAC, except River Kavart waters with MAC exceeding Cd, Cu and Zn;
- By mineralization level and standards for ion and heavy metal contents, the waters of Rivers Syunik, Artsvanic and those of Rivers Norashenik and Artsvanik conflux were characterized as satisfactory for agricultural land irrigation;
- River Barabatum waters were hazardous for use in irrigation due to high mineralization indices and ion (Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-) excesses vs. MAC. The waters of River Kavart and a rivulet on point KFB-6, too, were indicated as hazardous due to high mineralization level and ion (Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}) and heavy metal (Cd, Cu, Zn) excesses vs. MAC. Especially hazardous were the waters of the Artsvanik tailing repository aqueduct due to critical concentrations of Hg;
- Mixing of ore waters with surface streams brings to the increase in concentration of a number of compounds and heavy metals in the waters of River Voghchi left-bank tributaries. Chemical element concentrations in the waters did not reach MAC, nevertheless there exists a real ecological risk factor stepping from high coefficients of their cumulation in bio-environments;
- The volumes of metal transfer by separate streams were calculated. The maximal volumes were established for Rivers Norashenik and Artsvanik conflux.

Eco-toxicological studies of Kapan’s soils indicated that

- Basically, the city pollution was dominated by copper and lead, however no intense pollution of the entire territory of the city was established. Fields with maximal levels of heavy metal concentrations were localized in northern and central part of the city.

By geochemical indices of summary concentration of elements, the city territory pollution was attributed to weak and partially medium pollution;

- On the territory of the city, substantial excesses of elements of both I (As, Cd, Ni, Pb, Cr) and II-III (Cu, Zn, Mo) category of hazard vs. MAC were detected. Special attention should be given to left-bank part of the city with an emphasis on territories associated with industrial enterprises and - in some cases - with garages;
- Rain- and mudflows transferred substantial concentrations of ore elements (Cu, Mo, Ni) to the territory of the city;
- The basic share in toxic element transfer was indicated for As (2.5 MAC) on the city market site.

Eco-toxicological studies of agricultural crops indicated that

- The soils of the village of Syunik and the farm in River Norashenik alluvial plain were polluted by a set of heavy metals (Ni, Mo, Cu, Cr); soil-ground on Tejadin plot contained As;
- Agricultural crop pollution was dominated by Cr, Ni and Pb. Basically, the contents of the noted elements in the studied species were excessive vs. MAC.

Agricultural crops grown on the land of the village of Syunik, accumulated Hg besides ore elements.

The obtained data evidenced the hazard of their use for dietary purposes.

5.2. RECOMMENDATIONS

The obtained research outcomes indicated pollution of irrigation water, soils of agricultural lands and farm product by toxic elements. With regard for such pollution level and extension that threatens sustainable development of the territory, we consider it reasonable to execute the following activities.

Organizational actions

- to demand from Deno Gold Mining Company to cease unpurified ore water drainage to river network,
- to demand from the Kapan mining and dressing plant to provide de-mercurization of waters drained from the Artsvanik tailing repository,
- to apply to the RA Ministry of Nature Protection for instituting control over fulfillment of ecological safety requirements brought forward by the companies.

Research and diagnostic actions

- to perform a target geochemical mapping of the territory at sc.1:25000 so as to obtain a full picture of agricultural land pollution. To define the level of pollution spread by soil profile to the depth,
- as a matter of record, to detail levels of toxic element accumulation by diverse agricultural crops. To develop the best safe assortment of agricultural crops to be planted on polluted sites,
- to study eco-toxicological indices of fodder grasses on pollution-exposed territories and to provide eco-toxicological assessment of farm produce,
- to carry out a pilot express examination of children aimed to identification of risk groups exposed to the impact of heavy metals.

Technological actions

- to consider possibilities of application of available soil detoxification technologies. To perform case-specific experiments on the land of the village of Syunik,
- to suggest Deno Gold Mining Company putting into practice of well adopted to Armenia’s ore fields “mining geochemistry” methods for ore deposit forecast and evaluation, so as to mitigate environmental damage through best use of information space of existing adits and to reduce the volume of new mining and driving works.

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