NATIONAL ACADEMY OF SCIENCIES
THE CENTER FOR ECOLOGICAL-NOOSPHERE STUDIES

Assessing a risk of toxic elements discharge from an arsenic-containing substance repository site in the city of Alaverdi

OSCE Office in Yerevan

YEREVAN 2010

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

A. K. Saghatelyan

«3» 09 2010

REPORT

"Assessing a risk of toxic elements discharge from an arsenic-containing substance repository site in the city of Alaverdi"

Principal investigator

Dr. L. Sahakyan

Yerevan 2010

CONTENTS

1. INTRODUCTION

In the north of the city of Alaverdi, in River Madan (Lalvar) basin a repository site for As-containing substances was built in the 1980s (*Fig. 1*) called by local people "the arsenic grave".

LEGEND

the "As grave" site

Fig. 1. *The position of the "As grave" within the bounds of the city of Alaverdi*

For many years the repository site remained abandoned being exposed to erosion; today the isolation walls are almost destroyed (*Fig. 2*).

The ***project goal*** is to assess a possible discharge of toxic elements emphasizing *As* and *Hg* from the repository site (*Fig. 3*) on a base of the planned assessment of *As* and *Hg* contents in water, soil and bottom sediments.

It should be mentioned however that River Madan (Lalvar) basin homes lots of abandoned uncontrolled heaps *(Fig. 4)*. So, in the project's frame ***a task*** was set to define a share of the elements impact and their discharge from the *As* repository site and heaps.

Fig. 2. *Photos of "the As grave" site*

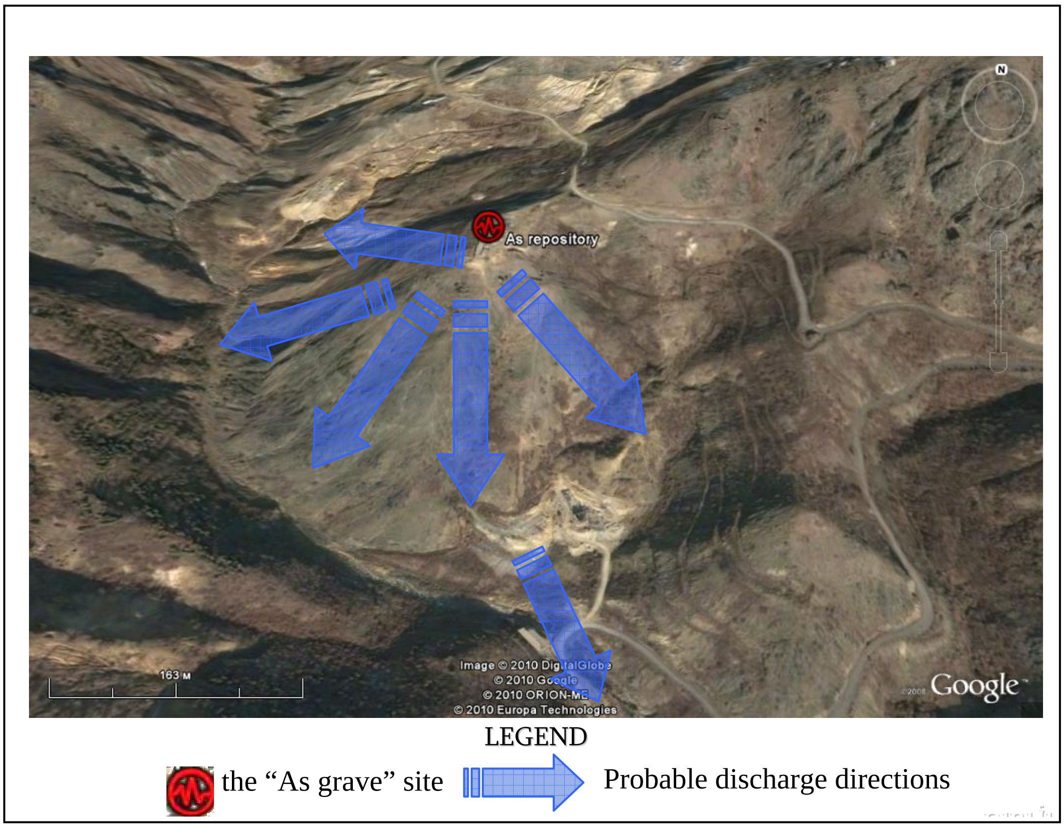
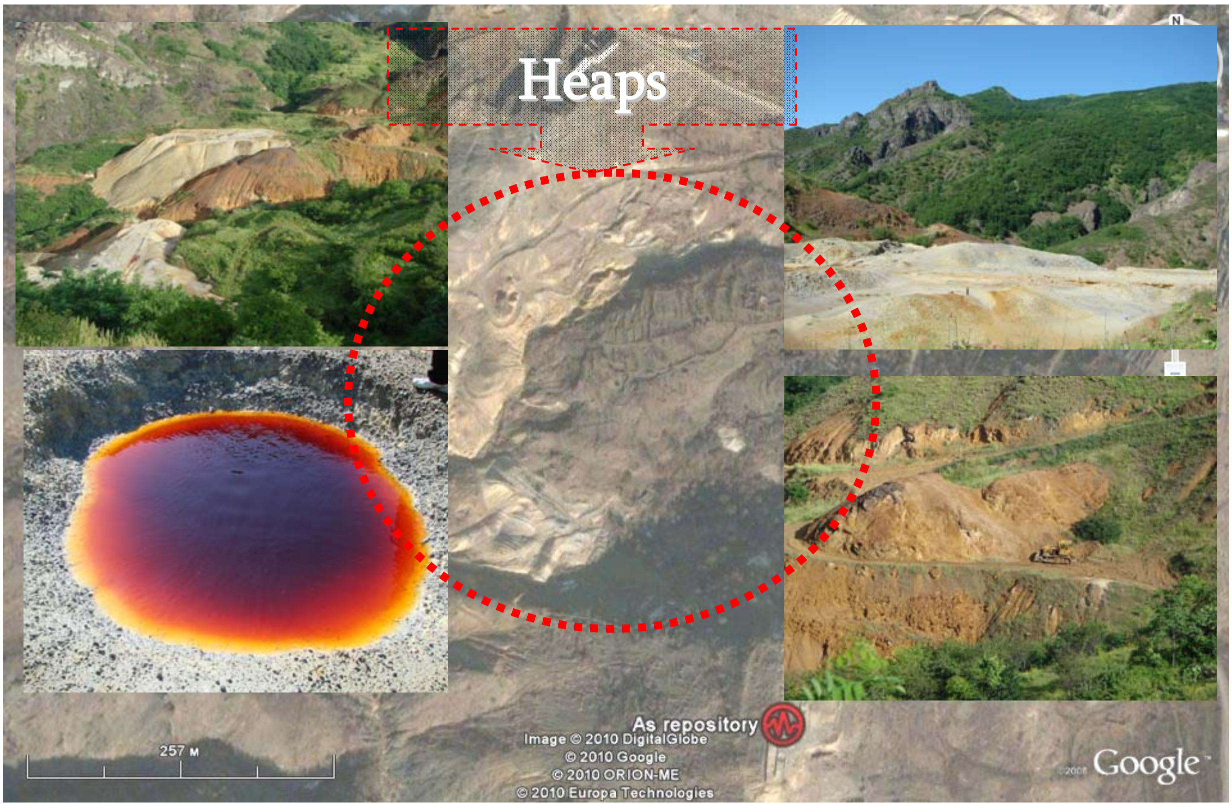


Fig. 3. *Probable directions of toxic element discharge from "the As grave" site*



LEGEND
the "As grave" site

Fig. 4. *Photos of abandoned heaps around "the As grave"*

The study was implemented by the Center for Ecological-Noosphere Studies of NAS RA under support of the OSCE Office in Yerevan.

2. GENERAL INFORMATION ON As

Arsenic (*As*) is a physiologically active and at the same time toxic non-metal; its index number is 33 and it is placed in the IV period V group of the D.I. Mendeleev periodic table (*Fig. 5*). The name of the element originates from Latin "arsenicum" or Greek "arsenikos", which means "yellow pigment".

There exist a large amount of *As* minerals – 368 mineral kinds – the most wide spread being arsenopyrite, lorandite- auripigment, auripigment, nickel, copper, cobalt etc. arsenides and sulfoarsenides (*Fig. 6*).

As is environmentally dangerous element and geo-chemically and ecologically has been poorly investigated. Due to its mobility and solubility *As* often enters the biosphere and man-made systems as well. *As* is not attributed to expensive utilized ore components to be utilized and is mostly involved in waste products and has profound pathogenic and technogenic effects. *As* freely travels throughout man-made environment, often transforming, polluting and poisoning the environment.

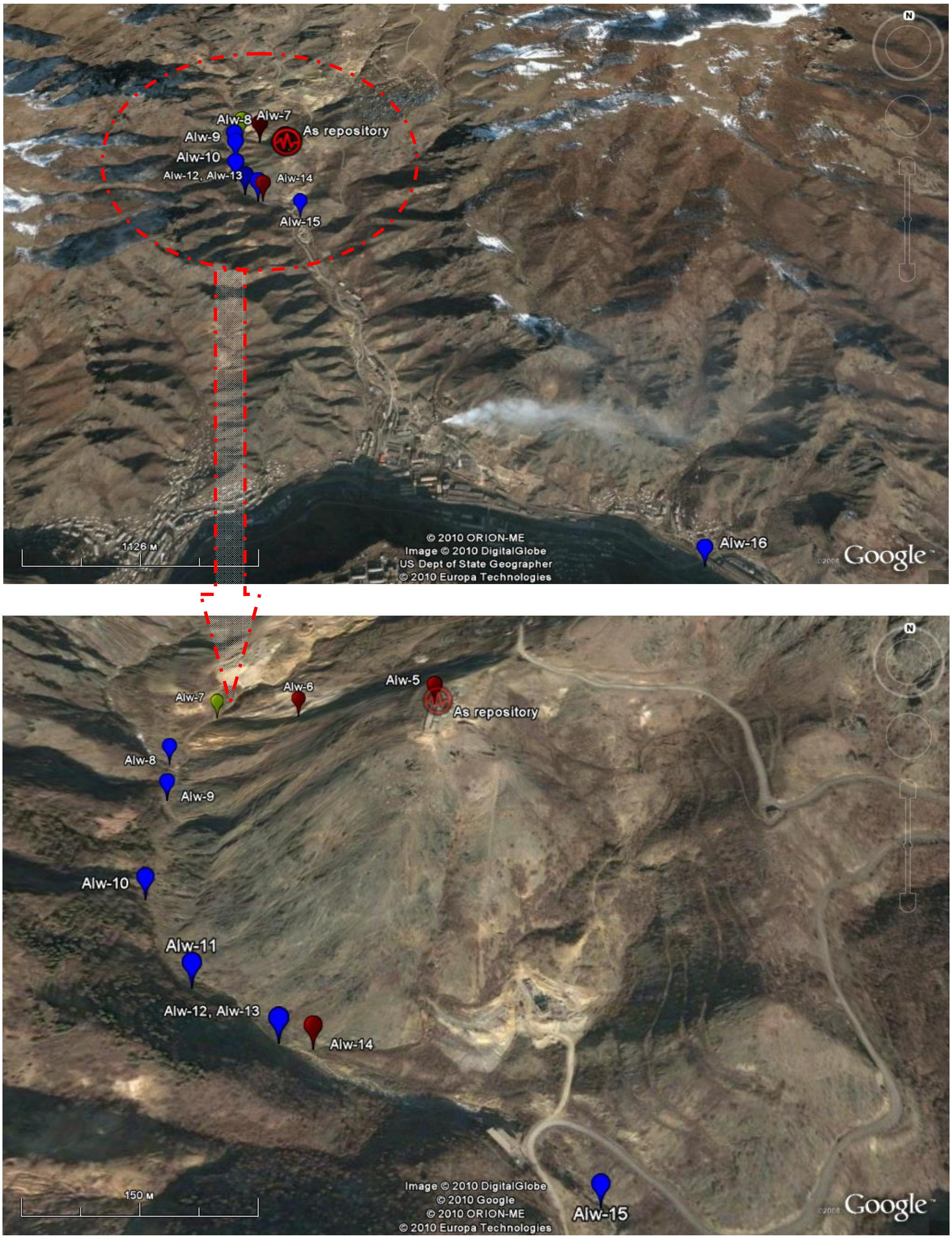
Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Fig. 5. *As and other toxic elements in the D.I.Mendeleev period table.*

Fig. 6. *Photos of some of As minerals*

3. RESEARCH MATERIAL AND METHODS

To assess toxic elements discharge from arsenic-containing element repository site in July 2010 relevant works were implemented on water, soil and bottom sediment sampling. Totally, collected were 11 water, 5 soil and 2 bottom sediment samples (*Fig. 7, 8, 9*).



LEGEND

As repository site

Water samples from the bed of Rivers Madan (Lalvar) and Debed (*Alw-8, 9, 10, 11, 12, 13, 14, 15, 16*)

Water flow samples from under the heaps (*Alw-7*)

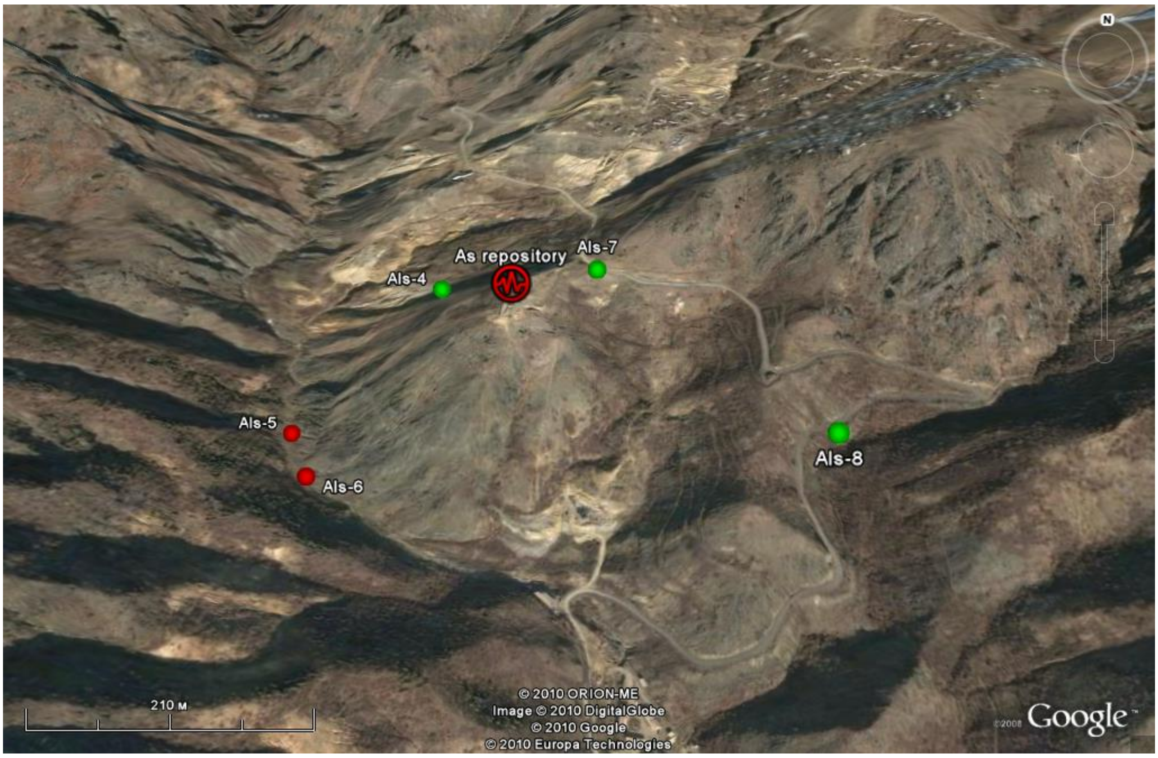
Water samples from the surface and from under the slope of As repository site (*Alw-5, 6, 14*).

Fig. 7. *A schematic map of water sampling*

Water was sampled with regard for a possible impact of heaps located around the repository site (*Fig. 7*). For that purpose, sampled was both rainwater directly from the surface (Alw-5) and stream water from under the repository slope (*Alw*-6, *Alw*-14), and stream waters from under the heaps (*Al*w-7), as well as waters from the major bed of River Madan (Lalvar) before (*Alw-8*) and after (*A/w-9, 10, 11, 12, 13, 15*) its confluence with a tributary and waters of River Debed (*Alw-16*).

Soil samples (*Fig. 8*) were of several types: on the slopes of the repository site beds of temporary flows are found which were dry during sampling, and so from there taken were sandy loam samples (*Als-5, 6)*; other soil samples were taken from periodically moistening slopes of the repository site (*A/s-4, 7, 8*).

Sampled were also bottom sediments (*A/b-1, 2*), from the major bed of River Madan (Lalvar) (*Fig. 9*).



LEGEND

As repository site

Sandy loam samples from the bed of temporary water flow (*Als-5, 6*)

Soil samples from the slopes of the repository site (*Als-4, 7, 8*)

Fig. 8 A schematic map of sandy loam and soil sampling

Water, soil and bottom sediment samples were then transported to the Central Analytical Laboratory of the Center for Ecological-Noosphere Studies NAS RA, treated and analyzed for

As and *Hg* contents through the atomic-absorption method (Perkin Elmer Aanalyst 800). Soil and bottom sediment samples were analyzed for total contents of *As* and *Hg*, and water samples – for concentrations of dissolved forms of the elements.

LEGEND

As repository site △ Bottom sediment samples (*Alb-1 ,2*).

Fig. 9 *A schematic map of water sampling*

Works on sample preparation and measurement for elements were implemented following ISO 9010 requirements [4, 5].

The actual contents of elements in different environments (soil, water) were then collated with maximal allowable concentrations (MAC) accepted in Armenia [1-3].

4. ASSESSING As AND Hg CONTENTS IN WATER

To determine water *pH* in-situ measurements were done which is important for the assessment of acidic-alkaline conditions of the given environment as such an indicator predetermines the behavior of *As* and *Hg*. *Arsenic* is maximally active in neutral and basic, and *Hg* – in acid mediums.

The measurements indicated (*Fig. 10*) that in *Alw-5* water sampled directly from the surface of the repository site had an acid medium (*pH*=3,81); in *Alw-6* and *Alw-7 pH* = 6,41 and 6,96, respectively – the medium was close to neutral; and in other sampling points *pH* varied between 7,25 and 8,06, i.e. the medium was basic.

Collating *pH* values of water samples with MAC [1] accepted in the RA for natural and fresh waters (*pH* between 6 and 9) indicated that only a rainwater sample from the surface of the repository site *Alw-5* disagreed with the accepted *pH* standards (*Fig. 11*).

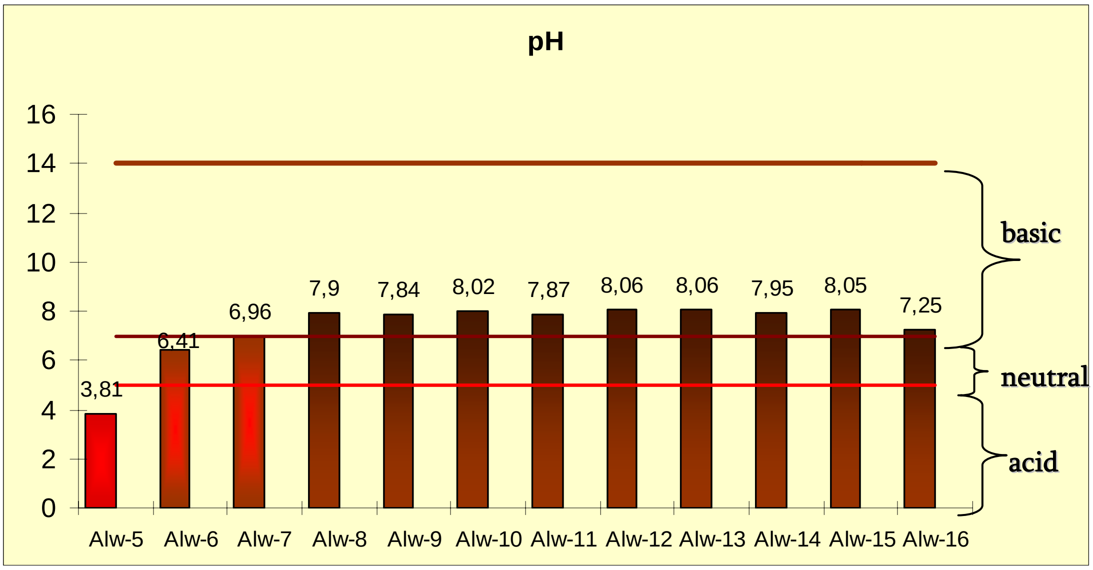


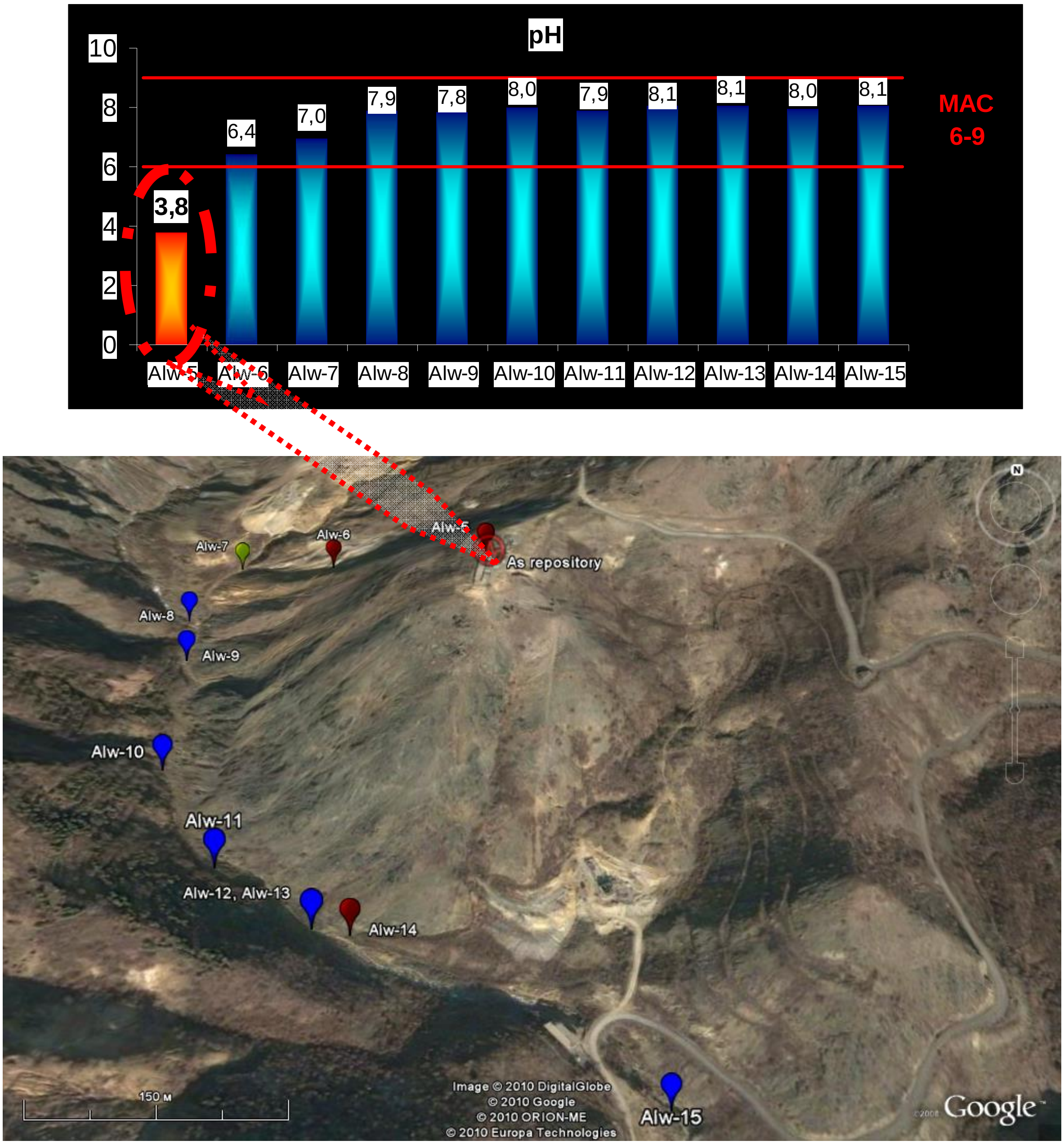
Fig. 10 *pH value of the analyzed water samples*

As was found out in the water samples *Alw-5, 6, 7, 11, 12* (*Fig. 12*). It is noteworthy that samples *Alw-5* and *Alw*-6 were collected directly from the surface and from under the slope of the *As*-containing elements repository. Presence of *As* in such samples evidences As discharge from the repository site. At the same time the medium acidity hampers active manifestation of processes of discharge.

As contents in sample *Alw*-7 – waters, flowing out from under the slope of the repository site evidences *As* discharge from the heaps, too. However samples *Alw*-11, 12, taken from River Madan (Lalvar) also displayed insignificant contents of As. No *As* was found out in the rest water samples. The latter is connected with extensive water intake from left tributaries of River Madan (Lalvar) and lowering of *As* concentration in river waters.

In all the analyzed water samples *As* contents were notably lower than MAC.

No *Hg* was found out in the analyzed water samples.



LEGEND

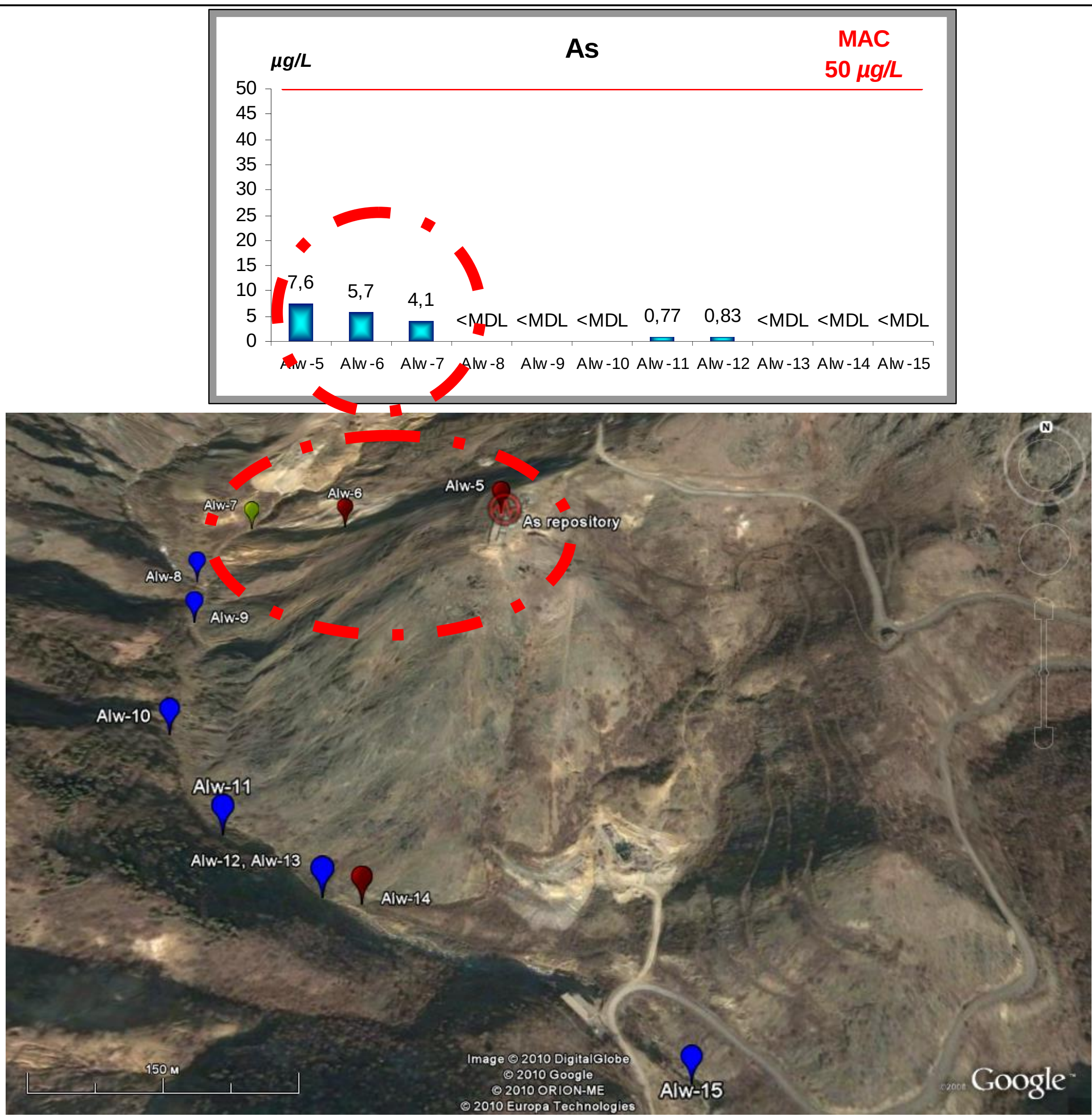
As repository site

Water samples from the bed of Rivers Madan (Lalvar) and Debed (*Alw-8,9,10,11,12,13,14,15,*)

Water flow samples from under the heaps (*Alw-7*)

Water samples from the surface and from under the slope of As repository site (*Alw-5, 6, 14*).

Fig. 11 *A pH vs. MAC value of the studied waters*



LEGEND

As repository site

Water samples from the bed of Rivers Madan (Lalvar) and Debed (*Alw-8,9,10,11,12,13,14,15,*)

Water flow samples from under the heaps (*Alw-7*)

Water samples from the surface and from under the slope of As repository site (*Alw-5, 6, 14*).

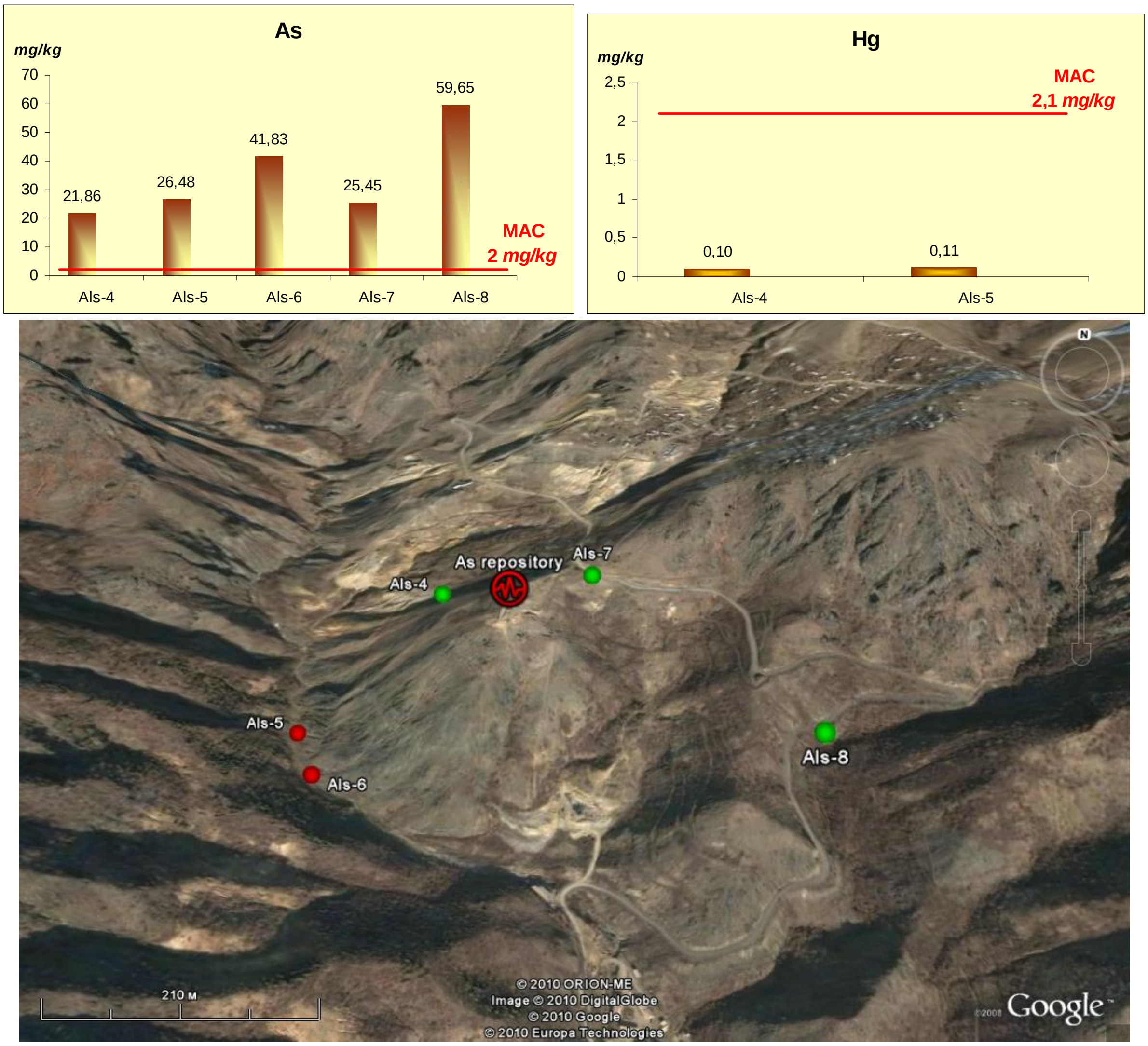
Fig. 12 *As contents in the analyzed water samples*

5. ASSESSING As AND Hg CONTENTS IN SOIL

As noted in paragraph 3, soil and sandy loam samples were taken respectively from the slope and beds of temporary water flows (*Fig. 8*). All the samples displayed high contents of *As* - 10,93

(*Als*-4) to 29,83 (*Als*-8) times excessive vs .MAC (2*mg/kg* [2, 3]) (*Fig. 13*). Such a phenomenon may be explained by geochemical peculiarities of the environments: as was mentioned earlier, acid medium hampers active migration of *As* and it is the reason by which *As* accumulates in soils and grounds.

Hg was found out in 2 samples: *Als*-4 (0,10*mg/kg*) and *Als*-6 (0,11*mg/kg*); however no excess vs. MAC (2,1*mg/kg* [2, 3]) was established (*Fig. 13*).



LEGEND

As repository site

Sandy loam samples from the bed of temporary water flow (*Als-5, 6*)

Soil samples from the slopes of the repository site (*Als-4, 7, 8*)

Fig. 13 *As and Hg contents in the analyzed sandy loam and soil samples*

6. ASSESSING As AND Hg CONTENTS IN BOTTOM SEDIMENTS

Bottom sediments like soils are known to be depositing environments. Soils are indicators of a man-made load on the air and bottom sediments – on waters. The structure of bottom sediments is similar to that of soils, so actual contents of elements were collated with respective MACs for soils.

The bottom sediment samples (*Fig. 9*) displayed both *As* and *Hg*, *As* contents in both samples being respectively 14,97 (*Alb*-1) and 12.29 (*Alb*-2) times excessive vs. MAC for soils (*Fig. 14*).

Hg contents did not exceed MAC values (*Fig. 14*).

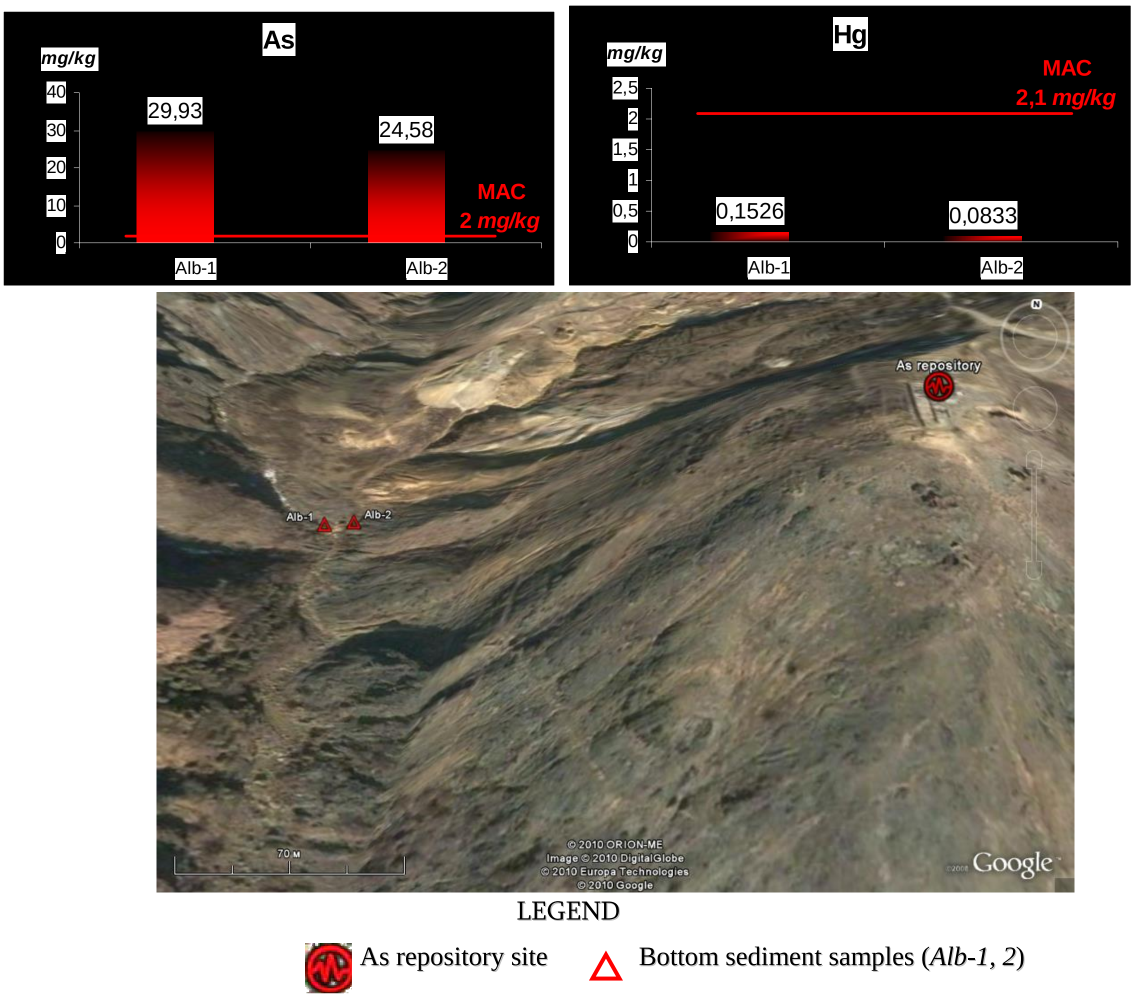


Fig. 14 *As and Hg contents in the analyzed bottom sediment samples*

7. CONCLUSIONS

The obtained research results support the following conclusions:

1. **The studied arsenic-containing elements repository site is located on a methodically right area as it lies in a geological formation containing high natural concentrations of As;**

2. **As was detected in all the soil and bottom sediment and 4 water samples (*Alw-5, 6, 7, 11, 12*);**

3. **Hg was detected in two soil (*Als-4, 5*) and bottom sediments samples (*Alb-1, 2*); its contents did not exceed MAC values.**

4. **As was found out in the rainwater samples collected from the surface of the repository site and sample of water flow from under the slope of the repository site as well as in the samples of water flow from the heaps; i.e. the discharge of elements from the repository site is added by *As* discharge from heaps. The determined contents did not exceed MAC for natural waters accepted in the RA.**

5. **The contents of *As* established in soil and bottom sediment samples were tens times excessive vs. MAC, this evidencing the active discharge of the noted element from the repository site. Free migration of As is hampered by acidity of waters predetermined by a large amount of sulfides in rocks.**

In order to prevent the discharge of toxic elements (As and Hg) from the As-containing elements repository site in the city of Alaverdi, isolation and drainage of the territory is advisable.

8. REFERENCES

1. ՀՀ Առողջապահության նախարարի 25 դեկտեմբերի 2002 թ. հրաման № 876 «Խմելու ջուր: Ջրամատակարարման կենտրոնացված համակարգերի ջրի որակին ներկայացվող պահանջներ: Որակի հսկողություն»: № 2-III-Ա 2-1 սանիտարական նորմերը և կանոնները հաստատելու մասին: Երևան, 2002, http://www.arlis.am/#
2. ՀՀ Առողջապահության նախարարի 25 հունվարի 2010 թ. հրամանը № 01-Ն «Հողի որակին ներկայացվող հիգիենիկ պահանջներ» № 2.1.7.003-10 սանիտարական կանոնները և նորմերը հաստատելու մասին: Երևան, 2010, http://www.arlis.am/#
3. ՀՀ Կառավարության 25 հունվարի 2005 թ. որոշում N 92-Նուղղ. «Հողային ռեսուրսների վրա տնտեսական գործունեության հետևանքով առաջացած ազդեցության գնահատման կարգը հաստատելու մասին» Երևան, 2010, http://www.arlis.am/#
4. Фомин Г.С., Фомин А.Г. Почва. Контроль качества экологической безопасности по меж дународным стандартам. Справочник. – М.: Изд-во “Протектор”, 2001, 304 с.
5. Analytical methods for atomic absorbtion spectrometry. PerkinElmer, BS EN ISO, 9001.