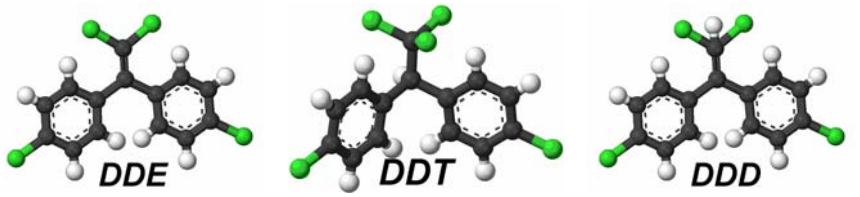
ANNEX 08

THE CENTER FOR ECOLOGICAL-NOOSPHERE STUDIES OF NAS RA

OSCE SUPPORTED PROJECT

ASSESSING A DISCHARGE OF CONTAMINANTS FROM THE NUBARASHEN TOXIC CHEMICALS REPOSITORY SITE



Yerevan 2010

ANNEX 08

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

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

_____ A. K. Saghatelyan

«__9__» ____September____ 2010

THE PROJECT REPORT

«ASSESSING A DISCHARGE OF CONTAMINANTS FROM THE NUBARASHEN TOXIC CHEMICALS REPOSITORY SITE»

Principal investigator

_____ **Dr of Sci. A.K. Saghatelyan**

Yerevan 2010

ANNEX 08

CONTENTS

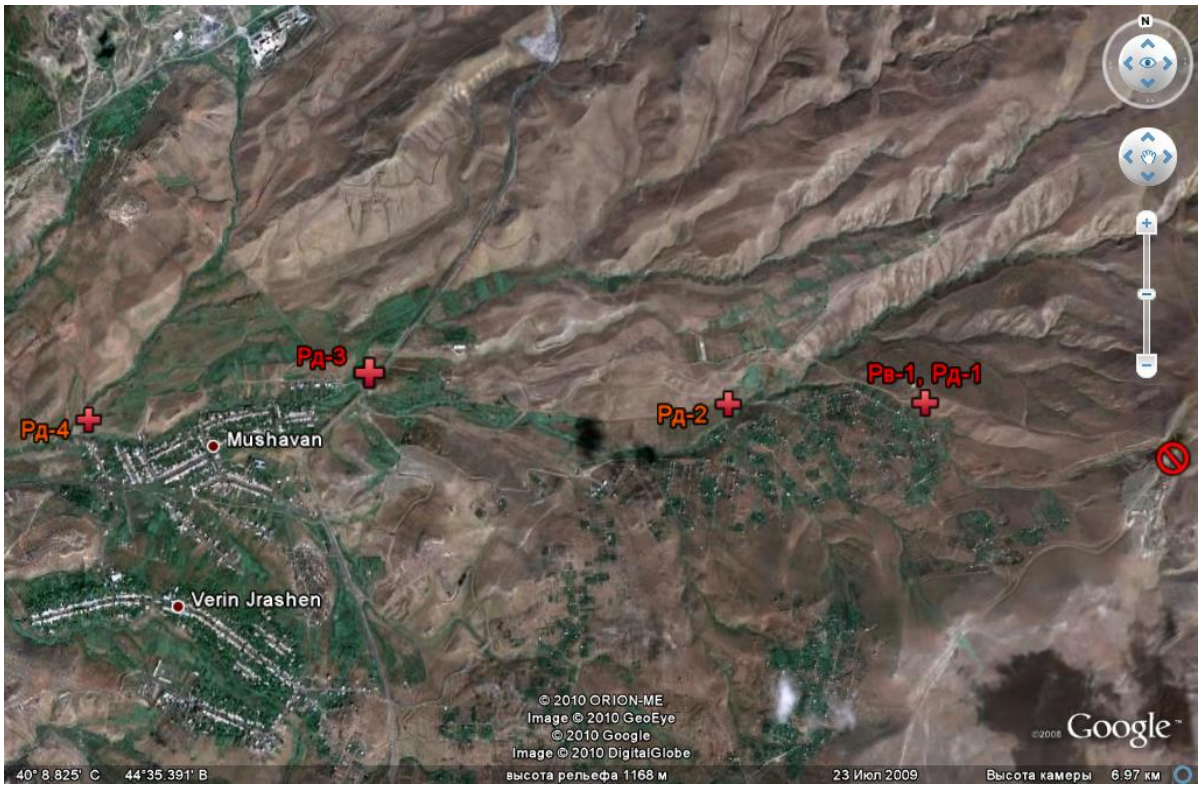
ANNEX 08

THE OUTCOMES OF PILOT INVESTIGATIONS OF CONTAMINANTS DISCHARGE FROM THE NUBARASHEN TOXIC CHEMICALS REPOSITORY SITE

In 2010 the Center of Ecological-Noosphere Studies NAS RA implemented episodic investigations of contaminants discharge from the Nubarashen toxic chemicals repository site.

The initial pilot study was implemented under support of the OSCE Office in Yerevan; sampling date – 17May, 2010 (*Fig. 1, 2*), reporting date – 27 May, 2010.

A map of localization of the Nubarashen repository and sampling points is given in *Figure 1.*



LEGEND

The repository

Sampling points

Рв-1 – Sampling point and number of water sample

Рд-1; 2; 3; 4 – Sampling points and ordinal numbers of bottom sediment samples

Fig.1 *A map of localization of the Nubarashen toxic chemicals repository and water, bottom sediments sampling points (date: 17.05.2010).*

ANNEX 08

Fig. 2. *A fragment of a water and bottom sediment sampling process*

In the frame of the project concentrations of As and Hg and three DDT isomers (p,p'-DDT, DDE, DDD) and lindane (γ-HCCH) were studied in the waters of a brook forming under the toxic chemicals repository, bottom sediments of the brook and a river the brook empties in. The results of analyses of the collected samples are visualized below in *Figures 3, 4* and *Tables 1, 2*.

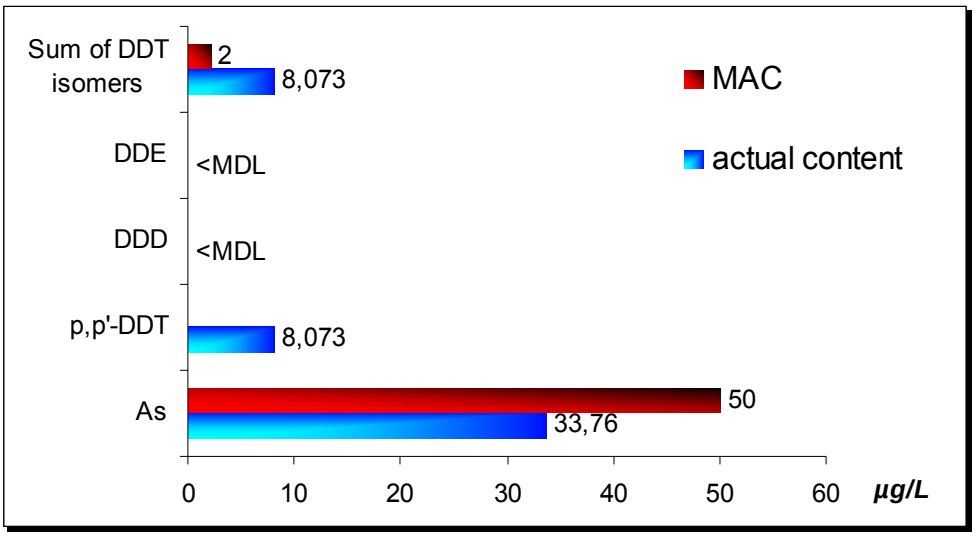


Fig. 3. *Concentrations of contaminants in the water of the brook and their collation with MAC [1]*

In the waters of the brook a p,p'-DDT isomer was indicated, summary contents of DDT isomers (8,073 *µg/L*) being 4,04 times excessive vs. the RA-accepted standards for natural waters (2 *µg/L* [1]).

The waters displayed also As, which concentrations (33,76 *µg/L*) were not excessive vs. the RA-accepted standards (50 *µg/L* [1]).

Bottom sediments displayed a DDE isomer; summary concentrations of DDT isomers (1164 *µg/kg*) showing a 11,64 time excess vs. MAC for soils (100 *µg/kg* [2]).

As concentrations in bottom sediments did not overstep the accepted MAC (2000 *µg/kg* [2]) for soils.

ANNEX 08

Hg and γ-HCCH (lindane) concentrations in the collected water and bottom sediment samples were lower than MDL (Minimum Detection Limit).

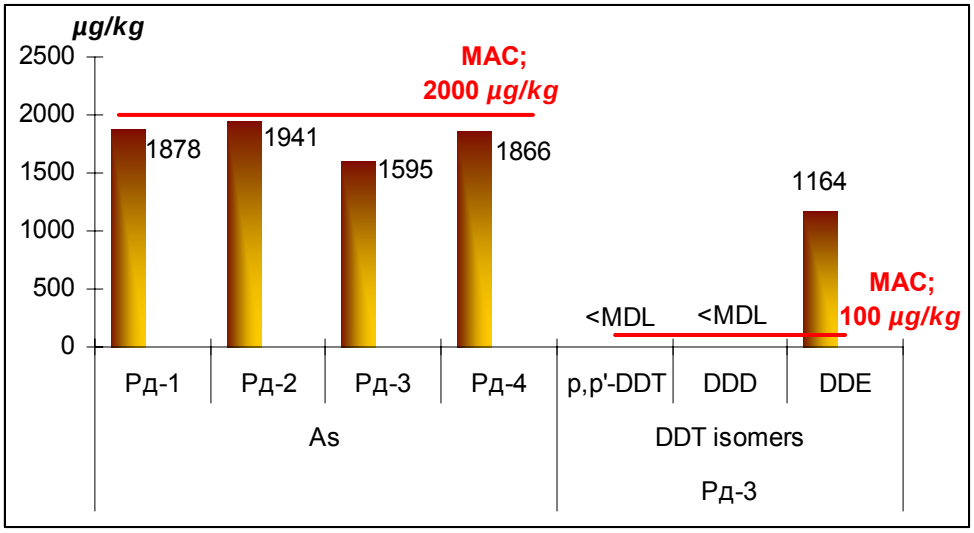


Fig. 4. *Concentrations of contaminants in bottom sediments and their collation with MAC [2]*

Table 1

Concentrations (µg/L) of contaminants in the waters of the brook forming under the toxic chemicals repository and their excesses vs. MAC [1]

			Sample number	**Рв-1**
Pollutant		MAC RA, *µg/L*	Concentration and excess vs. MAC	Geographical coordinates, distance from repository
				40°8'42"N; 44°36'31" E (1,1 *km* from repository)
As		50	concentration, *µg/L*	33,76
			excess vs. MAC	0,68
Hg		0,5	concentration, *µg/L*	<MDL[1]
DDT isomers	p,p'-DDT	–	concentration, *µg/L*	**8,073**
	DDD	–	concentration, *µg/L*	<MDL[2]
	DDE	–	concentration, *µg/L*	<MDL[2]
Sum of DDT isomers		2	concentration, *µg/L*	**8,073**
			excess vs. MAC	**4,04**
γ-HCCH (lindane)		2	concentration, *µg/L*	<MDL[2]

Note: MDL[1]= 0,6 *µg/L*; MDL[2]=10^{-2} *µg/L*.

ANNEX 08

Table 2

Concentrations of contaminants (μg/kg) in bottom sediments and their excesses vs. MAC [2]

Pollutant		MAC RA, *μg/kg*	Concentration and excess vs. MAC	Sample numbers	**Рд-1**	**Рд-2**	**Рд-3**	**Рд-4**
				Geographical coordinates, distance from repository				
					40°8'42" N; 44°36'31" E (1,1 *km* from repository)	40°8'44" N; 44°35'50"E (2,1 *km* from repository)	40°8'52" N; 44°34'33"E (4,0 *km* from repository)	40°8'48"N; 44°33'30"E (5,5 *km* from repository)
As		2000	concentration, *μg/kg*		1878,0	1941,0	1595,0	1866,0
			excess vs. MAC		0,94	0,97	0,80	0,93
Hg		2100	concentration, *μg/kg*		<MDL[1]	<MDL[1]	<MDL[1]	<MDL[1]
DDT isomers	p,p'-DDT	–	concentration, *μg/kg*		<MDL[2]	<MDL[2]	<MDL[2]	<MDL[2]
	DDD	–	concentration, *μg/kg*		<MDL[2]	<MDL[2]	<MDL[2]	<MDL[2]
	DDE	–	concentration, *μg/kg*		<MDL[2]	<MDL[2]	**1164,0**	<MDL[2]
Sum of DDT isomers		100	concentration, *μg/kg*		<MDL[2]	<MDL[2]	**1164,0**	<MDL[2]
			excess vs. MAC		–	–	**11,64**	–
γ-HCCH (lindane)		100	concentration, *μg/kg*		<MDL[2]	<MDL[2]	<MDL[2]	<MDL[2]

Note: MDL[1]=$6\cdot10^{-9}$ *μg/kg*; MDL[2]=10^{-10} *μg/kg*.

One more pilot investigation aiming the assessment of pesticide discharge from the Nubarashen toxic chemicals repository site was implemented by the order of «Armenian Women for Health and Healthy Environment» NGO; sampling date – 9 July 2010 (*Fig. 5*), reporting date – 19 July 2010.

Fig. 5. *A fragment of river water and wetland soil sampling process*

A map of water and wetland soil sampling points and their positions is given in *Fig. 6*.

ANNEX 08

LEGEND

Repository

Sampling points

Рв-3; 4 – Sampling points and ordinal numbers of water samples

Рд- 6; 7 – Sampling points and ordinal numbers of wetland soil samples

Fig. 6. *A schematic map of localization of the Nubarashen toxic chemicals repository and water and wetland soil sampling points (date: 9.07.2010).*

In the frame of the project investigated were concentrations of DDT pesticide isomers (p,p'-DDT, DDE, DDD) in the water of the river and soils neighboring wetlands. DDT isomers concentrations and their correlation with MAC [1, 2] RA are given in *Tab. 3, 4* and *Fig. 7*.

A p,p/-DDT isomer was established in one river water sample (Рв-3); its concentration (82,71 *μg/L*) being 41,4 times excessive vs. MAC (2 *μg/L* [1]) for natural waters.

One wetland soil sample displayed a DDE isomer; summary concentrations of DDT isomers in the soil (5100 *μg/kg*) being 51,0 times excessive vs. MAC RA (100 *μg/kg* [2]).

The concentrations of DDT isomers in the rest water and soil samples were lower as compared with MDL.

ANNEX 08

Table 3

Concentrations (μg/L) of DDT isomers in river waters and their excesses vs. MAC [1]

				Sample number	**Рв-3**	**Рв-4**
Pollutant		MAC RA, *μg/L*	Concentration and excess vs. MAC		Geographical coordinates, distance from repository	
					40° 8.769'N 44° 35.185'E (2,96 *km* from repository)	40° 8.643'N 44° 35.478'E (2,52 *km* from repository)
DDT isomers	p,p'-DDT	–	concentration, *μg/L*		**82,71**	<MDL
	DDD	–	concentration, *μg/L*		<MDL	<MDL
	DDE	–	concentration, *μg/L*		<MDL	<MDL
Sum of DDT isomers		2	concentration, *μg/L*		**82,71**	**–**
			excess vs. MAC		**41,355**	**–**

Note: *MDL=10^{-2} μg/L*

Table 4

Concentrations (μg/kg) of contaminants in wetland soils and their excesses vs. MAC [2]

				Sample number	**Рд-6**	**Рд-7**
Pollutant		MAC RA, *μg/kg*	Concentration and excess vs. MAC		Geographical coordinates, distance from repository	
					40° 8.553'N; 44° 37.072'E (0,25 *km* from repository)	40° 8.669'N; 44° 36.568'E (1,0 *km* from repository)
DDT isomers	p,p'-DDT	–	concentration, *μg/kg*		<MDL	<MDL
	DDD	–	concentration, *μg/kg*		<MDL	<MDL
	DDE	–	concentration, *μg/kg*		**5100**	<MDL
Sum of DDT isomers		100	concentration, *μg/kg*		**5100**	<MDL
			excess vs. MAC		**51,0**	–

Note: MDL=10^{-10} *μg/kg*

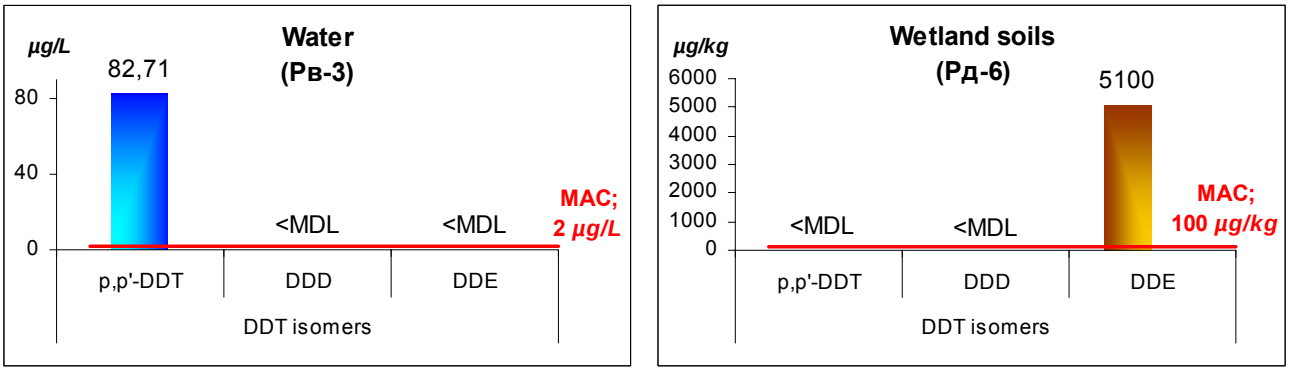
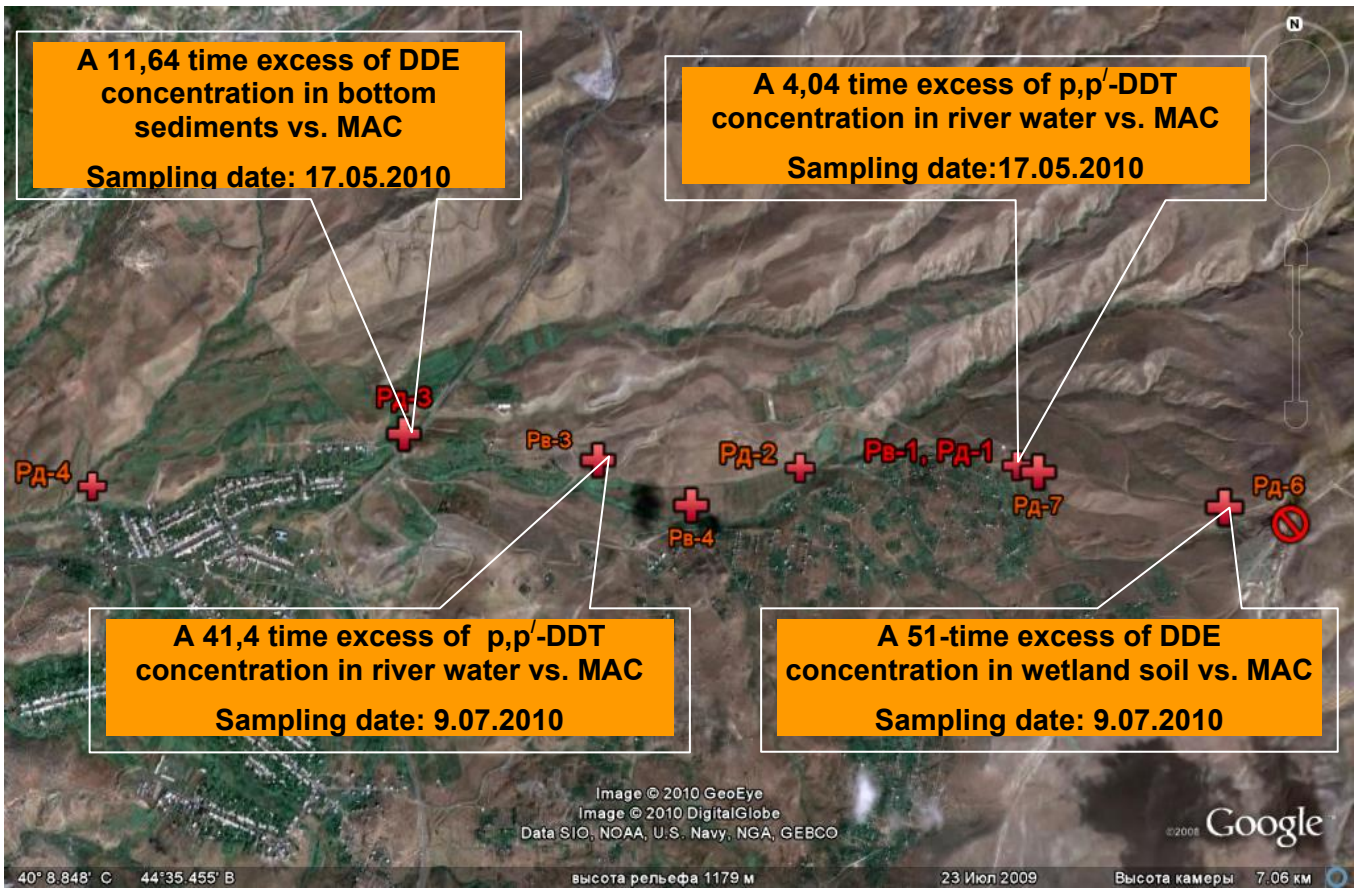


Fig. 7. *Concentrations of contaminants in river waters and wetland soils and their collation with MAC [1, 2]*

A summary schematic map of sampling and outcomes of the pilot investigations is given in *Fig. 8*.

ANNEX 08



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Repository

Sampling points

Рв-1; 3; 4 – Sampling points and ordinal numbers of water samples

Рд-1; 2; 6; 7 – Sampling points and ordinal numbers of bottom sediments and wetland soil samples

Fig. 8. *A schematic map of localization of the Nubarashen toxic chemicals repository, water, bottom sediment and wetland soil sampling points and the contaminants concentration excesses vs. MAC [1, 2]*

The results of a pilot stepwise sampling of the territory adjoining the Nubarashen toxic substance repository site allow concluding that

- ✓ The presence of a p,p/-DDT isomer in the waters of the brook and the river evidences the active discharge of the contaminant from the repository site in water medium,
- ✓ In summer low-water period the pesticide contents increase in river waters due to a decrease of the amount of precipitation and the concentrating of river solution,
- ✓ DDT in form of a DDE isomer accumulates in clayey bottom sediments and soils of neighboring wetlands.

So, in the result of the pilot investigations established was a fact of toxic chemicals discharge from the Nubarashen toxic substance repository site. The planned

detailing of investigations is aimed to indication of a radius of migration of contaminants and determination of their depositing media.

ASSESSING A DISCHARGE OF CONTAMINANTS FROM THE NUBARASHEN TOXIC CHEMICALS REPOSITORY SITE

The results of pilot investigations evidence a discharge of DDT isomers from the Nubarashen toxic chemicals repository site. With a view of indicating the distance of contaminants migration and their possible accumulation in depositing media, the Center for Ecological-Noosphere Studies NAS RA implemented more detailed studies under support of the OSCE Office in Yerevan.

To reach the stated goal, on August 3, 6, 2010 sampled were the waters and bottom sediments of Rivers Voghchaberd, Getar and Hrazdan as well as waters and bottom sediments of the Yerevanyan Lich. A schematic map of sampling is given in *Fig. 9*; *Fig.10* displays some episodes of field works.

Fig. 10. *Some episodes of field works*

Totally, the project envisaged collection of 20 samples of water and bottom sediment. However for completeness of assessment and with regard for the gravity of the situation, the Center for Ecological-Noosphere Studies collected and analyzed 14 additional samples at the expense of its home resources, total of 34 samples.

Water was sampled from a depth 15-20 *cm* with a 1-liter glass container. The container was washed up 3 times on the spot with the water to be sampled.

Bottom sediment samples weighted 0,7-1 *kg* were taken with rag bags.

Water and bottom sediment samples were analyzed for DDT isomers (p,p$^{/}$-DDT, DDE, DDD) concentrations in the accredited laboratory of the Center for Ecological-Noosphere Studies NAS RA.

Water samples were analyzed without any pretreatment on a gas chromatograph Trace DSQ employing a EPA method 608 [3].

ANNEX 08

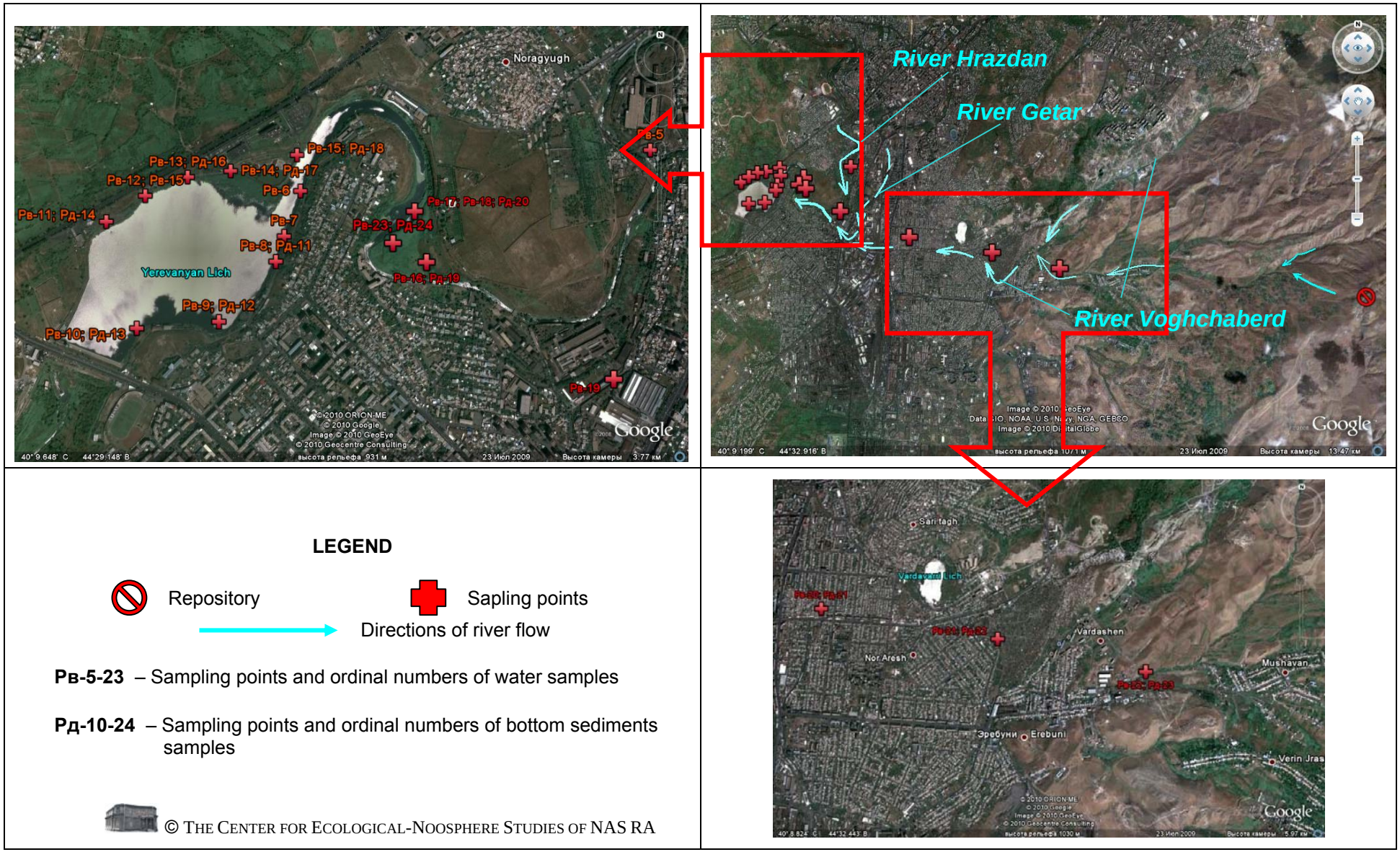

Fig. 9. *A schematic map of water and bottom sediment sampling points (sampling date: 3, 6 August, 2010)*

ANNEX 08

Bottom sediment samples were dried at a room temperature until air-dry state was reached. Then 2,5 *g* of sample were placed in a teflon container adding 30 *mL* of acetone and N-hexane mixture in a volumetric ratio 1:1. After that the containers were hermetically closed, then placed in a microwave extractor Milestone Start E and kept there for 20 min. at t^0120^oC [6]. After cooling the samples were analyzed on a gas chromatograph Trace DSQ through a EPA method 8081 [4, 5].

Geographical coordinates of the sampling points and the results of the analyses are given in *Tab. 5.*

Table 5

The results of water and bottom sediment analyses

№	Sampling date	Geographical coordinates	Distance from repository, *km*	DDT isomers			Sum of DDT isomers
				p,p′-DDT	DDE	DDD	
Water							
Рв-5	3 Aug. 2010	40° 9.850'N; 44°30.033'E	10,52	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-6	3 Aug. 2010	40° 9.783'N; 44° 29.009'E	11,91	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-7	3 Aug. 2010	40° 9.666'N; 44° 28.971'E	11,93	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-8	3 Aug. 2010	40° 9.571'N; 44° 28.935'E	11,98	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-9	3 Aug. 2010	40° 9.451'N; 44° 28.771'E	12,14	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-10	3 Aug. 2010	40° 9.437'N; 44° 28.534'E	12,47	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-11	3 Aug. 2010	40° 9.691'N; 44° 28.461'E	12,64	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-12	3 Aug. 2010	40° 9.736'N; 44° 28.539'E	12,55	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-13	3 Aug. 2010	40° 9.780'N; 44° 28.657'E	12,40	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-14	3 Aug. 2010	40° 9.811'N; 44° 28.787'E	12,22	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-15	3 Aug. 2010	40° 9.864'N; 44° 29.004'E	11,95	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-16	6 Aug. 2010	40° 9.583'N; 44° 29.367'E	11,35	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-17	6 Aug. 2010	40° 9.700'N; 44° 29.333'E	11,44	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-18	6 Aug. 2010	40° 9.700'N; 44° 29.333'E	11,44	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-19	6 Aug. 2010	40° 9.298'N; 44° 29.838'E	10,61	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-20	6 Aug. 2010	40° 9.047'N; 44° 30.953'E	8,98	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-21	6 Aug. 2010	40° 8.856'N; 44° 32.111'E	7,32	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-22	6 Aug. 2010	40° 8.721'N; 44° 33.069'E	5,94	<MDL[1]	<MDL[1]	<MDL[1]	–
Рв-23	6 Aug. 2010	40° 9.626'N; 44° 29.269'E	11,49	<MDL[1]	<MDL[1]	<MDL[1]	–
Bottom sediment							
Рд-10	3 Aug. 2010	40° 9.666'N; 44° 28.971'E	11,93	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-11	3 Aug. 2010	40° 9.571'N; 44° 28.935'E	11,98	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-12	3 Aug. 2010	40° 9.451'N; 44° 28.771'E	12,14	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-13	3 Aug. 2010	40° 9.437'N; 44° 28.534'E	12,47	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-14	3 Aug. 2010	40° 9.691'N; 44° 28.461'E	12,64	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-15	3 Aug. 2010	40° 9.736'N; 44° 28.539'E	12,55	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-16	3 Aug. 2010	40° 9.780'N; 44° 28.657'E	12,40	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-17	3 Aug. 2010	40° 9.811'N; 44° 28.787'E	12,22	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-18	3 Aug. 2010	40° 9.864'N; 44° 29.004'E	11,95	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-19	6 Aug. 2010	40° 9.583'N; 44° 29.367'E	11,35	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-20	6 Aug. 2010	40° 9.700'N; 44° 29.333'E	11,44	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-21	6 Aug. 2010	40° 9.047'N; 44° 30.953'E	8,98	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-22	6 Aug. 2010	40° 8.856'N; 44° 32.111'E	7,32	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-23	6 Aug. 2010	40° 8.721'N; 44° 33.069'E	5,94	<MDL[2]	<MDL[2]	<MDL[2]	–
Рд-24	6 Aug. 2010	40° 9.626'N; 44° 29.269'E	11,49	<MDL[2]	<MDL[2]	<MDL[2]	–

Note: $MDL^1=10^{-2}$ *μg/L*; $MDL^2= 10^{-10}$ *μg/kg*.

As seen from data provided in *Tab. 1*, concentrations of DDT isomers in the collected water and bottom sediment samples were lower than MDL.

Thus, DDT isomers in transitive and depositing media were detected within a 4 *km* distance from the toxic chemicals repository. Downstream the rivers of Voghchaberd, Getar, Hrazdan and in the waters and bottom sediments of the Yerevanyan Lich concentrations of pesticides were lower than MDL.

CONCLUSION

The obtained research results support the following conclusions:

- ✓ Established was a p,p/-DDT isomer discharge from the repository site in water medium,
- ✓ DDT in form of a DDE isomer accumulates in clayey bottom sediments of the rivers and soils of wetlands adjacent to the river
- ✓ DDT isomers in transitive and depositing media were established within a 4 *km* distance from the Nubarashen toxic chemicals repository; downstream the rivers of Voghchaberd, Getar, Hrazdan and in the waters and bottom sediments of the Yerevanyan Lich the concentrations of pesticides were lower than MDL.

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