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Toxic Hot Spots in Armenia

Monitoring and Sampling Reports

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CONTENT

FOREWORD

There are presented two reports about five selcted hot sposts in this publication. The data presented and discussed in these reports were obtained during a field visit and environmental sampling campaign conducted in Armenia in July 2010 and additional subsequent sampling conducted in autumn 2010. Both sampling campaigns represent an important part of a joint project of the Czech not-for profit organization Arnika Association and the Armenian non-governmental organization Armenian Women for Health and Healthy Environment (AWHHE) called "Scaling up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia", and conducted with the financial assistance of the European Union, Czech Development Agency, UNIDO, OSCE and other donors. The main goal of the project is to help rural communities in Armenia to implement sustainable agriculture and to eliminate the danger of chemical pollution in the Ararat and Armavir regions.

The field sampling was conducted by members of the Arnika Association, independent scientists and members of AWHHE and additional sampling in autumn 2010 was done by AWHHE. Selection of four obsolete pesticides stockpiles sites (Nubarashen, Jrarat, Masis and Echmiadzin) was based on previous Milieukontakt Oost Europa's report (Ritsema et al., 2006) and preliminary field visit by Arnika Association experts in March 2010 at some of these sites. In addition to these sites we decided to research also dumpsite of historic copper production waste close to Alaverdi in the north part of Armenia. Our main focus was on Persistent Organic Pollutants (POPs) as most serious contaminants at the sites, but chemical analyses didn't concentrate only on these chemicals.

The results presented in both following reports are based on analyses of 86 samples in total. Soil, swept, plaster, water, air and biological (food) samples were taken and you can find the specification for each location in the respective report. Samples were analyzed for:

- 21 OCPs (organochlorine pesticides) and their metabolites
- PCDD/Fs and DL PCBs (bioassay analyses in total TEQ – CALUX -TEQ), for chosen samples also congener specific analysis
- 222 pesticides and their metabolites (other than obsolete OCPs) plus 8 fenoxyalkane acid based pesticides for chosen samples
- 7 PCB congeners
- mercury and other heavy metals (6 chemicals).

We believe that the work presented in following reports will contribute significantly to implement the Stockholm Convention in Armenia and will serve as a pilot study for the work in other countries as well. We thank to all donors for their financial support and to International POPs Elimination Network (IPEN) for its support regarding expertise and continuous work on POPs.

In Prague, May – 8, 2011

Jindrich Petrlik
Executive Director, Arnika – Toxics and Waste Programme
on behalf of the joint Arnika – AWHHE project team

FINAL REPORT

on the results of environmental sampling conducted in Armenia in July - November 2010 as a part of the joint Czech-Armenian project "Scaling Up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia"

Alice Dvorská, Ph.D.

Brno, May 2011

SUMMARY

The data presented and discussed in this report were obtained during a field visit and environmental sampling campaign conducted in Armenia in July 2010 and additional subsequent sampling conducted in autumn 2010 as an important part of the project called “Scaling up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia”.

Armenia was characterized as a country with developed industry and agriculture in the past. Like all the republics of the former Soviet Union, organochlorinated pesticides were widely applied in Armenia until the ban in 1980s. Subsequently, the problem of areas contaminated by organochlorinated pesticides (agricultural lands, former pesticide storehouses, pesticide burials, dump sites, etc.) emerged.

The field visit in July 2010 was conducted by members of the Arnika Association, independent scientists and members of AWHHE. Sampling of air, soil and other solid matrices was conducted at five sites suspected to be persistent organic pollutant hotspots, i.e. one pesticide burial site site (Nubarashen), three former pesticide storage sites (Jrarat, Echmiadzin and Masis) and one dumpsite containing copper production waste (Alaverdi). Later, more air samples as well as biota samples were taken at the five sites by members of AWHHE. A total of 57 samples was obtained and analysed on the content of organochlorinated and other pesticides and polychlorinated dibenzo-p-dioxines and furanes. An inspection on the state and possible risk receivers (inhabitants, workers) at the sites was conducted, too.

Although the results of the here presented field visit in Armenia have to be considered preliminary and no risk analysis was conducted until now, the author of this study is convinced of the necessity to implement the following measures:

- immediately prevent people entering at least parts of the areas of the Jrarat, Masis, Echmiadzin and Nubarashen sites and stop the spread of contamination by persistent organic pollutants, which was pronounced very strongly especially in Jrarat,
- the pesticides in Jrarat should be repacked and removed as soon as possible,
- where people have to enter the mentioned and other sites and rooms, they should be consequently reminded to wear personal protection equipment,
- alternatives for the consumption of eggs especially in Echmiadzin and Jrarat should be discussed and people informed about ways how to minimize the exposure of domestic animals to POPs.
- These recommendations are undermined by the partly very high contamination by persistent organic pollutants found at some spots of the investigated sites.

The extent of the study was limited by financial, temporal and personal resources. A risk analysis supported by additional sampling where necessary should characterise and quantify the risks posed to humans and the environment by the pollution at the sites and further specify areas for decontamination and define the extent of decontamination. The lifetime exposure, and where appropriate the acute exposure of consumers to pesticide residues via food products, especially eggs in Echmiadzin and Jrarat, should be evaluated and the consumers immediately informed about the high POP levels found in their food.

ABBREVIATIONS

2,4-D – dichlorophenoxyacetic acid
AA – annual average
DDD – dichlorodiphenyldichloroethane
DDE – dichlorodiphenyldichloroethylene
DDT – dichlorodiphenyltrichloroethane
DDX – DDD, DDE, DDT
d.m. – dry matter
FAO – Food and Agriculture Organization
f.w. – fresh weight
HCH – hexachlorocyclohexane
IHPA – International HCH and Pesticides Association
IPEN – International POPs Elimination Network
LOD – limit of detection
LOQ – limit of quantification
MAC – maximum acceptable concentration
ML – maximum level
MRL – maximum residue level
NA – not analysed
ND – not detected
OCPs – organochlorinated pesticides
OSCE – Organization for Security and Cooperation in Europe
PCBs – polychlorinated biphenyls
PCDD/Fs – polychlorinated dibenzo-p-dioxines and furanes
POPs – persistent organic pollutants
SC – Stockholm Convention on Persistent Organic Pollutants
TEQ – Toxic equivalent

CONTENTS

1. INTRODUCTION

The results presented in this report were obtained during a field visit and sampling campaign conducted in Armenia in July 2010 and additional subsequent sampling conducted in autumn 2010. Both sampling campaigns represent an important part of the project „Scaling Up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia“. This is a joint project of the Czech not-for profit organization Arnika Association and the Armenian non-governmental organization Armenian Women for Health and Healthy Environment (AWHHE). The main goal of the project is to help rural communities in Armenia to implement sustainable agriculture and eliminate the danger of chemical pollution in the Ararat and Armavir regions. The project is focused on the finding of technical solutions to eliminate several hot spots contaminated by obsolete toxic pesticides out of which some are subject to the Stockholm Convention on Persistent Organic Pollutants (SC). The project also aims to help Armenia to implement the Convention.

The Stockholm Convention on persistent organic pollutants (POPs) was ratified by the National Assembly (Parliament) of the Republic of Armenia on October 22, 2003 (NIP, 2005). In accordance to the main provisions of the SC, each country that is a party to the Convention prohibits and/or takes legal and administrative actions required for the elimination, restriction of production and use of chemicals listed in Annexes A and B to the Convention, as well as on reduction or elimination of POPs releases resulting from intended or unintended production, as well as releases related to stocks and wastes containing POPs. The SC regulates the following pesticides: chlordecone, α-hexachlorocyclohexane, β-hexachlorocyclohexane, lindane (γ-hexachlorocyclohexane), pentachlorobenzene, DDT, aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. Further, it regulates these industrial chemicals: polychlorinated biphenyls, hexachlorobenzene, hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and pentabromodiphenyl ether. It also regulates unintentional by-products: polychlorinated dibenzo-p-dioxins, polychlorinated dibenzo-p-furans, α-hexachlorocyclohexane, β-hexachlorocyclohexane, pentachlorobenzene, hexachlorobenzene and polychlorinated biphenyls (SC, 2010).

Armenia was characterized as a country with developed industry and agriculture in the past. Leading industrial branches were machine-building industry, ferrous and non-ferrous metal processing, chemical, and petrochemical industry, ferrous and non-ferrous metallurgy, as well as industry of building materials. Armenia was also characterized by a developed agricultural production and was amongst the regions with intense pesticide application in the former Soviet Union. The total area load of pesticides averaged 9-35.5 kg ha^{-1}, exceeding the average all-union levels of pesticide application many times. Likewise all the republics of the former Soviet Union, organochlorine pesticides were widely applied in Armenia until the ban in 1980s. Subsequently, the problem of areas contaminated by organochlorinated pesticides (agricultural lands, former pesticide storehouses, pesticide burials, dump sites, etc.) emerged. The problem of an inappropriate use of obsolete pesticides is of no less urgency (NIP, 2005).

Although there exists information on more sites suspected to be significantly contaminated by obsolete pesticides in Armenia (Ritsema et al., 2006), only four (considered to be most significant) were chosen for sampling due to limited resources. Further, an industrial site suspected to be contaminated by PCDD/Fs was also visited and several samples were taken. According to the authors knowledge, sampling was previously conducted only at the burial site Nubarashen close to Yerevan and one sample was taken in the storage site Echmiadzin during the visit of Arnika Association members in March 2010. Nubarashen is the biggest and most known obsolete pesticides hot-spot in Armenia and has been previously subject to the of interest of various organizations (AWHHE, FAO, IHPA, IPEN).

The field visit in Armenia in July 22 – 28, 2010 was conducted by the following persons:

RNDr. Jindřich Petrlík – coordinator of survey
Mgr. Zora Kasiková – Arnika spokeswoman
RNDr. Alice Dvorská, Ph.D. – scientist at the Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno
Ing. Marek Šír – postgraduate student at the Institute of Chemical Technology, Prague
Ing. Zuzana Honzajková – postgraduate student at the Institute of Chemical Technology, Prague
Ondřej Petrlík – photographer

This survey in Armenia was conducted in close cooperation with AWHHE. Later in autumn 2010, members of AWHHE took additional samples. All the sampling and visits happened with the kind support of the storage site owners, the Aarhus Convention Centre in Alaverdi and Karine Yesayan from the Armenian Ministry of Agriculture.

2. SAMPLING CAMPAIGN

The first sampling campaign was conducted during a week-long stay in Armenia in the end of July 2010. Additional sampling was conducted in autumn 2010. Although the financial, temporal and personal resources of Arnika Association and AWHHE were limited, the in advance prepared sampling plan was trying to reflect the rules for a risk analysis of a contaminated area (MoE, 2005) to the best possible extent.

2.1 Weather conditions during sampling

During the sampling in July 22–28, 2010, there was no rain, weak wind, day temperatures reached 33 to 38° C and the days were sunny. Table 1 contains information on weather conditions during passive air sampling.

2.2 Sampling sites

The sampling was conducted at five sites suspected to be POP hot-spots, i.e. one pesticide burial site, three former pesticide storage sites and one dumpsite containing copper production waste. In and/or around all the pesticide storage buildings people without personal protection equipment were witnessed.

2.2.1 Nubarashen (40°08´34´´N, 44°37´02´´E)

The pesticide burial site Nubarashen is located about 20 km far from Yerevan. It was established as a dump of obsolete pesticides in 1982 or earlier and is owned by the City of Yerevan (Helps, 2010; Ritsema et al., 2006). It should contain cca 500 tonnes of pesticides out of which cca 190 tonnes should be DDT and 48 tonnes should be HCH (Helps, 2010). The site is guarded and further protected by a fence and warning signs (these measures are new, a destroyed fence and no guarding was reported previously; Petrlík, 2010). A drainage is built inside the fenced area, however, the water seems to flow out of the drainage behind the fence. The burial site is affected by landslides and other erosion processes which led to a migration of the burial site of more than ten meters in the past (AWHHE, 2005; Ritsema et al., 2006). This can be one of the reasons for the temporal and spatial (vertical and horizontal) fluctuations of DDT, DDE, DDD and HCH soil concentrations (some of them significantly exceeding Armenian legal standards) observed in the surroundigs of the burial site between 2003 and 2007 (Tadevosyan, 2010). This theory has to be proven as the number of point soil samples taken was low (AWHHE, 2010). Underground water sampling and a geophysical survey is planned to be conducted at Nubarashen by FAO or OSCE (AWHHE, 2010). Detailed information on the Nubarashen burial site can be found also in Helps (2010).

Livestock was reported to graze close to the burial site (AWHHE, 2010; Ritsema et al., 2006). A stream passing the burial site is a tributary to the river Getran, which empties into the river Razdan (which flows through Yerevan). This stream runs also through the closest settlement (summer houses partly occupied by refugees throughout the year) in a distance of cca 1 km from the burial site. The village Mushavan is in a distance of cca 2 km from the burial site, the 1500 villagers (AWHHE, 2005) are all permanent residents. The major source of food of the Mushavan and summer house residents is the market, a minor portion of food is of private production (AWHHE, 2004). Water, fruit, vegetable and cow milk samples were taken by AWHHE in three settlements in close proximity of the burial site in 2004 and analysed on the content of DDT and HCH . The samples did not exceed Armenian legal standards. Also breast milk samples were taken by AWHHE in two villages next to Nubarashen and for comparison also in other villages in the Ararat valley. Some breast milk samples exceeded the Armenian legal standards on DDT and HCH content for cow milk up to six times, however, the levels found in breast milk varied within the same range in all of the villages. Therefore, it was concluded that no direct linkage was found between the Nubarashen burial site and OCPs levels found in various matrices sampled in nearby villages (AWHHE, 2005). However, there are questions regarding the accuracy of these analytical data.

A nature reserve called Erebony was reported to be close the burial site (AWHHE, 2010) and birds of prey (ravens) were observed in the area during sampling in July 2010.

2.2.2 Jrarat (40°03´59´´N, 44°16´50´´E)

The formal governmental storage facility and distribution center for fertilizers and pesticides Jrarat (also sometimes referred to as Konstantin and Sisters LTD) is located cca 50 km from Yerevan. It consists of three buildings, out of which two are demolished. One of the demolished buildings still contains one roofed room, where canisters with methyl mercaptophos (a chemical agent to control insects which is toxic to humans and animals; The Free Dictionary, 2010) are stored (information provided by the owner). The middle part of the building contains rotten metal drums and spilled oils and the last part destroyed bags full of pesticides. The second completely destroyed building containes huge amounts of destroyed bags with a consolidated substance of predominantly white colour and crystalline structure. Evidence of a small fire was observed there. Rubble and pieces of asbestos roofing can be found all around the two destroyed buildings (Ritsema et al., 2006) and the area is also characterized by very heavy smell. The third (biggest) building in cca 100 m distance from the demolished buildings is preserved and according to the owner used for the storage of currently used fertilisers and not specified „biopreparates“. This building is locked and the windows and roof are quite preserved. Close to the site, a railroad is located, which was formerly used for pesticide transport. An estimation of the amount of hazardous waste stored at the Jrarat site can be found in Ritsema et al., 2006.

The site is owned by the former director of the distribution center, who established large ponds for breeding fish for the local market in the area. The concrete fish ponds filled with groundwater obtained from cca 150 m deep wells (Ritsema et al., 2006) are in cca 200 m distance from the three storage buildings. A small muddy fish pond also filled with groundwater is located cca 50 m from the two destroyed buildings. According to the owner, the fish are provided with Dutch feed.

The closest residential buildings are just behind a concrete wall surrounding the area, the closest village is cca 2 km far. There is no livestock grazing in the areal. A fruit tree orchard is located near the demolished buildings. The fish farm workers can freely walk around the site and dogs are rooming around. Women cutting grass and herbs for

TABLE 1 WEATHER CONDITIONS DURING PASSIVE SAMPLING OF AIR

SAMPLING INTERVAL	POP hot-spot	average temperature (°C)			description of weather	number of rainy days
		8:00	13:00	18:00		
26. 6.–23. 7. 2010[1]	Nubarashen[2]	23.0	32.5	33.0	clear sky until 12. 7., later occasional clouds	1
23. 7.–24. 8. 2010	Nubarashen[2]	22.2	32.3	32.4	clear sky until 13. 8. with one rain event, later rare clouds, winds and rain	4
7. 9.–31. 9. 2010	Jrarat	9.4	18.7	21.1	clear sky with occasional clouds until 22. 9., later changing conditions (clear sky, clouds, fogs, rain)	2
12. 10.–12. 11. 2010	Jrarat	3.4	13.2	12.3	changing conditions (often clear sky, often cloudy, occasional rain) until 31. 10., later clear sky with very few clouds	3
1. 9.–7. 9. 2010[3]	Jrarat	3.3	7.8	6.5	cloudy, rainy and changing conditions, occasionally clear sky	3

[1]weather records are available only for the period of 1.7.-23.7.2010, [2]weather records were taken at 9:00, 14:00 and 19:00 o´clock, [3]weather records are available only for the period of 4.9.-7.9.2010

consumption in the close vicinity of the storage sites were observed previously (Ritsema et al., 2006). The easy accessibility of the site was also confirmed by the theft of a passive air sampler installed there in September 2010. The wider surrounding of the Jrarat site is densely populated by storks. According to AWHHE, these birds have had problems with breeding in the last years, however, this information could not be confirmed.

2.2.3. Echmiadzin (39°56´38´´N, 44°33´12´´E)

The privately owned site is a farm with a former local distribution centre of pesticides. According to the owners, the vast majority of obsolete pesticides was already brought to a landfill (Ritsema et al., 2006). Two former obsolete pesticide storage rooms have a water-proof roof, closed windows, are locked and exhibited a moderately strong smell. They are part of a bigger hall. The first storage room was nearly empty, mostly empty packaging was found there. The floor of this room was covered by a pink powder and was swept recently. The second room was not swept, partly empty packaging was found there and old petrol lifters, too. In March 2010, Arnika members already visited this site and took one scratch-offs and sweepings sample in the second room. Significant concentrations (hundreds of mg per kg sample) of DDE and DDT were found (Šír, 2010). A sample of an aggregation found at the floor exhibited an elevated level of PCDD/Fs (62 ng PCDD/Fs-PCB TEQ kg^{-1}; BDS, 2010). The ceiling of both rooms was covered by an evaporated white substance. The owner and members of his family seemed to enter the rooms occasionally. An estimation of the amount of hazardous waste stored at the Echmiadzin site can be found in Ritsema et al., 2006.

A residential house occupated by 2 adults and 2 adolescents is in the close vicinity of the storage rooms. A fish pond filled by groundwater is located cca 50 m far from the storage rooms and a vegetable bed is right next to them. The family provides itself with privately grown vegetables, fruits, fish and eggs. Another residential building was observed behind a wall surrounding the area.

2.2.4 Masis (40°04´18´´N, 44°24´20´´E)

The privately owned storage facility is located in a former factory for processing, packing and distribution of agricultural products. The site was also used for the storage and distribution of pesticides in the past. Pesticides were stored in three separate rooms which are part of a large hall (Ritsema et al., 2006). A guard stays at the site for 24 hours per day and at least ten workers a day enter the area. The obsolete pesticides are not mixed up with currently used ones as was stated by the workers, but we weren´t allowed to enter and check the other rooms of the hall.

The biggest room with obsolete pesticides has no roof, windows are broken and it is closed by a metal gate locked by a padlock. It contains damaged drums and bags and a thick layer of powders of various colours (white, blue, pink and others) covers the floor. The wall between the biggest pesticide storage room and the rest of the hall is partly destroyed. The two smaller storage rooms are locked, not destroyed and there is a thin layer powder on the floor. Empty packaging of currently used pesticides (see Table 1) was found there and the rooms seemed to be entered and used occasionally. All the three pesticide storage rooms exhibited a strong smell. An estimation of the amount of hazardous waste stored at Masis can be found in Ritsema et al., 2006.

The guard´s house is located cca 100 m from the pesticide storage rooms, a residential house is located cca 50 m behind a concrete wall surrounding the area. Interestingly, the region around Masis was malarial in the past. We have no information, whether spraying of DDT was used as a measure preventing the spread of this disease.

2.2.5 Alaverdi (41°07´12´´N, 44°38´53´´E)

Alaverdi is a town in northern Armenia close to the border with Georgia and hosts the Alaverdi Mining and Metallurgical Plant built in 1980. This copper production facility was modernized in 1990. The ore is mined in the close surroundings of the factory and a part is imported from Mountain-Karabakh, too. An old dumpsite with cca 250 t of partly solidificated production waste is located about 1 km from the village Lernahank up of the town in a steep slope. There was no consistent investigation on the potential risk posed by this dumpsite conducted until now. Erosion and land slides are suspected to pose a risk, the possible impact of earthquakes on the dumpsite is investigated by the Armenian ministry of building industries (ACC, 2010). Air pollution (AC, 2010) and arsenic content in the production waste (ArmeniaNow.com, 2010) were until now identified as major risks connected with the copper mining and production in Alaverdi.

The old dumpsite consists of five not covered three-sided concrete enclosures containing sediment from production waste, solid pieces of waste, fly-ash, slag and rubble. Although the dumpsite is fenced, it can be entered easily just by bypassing the gate. The whole dumpsite exhibits a moderately strong smell. A brook runs down of the dumpsite in the valley and farther empties into the river Debed. Next to the brook, a small facility looking like a small mine or ore treatment area is located.

For photographs of the sampling site see Annex B. A detailed but older description of all the sites except Alaverdi can be found also in Ritsema et al., 2006.

2.3 Overview of samples

Table 2 provides a detailed description of samples (matrices, sampling points, type of samples and additional comments) taken at the five hot-spot sampling sites.

For detailed maps of each sampling site please see Annex A.

TABLE 2 DETAILED DESCRIPTION OF SAMPLES TAKEN AT FIVE SELECTED POP HOT-SPOTS

No. sample	Date	Sampling spot	Matrix	Type of sample	Comment
NUBARASHEN					
33[1,2]	23. 7. 2010	0–10 m far from fence in ditch (continuation of drainage)	soil	mixed sample out of 10 point samples	5 cm top soil. Smelly, eye irritating sample, white grains of chemicals observed
34[1]	23. 7. 2010	10 m far from fence, parallel to fence	soil	mixed sample out of 10 point samples	5 cm top soil
3A,3B[1,4]	26. 7. 2010	50 m far from fence, parallel to fence	soil	mixed sample out of 10 point samples	homogenization in bowl
1A,1B[1,4]	26. 7. 2010	45–55 m far from fence in ditch (continuation of drainage)	soil	mixed sample out of 10 point samples	homogenization in bowl
19[1]	26. 7. 2010	55-60 m far from fence in ditch with reed	sediment[5]	mixed sample out of 10 point samples	wet at some points
PAS-A[3]	26. 6.–23. 7. 2010	Mushavan village, 2 km far from burial site	air	passive	
PAS-B[3]	26. 6.–23. 7. 2010	Mushavan cottage settlement, 1,5 km far from burial site	air	passive	daily temperature records available
PAS-C[3]	23. 7.–24. 8. 2010	fence of burial site	air	passive	
PAS-D[3]	23. 7.–24. 8. 2010	250 m downhill of burial site, guards´s house	air	passive	the sampler was installed for 2 days inside guards´s house
38[1,2]	10. 11. 2010	Mushavan cottage settlement, 1,5 km far from burial site	eggs	mixed sample out of 5 eggs	freely roaming hens, maybe waste burning in household yard
39[1,2]	10. 11. 2010	Mushavan village, 2 km far from burial site	eggs	mixed sample out of 5 eggs	freely roaming hens, maybe waste burning in household yard
40[1]	10. 11. 2010	Mushavan village, 2 km far from burial site	cow milk	mixed sample out of milk from several cows	outside grazing cows, maybe waste burning in household yard
41[1]	10. 11. 2010	Mushavan village, 2 km far from burial site	cow cream	sample from one cow	outside grazing cow, maybe waste burning in household yard

No. sample	Date	Sampling spot	Matrix	Type of sample	Comment
			JRARAT		
35[2]	24. 7. 2010	side floor in big building	sweepings	mixed sample taken continuously along wall	
27[1]	24. 7. 2010	front wall 30-50 cm above floor in big building	plaster	mixed sample taken continuously from wall	peeling plaster with black film
29[1,2]	24. 7. 2010	floor up to 1 m from front wall in big building	sweepings	mixed sample taken continuously along wall	chlorine smell at two points, upper layer consisting probably of fertilisers and „biopreparates“ in use removed
31[1]	24. 7. 2010	floor up to 1 m from side wall in big building	sweepings	mixed sample taken continuously along half of wall	
25[1]	24. 7. 2010	floor around plastic barrels in big building	scratch-offs	mixed sample taken continuously around barrels	smell, barrels did not seem to leach after quick inspection, however, one point was wet
15[1]	26. 7. 2010	floor in back room of destroyed small building	sweepings	mixed sample taken continuously from floor	strong smell, spilled powders of white, yellow, brown, pink, black, yellow-green and grey colour
14[1]	26. 7. 2010	floor in middle room of destroyed small building	sweepings/ scratch-offs	mixed sample taken continuously from floor	greasy dark layer around rotten empty metal barrels, very strong smell
2[1]	26. 7. 2010	area between destroyed small building and totally ruined building next to it	soil	mixed sample out of 10 point samples	3-5 cm top soil, consolidated layer found deeper, sampling shovel slightly contaminated from sample 14
5[1]	26. 7. 2010	fish pond 50 m far from destroyed small building	sediment[5]	point sample taken from pond edge next to artesian water tributary	
9[1]	26. 7. 2010	fish pond 50 m far from destroyed small building	water	pond water taken from pond edge next to artesian water tributary	
7[1]	24. 7. 2010	concrete fish ponds 250 m far from big building	water	water outflowing from ponds	
PAS-E[3]	7. 9.–31. 9. 2010	office building	air	passive	
PAS-F[3]	12. 10.–12. 11. 2010	200 m far from destroyed buildings	air	passive	
PAS-G[3]	1. 9.–7. 9. 2010	between destroyed buildings	air	passive	
36[1]	11. 11. 2010	80 m far from storehouse	eggs	mixed sample out of 5 eggs	freely roaming hens, maybe waste burning in household yard
37[1]	11. 11. 2010	100 m far from storehouse	eggs	mixed sample out of 5 eggs	freely roaming hens, maybe waste burning in household yard
42[1,2]	11. 11. 2010	concrete fish pond 250 m far from storehouse	trout	mixed sample out of two trouts (livers and meat analysed separately)	fish sizes: 26.5/30[6] (age: 3+ years) and 28/32[6] (age: 3+ years)

No. sample	Date	Sampling spot	Matrix	Type of sample	Comment
			ECHMIADZIN		
21A, 21B[1,2,4]	24. 7. 2010	floor of room 1 of storage building	scratch-offs/ sweepings	mixed sample taken continuously along walls and under pallets	smell, floor was swept, close to walls pink, grey and white powders
22[1]	24. 7. 2010	floor of room 2 of storage building	scratch-offs	mixed sample taken from the whole floor	stronger smell than in room 1, floor was not swept, black, grey, yellow, yellow-green and white powders, old petrol lifters in room
26[1]	24. 7. 2010	vegetable bed next to storage building	soil	mixed sample out of 10 point samples	5 cm top soil layer, thin upper layer removed by inhabitant
8[1]	24. 7. 2010	well 50 m far from storage building	water	artesian	
11[1]	24. 7. 2010	fish pond 50 m far from storage building	water	pond	
28[1,2]	24. 7. 2010	fish pond 50 m far from storage building	sediment[5]	mixed sample out of 12 point samples	bottom of dry pond, 5 cm top sediment layer, wet under upper layer
45[1,2]	9. 11. 2010	Griboedov village, 10 m far from the pesticide storehouse	eggs	mixed sample out of 5 eggs	freely roaming hens
46[1,2]	9. 11. 2010	50 m far from the pesticide storehouse	eggs	mixed sample out of 5 eggs	freely roaming hens
			MASIS		
17[1]	26. 7. 2010	wall right from entrance in big room, up to 30 cm above floor	plaster	mixed sample taken continuously from wall	pink colour probably comming from pink substance found in nearby destroyed plastic barrel
24[1]	26. 7. 2010	surroundings of destroyed plastic barrel with pink substance in big room	scratch-offs	mixed sample taken continuously around plastic barrel	pink substance + scratch-offs, only upper layer sampled, however, layer of pink substance min. 10 cm deep
10[1]	26. 7. 2010	floor everywhere in big room except surroundings of destroyed plastic barrel	scratch-offs/ sweepings	mixed sample taken continuously from the whole floor	
16[1,2]	26. 7. 2010	whole floor in middle small room	scratch-offs	mixed sample taken continuously from the whole floor	pallets with white powder, bottles with dimethoat, empty packings of promethryn, methalaxyl and mancozeb
20[1]	26. 7. 2010	whole floor in outer small room	scratch-offs	mixed sample taken continuously from the whole floor	pallets with white powder, empty packings of cypermethrin, nabsabuzin, methalaxyl etc
18[1]	26. 7. 2010	1–3 m from walls of big and central small rooms	soil	mixed sample out of 10 point samples	3 cm top soil, consolidated layer found deeper
12[1]	26. 7. 2010	tap 100 m from storage rooms	water	artesian	
43[1]	10. 11. 2010	in direction from the storehouse to the center of Masis village; 300 m far from storehouse	eggs	mixed sample out of 5 eggs	freely roaming hens
44[1]	10. 11. 2010	300 m far from storehouse	cow milk	sample from 1 cow	free grazing cow

No. sample	Date	Sampling spot	Matrix	Type of sample	Comment
			ALAVERDI		
23[1,2]	27. 7. 2010	dumpsite close to Lernahank village, middle concrete enclosure	sediment from production waste	mixed sample out of 10 point samples	sampled area: 5x5 m, yellow, grey-black and brown wet mud, upper 1–2 cm removed, sampled up to 5 cm deep
32[1,2]	27. 7. 2010	dumpsite close to Lernahank village, middle concrete enclosure	slag	mixed sample out of few pieces	
32A[2]	27. 7. 2010	entrance of dumpsite close to Lernahank village	slag	mixed sample out of 2 pieces	
13[1,2]	27. 7. 2010	dumpsite close to Lernahank village, under small steep hill next to concrete enclosures	soil	mixed sample out of 8 point samples	sandy structure, sampled area: 2x6 m, upper 1–2 cm removed
30[1,2]	27. 7. 2010	dumpsite close to Lernahank village, in front of central concrete enclosure	ash/fly-ash	point sample	
6[1]	27. 7. 2010	brook 600 m far from dumpsite	water	point sample from brook edge	
4[1]	27. 7. 2010	brook 600 m far from dumpsite	sediment[5]	point sample from middle of brook	sandy structure
47[1,2]	12. 11. 2010	pond 200 m far from mercury burial site in Alaverdi town	trout	1 trout	fish size: 37/40[6]. Age: 4+ years. No water inflow to pond
48[1,2]	12. 11. 2010	Alaverdi town suburbs, 2 km far from the copper plant	eggs	mixed sample out of 5 eggs	freely roaming hens
49[1,2]	12. 11. 2010	Kobayr village, 30 km far from copper plant	eggs	mixed sample out of 5 eggs	freely roaming hens

[1]analysed in the laboratories of VŠCHT, Ústav chemie a analýzy potravin (Institute of Chemical Technology, Department of Food Chemistry and Analysis, Prague)
[2]analysed in BDS (BioDetection Systems B.V., Amsterdam) laboratories
[3]analysed in the laboratories of RECETOX (Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno). This research centre provided also the passive air samplers.
[4]two fractions obtained for two different analyses
[5]the fish ponds at Echmiadzin and Jrarat and stream at Nubarashen were probably of a temporary character (dry during substantial periods throughout the year). The „sediment" in the brook in Alaverdi consisted of sand. Generally, the matrix called sediment here was always very similar to the type of soil found at the particular locality.
[6]first (smaller) size is from mouth to tail fin base, second (larger) size is from mouth to tail fin end

2.4 Sampling and analytical methods

Samples of solid matrices were usually taken as mixed samples from the top layers. The sampling person changed gloves after taking each sample and rinsed the sampling shovel with tap water every time. After leaving each storage room / sampling area, the boots of sampling and helping persons were rinsed with tap water such that the contamination from one sampling spot did not affect the subsequent sampling. Air was sampled by passive air samplers, a device consisting of two stainless steel bowls attached to a common axis and forming a protective chamber for a polyurethane foam disc. Exposure times in orders of weeks enable the determination of many compounds from the POP group in air sampled by this cheap and simple method (Klánová et al., 2009). A trip blank was taken to ensure that no significant contamination of air samples occured during their transport, storage and analysis. Mixed biota samples were homogenised after transport to laboratory. For details please see Table 2.

Samples of solid matrices, water and sediments were filled into polyethylene sample cases. Cases with water and sediment samples were wrapped in aluminium foil. Polyurethane foam disks from passive air samplers were wrapped in two layers of aluminium foil and stored in a plastic bag. Eggs were stored in egg boxes wrapped in two polyethylene bags and later cooked. Milk and cream samples were stored in PET bottles. Fish samples were wrapped in two polyethylene bags. Soil, scratch-offs, sweepings and copper production waste samples were kept in room temperature, while water, sediment, air samples and eggs were stored in a fridge at 4-8°C during the stay in Armenia. Fish, milk and cream samples were stored in a freezer.

Samples determined for the analysis of PCDD/Fs were sent to a Dutch certified laboratory (BioDetection Systems B.V., Amsterdam). PCDD/Fs-PCB-TEQ were analysed as DR CALUX® TEQs and benchmarked against a 2,3,7,8-TCDD calibration curve. The samples were extracted by means of ASE (hexane:acetone, 90:10) extraction. The extracts were desulphurised and cleaned on an acid silica column. The cleaned extracts were dissolved in dimethyl sulfoxide (50 µl) and the DR CALUX® activity was determined after 24 hours exposure. All DR CALUX analysis results comply with EU requirements as indicated in COMMISSION REGULATION (EC) No 1883/2006 (laying down the sampling methods and the methods of analysis for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs). The content of PCDD/Fs and dioxin-like PCBs expressed as WHO-TEQ, I-TEQ and concentrations of individual congeners in sample 33 was determined at Eurofins / GFA GmbH Laboratories, Münster, Germany.

All samples except passive air samples were analysed on the content of OCPs and PCBs in a Czech certified laboratory (Institute of Chemical Technology, Department of Food Chemistry and Analysis). The analytes were extracted from water samples by microextraction into isooctane, from other non-biota samples by dichloromethane and from biota samples by means of hexane:dichloromethane (1:1). The extracts were cleaned by means of gel permeation chromatography (GPC). The identification and quantification of the analytes was determined by gas chromatography coupled with an electron capture detector or mass spectrometry detection. The residues of non-organochlorinated pesticides in these samples were extracted by means of QuEChERS coupled with cleaning by a mixture of primary and secondary amines (PSA), C18 and $MgSO_4$. These analytes were separated by liquid chromatography followed by a mass spectrometry detection (LC-MS/MS) making use of a triple quadrupole (QqQ). The analysis of water samples on non-organochlorinated pesticides was conducted by means of a direct injection after filtration through a microfilter and further analysed by the LC-MS/MS technique. The contents of heavy metals were determined by means of atomic absorption spectroscopy.

Passive air samples were analysed in the laboratories of the Research Centre for Toxic Compounds in the Environment (Masaryk University, Brno) on the content of OCPs and PCBs. The polyurethane foam discs were extracted with dichloromethane and the extracts fractionated on a sulphuric acid modified silica gel column. The content of the analytes was determined by gas chromatography coupled with an electron capture detector.

3. RESULTS

The results of chemical analyses are presented in Table 3. All samples of air and solid matrices except sample No. 35 were also analysed on the content of 7 PCBs (PCB 28, 52, 101, 118, 153, 138, 180) and exhibited a content lower than the detection limit. Samples 33 and 1A+1B were analysed also on the content of pesticides based on chlorinated phenoxyacids (2,4-D, 2,4,5-T, 2,4,5-TP, MCPA, mecoprop, MCPB, 2,4-DB and 2,4-DP), where all except 2,4-D exhibited concentrations lower than the detection limit. In some water samples only DDT and its metabolites were detected, the concentrations of other analytes were under the detection limits. POP levels in the trip blank for passive air samples were lower than the detection limit.

Table 3 Results of chemical analyses. < LOD: analyte concentration was below limit of detection. < LOQ: analyte concentration was below limit of quantification. NA: not analysed. For a better orientation, results for solid matrices are marked in brown, for water samples in blue, for biota samples in pink and for passive air samples in grey. Where the passive air sampling interval differed from 28 days, the numbers in square parentheses present concentrations recalculated for this standard sampling interval. All egg samples had a content of fat higher than 10 %, therefore concentrations are presented as lipid normalised results. Numbers in round parentheses present the percentage of fat in the biota samples. Malathion was analysed as the sum of malathion and malaoxon. Triadimefon was analysed as the sum of triadimefon and triadimenol. Dimethoat was analysed as the sum of dimethoat and omethoat.

TABLE 3 RESULTS OF CHEMICAL ANALYSES

	NUBARASHEN												
NO. SAMPLE	**33**	**34**	**1A + 1B**	**19**	**3A + 3B**	**PAS-A**	**PAS-B**	**PAS-C**	**PAS-D**	**38 (13,7)**	**39 (12.9)**	**40 (5.1)**	**41 (15.7)**
	ORGANOCHLORINATED PESTICIDES												
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg .kg^{-1}**	**ng.disc^{-1}**	**ng.disc^{-1}**	**ng.disc^{-1}**	**ng.disc^{-1}**	**µg.kg^{-1} fat**	**µg.kg^{-1} fat**	**µg.kg^{-1}**	**µg.kg^{-1}**
o,p´- DDD	24.215	0.019	0.682	0.003	< LOD	< LOD	< LOD	27.9 [23.7]	5.2 [4.4]	NA	NA	NA	NA
p,p´- DDD	103.841	0.059	3.241	0.014	< LOD	< LOD	< LOD	49.8 [42.3]	7.8 [6.6]	24.1	26.4	< LOD	< LOD
o,p´- DDE	NA	NA	NA	NA	NA	< LOD	< LOD	80.9 [68.6]	18.1 [15.4]	NA	NA	NA	NA
p,p´- DDE	16.699	0.484	0.673	0.004	0.028	14.9	14.0	125.7 [106.7]	43.0 [36.5]	62.0	100.0	4.5	12.4
o,p´- DDT	237.931	0.188	9.080	0.063	< LOD	< LOD	< LOD	251.1 [213.1]	21.8 [18.5]	55.5	57.4	< LOD	< LOD
p,p´- DDT	863.956	0.574	32.809	0.220	0.119	< LOD	< LOD	415.8 [352.8]	27.1 [23.0]	66.4	75.2	< LOD	3.5
aldrin	0.504	< LOD	2.328	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
dieldrin	< LOD	< LOD	< LOD	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
endosulfan sulphate	< LOD	< LOD	< LOD	< LOD	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
endosulfan α	1.188	< LOD	0.876	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
endosulfan β	4.153	< LOD	0.121	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
endrin	3.271	< LOD	0.112	0.001	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
HCH-alpha	109.312	0.030	0.351	0.001	< LOD	22.4	25.3	1998.3 [1695.5]	348.3 [295.5]	< LOD	5.4	0.2	0.3
HCH-beta	10.394	< LOD	0.654	0.001	< LOD	< LOD	< LOD	112.0 [95.0]	37.6 [31.9]	< LOD	3.1	< LOD	< LOD
HCH-gamma (lindane)	39.717	0.011	5.762	0.003	< LOD	< LOD	< LOD	514.3 [436.4]	104.6 [88.8]	5.1	67.4	0.3	3.0
HCH-delta	NA	NA	NA	NA	NA	< LOD	< LOD	176.7 [149.9]	11.6 [9.8]	NA	NA	NA	NA

NO. SAMPLE	33	34	1A + 1B	19	3A + 3B	PAS-A	PAS-B	PAS-C	PAS-D	38 (13,7)	39 (12.9)	40 (5.1)	41 (15.7)
heptachlor	< LOD	< LOD	< LOD	< LOD	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
heptachlor-endo-epox	< LOD	< LOD	< LOD	0.065	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
heptachlor-exo-epox	< LOD	< LOD	< LOD	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
hexachlorobenzene	4.167	< LOD	0.122	< LOD	< LOD	< LOD	< LOD	52.8 [44.8]	< LOD	10.2	8.5	0.3	0.6
hentachlorobenzene	NA	NA	NA	NA	NA	< LOD	< LOD	7.4 [6.3]	< LOD	NA	NA	NA	NA
oxychlordane	< LOD	< LOD	< LOD	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
cis chlordane	1.778	< LOD	< LOD	0.000	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
trans chlordane	3.253	< LOD	< LOD	0.001	< LOD	NA	NA	NA	NA	< LOD	< LOD	< LOD	< LOD
OTHER PESTICIDES													
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
ametryn	0.03	< LOD	< LOD	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
atrazine	9.49	< LOD	1.60	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
carbaryl	0.15	< LOD	0.05	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
carbendazim	0.19	< LOD	0.07	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
desmetryn	3.18	< LOD	1.00	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
malathion	0.02	< LOD	< LOD	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
phosalone	0.03	< LOD	< LOD	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
prometryn	14.96	< LOD	0.62	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
simazine	316.00	0.49	55.10	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
simetryn	< LOD	< LOD	0.15	< LOD	< LOD	NA	NA	NA	NA	NA	NA	NA	NA
2,4-D	2.343	NA	0.094	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PCDD/Fs, DIOXINLIKE PCBs													
Unit	**ng.kg^{-1} d.m.**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**pg.g^{-1} fat**	**pg.g^{-1} fat**	**NA**	**NA**
PCDD/F-PCB CALUX TEQ	6642	NA	NA	NA	NA	NA	NA	NA	NA	37	< LOQ	NA	NA

NO. SAMPLE	33	34	1A + 1B	19	3A + 3B	PAS-A	PAS-B	PAS-C	PAS-D	38 (13,7)	39 (12.9)	40 (5.1)	41 (15.7)
HEAVY METALS													
Unit	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**mg.kg^{-1}**	**mg.kg^{-1}**	**NA**	**NA**
mercury	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.001	< LOD	NA	NA
lead	NA	NA	NA	NA	NA	NA	NA	NA	NA	< LOD	< LOD	NA	NA
cadmium	NA	NA	NA	NA	NA	NA	NA	NA	NA	< LOD	< LOD	NA	NA
arsenic	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.01	0.01	NA	NA

NUBARASHEN, SAMPLE NO. 33

PCDD/Fs	ng.kg^{-1} d.m.	PCDD/Fs	ng.kg^{-1} d.m.	dioxin-like PCBs	ng.kg^{-1} d.m.
2,3,7,8-tetraCDD	1440	**2,3,7,8-tetraCDF**	123	**PCB 77**	99.4
1,2,3,7,8-pentaCDD	855	**1,2,3,7,8-pentaCDF**	9.03	**PCB 81**	8.13
1,2,3,4,7,8-hexaCDD	2490	**2,3,4,7,8-pentaCDF**	15.5	**PCB 105**	87.3
1,2,3,6,7,8-hexaCDD	203	**1,2,3,4,7,8-hexaCDF**	211	**PCB 114**	< LOQ
1,2,3,7,8,9-hexaCDD	222	**1,2,3,6,7,8-hexaCDF**	9.84	**PCB 118**	208
1,2,3,4,6,7,8-heptaCDD	3560	**1,2,3,7,8,9-hexaCDF**	< LOQ	**PCB 123**	< LOQ
octaCDD	27200	**2,3,4,6,7,8-hexaCDF**	62.2	**PCB 126**	31.5
WHO (1998)-PCDD/F TEQ excl. LOQ[1]	2680	**1,2,3,4,6,7,8-heptaCDF**	320	**PCB 156**	< LOQ
WHO (1998)-PCDD/F TEQ incl. LOQ[2]	2680	**1,2,3,4,7,8,9-heptaCDF**	46.3	**PCB 157**	< LOQ
WHO (2005)-PCDD/F TEQ excl. LOQ[1]	2680	**octaCDF**	609	**PCB 167**	< LOQ
WHO (2005)-PCDD/F TEQ incl. LOQ[2]	2680			**PCB 169**	< LOQ
I-TEQ (NATO/CCMS) excl. LOQ[1]	2280			**PCB 189**	< LOQ
I-TEQ (NATO/CCMS) incl. LOQ[2]	2280			**WHO (1998)-PCB TEQ excl. LOQ[1]**	3.19
				WHO (1998)-PCB TEQ incl. LOQ[2]	3.48

[1]TEQ value calculated by including the quantified congeners only
[2]TEQ value calculated by including the non-quantified congeners by taking their full value of LOQ

JRARAT

NO. SAMPLE	29	31	25	15	14	2	5	27	35	9	7
ORGANOCHLORINATED PESTICIDES											
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**NA**	**µg.l^{-1}**	**µg.l^{-1}**
o,p´- DDD	5.639	0.170	0.445	904.904	0.997	7.443	0.009	0.013	NA	< LOD	< LOD
p,p´- DDD	0.275	0.667	1.430	2341.893	2.622	27.994	0.023	0.018	NA	0.092	< LOD
p,p´- DDE	8.378	0.162	0.466	340.649	5.124	15.579	0.017	0.083	NA	< LOD	< LOD
o,p´- DDT	5.005	1.914	6.971	10735.934	7.440	73.516	0.220	0.112	NA	0.149	< LOD
p,p´- DDT	1.008	5.046	23.674	16982.959	22.094	256.909	0.547	0.164	NA	0.491	< LOD
aldrin	12.093	0.089	< LOD	1.889	0.325	0.114	0.000	0.032	NA	< LOD	< LOD
dieldrin	3.195	0.051	< LOD	< LOD	0.513	< LOD	0.000	< LOD	NA	< LOD	< LOD
endosulfan sulphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.022	NA	< LOD	< LOD
endosulfan α	0.264	< LOD	< LOD	< LOD	3.472	1.505	0.001	0.004	NA	< LOD	< LOD
endosulfan β	0.192	0.052	0.039	142.605	0.248	0.972	0.001	0.002	NA	< LOD	< LOD
endrin	0.138	0.020	0.083	42.307	0.177	1.037	0.002	< LOD	NA	< LOD	< LOD
HCH-alpha	0.536	0.004	0.096	3.876	0.053	0.845	0.001	0.566	NA	< LOD	< LOD
HCH-beta	0.168	0.013	0.212	0.814	0.676	3.868	0.002	0.110	NA	< LOD	< LOD
HCH-gamma (lindane)	1.007	0.046	0.163	219.304	0.446	21.367	0.005	0.042	NA	< LOD	< LOD
heptachlor	0.164	< LOD	< LOD	< LOD	6.399	< LOD	< LOD	< LOD	NA	< LOD	< LOD
heptachlor-endo-epox	3.805	3.071	21.460	11.218	0.471	< LOD	0.564	0.055	NA	< LOD	< LOD
heptachlor-exo-epox	< LOD	0.034	0.032	64.605	< LOD	< LOD	< LOD	0.012	NA	< LOD	< LOD
hexachlorobenzene	0.049	0.002	< LOD	< LOD	0.158	0.966	0.000	0.002	NA	< LOD	< LOD
oxychlordane	< LOD	< LOD	< LOD	2.068	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
cis chlordane	0.197	< LOD	< LOD	29.958	0.245	0.263	0.000	0.010	NA	< LOD	< LOD
trans chlordane	3.648	0.040	0.125	61.587	0.543	4.145	0.002	0.017	NA	< LOD	< LOD

NO. SAMPLE	29	31	25	15	14	2	5	27	35	9	7
OTHER PESTICIDES											
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**NA**	**µg.l^{-1}**	**µg.l^{-1}**
atrazine	< LOD	< LOD	< LOD	7.10	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
carbendazim	< LOD	< LOD	0.03	< LOD	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
chlorpyrifos(ethyl)	< LOD	< LOD	< LOD	0.04	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
cypermethrin	< LOD	< LOD	0.08	< LOD	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
lenacil	< LOD	< LOD	0.05	< LOD	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
malathion	< LOD	< LOD	< LOD	< LOD	0.08	< LOD	< LOD	< LOD	NA	< LOD	< LOD
metalaxyl	< LOD	< LOD	0.02	0.14	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
permethrin	< LOD	< LOD	< LOD	0.03	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
phosalone	0.03	0.04	0.28	0.09	0.40	< LOD	< LOD	< LOD	NA	< LOD	< LOD
prometryn	< LOD	< LOD	0.06	1.10	< LOD	0.04	< LOD	< LOD	NA	< LOD	< LOD
propargite	< LOD	< LOD	0.04	0.06	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
simazine	< LOD	< LOD	1.44	4640.00	0.29	0.07	< LOD	< LOD	NA	< LOD	< LOD
simetryn	< LOD	< LOD	< LOD	0.07	0.02	< LOD	< LOD	< LOD	NA	< LOD	< LOD
triadimefon	< LOD	< LOD	0.03	0.04	0.03	0.03	< LOD	< LOD	NA	< LOD	< LOD
trichlorfon	< LOD	< LOD	0.03	< LOD	< LOD	< LOD	< LOD	< LOD	NA	< LOD	< LOD
PCDD/Fs, DIOXINLIKE PCBs											
Unit	**ng.kg^{-1} d.m.**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**ng.kg^{-1} d.m.**	**NA**	**NA**
PCDD/F-PCB CALUX TEQ	2.0	NA	NA	NA	NA	NA	NA	NA	5.3	NA	NA

JRARAT

NO. SAMPLE	PAS-E	PAS-F	PAS-G	36 (12.9)	37 (13.2)	42 (2.2)
ORGANOCHLORINATED PESTICIDES						
Units	**ng.disc^{-1}**	**ng.disc^{-1}**	**ng.disc^{-1}**	**µg.kg^{-1} fat**	**µg.kg^{-1} fat**	**µg.kg^{-1}**
o,p´- DDD	8.9 [10.4]	63.7 [55.7]	39.4 [157.6]	NA	NA	NA
p,p´- DDD	8.5 [9.9]	61.7 [54.0]	33.6 [134.4]	26.4	25.0	1.1
o,p´- DDE	21.0 [24.5]	227.4 [199.0]	148.9 [595.6]	NA	NA	NA
p,p´- DDE	120.3 [140.4]	503.9 [440.9]	308.0 [1232.0]	851.9	497.0	2.3
o,p´- DDT	36.9 [43.1]	601.3 [526.1]	318.5 [1274.0]	< LOD	< LOD	< LOD
p,p´- DDT	26.6 [31.0]	539.1 [471.7]	231.7 [926.8]	45.0	111.4	1.6
aldrin	NA	NA	NA	< LOD	< LOD	< LOD
dieldrin	NA	NA	NA	< LOD	< LOD	< LOD
endosulfan sulphate	NA	NA	NA	< LOD	< LOD	< LOD
endosulfan α	NA	NA	NA	< LOD	< LOD	< LOD
endosulfan β	NA	NA	NA	< LOD	< LOD	< LOD
endrin	NA	NA	NA	< LOD	< LOD	< LOD
HCH-alpha	45.5 [53.1]	77.8 [68.1]	68.5 [274.0]	< LOD	1.5	< LOD
HCH-beta	< LOD	24.0 [21.0]	14.6 [58.4]	< LOD	0.8	< LOD
HCH-gamma (lindane)	< LOD	54.2 [47.4]	41.1 [164.4]	7.8	53.8	1.2
HCH-delta	< LOD	< LOD	< LOD	NA	NA	NA
heptachlor	NA	NA	NA	< LOD	< LOD	< LOD
heptachlor-endo-epox	NA	NA	NA	< LOD	< LOD	1.1
heptachlor-exo-epox	NA	NA	NA	< LOD	< LOD	0.5
hexachlorobenzene	< LOD	< LOD	< LOD	4.7	5.3	0.1
pentachlorobenzene	< LOD	< LOD	< LOD	NA	NA	NA
oxychlordane	NA	NA	NA	< LOD	< LOD	< LOD
cis chlordane	NA	NA	NA	< LOD	< LOD	< LOD
trans chlordane	NA	NA	NA	< LOD	< LOD	< LOD

NO. SAMPLE	PAS-E	PAS-F	PAS-G	36 (12.9)	37 (13.2)	42 (2.2)
PCDD/Fs, DIOXINLIKE PCBs						
Unit	**NA**	**NA**	**NA**	**NA**	**NA**	**pg.g^{-1} f.w.**
PCDD/F-PCB CALUX TEQ	NA	NA	NA	NA	NA	0.22
HEAVY METALS						
Unit	**NA**	**NA**	**NA**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**
mercury	NA	NA	NA	< LOD	0.002	0.021
lead	NA	NA	NA	< LOD	< LOD	< LOD
cadmium	NA	NA	NA	< LOD	< LOD	< LOD
arsenic	NA	NA	NA	0.02	0.01	0.36

ECHMIADZIN

NO. SAMPLE	21A + 21B	22	26	28	8	11	45 (11.7)	46 (12.7)
ORGANOCHLORINATED PESTICIDES								
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**µg.l^{-1}**	**µg.l^{-1}**	**µg.kg^{-1} fat**	**µg.kg^{-1} fat**
o,p´- DDD	< LOD	< LOD	0.008	0.003	< LOD	< LOD	NA	NA
p,p´- DDD	1.779	< LOD	0.024	0.012	0.087	< LOD	46.2	46.5
p,p´- DDE	0.456	191.893	0.018	0.003	< LOD	< LOD	4983.8	4896.9
o,p´- DDT	4.283	346.297	0.079	0.073	0.159	< LOD	120.5	114.2
p,p´- DDT	11.237	46.026	0.219	0.224	0.423	< LOD	450.4	686.6
aldrin	1.491	150.001	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
dieldrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
endosulfan sulphate	< LOD	4.174	< LOD	0.009	< LOD	< LOD	< LOD	< LOD
endosulfan α	0.447	7.595	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
endosulfan β	0.059	9.708	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
endrin	0.056	5.349	< LOD	0.001	< LOD	< LOD	< LOD	< LOD

NO. SAMPLE	21A + 21B	22	26	28	8	11	45 (11.7)	46 (12.7)
HCH-alpha	0.298	6.014	0.091	0.000	< LOD	< LOD	< LOD	< LOD
HCH-beta	0.497	6.219	< LOD	0.001	< LOD	< LOD	< LOD	< LOD
HCH-gamma (lindane)	4.326	< LOD	0.015	0.001	< LOD	< LOD	20.5	22.0
heptachlor	< LOD	< LOD	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
heptachlor-endo-epox	7.816	3.263	< LOD	0.006	< LOD	< LOD	< LOD	< LOD
heptachlor-exo-epox	< LOD	< LOD	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
hexachlorobenzene	0.102	< LOD	0.006	0.000	< LOD	< LOD	6.0	7.1
oxychlordane	0.079	1.620	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
cis chlordane	< LOD	11.048	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
trans chlordane	< LOD	109.446	< LOD	0.000	< LOD	< LOD	< LOD	< LOD
OTHER PESTICIDES								
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**µg.l^{-1}**	**µg.l^{-1}**	**NA**	**NA**
buprofezin	< LOD	0.05	< LOD	< LOD	< LOD	< LOD	NA	NA
carbendazim	187.00	75.10	0.02	< LOD	< LOD	< LOD	NA	NA
chlorpyrifos(ethyl)	< LOD	0.26	< LOD	< LOD	< LOD	< LOD	NA	NA
cypermethrin	2.59	1367.00	0.54	< LOD	< LOD	< LOD	NA	NA
deltametrin	< LOD	8.70	< LOD	< LOD	< LOD	< LOD	NA	NA
desmetryn	0.08	< LOD	< LOD	< LOD	< LOD	< LOD	NA	NA
dichlorvos	< LOD	0.03	< LOD	< LOD	< LOD	< LOD	NA	NA
dimethoate	< LOD	11.40	< LOD	< LOD	< LOD	< LOD	NA	NA
ethion	< LOD	0.27	< LOD	< LOD	< LOD	< LOD	NA	NA
imidacloprid	< LOD	< LOD	0.14	< LOD	< LOD	< LOD	NA	NA
lenacil	15.90	0.31	< LOD	< LOD	< LOD	< LOD	NA	NA
malathion	< LOD	0.05	< LOD	< LOD	< LOD	< LOD	NA	NA
metalaxyl	55.30	74.50	< LOD	< LOD	< LOD	< LOD	NA	NA
metribuzin	0.30	0.08	< LOD	< LOD	< LOD	< LOD	NA	NA

NO. SAMPLE	21A + 21B	22	26	28	8	11	45 (11.7)	46 (12.7)
oxadixyl	< LOD	3.10	< LOD	< LOD	< LOD	< LOD	NA	NA
permethrin	< LOD	3.10	< LOD	< LOD	< LOD	< LOD	NA	NA
phosalone	3.24	378.00	< LOD	< LOD	< LOD	< LOD	NA	NA
pirimiphos-ethyl	< LOD	0.07	< LOD	< LOD	< LOD	< LOD	NA	NA
pirimiphos-methyl	< LOD	0.03	< LOD	< LOD	< LOD	< LOD	NA	NA
prometryn	1.77	6.40	< LOD	< LOD	< LOD	< LOD	NA	NA
propachlor	1.30	0.04	< LOD	< LOD	< LOD	< LOD	NA	NA
propiconazole	< LOD	0.14	< LOD	< LOD	< LOD	< LOD	NA	NA
simazine	20.40	0.06	< LOD	< LOD	< LOD	< LOD	NA	NA
simetryn	< LOD	0.07	< LOD	< LOD	< LOD	< LOD	NA	NA
triadimefon	62.40	64.70	< LOD	< LOD	< LOD	< LOD	NA	NA
trichlorfon	< LOD	0.71	< LOD	< LOD	< LOD	< LOD	NA	NA
PCDD/Fs, DIOXINLIKE PCBs								
Unit	**ng.kg^{-1} d.m.**	**NA**	**NA**	**ng.kg^{-1} d.m.**	**NA**	**NA**	**pg.g^{-1} fat**	**pg.g^{-1} fat**
PCDD/F-PCB CALUX TEQ	869	NA	NA	1.9	NA	NA	24.8	20.9
HEAVY METALS								
Unit	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**mg.kg^{-1}**	**mg.kg^{-1}**
mercury	NA	NA	NA	NA	NA	NA	0.001	< LOD
lead	NA	NA	NA	NA	NA	NA	< LOD	< LOD
cadmium	NA	NA	NA	NA	NA	NA	< LOD	< LOD
arsenic	NA	NA	NA	NA	NA	NA	0.01	0.01

MASIS									
NO. SAMPLE	17	24	10	16	20	18	12	43 (14.6)	44 (4.3)
ORGANOCHLORINATED PESTICIDES									
Unit	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	µg.l^{-1}	µg.kg^{-1} fat	µg.kg^{-1}
o,p´- DDD	< LOD	0.848	1.513	0.079	4.488	0.012	< LOD	NA	NA
p,p´- DDD	0.007	0.570	1.507	0.099	0.608	0.012	0.054	22.6	1.1
p,p´- DDE	0.001	0.408	3.492	0.164	9.324	0.028	< LOD	233.6	4.4
o,p´- DDT	0.001	1.346	5.765	0.271	6.735	0.057	0.059	< LOD	< LOD
p,p´- DDT	0.179	2.893	10.068	0.385	35.838	0.230	0.182	125.3	1.2
aldrin	< LOD	0.386	1.702	0.033	111.186	< LOD	< LOD	< LOD	< LOD
dieldrin	< LOD	0.432	0.023	< LOD	41.812	< LOD	< LOD	< LOD	< LOD
endosulfan sulphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
endosulfan α	0.003	6.339	0.108	< LOD	3.602	< LOD	< LOD	< LOD	< LOD
endosulfan β	< LOD	< LOD	0.083	< LOD	0.256	< LOD	< LOD	< LOD	1.0
endrin	< LOD	0.625	0.080	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HCH-alpha	1.002	3079.626	0.305	0.013	0.027	0.007	< LOD	< LOD	< LOD
HCH-beta	0.340	398.426	0.260	0.009	0.161	0.009	< LOD	< LOD	< LOD
HCH-gamma (lindane)	0.040	204.873	0.163	0.008	0.018	< LOD	< LOD	13.0	0.6
heptachlor	< LOD	1.665	4.414	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
heptachlor-endo-epox	0.079	< LOD	6.640	0.127	81.834	< LOD	< LOD	< LOD	< LOD
heptachlor-exo-epox	< LOD	< LOD	0.103	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
hexachlorobenzene	< LOD	0.828	< LOD	0.001	0.004	< LOD	< LOD	2.7	0.2
oxychlordane	< LOD	< LOD	0.065	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
cis chlordane	0.010	< LOD	0.165	0.004	< LOD	< LOD	< LOD	< LOD	< LOD
trans chlordane	< LOD	0.475	1.399	0.064	2.929	< LOD	< LOD	< LOD	< LOD
OTHER PESTICIDES									
Unit	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	µg.l^{-1}	NA	NA
ametryn	< LOD	< LOD	0.35	0.30	0.39	< LOD	< LOD	NA	NA
atrazine	< LOD	< LOD	13.50	0.04	< LOD	< LOD	< LOD	NA	NA

NO. SAMPLE	17	24	10	16	20	18	12	43 (14.6)	44 (4.3)
carbendazim	< LOD	0.03	0.20	0.64	32.50	0.03	< LOD	NA	NA
chlorpyrifos(ethyl)	< LOD	0.05	32.40	17.90	0.55	< LOD	< LOD	NA	NA
cypermethrin	< LOD	< LOD	0.65	887.00	43.30	< LOD	< LOD	NA	NA
deltametrin	< LOD	0.06	0.49	116.00	400.00	< LOD	< LOD	NA	NA
desmetryn	1.60	0.82	0.21	0.03	0.04	< LOD	< LOD	NA	NA
dichlormid	< LOD	< LOD	0.32	< LOD	< LOD	< LOD	< LOD	NA	NA
dimethoate	< LOD	< LOD	< LOD	0.10	< LOD	< LOD	< LOD	NA	NA
ethion	< LOD	< LOD	0.03	0.45	< LOD	< LOD	< LOD	NA	NA
imidacloprid	< LOD	< LOD	< LOD	0.92	< LOD	< LOD	< LOD	NA	NA
lambda-cyhalothrin	< LOD	< LOD	< LOD	73.70	19.50	< LOD	< LOD	NA	NA
lenacil	0.40	191.00	0.03	0.09	0.10	< LOD	< LOD	NA	NA
malathion	< LOD	< LOD	< LOD	0.03	< LOD	< LOD	< LOD	NA	NA
metalaxyl	< LOD	0.02	< LOD	152.00	7.20	0.06	< LOD	NA	NA
metribuzin	< LOD	< LOD	< LOD	0.19	0.20	< LOD	< LOD	NA	NA
oxadixyl	< LOD	< LOD	< LOD	19.40	1.10	< LOD	< LOD	NA	NA
penconazole	< LOD	< LOD	< LOD	4.80	< LOD	0.12	< LOD	NA	NA
pendimethalin	< LOD	< LOD	< LOD	264.00	3.60	< LOD	< LOD	NA	NA
permethrin	< LOD	< LOD	< LOD	41.90	6.60	< LOD	< LOD	NA	NA
phosalone	< LOD	1.50	917.00	804.00	9.70	< LOD	< LOD	NA	NA
phosmet	< LOD	< LOD	< LOD	1.50	43.30	93.00	< LOD	NA	NA
phoxim	< LOD	0.02	0.13	< LOD	< LOD	< LOD	< LOD	NA	NA
pirimiphos-ethyl	< LOD	< LOD	< LOD	0.10	< LOD	< LOD	< LOD	NA	NA
pirimiphos-methyl	< LOD	< LOD	< LOD	252.00	2.30	< LOD	< LOD	NA	NA
prometon	< LOD	< LOD	1.20	< LOD	0.09	< LOD	< LOD	NA	NA
prometryn	< LOD	5.10	1267.00	78.40	149.00	0.17	< LOD	NA	NA
propachlor	2.10	0.17	9700.00	20.50	0.15	0.05	< LOD	NA	NA
propargite	< LOD	< LOD	0.06	0.49	371.00	0.34	< LOD	NA	NA
propiconazole	< LOD	< LOD	< LOD	4.70	0.57	< LOD	< LOD	NA	NA

NO. SAMPLE	17	24	10	16	20	18	12	43 (14.6)	44 (4.3)
syridaben	< LOD	< LOD	< LOD	8.80	0.95	< LOD	< LOD	NA	NA
simazine	0.05	0.36	651.00	0.27	0.04	0.03	< LOD	NA	NA
simetryn	< LOD	< LOD	< LOD	< LOD	0.02	< LOD	< LOD	NA	NA
triadimefon	< LOD	0.37	0.65	253.00	79.80	0.22	< LOD	NA	NA
trichlorfon	< LOD	< LOD	< LOD	0.07	< LOD	< LOD	< LOD	NA	NA
PCDD/Fs, DIOXINLIKE PCBs									
Unit	**NA**	**NA**	**NA**	**ng.kg^{-1} d.m.**	**NA**	**NA**	**NA**	**NA**	**NA**
PCDD/F-PCB CALUX TEQ	NA	NA	NA	30	NA	NA	NA	NA	NA
HEAVY METALS									
Unit	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**mg.kg^{-1}**	**NA**
mercury	NA	NA	NA	NA	NA	NA	NA	0.001	NA
lead	NA	NA	NA	NA	NA	NA	NA	< LOD	NA
cadmium	NA	NA	NA	NA	NA	NA	NA	< LOD	NA
arsenic	NA	NA	NA	NA	NA	NA	NA	0.01	NA

ALAVERDI

NO. SAMPLE	23	32	30	13	4	6[1]	47 (12.5)	48 (12.6)	49 (15.5)
ORGANOCHLORINATED PESTICIDES									
Unit	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**	**µg.l^{-1}**	**µg.kg^{-1}**	**µg.kg^{-1} fat**	**µg.kg^{-1} fat**
o,p´- DDD	0.012	NA	NA	< LOD	< LOD	NA	NA	NA	NA
p,p´- DDD	0.009	NA	NA	< LOD	< LOD	NA	< LOD	27.0	21.3
p,p´- DDE	0.003	NA	NA	< LOD	< LOD	NA	6.4	100.8	166.5
o,p´- DDT	0.062	NA	NA	< LOD	< LOD	NA	< LOD	511.1	56.8
p,p´- DDT	0.161	NA	NA	< LOD	< LOD	NA	4.0	83.3	160.6
aldrin	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD

NO. SAMPLE	23	32	30	13	4	6[1]	47 (12.5)	48 (12.6)	49 (15.5)
dieldrin	0.002	NA	NA	< LOD	< LOD	NA	1.8	< LOD	< LOD
endosulfan sulphate	< LOD	NA	NA	< LOD	< LOD	NA	0.2	< LOD	< LOD
endosulfan α	< LOD	NA	NA	< LOD	< LOD	NA	0.2	< LOD	< LOD
endosulfan β	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD
endrin	< LOD	NA	NA	< LOD	< LOD	NA	5.2	< LOD	< LOD
HCH-alpha	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD
HCH-beta	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD
HCH-gamma (lindane)	< LOD	NA	NA	< LOD	< LOD	NA	5.9	15.1	17.4
heptachlor	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD
heptachlor-endo-epox	7.677	NA	NA	< LOD	< LOD	NA	2.7	< LOD	< LOD
heptachlor-exo-epox	< LOD	NA	NA	< LOD	< LOD	NA	1.2	< LOD	< LOD
hexachlorobenzene	< LOD	NA	NA	< LOD	< LOD	NA	1.3	2.4	1.9
oxychlordane	< LOD	NA	NA	< LOD	< LOD	NA	2.4	< LOD	< LOD
cis chlordane	< LOD	NA	NA	< LOD	< LOD	NA	0.5	< LOD	< LOD
trans chlordane	< LOD	NA	NA	< LOD	< LOD	NA	< LOD	< LOD	< LOD
PCDD/Fs, DIOXINLIKE PCBs									
Unit	**ng.kg^{-1} d.m.**	**ng.kg^{-1} d.m.**	**ng.kg^{-1} d.m.**	**ng.kg^{-1} d.m.**	**NA**	**NA**	**pg.g^{-1} f.w.**	**pg.g^{-1} fat**	**pg.g^{-1} fat**
PCDD/F-PCB CALUX TEQ	508.0	1120	18	9.5	NA	NA	0.67	11.9	7.3
HEAVY METALS									
Unit	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**mg.kg^{-1}**	**mg.kg^{-1}**	**mg.kg^{-1}**
mercury	NA	NA	NA	NA	NA	NA	0.06	0.001	0.002
lead	NA	NA	NA	NA	NA	NA	< LOD	< LOD	< LOD
cadmium	NA	NA	NA	NA	NA	NA	< LOD	< LOD	< LOD
arsenic	NA	NA	NA	NA	NA	NA	1.17	0.03	0.02

[1]This sample was analysed only on non-chlorinated pesticides, no detectable levels were found

4. DISCUSSION

4.1 Legal standards

The pollutant concentrations determined in the samples from all sites have to be compared to maximum allowed concentrations of these pollutants as defined in various national and international decrees and laws. Armenian, Czech and German standards (Table 4) were used to discuss the pesticide and PCDD/Fs levels found in soils. No POP and pesticide maximum level are defined for soil in the EU legal standards. Armenian, Czech and EU standards (Table 5) were used to discuss the findings in water samples and Armenian and EU standards to discuss pollutant levels in food (Table 6).

TABLE 4 LIMIT CONCENTRATION VALUES FOR ORGANOCHLORINATED AND OTHER PESTICIDES AND PCDD/Fs IN VARIOUS TYPES OF SOILS EXPRESSED IN mg.kg^{-1} DRY WEIGHT.

	agricultural soils				residential	industrial + commercial	all soils except agricultural soils			
	Armenian MPL[1]	Czech risk based MAC[3]	Czech MAC[4]	Czech preventive value[5]	Germany	Germany	Czech criterion A[2]	Czech criterion B[2]	Czech criterion C-residential[2]	Czech criterion C-industrial[2]
OCPs individual			0.01				0.05	2	2.5	10
OCPs sum			0.1							
Other pesticides indiv.			0.01				0.05	3	4	12
Other pesticides sum			0.1							
HCH	0.1									
α, β, γ-HCH individual		1								
α, β, γ-HCH sum				0.01						
HCH-mix or β-HCH					10[6]	400[6]				
DDE		10		0.025						
DDD		10		0.02						
hexachlorobenzene	0.03	1		0.02	8[6]					
endosulfan	0.1									
heptachlor	0.05									
atrazine	0.01									
permetryn	0.05									
simazine	0.2									
malathion	2.0									
methalaxyl	0.05									
aldrin					4[6]					
PCDD/Fs I-TEQ (ng.kg^{-1})	3[8]	100		0.001	1000[7]	10 000[7]	1	100	500	10 000

[1]Maximum permissible levels. Hygienic Requirements for Soil Quality: Sanitary Code and Guidelines N 2.1.7.003-10 (Appendix to the Order N 01-N of 25 January, 2010 of the RA Minister of Health)
[2]Soil, ground water and soil air pollution criteria according to the methodological guidelines of the Czech Ministry of Environment of 31 July 1996. This criteria are not legally binding, however, often applied in the Czech Republic on a voluntary basis. Criteria A approximately correspond to the natural concentration level of the chemical substance in the environment. The exceedance of criteria A is considered as a contamination of the particular environmental compartment except in areas with a naturally higher abundance of the chemical substance. If criteria B are not exceeded, the contamination is not considered sufficiently significant to justify the need for more detailed information on the contamination, e.g. to start an investigation or monitoring of the contamination. Criteria B are considered a contamination level that may have negative impacts on human health and individual environmental compartments. It is necessary to gather additional information to find out, whether the site represents a significant environmental burden and what risks it does pose. Criteria B are therefore designed as intervention levels which, when exceeded, justify the demand for further investigation on the contamination. The exceedance of criteria B requires a preliminary assessment of risks posed by the contamination, the identification of its source and reasons and according to the investigation results a decision on further investigation and start of a monitoring campaign. The exceedance of criteria C represents a contamination which may pose a significant risk to human health and environmental compartments. The risk level can be determined only by a risk analysis. The recommended levels of remediation target parameters resulting from the risk analysis can by higher than criteria C. In addition to the risk analysis, assessments of technical and economic aspects of the problem solution are necessary documents for the decision on the type of remedial measures.
[3]Maximum acceptable concentrations of pollutants in the arable or mould layer of agricultural soils determined according to risk levels. Proposal of the ammendatory act of decree 13/94 Sb. When exceeded, these MACs indicate a direct risk to humans and animals when present at the site. These criteria did not went into force up to now.
[4]Maximum acceptable concentrations of pollutants in agricultural soils according to decree 13/94 Sb. These are often exceeded also in the Czech Republic.
[5]Upper limit of natural or diffuse anthropogenic background. Criteria decisive for the protection of soil against risk inputs. Inputs should be monitored, a risk analysis is not necessary. Proposal of the ammendatory act of decree 13/94 Sb.
[6]Trigger values pursuant to § 8 paragraph 1 sentence 2 No. 1 Federal Soil Protection Law for the direct intake of pollutants at playgrounds, in residential areas, parks and recreational facilities, and industrial and commercial real properties.
[7]Action values pursuant to § 8 paragraph 1 sentence 2 No. 2 Federal Soil Protection Law for the direct intake of dioxins/furanes at playgrounds, in residential areas, parks and recreational facilities, and industrial and commercial real properties. In the event of dioxin-containing lye-residues from copper slate, the action values shall, due to the low resorption in the human organism, be applied not directly to protect human health but rather to ward off danger for a long time.
[8]not expressed as TEQ, units are ng.kg^{-1}

TABLE 5 LIMIT CONCENTRATION VALUES FOR DDT AND IT´S METABOLITES IN VARIOUS TYPES OF WATER EXPRESSED IN $\mu g.l^{-1}$.

	drinking water		ground water			surface water
	Armenian MPL[1]	EU[3]	Czech criterion A[2]	Czech criterion B[2]	Czech criterion C[2]	EU[4] AA
Individual OCPs[5]			0.01	0.1	0.2	
Pesticides individual[6]		0.1				
Pesticides sum		0.5				
DDT	2					
p,p´-DDT						0.01
DDT total[7]						0.025

[1]Order No 876 on Approval of No 2-III-A2-1 Sanitary Code and Regulations on"Drinking Water": Hygienic Requirements for Water Quality of the Centralized Water Supply Systems: Quality Control" (25 December, 2002, c. Yerevan).
[2]Soil, ground water and soil air pollution criteria according to the methodological guidelines of the Czech Ministry of Environment of 31 July 1996. This criteria are not legally binding, however, often applied in the Czech Republic on a voluntary basis. Criteria A approximately correspond to the natural concentration level of the chemical substance in the environment. The exceedance of criteria A is considered as a contamination of the particular environmental compartment except in areas with a naturally higher abundance of the chemical substance. If criteria B are not exceeded, the contamination is not considered sufficiently significant to justify the need for more detailed information on the contamination, e.g. to start an investigation or monitoring of the contamination. Criteria B are considered a contamination level that may have negative impacts on human health and individual environmental compartments. It is necessary to gather additional information to find out, whether the site represents a significant environmental burden and what risks it does pose. Criteria B are therefore designed as intervention levels which, when exceeded, justify the demand for further investigation on the contamination. The exceedance of criteria B requires a preliminary assessment of risks posed by the contamination, the identification of its source and reasons and according to the investigation results a decision on further investigation and start of a monitoring campaign. The exceedance of criteria C represents a contamination which may pose a significant risk to human health and environmental compartments. The risk level can be determined only by a risk analysis. The recommended levels of remediation target parameters resulting from the risk analysis can by higher than criteria C. In addition to the risk analysis, assessments of technical and economic aspects of the problem solution are necessary documents for the decision on the type of remedial measures.
[3]EU drinking water directive 98/83/EC of 3 November 1998
[4]Annual average. Directive 2008/105/EC of the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. The AA values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.
[5]except methoxychlor
[6]except aldrin, dieldrin, heptachlor and heptachlorepoxid
[7]sum of p,p´-DDT; o,p-DDT; p,p´-DDE; p,p´-DDD

TABLE 6 LIMIT CONCENTRATION VALUES FOR ORGANOCHLORINATED AND OTHER PESTICIDES AND PCDD/Fs IN VARIOUS TYPES OF FOOD.

	Chicken eggs			Cow milk and cream			Trout	
	Armenian MPL[1]	EU MRL[2]	EU ML[3]	Armenian MPL[1]	EU MRL[2]	EU ML[3]	Armenian MPL[1]	EU ML[3]
Unit	$mg.kg^{-1}$	$\mu g.kg^{-1}$ fat	$pg.g^{-1}$ fat	$mg.kg^{-1}$	$mg.kg^{-1}$	$pg.g^{-1}$ fat	$mg.kg^{-1}$	
DDT[4]	0.1			0.05			0.3	
DDT total[5]		500			0.04			
HCHs[6]	0.1			0.05			0.03	
HCH – gamma (lindane)		100			0.001			
HCB		200			0.01			
endrin		50			0.0008			
endosulfan[7]		500			0.05			
heptachlor[8]		200			0.004			
PCDD/Fs	0.000003			0.000003			0.000004	
WHO-PCDD/Fs TEQ			3.0			3.0		4.0 pg g^{-1} f.w.
WHO-PCDD/Fs-PCB TEQ			6.0			6.0		8.0 pg g^{-1} f.w.
mercury								0.50 $mg.kg^{-1}$

[1]Hygienic Requirements for Food Raw Material and Food Value: Hygienic Guidelines N 2-III-4.9-01-2010 (approved by the Order N 06N of 10.03.2010 of the RA Minister of Health.
[2]Regulation (EC) N°149/2008. Maximum residue level (MRL) means the upper legal level of a concentration for a pesticide residue in or on food or feed set in accordance with the Regulation, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers.
[3]Regulation (EC) N°1881/2006. TEQ value calculated by including the non-quantified congeners by taking their full value of LOQ. Foodstuffs containing a contaminant at a level exceeding the maximum level (ML) should not be placed on the market.
[4]sum of DDT, DDE and DDD
[5]sum of p,p´-DDT, o,p´-DDT, p,p´-DDE and p,p´-DDD
[6]sum of HCH-alpha, HCH-beta, HCH-gamma and HCH-delta
[7]sum of alpha- and beta-isomers and endosulfan-sulphate
[8]sum of heptachlor and heptachlor epoxide

The content of POPs in samples of solid matrices was also compared to the provisional low POPs content for wastes defined under the Basel Convention on the control of transboundary movements of hazardous wastes and their disposal: 50 $mg.kg^{-1}$ for aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene and 15 µg TEQ PCDD/Fs kg^{-1}. According to the Convention, wastes consisting of, containing or contaminated with POPs above the low POP content should be

disposed of in such a way that the POP content is destroyed or irreversibly transformed or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option (BC, 2008).

4.2 Background POP levels

POP levels determined in passively taken air samples cannot be compared directly to legal standards as they are expressed in not comparable units (ng disc^{-1} instead of ng m^{-3}). The best way is to use passive air sampling results from other sites for comparison. Table 7 lists POP levels measured in air at the central European background site Košetice, Czech Republic (Genasis, 2011). Košetice is located in a moderately warm and moderately humid upland zone with a mean annual temperature of 7° C, an annual total precipitation of 621 mm and 1800 hours of sunshine per year. POP levels found in Košetice are higher than at background stations in northern Europe, thus reflecting the high density of urban areas, agriculture and industry in the Czech Republic and central Europe (Holoubek et al., 2007).

TABLE 7 POP LEVELS DETERMINED IN PASSIVE AIR SAMPLES IN KOŠETICE, CZECH REPUBLIC (ng.m^{-3}).
The values are medians of samples taken in the period 2005-2009. The samplers were exposed to air during standard sampling intervals of 28 days.

Pollutant	Median level	Pollutant	Median level
o,p´- DDD	0.10	HCH-alpha	2.83
p,p´- DDD	0.32	HCH-beta	0.53
o,p´- DDE	0.10	HCH-gamma (lindane)	4.91
p,p´- DDE	5.91	HCH-delta	0.10
o,p´- DDT	0.10	Hexachlorobenzene	13.98
p,p´- DDT	0.60	Pentachlorobenzene	2.30

Eggs from free-range hens often exhibit a higher level of POP contamination compared to eggs from poultry farms. It was postulated that environmental pollution is the origin of the higher contamination of eggs from private owners (van Overmeire et al., 2006).

Therefore, levels of DDX in eggs from poultry farms are listed in Table 8 to give a clue on „background" levels. For a further discussion about various levels of DDX in chicken eggs please see IPEN (2009).

TABLE 8 MEAN CONCENTRATIONS OF DDX IN CHICKEN EGGS AT TWO POULTRY FARMS (µg.kg^{-1} FAT)

Site	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	o,p´-DDT	p,p´-DDT	DDT total[3]
Osaka, Japan[1]	NA	69	NA	ND	ND	37	106
Beijing, China[2]	0.17	15.0	0.67	8.97	0.75	4.97	29.7

NA – not analysed
ND – not detected
[1]Furusawa and Morita, 2000; only egg yolk considered
[2]Tao et al., 2009
[3]sum of p,p´-DDT, o,p´-DDT, p,p´-DDE and p,p´-DDD

4.3 Nubarashen

The highest concentrations of pesticides among the samples taken at the Nubarashen burial site were observed in sample 33 taken in the left ditch just behind the fence (0-10 m). The highest concentration was observed for p,p´-DDT (864 mg.kg^{-1}), which exceeds the Armenian soil MPLs for this substance by almost 9000 times. The Czech criterion C for industrial soils as well as the proposed Czech risk based MACs was exceeded by almost 90 times for p,p´-DDT and up to 20 times by the content of other DDX in the sample. This sample also contains high concentrations of HCHs which exceed the Armenian soil MPLs for these substances by 100–1000 times. The Czech criterion C for industrial soils is exceeded by the content of HCHs in this sample up to 10 times and the proposed Czech risk based MACs up to 100 times. This sample exhibited also significant concentrations of other pesticides, e.g. endosulfan, atrazine, malathion and simazine, where the concentration of the last one exhibited the Armenian MPLs by about 1500 times and the Czech criterion C for industrial soils by 26 times. The concentration of the pesticide 2,4-D exceeded the Czech MAC for agricultural soils by 230 times and is close to the Czech criterion B.

Sample 33 was characterized also by a high content of PCDD/Fs and dioxin-like PCBs. The PCDD/Fs-PCB CALUX TEQ (6642 ng.kg^{-1}) significantly differs from the WHO-PCDD/Fs TEQ (2680 ng.kg^{-1}), I-TEQ (NATO/CMSS) (2280 ng.kg^{-1}) and WHO-PCB TEQ (3.19–3.48 ng.kg^{-1}). The reason could be an insufficient homogenization of the sample which was characterized by the occurrence of white grains of pure chemicals and a strong, eye-irritating smell. The I-TEQ (NATO/CMSS) is well above the Czech criterion C and German legal standards for residential areas. The proposed Czech risk based MAC for PCDD/Fs is exceeded by 20 times in this sample. The high levels of PCDD/Fs in this sample could be at least partially explained by dioxin impurities in various pesticides. Masunaga et al. (2001) found significant PCDD/Fs impurities in pentachlorophenol dominated by OctaCDD and 1,2,3,4,6,7,8,9-HeptaCDD. This dioxin pattern was also found in sample 33 and although pentachlorophenol was not analysed in the sample, it was reported to be buried at Nubarashen in significant amounts (8,7 t; Helps, 2010). PCDD/Fs impurities can be also found at varying levels in pesticides based on chlorinated phenoxyacids, e.g. 2,4-D (Kluyev, 1996), whose concentration in sample 33 exceeded the Czech MAC for agricultural soils by 230 times and is close to the Czech criterion B.

Up to 55 m from the fence (sample 1A+1B), the ditch is still characterised by high p,p´-DDT levels (33 mg.kg^{-1}) exceeding all the above mentioned legal standards by far and also the content of other OCPs is significant. The concentration of simazine exceeds the Armenian MPLs about 270 times. The DDT content in this sample is also well above the provisional low POPs content for wastes as defined under the Basel Convention. Samples taken elsewhere in the close surroundings of the burial site (i.e. not in the left ditch, samples no. 19, 34 and 3A, 3B) behind the fence up to 60 m distance exhibit concentrations of DDX (dominated by p,p´-DDT) up to hundreds of mg.kg^{-1} which almost always exceed the Armenian soil MPLs but not the Czech criterion B or risk based MACs. Out of these samples, only sample 34 was characterized by a significant level of simazine (exceeding the Armenian MPL by 2.5 times), other non-chlorinated pesticides were not detected in these samples.

The air contamination is decreasing by distance from the burial site. The DDX and HCHs levels determined at the fence of the site (sample PAS-C) are 100 and 300 times higher, respectively, than long-term central European background levels. At a distance of 250 m (sample PAS-D), these are still exceeded by 17 and 60 times for DDX and HCHs, respectively. Passive air samples (PAS-A and PAS-B) taken farther in the village of Mushavan exhibit much lower OCPs levels, which are however still significantly higher than the central European background. Unfortunately, Armenian air POP background levels for better comparison were not available when finishing this report.

DDX and HCHs levels in both pooled egg samples taken from free-ranging hens in 1.5-2 km distance from the burial site were below Armenian and EU legals standards, however, they were 2-8 times higher than background DDX levels (Table 8). PCDD/F-PCB CALUX TEQ levels exceeded EU MLs expressed as WHO-PCDD/Fs-PCB TEQ more than 6 times, however, the source of this contamination is not easy to interpret. Both households may burn their waste in the yards, where chicken may have access to. Therefore, the burial site cannot be suspected as the only major source for the dioxin contamination of the eggs. OCP levels determined in cow milk and cream samples did not exceed Armenian and EU legal standards.

4.4 Jrarat

The samples taken from the floor inside the big preserved storage room (No. 29, 31, 25 and 35) are characterised by elevated levels of POPs, which do not exceed the provisional low POP content for waste but do exceed the Czech criterion C for industrial soils by two times (in the case of DDT and heptachlor) in sample 25 taken in the surroundings of plastic barrels with supposedly re-packed POPs (information provided by the owner of the site). Sample No. 29 taken along the front wall is characterised by a high concentration of aldrin (12 mg.kg^{-1}).

The central room in the demolished small storage building exhibits elevated concentrations of DDT (22 mg.kg^{-1}) and its metabolites (up to 7 mg.kg^{-1}) as well as endosulfan α (3.5 mg.kg^{-1}) and heptachlor (6 mg.kg^{-1}) (sample 14). The provisional low POP content for waste is not exceeded, however the Czech criterion C for industrial soils is exceeded by two times in the case of DDT. The situation is extremely serious in the last room in this demolished building (sample No. 15). Extremely high concentrations of DDT and its metabolites of up to tens of g.kg^{-1} were detected here on the floor together with concentrations in the order of tens and hundreds of mg.kg^{-1} of other OCPs. This room is also heavily contaminated by simazine (4640 mg.kg^{-1}).

The soil between the two demolished buildings is heavily contaminated by OCPs. The concentration of DDT exceeds the provisional low POP content by 5 times and concentrations of other OCPs exceed the Czech criterion C for industrial soils, too. The sediment in the fish pond 50 m far from the demolished buildings is characterised by elevated levels of DDT, its metabolites and heptachlor endo epoxide (hundreds of mg kg^{-1}), however, this sample was a point sample and thus cannot be considered representative. Water (sample No. 9) flowing into the fish pond exhibited DDX concentrations exceeding the EU AA standards for surface water many times. The water supplying the concrete fish ponds 250 m far from the storage buildings did not contain any detectable pesticide concentrations.

The extremely high DDT levels found in the demolished building are reflected in the high contamination of air in the very close surroundings (sample PAS-G, 600 times higher DDX concentrations compared to European background levels). Also air sampled 200–250 m far from the storage rooms (samples PAS-E and PAS-F) exhibit high DDT concentration, although they are an order of magnitude lower than in sample PAS-G. Also pooled egg samples taken from hens freely roaming in 80–100 m distance from the storehouses (without direct access to the storehouse) exhibit DDX levels which exceed EU MRLs up to 2 times and are close to or slightly exceed Armenian MPLs.

4.5 Echmiadzin

Samples of scratch-offs (No. 21A, 21B and 22) taken at the floors of the storage rooms exhibited significant levels of OCPs (DDT and its metabolites, endosulfanes, HCHs, heptachlor, chlordane) and other pesticides (carbendazim, cypermethrin, dimethoat, lenacil, methalaxyl, phosalon, simazine, triadimefon and a few more). The floor in room 1 can pose a significant risk to the health of people entering the room due to p,p´-DDT and lindane concentrations which are close to the proposed Czech risk based MACs for soils. The PCDD/Fs-PCB TEQs (869 ng PCDD/Fs-PCB TEQs kg^{-1}) exceeds the Czech criterion C for residential soils by 1.7 times and the proposed Czech risk based MAC for soils by almost 9 times.

While the POP levels in the scratch-offs in room 1 did not exceed the provisional low POPs content for wastes, the situation is even more serious in room 2. Here, concentrations up to hundreds of mg.kg^{-1} were detected for p,p´-DDE and o,p-DDT (192 and 346 mg.kg^{-1}, respectively). The concentration of p,p´-DDT (46 mg.kg^{-1}) is very close to the low POP content level for waste. The concentrations of aldrin (150 mg.kg^{-1}) and trans-chlordane (109 mg.kg^{-1}) exceeds this standard by 3 and 2 times, respectively. High concentrations of cypermethrin and phosalone (1367 and 378 mg.kg^{-1}, respectively) were found in the scratch-offs from the floor in room 2, too.

The soil sample (No. 26) taken from the vegetable bed right next to the storage rooms exhibited a concentration of p,p´-DDT (0.22 mg.kg^{-1}) exceeding the Armenian soil MPL by 2 times and the Czech MAC for agricultural soil by 22 times. This legal standard is also slightly exceeded by some DDT metabolites, α-HCH and lindane. However, the Czech MACs are known to be often exceeded also in the Czech Republic, too. The most prevalent pesticide found in the sample was cypermethrin (0.54 mg.kg^{-1}). This sample is characterized by a level of contamination that demands a prevention of further pollutant inputs (according to the Czech preventive values).

The water sampled (sample No. 11) from a fish pond cca 50 m far from the storage building exhibited no detectable pesticide concentrations, however, groundwater taken from a tap (sample No. 8) exhibited slightly elevated concentrations of p,p´-DDT and o,p-DDT, which did not exceed the Armenian MPL for water but did exceed the EU drinking water standards up to 4 times. It is not clear, whether the groundwater becomes polluted by DDT already in the soil or when pumped through the bore which may be constructed out of polluted material. The fish pond sediment (sample No. 28) exhibited slightly elevated levels of p,p´-DDT (0.224 mg.kg^{-1}).

Pooled egg samples (No. 45 and 46) taken from hens freely roaming in 10 – 50 m distance from the storage rooms exhibited very similar POP concentrations. DDX levels heavily exceed the EU MRLs (11 times) and slightly exceed Armenian MPLs. PCDD/F-PCB CALUX TEQ levels exceeded EU MLs expressed as WHO-PCDD/Fs-PCB TEQ about 4 times. According to the information given by the chicken owners, the animals cannot enter the storage rooms. Therefore, another source of the high contamination found in the eggs has to be investigated. A possibility could be the depositing of dust swept out of the storage room in the nearby area, where chicken do freely roam. However, this hypothesis was not confirmed by the owners.

4.6 Masis

Three samples were taken from inside the biggest storage room. The scratch-offs and sweepings sample taken from the whole floor (sample No. 10) exhibits high levels of of DDT (10 mg.kg^{-1}) and its metabolites and heptachlor. Further, this sample is heavily contaminated by propachlor, prometryn, phosalone and simazine (9700, 1267, 917 and 651 mg.kg^{-1}, respectively). Sample 24 was taken in the close vicinity of a destroyed plastic barrel containing pink powder and is dominted by α-HCH (3080 mg.kg^{-1}) and concentrations of β-HCH and lindane lower by one order. Significant concentrations of lenacil (191 mg.kg^{-1}) were detected, too. The character of sample 24 is reflected in sample 17 (plaster from around the drum) by hundreds of mg.kg^{-1} of the respective pesticides detected. The Czech criterion C for industrial soils as well as the proposed Czech risk based MAC is heavily exceeded in this room especially by HCHs which (when applying the preliminary the low POPs content for waste also on HCH concentrations) poses a demand for appropriate clean-up measures.

The floors in the two smaller storage rooms are less contaminated than in the bigger room. However, the floor in the central room (sample 16) exhibits DDX levels of hundreds of mg.kg^{-1} and levels of non-chlorinated pesticides exceeding the Czech criterion C for industrial soils by about 70 times in the case of cypermethrin and phosalone and by 20 times and less for several other pesticides. The scratch-offs taken from the floor in the last small storage room (sample 20) can be considered POP contaminated waste (the preliminary low POPs content for waste is exceeded up to 2 times by aldrin and heptachlor and approached by the content of dieldrin an DDT). High concentratios of deltametrin, propargite and prometryn (400, 371 and 149 mg.kg^{-1}, respectively) were found here, too.

The contamination in the storage rooms seems to spread out of them. Tens and hundreds of mg.kg^{-1} of DDX were detected in soil along the outer walls (exceeding the Armenian MPL for soils two times in the case of DDT) and in groundwater taken from a tap cca 100 m far from the storage rooms (DDT levels not exceeding the Armenian MPL for water but exceeding the EU drinking water standards by two times). It is not clear, whether the groundwater becomes polluted already in the soil or when pumped through the bore which may be constructed out of polluted material. A pooled egg sample taken 300 m far from the storage house exhibited POP levels under Armenian and EU legal standards, however, DDX levels were 3-12 times elevated compared to background concentrations (Table 8). A milk sample from one cow grazing 300 m far from the storehouse did contain OCPs levels well under Armenian and EU legal standards.

4.7 Alaverdi

Detectable levels of DDT and its metabolites and especially heptachlor-endo-epoxide were found in the sediment from production waste in the middle of the concrete enclosure (sample No. 23). The concentration of heptachlor-endo-epoxide exceeds the Czech criterion B by almost three times and the proposed Czech preventive value for DDT is exceeded by 5 times. High PCDD/Fs-PCB TEQs were found in samples 23 and 32 (508 and 1120 ng.kg^{-1}, respectively), both of them taken in the middle concrete enclosure. These – when compared to the legal standards expressed in PCDD/Fs I-TEQ – exceed the Czech risk based MAC and also criterion B by 5 and 10 times, however, they are well under the Czech criterion C for industrial sites. Levels of PCDD/Fs-PCB TEQs well above the Czech criterion A and the proposed Czech preventive values (when compared to these standards expressed in PCDD/Fs I-TEQ) were found in front of the concrete enclosures (samples No. 30 and 13). The determined PCDD/Fs-PCB TEQ could not be compared to Armenian legal standards as these are not expressed as TEQs. No detectable levels of non-chlorinated pesticides were detected in the water and sediment samples (No. 6 and 4) taken in the brook cca 600 m down the hill from the dumpsite. These samples were not analysed on the content of OCPs and PCDD/Fs.

DDX and HCHs levels in a pooled egg sample taken from Kobayr village (30 km from Alaverdi) did not exceed Armenian and EU legal standards, while DDX levels in a pooled egg sample taken from Alaverdi suburbs were close to Armenian MPLs and slightly exceeded EU MPLs. The eggs were layed by freely roaming hens fed by bought feeding as well as food remainings. As there is no other relevant information available, it is not possible to speculate on the sources of POPs in eggs from the Alaverdi suburbs as these weren´t taken in the close surroundings of POP hot-spots. PCDD/F-PCB CALUX TEQ levels exceeded EU MLs expressed as WHO-PCDD/Fs-PCB TEQ. A meat sample out of one trout taken from a pond near the mercury burial site in Alaverdi did not exhibit PCDD/Fs and mercury levels that would suggest concern.

5. CONCLUSION

5.1 Sampling sites

The following conclusions can be made on the contamination levels found at the sampling sites:

Nubarashen: immediately behind the fence down the slope in the left ditch (which seems to receive the majority of rain- and meltwater from the drainage) the soil has been found to be heavily contaminated by DDT, HCHs, some non-chlorinated pesticides and PCDD/Fs. The high levels of PCDD/Fs can be at least partially explained by buried pesticides containing PCDD/Fs impurities. The overall contamination is still significant in this ditch 55 m far from the fence. The levels found suggest an urgent need for a risk analysis as they may pose a risk to human health and animals when present in this area. Elsewhere down the slope up to 60 m distance from the fence, elevated levels of DDX (dominated by p,p´-DDT) were found in soils which are close to the Armenian MPLs. It can be concluded that the major contamination was found in the left ditch suggesting outwash of the pesticides from the burial site by rain- and meltwater. Significant contamination was found also in soils outside the left ditch. The dominant OCPs were DDX and HCHs, while the non-chlorinated pesticides were dominated by simazine. The contamination is decreasing by distance from the fence, however, some OCPs are present in concentrations above Armenian soil MPLs also in the distance up to 60 m from the fence.

All the soil and sediment samples taken at Nubarashen were mixed surface samples such that a spatial horizontal distribution of the pesticides could be determined down the slope of the burial site. However, information on the vertical distribution of pollutants is of crucial importance also due to the unpredictable character of the possible contamination of the environment around Nubarashen burial site (Tadevosyan, 2010). The vertical distribution was studied by Honzajková and Šír (2010), who found DDX levels in the order of hundreds $mg.kg^{-1}$ up to 1,5 m depth immediately behind the fence down the slope in the left ditch.

The very high air contamination determined at the fence of the burial site is significantly decreasing by distance, however, OCPs concentrations are still significantly elevated up to 2 km distance from the site. Although the level of PCDD/Fs and dioxin-like PCB toxicity found in eggs sampled in Mushavan cannot be directly compared to legal standards, the high levels of TEQ suggest that these eggs are not suitable for consumption. However, the source of these PCDD/Fs levels does not necessarily have to be the burial site, e.g. burning of household waste or biomass can contribute significantly, too.

Jrarat: The floor in the preserved big storage room in this area exhibits levels of OCPs which may pose a risk to human health. The situation is extremely serious in the small demolished storage building cca 100 m far which is characterised by an extremely strong smell due to the inappropriate storage of methyl mercaptophos (information provided by the owner) and numerous destroyed bags full of pesticides. Although not sampled, the situation is suspected to be similarly serious in the second (bigger) demolished building right next to it which was observed to contain dozens of destroyed bags probably containing pesticides, too. The soil between these two demolished buildings is heavily contaminated by DDX as well as other OCPs and can be considered POPs waste demanding appropriate clean-up measures.

The contamination from the demolished buildings seems to spread also to the nearby muddy fish pond. The water supplying the concrete fish ponds 250 m far from the storage buildings did not contain any detectable pesticide concentrations and thus is probably suitable for commercial fish breeding. Also, a pooled meat sample out of two commercially bred trouts did not exhibit pollutant levels that would suggest concern. However, the spread of OCPs by air to the wider surroundings is reflected in the concentration gradient determined by passive air sampling and elevated DDX levels in eggs from hens freely roaming behind the wall surrounding the storage site.

Echmiadzin: The floors of both storage rooms exhibited a significant contamination by OCPs and several other pesticides. The situation is serious especially in room 2, where the scratch-offs can be considered POPs waste demanding appropriate clean-up measures. The lower contamination in room 1 could be caused by sweeping of the floor by the inhabitants before the sampling. Still, when entered, the floor contamination in this room may pose a significant risk to human health especially due to a high PCDD/Fs-PCB TEQ.

The contamination from both storage rooms seems to spread out of the storage building. There are doubts, whether the soil from the vegetable bed right next to this building is suitable for agricultural practice. The fish pond area cca 50 m far from the storage building is characterized by slightly elevated levels of DDT. Eggs taken from hens freely roaming in close surroundings of the storehouse exhibited extremely high DDX concentrations, although the owners deny a direct contact of the hens with the POPs waste inside the storehouse. The consumption of these eggs is suspected to pose a significant health risk also due to high levels of PCDD/Fs and dioxin-like PCB toxicity.

Masis: The biggest storage room may pose a risk to human health when entered and contains waste heavily contaminated by HCHs and other pesticides. The floor in the central small storage room is heavily contaminated by other pesticides (non-OCPs) and the scratch-offs from the last small storage rooms can be considered POPs contaminated waste indicating a demand for appropriate clean-up measures. The contamination in the storage rooms seems to spread out of them (elevated levels of DDX were detected in soil along the outer walls and in groundwater taken from a tap cca 100 m far from the storage rooms).

Alaverdi: the production waste sediment in the middle concrete enclosure exhibited levels of concentrations of some OCPs demanding a prevention from further input of these substances to the site and a possible preliminary risk analysis. Inside the enclosure, PCDD/Fs-PCB TEQs suggesting a risk to humans and animals and the need for a preliminary risk analysis were detected. Outside of the enclosure, PCDD/Fs-PCB TEQs levels suggesting a prevention of further PCDD/Fs inputs were found. The elevated POPs levels found in egg samples remain to be interpreted.

5.2 Limitations of the study

The major limitations of the study are the limited financial, temporal and personal resources. Therefore, only a first estimation on the pollution level and character at the visited sites based on a not sufficient number of samples could be derived. A first impression of the situation including potentially threatened persons and environmental compartments was obtained, however, future investigations in this field are needed, too. The here presented results cannot be considered exhausting, rather supporting the need for an extended investigation in future. Still, heavy contamination was found at some investigated spots and immediate action at these spots is therefore justified also without additional sampling.

The comparison of pollutant concentration levels found in the samples with legal standards has also its limitations. Each of the legal standard is defined in a different way and for a different purpose. In addition, there do not exist legal standards for some of the pollutants and matrices sampled. The estimation of a potential risk to humans and the environment cannot be conducted by consulting legal standards only, an extensive risk analysis based on a sufficient number of samples and exhausting description of the state of the area and the potential risk receivers is crucial.

5.3 Suggestions for future actions

A future extensive sampling campaign should be conducted at the here discussed sites including parts of these sites that could not be sampled in July 2010 (e.g. the surroundings of the railroad and the totally demolished building in Jrarat). A hydrological and geological survey should be conducted at the sites, too, such that a risk analysis can be conducted. The risk analysis should characterise and quantify the risks posed to

humans and the environment by the pollution at the sites and further specify areas for decontamination and define the extent of decontamination.The lifetime exposure, and where appropriate the acute exposure of consumers to pesticide residues via food products, especially eggs in Echmiadzin, Jrarat and Nubarashen, should be evaluated. High dioxin levels found in eggs sampled close to the Nubarashen burial site are not easy to interpret, however, the hen breeders should be informed about the findings and various possible dioxin sources, not only from the burial site, but especially from domestic activities (burning of waste etc). Alternatives for the consumption of these eggs should be discussed.

Although the results of the here presented study have to be considered preliminary and no risk analysis was conducted up to now, the author of this study is convinced of the necessity to take immediate action by implementing at least simple measures to prevent people entering some of the visited sites and to stop the spread of pollution to their surroundings. This applies especially for the demolished buildings in Jrarat, where a significant spread of POPs to its wider surroundings was demonstrated by gradient sampling in different environmental matrices. Further, room 2 in the storage building in Echmiadzin, the biggest storage room in Masis and the immediate surroundings of the Nubarashen burial site need to be secured. Where people have to enter these and the other sites and rooms, they should be consequently reminded to wear personal protection equipment. The POPs found in the destroyed buildings in Jrarat should be repacked and removed as soon as possible. These recommendations are justified by the partly very high POP contamination found at some spots of the investigated sites.

ACKNOWLEDGEMENTS

The field survey and sampling was conducted as a part of the project „Scaling Up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia“ financed by European Union, Czech Development Agency, IPEN and other donors, and could not happen without the kind support of the storage site owners and the Aarhus Convention Centre in Alaverdi, Armenia. Indispensable assistance on-site was also given by the colleagues from AWHHE and Karine Yesayan from the Armenian Ministry of Agriculture.

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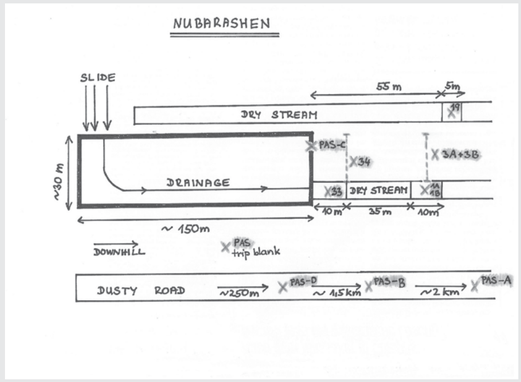
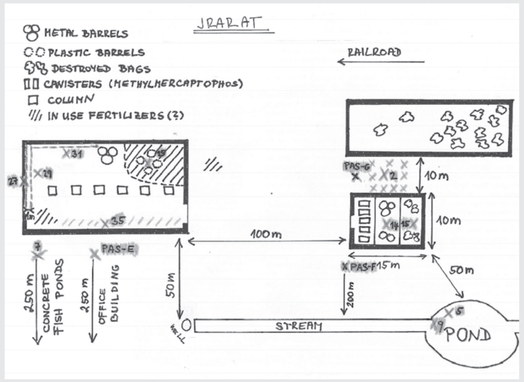
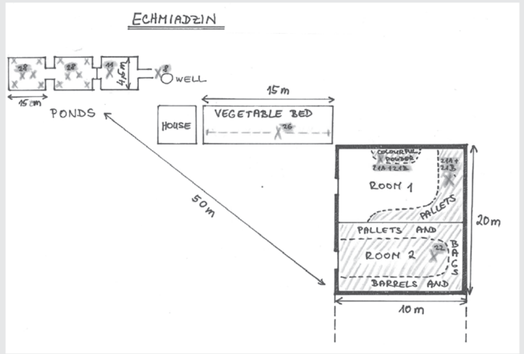
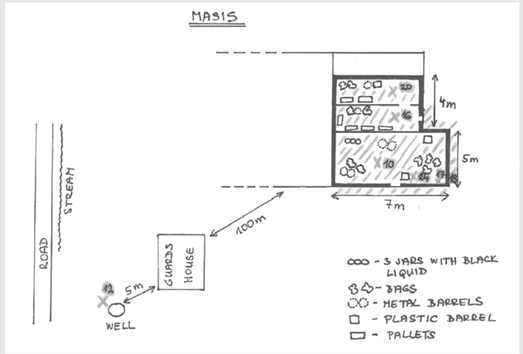
ANNEX A. SAMPLING PLANS

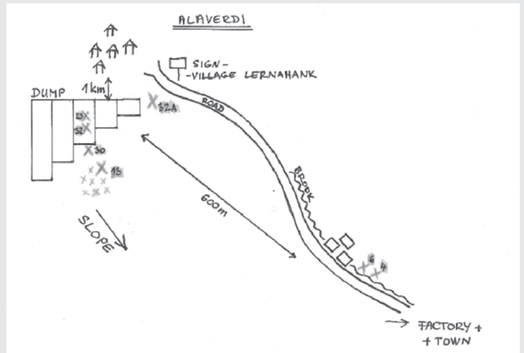
The sampling plans were drawn by Alice Dvorská according to drawings taken at the sites by her, Jindřich Petrlík and Zora Kasiková. The sites of biota sampling are not depicted in the plans, for details see Table 2.











ANNEX B. PHOTOGRAPHS OF SAMPLING SITES

The photographs were taken by Ondřej Petrlík and Jindřich Petrlík.

Nubarashen

The landslide is visible on the slope behind the fenced area.

Yerevan suburbs can be seen on the horizon when looking from the pesticide burial ground.

Sample No. 33 was taken in the ditch next to the fence.

Sample No. 33 contained grains of pure chemicals.

Jrarat

Big quite well preserved storage building used for the storage of currently used fertilisers and not specified „biopreparates" (information provided by the owner).

Sampling in the big storage room.

Central room of small demolished building where sample No. 14 was taken.

Room of small demolished building where sample No. 15 was taken.

Demolished building (look from the „inside"), where numerous bags probably containing pesticides were found. No samples were taken here.

Echmiadzin

View of the area of the family farm. The residential house and vegetable beds are right next to the storage rooms.

Storage room 2 where sample No. 22 was taken.

Storage room 1 where sample No. 21A, 21B was taken.

Masis

View of the commercially used facility. The pesticide storage rooms are located at the end of the hall.

Small central storage room where sample No. 16 was taken.

Big storage room with destroyed roof where samples No. 10, 24 and 17 were taken.

Taking of sample No. 24.

Alaverdi

View of the valley where the Alaverdi mining and metallurgical plant is situated.

Concrete enclosures containing copper production waste at the dumpsite close to the village Lernahank.

final report

PESTICIDE MONITORING IN ARMENIA

visit of the surroundings of Yerevan, Echmiadzin and Alaverdi, July 22–28, 2010

Ing. Zuzana Honzajková, Ing. Marek Šír

Institute of Chemical Technology in Prague, November 2010

CONTENTS

INTRODUCTION

In cooperation with the Czech non-profit organisation Arnika, we visited Armenia in July 2010. The purpose of our visit was monitoring of pesticide contamination in selected localities. In Armenia, the mission was prepared and organised by a local non-governmental organisation Armenian Woman for Health & Healthy Environment (AWHHE).

Our team visited in total four localities where pesticides were present. These localities were, in particular, storages serving for pesticide distribution and storing in the past. The localities included one dumping site of pesticide residues and wastes contaminated by pesticides, which is partially secured at present. Further, we visited a disposal site of wastes from a metallurgical plant processing copper ore.

The present report comprises detailed description of the visited localities and taken samples. Preliminary conclusions concerning the nature of contamination and possible risks ensuing from it are presented for each of the localities. An annex to the report states results of analyses of all the taken samples, and comparison with pollution criteria.

METHODOLOGY OF SAMPLING AND SAMPLE ANALYSIS

Several samples were taken in each of the localities. Mostly, mixed samples were taken, formed by several partial samples taken in various places of the given locality. We always endeavoured to take a sample representing the given whole to the maximum possible level. Systematic sampling, including depth profiles, was carried out in one of the localities. The samples were taken by means of a shovel into plastic sample containers with screw lids. Soil samples were stored at room temperature, water samples were stored in a refrigerator in the dark. The number and description of the taken samples is stated below in the parts of the text concerning the individual localities.

Sample analysis were carried out in laboratories of the Institute of Chemical Technology in Prague. For the analysis, there was used an efficient method, verified in the long term, of extraction by hexane in ultrasound, and subsequent analysis of the extract by gas chromatography.

In the laboratory, sample homogenization was carried out at first. Subsequently, a representative part of the sample was taken for analysis, specifically, 2.5 g of the sample. The sample was placed, together with 10 ml of hexane, into an extraction bottle, and extracted in ultrasound water bath for the period of 20 minutes. Subsequently, the extract was analysed by means of a gas chromatograph with ECD detector. Results of analyses of all the samples are presented in tables in an annex in the end of this document.

VISITED LOCALITIES

Our aim was to monitor occurrence of pesticides in four localities in the vicinity of Yerevan. The localities were places contaminated by pesticides because of the former activities (dumping site, storages, sale places). Further, heavy metals contamination was monitored in the neighbourhood of the disposal site of waste from a metallurgical plant in the vicinity of the city Alaverdi.

Nubarashen

Sampling date: July 23, 2010, July 26, 2010

The dumping site is located ca 20 km from Yerevan, the capital of Armenia, cca 1 kilometre from the closest residential houses. It served for disposal of pesticide residues and wastes contaminated by pesticides. Unfortunately, the dumping site is located on a hill, and, thus, rainwater and leachate from the dumping site flow down in the direction of the close, lower situated, residential houses. At present, the dumping site is sealed and fenced, the territory under the dumping site is accessible, covered by grass and shrubs, marks of livestock grazing are visible there.

Samples taken

In this locality, the territory under the dumping site was sampled systematically. The places of sampling are depicted in Figure 1. There were taken 9 samples from the surface, and three samples from each of the three profiles parallel with the lower base of

the dumping site. During taking of surface samples (samples N1 - N9), soil overburden was removed at first. Subsequently, cca 250 g of soil was taken by means of a shovel, from the depth of at most 5 cm. In the places designated N1, N4 and N7 in Figure 1, in total 8 depth samples were taken from drill holes in the profile vertical to the lower base of the dumping site. The samples were taken from the depth 0.5 m, 1 m and 1.5 m. Manual drilling equipment with Edelman drill was used for the sampling. Sample of 250 g was taken from each of the depth profiles.

Results and risk assessment

In the surface samples, pesticide concentrations were found reaching hundreds of milligrams to units of grams per a kilogram of soil. Especially 4,4´-DDT, 2,4´-DDT, 4,4´-DDE, alpha-HCH, and beta-HCH were found. In the vicinity of the dumping site, high pesticide contamination was found also in the whole depth profile, in the order of hundreds mg of DDT per kg of soil, even in the depth of 1.5 m under the surface.

From these results, it is obvious that massive pesticide releases from the body of the dumping site were taking place in the past. Under the dumping site, a channel is visible through which water flows off the dumping site during rain periods. In this channel, the highest levels of pesticide concentrations were found (samples N1, N4, and N7).

The spreading contamination in the surroundings of the dumping site represents considerable risk for the environment and people living in the vicinity. It is also very likely that pesticides enter the food chain, because marks of livestock grazing were found in close vicinity of the dumping site where also the highest DDT concentrations were detected.

Covering and fencing the dumping site partially prevented direct exposure of people and livestock, but spreading into the environment could still continue. Thus, sealing the dumping site does not represent a solution of the problem. It will be necessary to decontaminate the whole territory of the dumping site, in order to prevent possible risks.

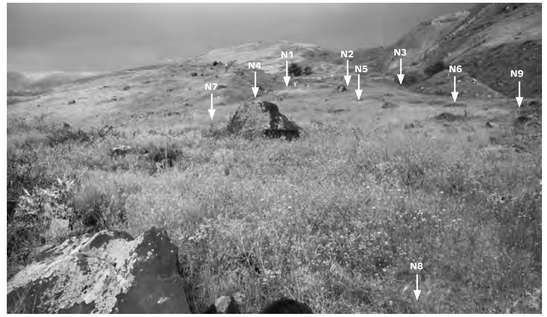


Figure 1: Places where surface samples were taken under the Nubarashen dumping site. *Author: Z. Honzajková*

Echmiadzin

Sampling date: July 24, 2010

In this locality, 2 storages are located where fertilizers and pesticides were handled. In close vicinity of the storages, vegetable patches are found, and small ponds for trout breeding are located cca 30 metres from the storages. The storages form part of a local farm where people live permanently, and which is located also in close vicinity of the storages.

The storages had been partially cleared already, however, pesticide residues were noticeable on floors and shelves. The presence of pesticide residues was proved also by strong smell. In close vicinity of one of the storages, there was a patch where local people grew vegetables.

Samples taken

In total, 5 samples were taken. In each of the both storages, one mixed sample of the material swept from the floor was taken, and, further, there was taken one mixed sample of the soil from the patches in the vicinity of the storage, a sample of sediment from an empty pond for trout breeding, and a sample of water from another breeding pond.

Results and risk assessment

In the material swept from the floors of the storages, high HCH and DDT concentrations were found, in the order of up to hundreds $mg.kg^{-1}$. In the surrounding soil and water, increased concentrations of HCH and DDT and its derivatives were also detected, in comparison with the background levels. Pesticide contamination was not proved in water from the pond. Lack of information of the local inhabitants on the hazardous properties of these substances represents the highest risk. They handle the material deposited in the storages without any protective equipment. The first storage had been swept recently. The pesticides may enter the surrounding environment also through this handling. There exists a risk of contamination of agricultural soil and crops, and contamination of breeding ponds, with the possibility of accumulation of these hazardous substances in fish meat. A further risk is pesticide accumulation in eggs of hens bred there.

Figure 2: First storage, closest to the vegetable patches. *Author: M. Šír*

Masis, Berriutyun LTD Masis

Sampling date: July 26, 2010

The locality is used for handling of fertilizers. A big storage with corresponding facilities and railway siding is present here. At present, the storage is still used for storing fertilizers. Two small storages, where pesticides and fertilizers were handled, are located next to the big storage used up to now. The first of the small storages is a ruined building without roof, freely accessible. In this room, bags and barrels with pesticides and fertilizers are present. The barrels are rusted through, and the bags are torn. Thus, their content is spilled loosely on the floor. The room does not have a roof, and, thus, these wastes are exposed to rain and weather influences.

The second of the small storages is formed by two rooms, and it is generally secured. In the past, this place served for sale of pesticides and fertilizers, the rooms are partially cleared, pesticide and fertilizer residues are spilled on the floor (see Figure 4). In the both rooms, strong pesticide smell was noticeable.

Figure 3: Storage serving for storing fertilizers in the locality Masis. *Author: M. Šír*

Samples taken

In total, 5 samples were taken in this locality. A mixed sample from the bags, and another one from the floor, were taken in the first storage. A mixed sample of the material swept from the floor was taken in the second storage. Further, there were taken a mixed sample of plasters from the both storages, and a mixed sample of soils in close vicinity of the storages, cca 10 metres from the storages.

Results and risk assessment

In the samples from the storages, alpha-HCH, beta-HCH and gamma-HCH is found predominantly, in concentrations up to the order of units $g.kg^{-1}$. Plasters from the storages are contaminated predominantly by beta-HCH and 4,4´-DDT. In the vicinity of the storages, increased concentrations of DDT and DDE were found. Thus, the analyses confirmed that pesticides were present in the both small storages in high concentrations.

The situation presents risks mainly for the employees working in the locality. In the first, freely accessible, room with the pesticides, cigarette ends were found on the floor, originating, with the highest likeliness, from the employees. They move here without any protective equipment, and this presents a huge health risk for them. Contamination of the stored fertilizers, and of landscape in the vicinity, represents another risk.

Jrarat

Sampling date: July 24 and July 26, 2010

A big storage of fertilizers, serving also as a pesticide storage in the past, is found in the locality. The storage is locked, and accessible only with consent of the owner. Pesticide residues in barrels, and fertilizers in bags, are found in the storage. Further, ruins of a small storage, without a roof, are found in the locality. The small storage is filled with barrels and bags with fertilizers and pesticides. A railway siding, which served for handling of fertilizers and pesticides, is located close to the storages. Further, a pond for trout breeding is found cca 50 m from the small storage.

Figure 5: Interior of the building of the big storage.
Author: Z. Honzajková

Figure 6: Ruins of the small storage where torn bags with crude DDT were found.
Author: M. Šír

Figure 7: View of a part of the small storage, with barrels containing waste contaminated with DDT.
Author: M. Šír

Samples taken

In total, 8 samples of solid substances were taken in this locality. There were taken 3 mixed samples of the material swept from the floor, and plaster, in the big storage, and, further, 2 samples in the small storage, samples of soils in the vicinity of the big storage and of the small one, and, finally, water from the breeding pond located nearby.

Results and risk assessment

Results of analyses proved that the powder in the torn bags in the ruined storage is essentially a raw pesticide DDT. The sample contained in total 647 g of pesticides per kg, majority of them was formed by 4,4-DDT (515 $g.kg^{-1}$), and 2,4-DDT (100 $g.kg^{-1}$). Further, the sample contained by-products and decomposition products of DDT, including predominantly DDD and DDE, the toxicity of which is similarly high as in the case of DDT. The estimated stored amount is in the order of hundreds of kilograms.

The rusted-through barrels contain wastes contaminated by DDT. The fertilizers stored in the big storage come in contact with spilled pesticide residues, and with raw pesticides in inadequate packaging. In the material swept under the barrels with pesticides, high concentrations of DDT, DDD and DDE were found, in the order of tens $g.kg^{-1}$. Also the plasters in the storage are contaminated, predominantly by DDT.

The risk is obvious at first sight, because the building where pesticides are deposited is ruined, and without a roof. Only parts of walls remained of the building. The pesticides are deposited, practically, in open landscape. Rain and wind cause transport of pesticides into the surrounding landscape. This was confirmed also by the results of analysis of a soil sample from the vicinity of the storage. In total 280 mg of DDT, DDE and HCH per kg was found in this sample. This corresponds to values for a highly contaminated territory.

One of the further big risks is the possibility of contamination of breeding ponds in close vicinity of the storage (see Figure 9). In view of the possibility of accumulation of these persistent pollutants in animal adipose tissues, it would be recommendable to carry out an analysis of fish meat taken from several samples of fish.

Alaverdi

Sampling date: July 27, 2010

Several concrete structures are located in the locality, serving in particular for disposal of slag and fly ash from a nearby metallurgical plant processing copper ore. Some of the structures are already full, and covered by grass and shrubs. The disposal site is located in hilly area above the town Alaverdi.

Samples taken

3 samples of solid material were taken. A sample of metallurgical waste, and a sample of fly ash with slag, were taken in the structures. Further, a soil sample was taken in the vicinity under the disposal site.

Results and risk assessment

As expected, high percentage of metals, namely of copper, lead, zinc, cadmium, chromium and arsenic, was found in waste and slag from the metallurgical plant. However, high concentrations of heavy metals were found also in the soil sample taken in the distance cca 20 m from the disposal site, out of the actual disposal site area. The surrounding environment is contaminated in particular by lead, cadmium and arsenic. These hazardous substances are being washed out of the disposal site by rain precipitations, and are spreading downhill towards the town Alaverdi, the suburbs of which are located in the order of hundreds of metres from the disposal site. The neighbourhood of the disposal site is freely accessible.

ANNEXES

In the tables, the found out concentrations can be compared with contamination criteria for soils and underground water according to the Methodical Instruction of the Ministry of Environment of the Czech Republic. The amounts of pesticides in many localities exceed the criterion C several times.

Criterion **A**

For OCPs = 0.05 mg.kg^{-1} of dry matter

Criterion A levels correspond approximately to natural content of the monitored substances in nature (in connection with the usual sensitivity limit of analytical determination). When criteria A are exceeded, it is regarded as pollution of the corresponding environmental component, with the exception of areas with naturally higher content of the monitored substances. However, if criteria B are not exceeded, the pollution is not regarded as significant to the extent that it would be necessary to obtain more detailed data for its assessment, i.e., to start investigation or to monitor the pollution.

Criterion **B**

For OCPs = 2 mg.kg^{-1} of dry matter

Exceeding of criteria B is regarded as pollution that may have adverse impacts on human health and the individual environmental components. It is necessary to collect further data for assessment whether the case presents a significant environmental burden, and what are the risks connected with it. Thus, criteria B are set as intervention limits, exceeding of which means that it is necessary to deal with the pollution further. If criteria B are exceeded, it is necessary to preliminarily assess risks ensuing from the found out pollution, to determine its source and causes, and, depending on the results, to decide on further investigation or start of monitoring.

Criteria **C**

For OCPs: residential areas: 2.5 mg.kg^{-1} of dry matter; recreational areas: 5 mg.kg^{-1} of dry matter; industrial areas: 10 mg.kg^{-1} of dry matter for sum of DDT and its metabolites – all land use areas: 2,5 mg.kg^{-1} of dry matter

Exceeding of criteria C is regarded as pollution that may represent a significant risk of endangering human health and environmental components. Seriousness of the risk may be confirmed only by its analysis. Recommended values of target parameters for decontamination may be also higher than the stated criteria C, depending on the results of risk analysis. Documents necessary for deciding on the method of corrective measure are formed, in addition to the risk analysis, by studies evaluating technical and economic aspects of the proposed solution.

Criterion values are valid in case of OCPs for each pesticide separately.

However, not so strict criteria are valid in Armenia yet. When assessing the pollution level, the so-called Provisional Low POPs Content Level may be taken into consideration, this level being 50 mg.kg^{-1}. The value 50 mg means weight of each pesticide contained in a sample separately.

TABLE 1: SUMMARIZED RESULTS OF ANALYSES AT NUBARASHEN DUMPING SITE

underground samples taken in three profiles down the hill from the dumping site. Samples were taken from the drill hole.

Locality	NUBARASHEN							
Sample Description	NV1	NV2 soil samples - first profile	NV3	NV4	NV5 soil samples - second profile	NV6	NV7 soil samples - third profile	**Criterion C** residential; recreational; industrial
Depth (m)	**0.5**	**1.0**	**1.5**	**0.5**	**1.0**	**0.5**	**1.0**	
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg^{-1} d.m.)							
alpha-HCH	2.40	5.35	6.8	-	0.06	-	-	2.5; 5; 10
beta-HCH	1.37	1.61	0.87	0.03	0.04	-	0.01	2.5; 5; 10
gamma-HCH	0.49	0.06	0.01	-	-	-	-	2.5; 5; 10
HCB	1.23	0.50	0.30	-	-	-	-	2.5; 5; 10
heptachlor	0.06	0.01	-	-	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	0.07	0.03	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	-	-	-	-	-	-	-	2.5; 5; 10
dieldrin	-	-	-	-	-	-	-	2.5; 5; 10
endrin	-	0.02	0.07	-	-	-	-	2.5; 5; 10
2,4´-DDE	0.24	0.19	0.61	-	0.01	-	0.01	2.5; 5; 10
4,4´-DDE	1.37	1.30	2.40	0.03	0.09	0.02	0.08	2.5; 5; 10
2,4´-DDD	1.32	0.41	1.88	-	-	-	0.01	2.5; 5; 10
4,4´-DDD	4.15	1.52	13.36	0.04	0.02	0.01	0.02	2.5; 5; 10
2,4´-DDT	17.8	7.33	24.54	0.11	0.05	0.01	0.06	2.5; 5; 10
4,4´-DDT	148.31	64.18	214.12	0.79	0.35	0.08	0.59	2.5; 5; 10
DDT	173.19	74.93	256.91	0.97	0.52	0.12	0.77	2.5
TOTAL	**178.10**	**82.51**	**264.23**	**1.1**	**0.62**	**0.13**	**0.79**	

TABLE 2: SUMMARIZED RESULTS OF ANALYSES AT NUBARASHEN DUMPING SITE –
surface layer samples taken in several profiles down the hill from the dumping site.

Locality	NUBARASHEN										**Criterion C** residential; recreational; industrial
Sample Description	N1	N2	N3	N4	N5	N6	N7	N8	N9	NS	
	soil samples - surface										
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg^{-1} d.m.)										
alpha-HCH	248.36	0.12	0.72	10.90	0.07	0.77	0.21	0.12	0.11	-	2.5; 5; 10
beta-HCH	45.50	-	2.11	14.75	0.03	2.3	0.12	0.42	0.05	0.01	2.5; 5; 10
gamma- HCH	67.94	0.01	-	2.19	0.00	-	0.02	0.02	0.02	-	2.5; 5; 10
HCB	9.80	-	0.30	3.92	-	0.34	0.17	-	-	-	2.5; 5; 10
heptachlor	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
dieldrin	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
endrin	2.17	-	-	-	-	-	-	-	-	-	2.5; 5; 10
2,4´-DDE	30.81	5.95	1.4	7.58	-	0.48	0.68	-	0.38	-	2.5; 5; 10
4,4´-DDE	30.49	30.69	5.57	27.51	0.03	2.33	4.97	0.14	5.80	-	2.5; 5; 10
2,4´-DDD	36.57	0.39	1.13	11.85	-	1.8	0.28	0.07	0.07	-	2.5; 5; 10
4,4´-DDD	152.93	0.18	4.24	51.47	-	4.3	0.78	0.28	0.06	0.01	2.5; 5; 10
2,4´-DDT	664.89	3.63	15.69	177.19	0.01	16.57	4.60	0.89	1.00	-	2.5; 5; 10
4,4´-DDT	4045.22	6.45	115.31	1250.78	0.04	100.25	18.5	5.13	1.87	-	2.5; 5; 10
DDT	4960.91	47.29	143.34	1526.38	0.08	125.73	29.81	6.51	9.18	0.01	2.5
TOTAL	**5334.68**	**47.30**	**146.11**	**1558.15**	**0.19**	**127.89**	**29.87**	**7,05**	**9.35**	**0.02**	

TABLE 3: RESULTS OF ANALYSES FOR SAMPLES TAKEN IN OBSOLETE PESTICIDES STORAGE NEAR ECHMIADZIN AND ITS VICINITY.

Locality	ECHMIADZIN				**Criterion C** residential; recreational; industrial	ECHMIADZIN
Sample Description	E1 storage 1 - sweepings	E2 storage 2 - sweepings	E3 patch near the storage - soil	E4 trout pond - sediment		EV trout pond - water
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg^{-1} d.m.)					µg.kg^{-1}
alpha-HCH	2.27	7.36	0.06	0.06	2.5; 5; 10	0.29
beta-HCH	34.95	7.17	0.05	0.05	2.5; 5; 10	-
gamma-HCH	31.73	-	-	-	2.5; 5; 10	-
HCB	1.1	41.92	-	-	2.5; 5; 10	0.02
heptachlor	-	4.13	-	-	2.5; 5; 10	-
heptachlor exo-epoxide					2.5; 5; 10	
alpha-endosulfan	15.31	329.25	-	-	2.5; 5; 10	-
beta-endosulfan	-	106.81	-	-	2.5; 5; 10	-
dieldrin	-	3.28	-	-	2.5; 5; 10	-
endrin	-	83.93	-	-	2.5; 5; 10	-
2,4´-DDE	0.52	361.72	-	0.01	2.5; 5; 10	-
4,4´-DDE	0.73	499.81	0.03	0.01	2.5; 5; 10	-
2,4´-DDD	-	30.90	0.04	-	2.5; 5; 10	-
4,4´-DDD	0.35	279.45	-	-	2.5; 5; 10	-
2,4´-DDT	2.30	610.22	0.01	-	2.5; 5; 10	-
4,4´-DDT	8.55	-	0.02	-	2.5; 5; 10	0.01
DDT	12.45	1782.10	0.10	0.02	2.5	0.01
TOTAL	**97.72**	**2358.57**	**0.20**	**0.13**		**0.31**

TABLE 4: RESULTS OF ANALYSES FOR SAMPLES TAKEN IN OBSOLETE PESTICIDES STORAGE IN MASIS AND ITS VICINITY.

Locality	MASIS					Criterion C residential; recreational; industrial
Sample Description	M1 storage 1 - sweepings	M2 storage 1 - pink material	M3 sotrage 2 - sweepings	M4 storage 1 and 2 - plaster	M5 vicinity of the storages - soil	
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg^{-1} d.m.)					
alpha-HCH	6.65	4145.98	1.44	4.19	0.06	2.5; 5; 10
beta-HCH	10.35	4795.80	4.1	30.12	0.20	2.5; 5; 10
gamma-HCH	1.51	3587.43	7.84	0.26	0.01	2.5; 5; 10
HCB	0.03	25.98	0.15	-	-	2.5; 5; 10
heptachlor	-	26.29	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	3.83	-	-	0.01	2.5; 5; 10
alpha-endosulfan	-	24.22	-	-	0.02	2.5; 5; 10
beta-endosulfan	8.2	5.1	1.13	0.20	0.19	2.5; 5; 10
dieldrin	1.1	1.85	-	-	0.07	2.5; 5; 10
endrin	-	-	-	-	-	2.5; 5; 10
2,4´-DDE	45.11	10.42	4.65	0.40	0.07	2.5; 5; 10
4,4´-DDE	55.70	8.88	6.34	0.73	0.58	2.5; 5; 10
2,4´-DDD	5.60	9.92	5.18	0.59	0.19	2.5; 5; 10
4,4´-DDD	1.67	12.31	0.99	0.94	0.02	2.5; 5; 10
2,4´-DDT	70.59	31.57	4.76	3.97	0.14	2.5; 5; 10
4,4´-DDT	18.72	14.74	11.17	16.52	0.38	2.5; 5; 10
DDT	197.39	87.84	33.09	23.15	1.38	2.5
TOTAL	**224.96**	**12704.23**	**47.67**	**57.91**	**1.94**	

Locality	JRARAT								Criterion C residential; recreational; industrial
Sample Description	J1 big storage – sweepings from the floor	J2 big storage - sweepings under barels	J3 big storage - powder from the cover of the barrels	J4 big storage - plaster	J5 vicinity of the big storage - soil	J6 small storage without a roof - mixed sample from the bags	J7 small storage without a roof - mixed sample from the barrels	J8 vicinity of the small storage without a roof - soil	
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg^{-1} d.m.)								
alpha-HCH	0.67	14.41	0.26	-	0.06	210.99	0.75	7.55	2.5; 5; 10
beta-HCH	0.25	19.25	0.74	-	0.08	19.25	3.14	13.42	2.5; 5; 10
gamma-HCH	-	377.46	0.27	-	-	1609.47	0.47	1.30	2.5; 5; 10
HCB	-	-	0.05	-	-	-	0.36	-	2.5; 5; 10
heptachlor	-	-	-	-	-	-	28.40	-	2.5; 5; 10
heptachlor exo-epoxide	0.03	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	-	-	-	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	0.02	16.68	-	-	0.02	16.68	12.00	-	2.5; 5; 10
dieldrin	-	0.24	-	-	-	0.24	-	-	2.5; 5; 10
endrin	-	-	-	-	-	-	-	-	2.5; 5; 10
2,4´-DDE	0.07	78.03	-	-	0.10	204.56	153.10	9.6	2.5; 5; 10
4,4´-DDE	0.19	430.01	0.94	0.18	0.26	1925.96	474.67	40.94	2.5; 5; 10
2,4´-DDD	0.05	1704.72	-	0.23	0.04	5286.43	31.54	4.21	2.5; 5; 10
4,4´-DDD	0.32	6256.25	-	-	0.01	23087.13	18.4	10.10	2.5; 5; 10
2,4´-DDT	0.30	5855.78	15.16	1.68	0.06	99479.88	332.87	30.3	2.5; 5; 10
4,4´-DDT	0.49	12485.27	70.32	9.14	0.12	515918.01	297.49	163.46	2.5; 5; 10
DDT	1.42	26810.06	86.42	11.23	0.59	645901.97	1308.07	258.61	2.5
TOTAL	**2.40**	**27238.09**	**87.76**	**11.22**	**0.75**	**647758.6**	**1352.83**	**280.06**	

Locality	ALAVERDI								
Sample Description	A1 solid waste from metallurgical plant	A2 fly ash, slag	A3 soil, vicinity of the disposal site	**Criterion**	**A**	**B**	**C**	**C**	**C**
				Land use specification	-	-	residential	recreational	industrial
SUBSTANCE	CONTENT IN DRY MATTER ($mg.kg^{-1}$)			LIMIT VALUES	CONTENT IN DRY MATTER ($mg.kg^{-1}$)				
Pb	12060	19820	1374	**Pb**	80	250	300	500	800
Zn	155	2644	133	**Zn**	150	1500	2500	3000	5000
Cu	48120	61170	1022	**Cu**	70	500	600	1000	1500
As	1765	7514	453	**As**	30	65	70	100	140
Cr	112	92	59	**Cr**	130	450	500	800	1000
Fe	21000	174800	99700	**Fe**	-	-	-	-	-
Cd	12	94	1.3	**Cd**	0.5	10	20	25	30

COLOUR PHOTOS

View at Yerevan, capital of Armenia, with Ararat behind. The Yerevan was also place of preparation for all sampling and it is city, where is located office of AWHHE, one of two partner NGOs participating in this project. *The photographs were taken by Ondřej Petrlík.*

Czech sampling team at hot spot in Echmiadzin. From the left side: Alice Dvorská, Jindřich Petrlík, Marek Šír, Zuzana Honzajková.

Obsolete pesticides residues such as DDT or lindane were found also in famous Armenian lake Sevan however it was published in other studies (e.g. in the National Implementation Plan for the Stockholm Convention on POPs of the Republic of Armenia).

Sampling in the ruined building of the storage in Jrarat. The rest of pesicides (most likely DDT) is vissible behind the persons.

Sampling inside the big storage building. High levels of obsolete pesticides residues were found also in samples from this building.

Ruins of the former pesticides storage with stockpile of obsolete DDT.

Sampling in surrounding of damaged drums.

Alice Dvorska is showing one of taken samples in Jrarat on this photo.

NUBARASHEN

Sampling at Nubarashen site by drill with help of worker from Center for Noosphere and Ecological Studies based in Yerevan.

Sampling downhill from the burial site in July 2010. Smell was so strong that respirator were needed for persons taking samples. There are Alice Dvorská and Jindřich Petrlík at this photo.

Passive air sampling device was installed at July - 23rd, 2010 on the fence of burial site. This device consists of two stainless steel bowls attached to a common axis and they form a protective chamber for a polyurethane foam disc as well.

There were dumped 500 metric tonnes of obsolete pesticides since 1982 in the valey near Nubarashen. A landslide occured later on and original burial site was damaged including bags with pesticides what leads to serious contamination in the surrounding. The burial site was covered by soil, fenced, and is guarded since spring 2010 in order to prevent further unpredictable damage by irresponsible persons.

ECHMIADZIN

Storage room 2 with some drums and bags with pesticides left.

Obsolete pesticides storage building near Echmiadzin and Griboedov.

Storage room 1 where sample 21A, 21B was taken. The floor was covered by layer of pink-velvet pesticide residue.

We found also death bird in the storage room 2.

Sampling at the vegetable bed next to storage building with assistance of man living in house within the broader area of the obsolete pesticides storage.

MASIS

Sampling in obsolete pesticides storage in Masis. The biggest room with residues of obsolete pesticides in damaged bags.

View at obsolete pesticides strage from outside. The room with no roof is in the left part of this photo, the extension of the larger building.

Small central storage in Masis.

Another small room of the storage.

”The European Union is made of 27 Member States who have decided to gradually link together their know-how, resources and destinies. Together, during a period of enlargement of 50 years, they have built a zone of stability, democracy and sustainable development whilst maintaining cultural diversity, tolerance and individual freedoms. The European Union is committed to sharing its achievements and its values with countries and peoples beyond its borders”. The European Commission is the EU’s executive body.

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