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project

ENABELING ACTIVITIES TO FACILITATE EARLY
ACTION ON THE IMPLEMENTATION OF THE
STOCKHOLM CONVENTION ON PERSISTENT ORGANIC
POLLUTANTS (POPS) IN THE REPUBLIC CROATIA

Under project

INVENTARISATION OF PERSISTENT ORGANIC POLLUTANTS - PESTICIDES IN THE REPUBLIC OF CROATIA

Project coordinator: dr. sc. Darka Hamel
Project expert co-workers - phytopharmaceuts:
m. sc. Goran Hrlec, b. sc. Gorana Hrlec

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PESTICIDES – PERZSITANT ORGANIC POLUTANTS – REVIEW OF THE SITUATION

1. POPs PESTICIDES – REVIEW OF THE SITUATION IN CROATIA

1.1. INTRODUCTION

Persistent organic pollutants (POPs) are toxic organic substances, mostly of synthetic origin, resistant to photolytic, biological and chemical degradation. Due to the toxicity and persistence additional problem performs their accumulation in living organisms in fat tissue and they unchangeable are easily spread on great distances where they have never been used. In the medium of the last century they were produced and used in large quantities and due to this large amounts were spread in the environment. Due to its persistence they perform long-term pollution for the environment in the world.

Due to the period of production and application of POPs in Republic of Croatia we can have three groups:

POPs never used in Croatia (mirex)

POPs produced and used in large quantities (DDT, hexachlorobenzen, clordan, heptachlor, aldrin, dieldrin, endrin, toxafen)

POPs which usage was banned recently (lindan)

Status of POPs pesticides in Republic of Croatia is shown in Table 1.

Table 1. Active ingredients of POPs pesticides and years of banning

AKTIVE INGREDIENT	PERMISION SINCE YEAR	BANED IN YEAR
HCB	1962.	11. 7. 1980.
toxafen	1957.	27. 4. 1982.
Endrin	1957. (From 1971. only as a rodenticide)	29. 5. 1989.
Aldrin	1958.	1972.*
Dieldrin	1958.	1972.*
Heptachlor	1956.	7/1973.*
Hexaklorciklohexan (HCH)	1944.	1972.*
DDT	1944.	In agriculture 1972.*
Lindan	1944.	July 2001.
Mirex	Not registered in Republic of Croatia	
Dicofol	1949.	2001.

*National Journal of SFRY 19/1972

When it was decided to ban any active ingredient it was allowed to applicate available amounts to prevent pollution with the remained stock.

Many restrictions were prescribed on October 21, 1971 about pesticide application according to the dates of seeding, next crop, application in the determined crops and were allowed for application only against some pests.

Due to banning of POPs pesticides about 20 –30 years ago it can be expected that amount of POPs pesticides in environment and humans as well, in Croatia are lower than in developed countries where they were used in larger amounts. Inventarisation of POPs pesticides should give clear and combined data about the

status of these substances in Croatia and/or their movement in the environment. According to the situation it will be possible to understand what activities have to be performed.

1.2. INSTITUTIONS AND LEGISLATION

Due to the application pesticides in Croatia can be used for next purposes:

- Protection of plants and products
- Protection of animals against pest
- Protection of humans against pests
- In public health sector
- Protection of wood and textile
- Application in homes (spray with small amount of active ingredient)

Pesticides are registered due to several acts and regulations in responsibilities of different ministries in Croatia. There are different institutions that due to their studies recommend application of pesticides and responsible ministry issues permission for registration. Also exists regulation on banning of pesticides. List of regulations is shown in Table 2.

Table 2. List of regulations that prescribe marketing, import, export, application, storage, disposal and recycling of pesticides

Plant protection
Plant protection act 10/94
Regulations of conditions and way of placing on the market of plant protection products 75/98
Regulations on plant health inspection and inspection of plant protection products in transboundary movement 12/95
Toxic substances
Act of toxic substances 27, 39, 55/1999
Regulations on placing toxic substances in groups of hazard 47/1995
Regulation on labelling of toxic substances on the market 47/1999
Regulation on measure protections in institutions using toxic substances for scientific research 148/99
List of registered toxic substances 7/2001
List of toxic substances to be used in public health for disinfections, desinsections, deodorisation and decontamination 151/2002
Regulation on packaging and handling with packages for toxic substances 39/2003
Regulation on small amounts of toxic substances for laboratory and scientific research 39/2003
Water
Water act
Regulation on dangerous substances in water 78/98
State plan for water protection 8/99
Regulation on water classification 77/98
Regulation on quality of drinking water 46/94
Veterinary
Veterinary medicines and veterinary medical supply 79/98

Regulation on quality check of veterinary medicines, medical additives, medical supplies, manner of storing and recording of provided checking of quality 148/99
List of veterinary medicines, medical additives and veterinary medical supplies registered for application 73/2000
Regulation on band veterinary medicines for application on animals which meat and products are used for consumption 4/2002
<i>Environment</i>
Environment protection act 82/1994
<i>Agriculture</i>
Agricultural land act 66/2001 and 82/2002
Regulation on protection of agricultural land 15/92

1.2.1. Ministry of health responsibilities

Ministry of health is responsible for issuing:

Permission for import of registered active ingredients for formulation of different pesticides

Permission for import of ready-made products for public health

Decision for placing active ingredients on list of toxic substances

Decision on placing pesticides in groups according to the toxicity

Determining of maximum allowed quantities of pesticides that may be found in products on the market

Permission for use of pesticides in homes

According to the Toxic substances act registered are institutions for toxicological analyses of active ingredients and ready-made pesticides and efficacy studies of pesticides on harmful organisms in public health. The longest registration of active ingredient is 10 years.

Physical chemical analyses of pesticides as well as residues in food perform Institute for public health of Republic Croatia whereas county institutes make survey of residues in food.

1.2.2. Responsibilities of Ministry of agriculture and forestry

Ministry of agriculture and forestry is responsible for the registration of plant protection products and animal protection products.

In the Institute for plant protection in agriculture and forestry of Republic Croatia studied are biological efficacy and physical-chemical analyses of plant protection products as well as pesticides used in public health and veterinary. Sometimes are surveyed pesticides residues in water, soil, plants and products.

Plant protection product can be registered maximum on 10 years whereas in case of bad influence on the environment and human health changes can be made earlier.

List of forbidden substances that includes POPs pesticides is prepared and it will be published soon.

According to the mentioned statements there is no import or export of POPs pesticides.

1.3. PAST, RECENT AND FORESEEN PRODUCTION AND USE OF POPS PESTICIDES

1.3.1. Past production of POPs

DDT production started in 1943, whereas dust production started in 1946. Production of pesticides exclusive copper sulphate increased from 858 to 7114 t, in the period from 1951 to 1957.

However the only available information was import of 1435 t of plant protection products and active ingredients.

Pesticides production was small and large amounts were imported. Due to the lack of data imported amounts of active ingredients are not presented specified.

Data for the period after 1957 are incomplete and are based on different sources like plans, import, production and used amounts of plant protection products.

Three producers of POPs and other pesticides were in Croatia. These were Chromos that placed 27 POPs pesticides on the market, Pliva one and Radonja 4. Two producers from Slovenia had 27 products, three producers from Serbia had 17 products, and one from Macedonia had 11 products whereas there were 8 products from different producers from other countries.

Pesticide production was increasing and about 70000 t were produced in 1981 whereas production declined to 55000 t in 1985. Due to the insufficiency of foreign currency the production decreased although production of 75000 t was foreseen for the period 1982 to 1987.

1.2.3. Temporary production of POPs

Temporary POPs pesticides are not produced nor import of active ingredients that will be used for new formulation of POPs pesticides.

Three producers of pesticides Chromos Agro, Veterina and Herbos exist in Croatia. Production consists of formulation of pesticides from imported active ingredients according to the registration file or it is only placed in suitable package or is imported a ready-made product. Already products prepared for the market import many firms as well as representatives foreign producers or distributors of pesticides. At the same time only Herbos is synthesizing active ingredient atrazin used in herbicides.

Decreasing of pesticides production is continued and in 1991 production was 9741 t of plant protection products whereas 4571 t were insecticides.

Many pesticides have been registered as replacement for toxicologically improper pesticides including POPs in Croatia. 93 active ingredients from groups of piretroids, organo-phosphates, carbamates as well as *Bacillus thuringiensis* and other toxicologically acceptable groups have been used as alternatives to POPs.

1.3.3. Future production of POPs

Future production is not expected due to absence of POPs on the list of allowed toxic substances. However, list of forbidden substances including POPs is prepared. POPs pesticides production and marketing will be band after ratification of Stockholm convention.

1.3.4. Use of POPs

POPs pesticides were used according to the label. As alternatives used were pesticides of smaller toxicity and danger and of better ecological characteristics. Recently used pesticides are less persistent. In process of registration decisions by WHO, FAO, EPA, EU directives are compared.

1.3.4.1. Past usage

Pesticides in agriculture were applied on the whole surface and mostly by using dusts.

Due to application on many crops and against many pest big amounts of POPs pesticides were used.

Oscillation of application of organochlorine insecticides was due to the climatic changes, crop rotation, and insufficient foreign currency for import of active ingredients or ready-made products, resistance appearance, forecasting program and integrated plant protection. Due to mentioned environment pollution was decreased.

1.3.4.2. Temporary usage

Due to the mentioned banning POPs pesticides are not used.

1.3.4.3. Future usage

Use of POPs is not foreseen according to the existing and future regulations.

1.4. IMPORT AND EXPORT

1.4.1. Imported amounts of POPs in the past

Past amounts of import of pesticides are not available. As guide to the imported quantities used amounts can be surveyed.

1.4.3. Past export

Data about exported POPs pesticides are not available.

1.4.3. Import of POPs pesticides

It is allowed to import substances from the list of toxic substances or ready-made registered products. Border inspection allows import due to the permission of the responsible ministry and register of registered pesticides. Custom inspection has information through responsible ministries that help them during the official survey and according to this it is not expected to have problems.

There is also small possibility for smuggle of POPs pesticides because most of them are forbidden in the neighbouring countries.

Regulations concerning selling of pesticides in agricultural and veterinary pharmacies prescribe that only registered products are allowed for selling.

Table 4. Used active ingredients in kg/ year in agriculture in Croatia

Year	ALDRIN	DDT in agriculture	DIELDRIN	ENDRIN	HEPTACLOR	KLORDAN	TOXAFEN	KELEVAN
1962							5 200	
1963							6 400	
1964	48 353	1 784	610				5 395	
1965	9 982	1 196	186				1 728	
1966	13 448	14 051	5 298					
1967	53 400	16 325	1 980	120			5 375	
1968	496	4 183	142		370		2 025	
1969	64 821	6 051	284		1 175		2 250	0
1970	39 260	5 450	132		1 264		1 625	12 375
1971	21 840	4 296	1 278		2 336		2 463	7 876
1972	0	1 078	0		0	0	2 765	3 562
1973	0	0	0		0	0	3 953	5 400
1974	0	0	0		0	0	1 573	5 625
1975	0	0	0		0	0	3 604	47 880
1976	0	0	0		0	0	4 420	104 100
1977	0	0	0		0	0		1 350

1.5. EXISTING STOCKPILES, WASTE THAT CONTAINS POPs PESTICIDES, LOCATIONS FOR DISPOSAL AND CONTAMINATED SITES

POP pesticides were forbidden many years ago and they don't perform problem for human and animal health and the environment as well.

1.5.1. Existing stock pails of POPs pesticides

Questioning of the biggest users of pesticides has not shown existing of POP pesticides.

1.5.2. Waste with POPs pesticides

Pesticides that are used do not contain POPs and there is not possibility to develop waste that contains POPs. Special disposal for the POPs were not foreseen. It can be supposed that if the POPs were discard some 20 to 30 years ago that they are covered with heaps of rubbish. An exception could be appearance of empty pesticides packages in some storehouses.

1.5.3. Locations for discarding POPs pesticides

Due to the existing regulations no disposal for POPs are foreseen. Taking into account that other POPs exist disposal should be prepared. In such case these disposal could be used for discarding of POPs pesticides.

1.5.4. Contaminated locations with POPs pesticides

Locations contaminated with POPs pesticides are not known. Lasting period of this project and financing has not been sufficient that contaminated locations could be found.

Accepting that pesticides were used according to the allowed dosages there is no possibility of finding locations with pollution with POPs pesticides.

According to the available data there is no danger for humans and environment caused by POPs pesticides.

1.6. CURRENT MENAGEMENT (PRODUCTION, USAGE, STOCKS AND WASTE OF POPS PESTICIDES)

1.6.1. Experience so far with management of POPs pesticides

POP pesticides were used in agriculture, forestry, veterinary and public health according to the label. Explained were application methods, discarding of remained pesticide and package.

1.6.2. Behaviour and practise of traders

Traders behave according to the proscribed regulations.

1.6.3. Behaviour of users of POPs pesticides

Pesticides were used according to the label taking into account MRL and post treatment period.

MRL for pesticides were proscribed for the first time in 1969.

Since 1970 there are no recommendations for application of organochlorine pesticides on vegetables, alpha alpha, fruit trees after blossoming and in storehouses.

Guidance for last treatments of plants and plant products were announced in 1970.

1.7. CURRENT CAPACITIES/POTENTIAL AND EXPERIENCE SO FAR WITH POPs PESTICIDES

1.7.1. Current capacities/potential

According to the regulations all POPs pesticides are on the list of forbidden substances and are not on the list of toxic substances and there is no abilities that they will be imported, exported, produced or on any other way placed on the market.

1.7.2. Experience so far with POPs pesticides

Experience so far with POPs pesticides show interest for checking of residues in water, soil, plants, animals and humans.

1.8. RESPONSIBILITIES AND DUTIES

List of forbidden substances is main regulation based on the Act of toxic substances and bans any use and marketing of POPs pesticides. With this act ordered is how to dispose waste of pesticides. Some misunderstanding is between Ministry of agriculture and forestry, Ministry of health and Ministry of environment and physical planning concerning disposal and recycling of empty packages. Very important problem exists because the only one incinerator for dangerous substances is closed.

2. REVIEW OF CONTAMINATED LOCATIONS WITH POPs PESTICIDES

2.1. INTRODUCTION

There is no obligation of checking POPs pesticides in the environment. This means pollution of soil, plants and plant products, meat, milk and products. Also locations for disposal of POPs pesticides and waste of similar origin are not determined.

2.2. INSTITUTIONAL AND REGULATORY FRAMEWORK

There is no national institution that will obtain jobs as well as finance sources for identification, estimation, ordered priorities, cleaning and contaminated locations.

2.3. LOCATIONS CONTAMINATED WITH POPs PESTICIDES

According to the available data that are incomplete and often not uniform contaminated sites with POPs pesticide were not found till now.

2.4. PRELIMINARY IDENTIFICATION OF PRIORITY LOCATIONS

According to the collected data that generally show places of application of POPs pesticides in some regions of Croatia it would be possible to determine areas and make survey if any POPs pesticides residues are present.

2.5. CURRENT CAPACITY OF DISPOSAL AND EXPERIENCES SO FAR

Due to the possibility that small amounts of POPs pesticides can appear it should not be a problem to find proper place for disposal. Environment protection act prescribes that polluter pays for a caused pollution. There is not organized recycling of POPs pesticides.

2.6. RESPONSIBILITIES AND DUTIES

According to the existing legislation disposal for POPs pesticides must be ordered in the regulations of environment protection.

2.7. INTERNATIONAL EXPERIENCE AND PRACTISE – REVIEW

Inventarisation of POPs pesticides is provided in countries in transition as well as developing countries with a support of developed countries or international organizations. Inventarisation and national action plans are also in course in EU and OECD countries. POPs pesticides are not problem of one special country but due to spreading they make a global problem.

We were present in preparing and accepting Stockholm convention and attended seminars on POPs pesticides.

3. CURRENT STATUS CONCERNING POPs PESTICIDES

Collected data used to present current status of POPs pesticides mostly correspond to the period after 1990.

Accepting of adequate new legislation, as amendments to existing acts and new regulations are important condition in preventing registration of POPs pesticides. Important is to determine national monitoring program in all of the elements of the environment because of introduction into status of POPs pesticides and recognising problems that can appear due to their residues.

Licence for plant protection product can't be issued if active ingredient is placed in list 2 (Annex 2) EU Council directive 91/414. This is an obstacle for registration of ecologically unacceptable active ingredients.

Maximum residue levels (MRL) of POPs pesticides are determined in Regulation concerning amount of pesticides, toxins, mycotoxins, metals and histamines and other similar compounds that are allowed in commodities and other conditions regarding quality of commodities and objects of general use (N. N. 45/98). In table 5 are shown MRL for POPs pesticides.

Table 5. MRL values for POPs pesticides

POPs pesticide	MRL (mg/kg)	Commodity
Aldrin (alone or together with dieldrin, expressed as dieldrin)	0.2 0.02 0.01 0.006	Meat and products Eggs and products Cereals and products Milk and products
DDT and metabolites	1 0.1 0.05 0.04	Meat and products Eggs and products, vegetables, plant oil cereals Milk and products
Dieldrin	-	-
Endrin	0.05 0.01 0.001	Meat, eggs and products Fruit, vegetables, cereals Milk and products
Hexachlorobenzene	0.2 0.1 0.05 0.02	Meat and products Dried plants, tea Fruits, vegetables, plant oils Eggs and products

	0.01	Milk and products, cereals
Heptachlor and heptachlorepoxyd	0.2 0.01 0.02 0.004	Meat and products Cereals, fruits, vegetables Eggs and products Milk and products
Chlordan	No residues	
Mirex	-	
Toxaphene	No residues	

Health control checks and quality checks of commodities and objects of general concern are done according to guidelines of Ministry of health and the Law concerning quality of commodities and objects of general concern (N. N. 1/97). Annually around 80 000 samples of commodities and objects of general concern from import or domestic origin are analysed for determination of microbiological and chemical properties. In table 6 is shown percentage of samples positive to HCB and DDT.

Table 6: Percentage of samples positive to HCB and DDT (1992-1996.)

Type of sample and period of sampling		Percentage of samples positive to HCB	Percentage of samples positive to DDT
Beef	-from import 1992-96	52	81
	-from domestic production 1992-96	19	50
	-from domestic production 1985/86	33	92
Pork	- from import 1992-96	39	82
	- from domestic production 1992-96	16	41
	- from domestic production 1985/86	7	80
Poultry	- from import 1992-96	43	50
	- from domestic production 1992-96	25	55
Fish	- from import 1992-96	25	91
	- from domestic production 1992-96	27	100

Average measured concentrations of DDT in imported meat were in range 0,041-0,059 mg/kg and in domestic meat in range 0,013-0,014 mg/kg. DDE was present in 34,57 % of meat samples of domestic origin and 75-76,25 % samples of imported meat. Comparison of obtained results show decreasing of concentrations of organochlorine pesticides in meat from domestic production. In 1985/1986 median concentrations of DDT in pork was 0,018 mg/kg and in this analysis it was 0,001 mg/kg. There was no sample with DDT concentration above MRL. Comparing analytical results of commodities from 1989. with those in 1999. the decreased trend of number of samples containing POPs pesticides above MRL is evident.

Levels of DDT in imported and domestic fish were not significantly different. One sample from import and one of domestic origin contained DDT above MRL. In table 7 are summarized results of analysis of meat and fish on presence of DDT and metabolites.

Table 7: Results of analysis of samples of meat and fish on presence of DDT and metabolites

	DDT and metabolites in beef mg/kg on fat content			DDT and metabolites in pork mg/kg on fat content		
	Import 1992-96	Domestic production 1992-96	Domestic production 1985/86	Import 1992-96	Domestic production 1992-96	Domestic production 1985/86
Number of	80	122	63	72	81	75

samples						
Average value	0,059	0,013	0,051	0,041	0,014	0,052
Median	0,029	0,001	0,018	0,015	0	0,009
Range	0-0,427	0-0,157	0-0,571	0-0,265	0-0,235	0-0,626

	DDT and metabolites in poultry mg/kg on fat content		DDT and metabolites in fish mg/kg on edible part of fish	
	Import 1992-96	Domestic production 1992-96	Import 1992-96	Domestic production 1992-96
Number of samples	14	20	44	33
Average value	0,022	0,017	0,0087	0,0103
Median	0,003	0,004	0,0016	0,0041
Range	0-0,088	0-0,0089	0-0,1698	0,0002-0,159

Residues of organochlorine compounds in human milk are monitored since 1977. from mothers not occupationally exposed to these compounds in different locations. All analysed samples contained DDE whereas other pesticides and their metabolites (DDT, DDD, HCH isomers and HCB) were not found in all samples. In table 8 are shown results of analysis of human milk in period 1977-1998.

Table 8: Median concentrations ($\mu\text{g}/\text{kg}$ on milk fat or $\mu\text{g}/\text{kg}$ on milk*) of POPs pesticides in human milk in period 1977-1998. in Zagreb (N-number of samples)

POPs pesticide	1977/79* N=34	1977/79* N=37	1981/82 N=50	1985 N=18	1986/87 N=41	1987/89 N=22
HCB	-	-	210	210	120	60
DDE	30	63	1900	1060	1480	620
DDD	0	3	-	0	0	0
DDT	0	0	180	130	70	0

POPs pesticide	1987/90 N=40	1990/91 N=30	1991/93 N=54	1994/95 N=54	1996/98 N=43
HCB	31	20	15	11	15
DDE	491	450	282	247	409
DDD	0	0	0	0	0
DDT	0	0	0	9	9

During this long monitoring period trend of decreasing levels of these compounds in human milk are observed.

Daily intakes were calculated based on results of analysis of commodities, human milk and questionnaire on consumption habits of certain population groups (table 9).

Table 9: Calculated daily intakes of POPs pesticides (ng/kg body weight). Single values are calculated from average values or median concentrations in commodities and ranges from maximum and minimum values

Origin of commodity and population group	HCB	DDT type compounds
Fish (river Kupa) -fishermen 1985/88.	-	0-158

Fish (from market)		
-adults 1992.	-	-
-adults 1992/96.	0,5	10,0
Mixed diet 1987/89		
-adult women	2-700	200-1200
-dojilje	2-1100	500-2400
Human milk		
-infants		
-1981/82	0-2400	700-25100
-1987/95	-	1620

Acceptable daily intake (ADI) of DDT type compounds is 20 µg/kg body weight of adult person and ADI value for HCB is withdrawn.

Collecting data on POPs pesticide residue levels in ground and underground waters started in late seventies. These results also show decreasing trend of POPs residue levels and in 1993-1994. these levels were <0,5 do 2 ng/dm³. According to data of drinking water quality checks in 2001. 7,2 % of samples did not have good chemical quality properties. Reasons for poor quality were presence of nitro-salts, iron or manganese, but not pesticides.

The most data on POPs residue levels in Adriatic sea is collected for DDT and metabolites in Rijeka bay, which is characterized with slow exchange of water mass. In monitoring of DDT and metabolites in Croatian see from 1977-1987. levels were in range <0,06-104,9 ng/dm³. Concentrations of DDT group compounds were decreasing during this monitoring and in 1987 were at the level of detection. Average DDT concentration in see sediment was 3,7 ng/g of dried sample in 1997.

Indicator of recent use of DDT is DDE/DDT concentration ratio and if there is no new input of DDT in environment than the ratio value is increasing with time. For estimation of geographic distribution of POPs pesticides analytical results from pine needle were taken because of its widespread and in order to make comparison with other literature sources. DDE/DDT ratio was 2,0 and there was no new input of DDT in the environment in 1992 and 1995. Calculated DDE/DDT ratio for air measured in Zagreb was low (1,0 and 0,64) as a consequence of long distance transport of these compounds.

It is important to mention that besides inadequate monitoring also equipment in laboratories is insufficient and employees are not experienced and trained.

Conclusion

According to the collected data POPs pesticides are not produced and not used in Croatia.

Permanently are checked POPs pesticides residues in water according to the regulations whereas for monitoring of other elements of the environment there are not prescribed regulations.

There are oscillations in usage of organochlorine insecticides in the past due to the climatic changes, crop rotation, and insufficiency of foreign currency for import of active ingredients or ready-made products, resistance and work of forecasting and application of integrated plant protection.

However there are data collected through different projects and inspection samples analyses, but this is not provided regularly in frames of national monitoring program.

Oscillation of application of organochlorine insecticides was due to the climatic changes, crop rotation, and insufficient foreign currency for import of active ingredients or ready-made products, resistance appearance, forecasting program and integrated plant protection. Due to mentioned environment pollution was decreased.

Due to mentioned it is necessary to adopt regulations for permanent checking of POPs pesticides residues in all of the elements of the environment.

Also it is necessary to have data collected in the central register.

It is necessary to repair incinerator for dangerous substances.

To provide monitoring it is necessary to have sophisticated equipment and trained experts.