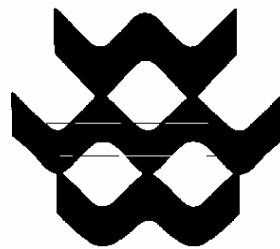


**PLANT PROTECTION INSTITUTE  
POLAND**



**TAUW MILIEU BV  
THE NETHERLANDS**

# **4th FORUM HCH AND UNWANTED PESTICIDES**

**15-16 January 1996  
POZNAN, POLAND**

**International co-operation of experts for the solution of the  
hexachlorocyclohexane  
and unwanted pesticides problems**

**PROCEEDINGS**

**Poznan, 1997**



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## OPENING GREETINGS

Stefan PRUSZYNSKI

Ladies and Gentlemen, our dear Guests!,

It is my honour and pleasure to welcome you to Poznan on the international conference IV<sup>th</sup> HCH Forum on behalf of the organizers, Plant Protection Institute staff and myself. Giving the Plant Protection Institute the opportunity of organizing this meeting is treated by us as a privilege and approval of our co-workers' activities in earlier HCH Forum works.

Meeting in Poznan is however of quite a different character because it is the first time when the specialists associated in HCH Forum meet in the country that, until quite recently, belonged to the so called „socialistic camp”. I am quite sure that political problems should not be involved in our meeting, nevertheless it should be emphasized that the principles of economy organization, and mainly central system of planning and distribution of plant protection products highly affected arising of the phenomena unknown in Western European countries. I have in mind the decision taken at the beginning of the seventies concerning the construction of tombs which are places of storage for unwanted plant protection products and pesticide waste. Central decisions and often the lack of imagination caused the problem signalized by our co-workers during your earlier meetings, the problem, which will be presented and discussed now.

It would be a simplification to burden only the system and its authorities with the responsibility for the tombs and other places of pesticide storage. The occurrence of this problem was also highly affected by such decisions as the withdrawal from use of some groups of plant protection products (DDT, arsenic compounds, mercuric seed dressings) as well as by the structure of Polish agriculture.

Hence Polish administrative authorities and Polish plant protection are presently facing a problem which is very difficult to solve. The last few years are characterized by considerable improvements and we feel sure that the debates of IV HCH Forum will allow to work out the optimal solutions for the future.

Other countries of Central and Eastern Europe in which similar situation exists in various degree and range are also interested in the development of methods of solving the problem of tombs. That is why the representatives of these countries take part in our meeting. Territorial extension of interest in HCH Forum for practically the whole Europe seems to be one of the most important achievements of this meeting.

Ladies and Gentlemen!, Discussing the problem of tombs, that is the risk to the natural environment and humans caused by agriculture and plant protection, I must emphasize the efforts of plant protection science and practice undertaken in Poland and other countries of Central and Eastern Europe which aim at the elimination and reduction of possible adverse effects of the use of plant protection chemicals.

In Poland there are the following examples of such an approach to plant protection: the organization of a system of plant protection products authorization meeting international requirements; all-Polish monitoring of plant protection products residues; all-Polish registration of the most important pests and diseases occurrence; studies carried out for 20 years on the effect of

intensive plant protection on various components of the environment; guidelines for integrated pest management; studies on biological and other non-chemical methods of plant protection and their implementation.

Together with these multidirectional activities intensive works aiming at the solution to the problem of tombs undertaken during last years are carried out.

Discussing the problem of tombs it should be emphasized that it occurred in the country where the use of plant protection products had always been much lower than in countries of developed agriculture.

Ladies and Gentlemen! The materials you have received also consist of some information on the Plant Protection Institute where our meeting takes place. I would like to encourage you to read this information and in case of interest in some of Institute's activities — to direct visits in its departments.

Ladies and Gentlemen! Expressing my satisfaction of your coming and participation in IVth HCH Forum I wish you fruitful debates and new solutions to the problem so difficult yet important from the point of view of plant protection and the environment protection. I also would like to wish you a nice stay in our town and in our centre.

## OPENING GREETINGS

Bram de Borst

Ladies and Gentlemen, Dear Participants of the IVth HCH FORUM!

On behalf of the participants I want to thank the Plant Protection Institute in Poznan for their hospitality and their large efforts in organizing this IVth HCH FORUM. It is a great pleasure to see that so many people accepted the invitation to attend this forum.

The HCH-FORUM is an initiative of an international group of experts, working on the field of HCH and chlorinated pesticides. Meetings have been organized in Zwolle (1992), Magdeburg (1993) and Bilbao (1994). The scope of the HCH-FORUM is to exchange information on :

- risk assessment
- investigation strategy
- remediation strategy
- development of technological solution

Participants are working with universities, research institutes, authorities, industry, contractors and consultants.

The HCH-FORUM is stimulating the attendees in developing solutions on 'how to deal with contamination, originated from HCH and other chlorinated pesticides'.

The first HCH-FORUM, an inventory was made up of the main problems, thus concluding in the scope of the HCH-FORUM as stated above. From the presented papers of the second forum, the extend of the problem was stated as a global problem. It was also concluded that different contaminated sites, varying from production sites to diffuse contamination over large areas, need differentiation in solutions. A first presentation on technical solution was given. The third forum stipulated the progress in concepts, strategies and technical solutions. Presentation were given on biodegradation, (physico-chemical) and extraction technologies.

Needs were identified for coordination of research programmes and international fund raising for broadly applicable research projects.

The fourth HCH-FORUM here in Poznan brings together a large group of experts from 17 different countries. The progress in strategies and technologies will be presented. We look forward to have a stimulating exchange of experiences, expecting that this will offer each participant new and better ideas how to improve solutions for the problem of chlorinated pesticides.

This result will be achieved only by an active participation of all attendees. This means that the future cooperation and developments depends on the initiative and input of the participants.

I wish you a fruitful discussion and exchange of experiences!

## OBSOLETE, UNWANTED AND/OR BANNED PESTICIDES

### A. Wodageneh

Large quantities of obsolete, unwanted and banned pesticides have accumulated over the years in many countries and currently they are posing serious environmental problems. These are hazardous wastes which have become major sources of environmental pollution. There is a growing sense of a global concern and urgency on how to combat the hazard. People in developing countries are most affected because of widespread exposure basically as a result of lack of understanding of the inherent danger of pesticides in general. The FAO estimate of obsolete pesticides in Africa and the Near East alone is in the range of 20,000 tons. The immediate concern is not only HCH/BHC but the overall problem of obsolete pesticides in general. The focus should not be limited only to obsolete stocks that have so far accumulated in the environment but urgent action need to be taken to prevent further accumulation. Unless global awareness is developed to rectify this fundamental and serious environmental and health hazard, the problem will be both complicated and devastating and moreover the damage will be irreversible. The consequences would be far reaching leading to more serious environmental problems than can be anticipated. If the opportunities to tackle the situation are postponed, there would be little or no alternatives for reversing the damage.

### ACTIVITIES UNDERTAKEN OR IN PROGRESS

With the financial assistance from the Government of the Netherlands, has July 1994 FAO has been able to initiate a two year project on „Prevention and Disposal of Unwanted Pesticide Stocks in Africa and the Near East”. Among other things, it has been able to compile results of survey of obsolete pesticides from a number of countries in Africa and Near East. A total of 38 countries have been covered 33 of which are from Africa and 5 from the Near east. The result of the inventory indicated the existence of nearly 10,000 tonnes only in the countries so far covered.

Though inventories of obsolete pesticides obtained from the different countries are made up hundreds of different active ingredients, of the total of nearly 10,000 tonnes identified, nearly 3,000 tonnes or 35.51% is HCH (BCH) and 229 tonnes or 2.95% is Lindane. The following graph shows clearly the proportion of each.

The inventory does not include contaminants such as contaminated soils, containers and materials which from experience are expected to be around 50% above the actual amount of obsolete pesticides.

Although HCH contamination is most common and widespread particularly in Eastern Europe, the above graph indicates that HCH also contributes to environmental contamination in Africa and the Near East. This is part of the inventory covering region under Project GCP/INT/572/.NET and is not yet complete as several African countries are still under investigation in order to determine the overall situation of obsolete pesticides in the remaining countries of two regions.



The following technical guidelines have been prepared and distributed.

- English, French and Arabic version of „Prevention of Accumulation of Obsolete Pesticide Stocks”
- English version of „Disposal of Bulk Quantities of Obsolete Pesticides in Developing Countries” This was produced in cooperation with UNEP, and WHO and
- English version of „Pesticide Storage and Stock Control Manual”. All the guidelines will be available in French, Spanish and Arabic translations.

Pilot disposal operations are initiated in three countries, namely, Yemen, Zambia and Seychelles. The operation in Yemen is being completed involving 262 tonnes while disposal in Zambia and Seychelles will be finalized in 1997.

It is the aim of FAO to formulate programmes, to mobilize and enhance a plan of action for a collaborative international effort and, where possible, to continue in-country activities aimed at reducing the accumulation of obsolete pesticides and risk to human health and the environment.

#### THE NEED FOR URGENT DISPOSAL OF OBSOLETE PESTICIDES

Disposal of obsolete pesticides is neither simple nor cheap. It requires basic technical skill and expertise. Developing countries neither have the facilities nor the finance. They need to be assisted both technically and financially. Collaboration of both donors and recipient countries is prerequisite. Commitment and financial support are fundamentally important for a solution of such major environmental disaster. A table of obsolete pesticide inventory and disposal operations completed in Africa and the Near East, is given on the following page.

Although the beginning has been made in the right direction, the solution to the problem is still far away. A summary table of obsolete pesticides inventory from 31 countries in Africa and the Near East and two tables one each on HCH (BCH) and Lindane are attached. Although an effort can be made to demonstrate the worst environmental damage inflicted upon each and every country, in order to minimize the human health hazard, much more effort will be required to clean up and dispose of all identified obsolete pesticides along with their contaminants. However, it must be understood that whatever solution might be justifiably acceptable and considered appropriate, it should be implemented. However, whatever can be made, nothing tangible can be achieved without a concerned global effort and undertaking.

## Inventory of obsolete and unwanted pesticide stocks by country ( project GCP/INT/572/NET )

No	Country	No sites affected	No of different pesticide	Total in (tonnes)	Total disposed of (tonnes)	Agencies involved in disposal
AFRICA						
1	Benin	20	±21	67		
2	Botswana	1	7	25		
3	Burkina Faso	24	57	54		
4	Burundi	2	5	58		
5	Cameroon	20	10	225		
6	Cape Verde	3	12	23		
7	Congo	7	1	2		
8	Eq. Guinea	22	17	146		
9	Eritrea	29	58	158		
10	Ethiopia	143	±70	426		
11	Gambia	±7	> 5	23		
	Guinea Bissau	4	9	9		
14	Madagascar	4	14	76	70	GTZ
15	Malawi	11	29	127		
	Mali(Provisional)	28	9	125		
16	Mauritania	13	11	257		
17	Morocco	25	±170	2,265		
18	Mozambique	48	±150	443	160	GTZ
19	Namibia	1	1	245		
20	Niger	±15	29	52	60	USAID/GTZ/Shell
22	Sao Tome/Princ.	1	3	3		
23	Senegal	8	±21	274		
	Seychelles	1	37	10		

No	Country	No affected sites	No of different pesticide	Total in (tonnes)	Total disposed of (tonnes)	Agencies involved in disposal
24	S/Africa	several		±30	390	
	Sudan	44	±80	657		
25	Swaziland	2	35	9		
	Tanzania		DNOC	inventory	55	GTZ
27	Togo	7	>20	85		
28	Tunisia	21	various 5	882		
29	Uganda		Deldrin	inventory	50	FAO
	Zaire	5	11	591		
30	Zambia (*)	6	±51	336		FAO/DGIS/ GTZ
31	Zanzibar	Several	±	100		280 DGIS
NEAR EAST						
1	Iraq	16	5	232		
2	Lebanon	Several	Several		189	
3	Qatar	1	7	5		
4	Syria	20	13	323		
5	Yemen	>20	±130	262	262	FAO/KfW
	Total			9,030	937	

## NOTE:

The above is a compilation of results of inventories up to September 1996. The figures do not include quantities of contaminated soils and materials which can be substantial and thus the final total should be expected to be much higher.

HCH Identified in a few countries of Africa (Survey will continue)

N.B. Question marks indicate either unspecified or unknown

Country	Location	Quantity	Unit	Formulation	Year	Origin
Benin	Natitingou	24,000	kg	?	1980	?
Burkina	Koupela	5	kg	?	?	Maduco
" "	Ouhaigoua	770	kg	?	1986	?
Ethiopia	?	85,373	kg	?	?	?
Morocco	?	1,995,065	kg	?	?	?
Namibia	Keetmanshoop	245,000	kg	?	?	S/Africa
Niger	Niamey	650	kg	?	?	?
Senegal	Richard Toll	625	kg	?	1973	?
" "	St. Louis	25,000	kg	?	1974	?
S. Africa	several	128,837	kg	?	?	?
Tunisia	Beja	300	kg	?	?	?
" "	Gabes	21,000	kg	?	?	?
" "	Gafsa	60,000	kg	?	?	?
" "	Jendouba	2,000	kg	?	?	?
" "	Kairouan	11,000	kg	?	?	?
" "	Kasserine	450	kg	?	?	?
" "	Lekef	4,000	kg	?	?	?
" "	Medenine	22,000	kg	?	?	?
" "	Monastir	3,000	kg	?	?	?
" "	Sfax	12,000	kg	?	?	?
" "	Sidi Bouzid	1,500	kg	?	?	?
" "	Silana	1,250	kg	?	?	?
" "	Sousse	100,000	kg	?	?	?
" "	Yunis	50,000	kg	?	?	?
" "	Zaghuan	4,000	kg	?	?	?
	TOTAL	2,757,827	kg	?	?	?
TOTAL		2,758	Tonnes			

Lindane identified in a few countries of Africa (Survey will continue)

Country	Location	Quantity	Unit	Formulation	Year	Origin
Burkina Faso	Ougadougou	2	kg	?	1987	Callivoire
Cameroon	Abong Mbaang	14,190	kg	?	1988/89	Rhone
" "	Bamenda/Nkwen	14,000	kg	?	1988	Rhone
" "	Bafoussan	60,000	kg	?	1985	Rhine
" "	Kumba	4,180	kg	?	1987	Callope S. Africa
Eritrea	Agordat	1,000	kg	?	1974	?
" "	Adi Tecezan	1,350	kg	?	?	?
" "	Nacfa	600	kg	?	?	?
" "	Ghinda	1,350	kg	?	?	?
" "	Alghidir	1,125	kg	?	?	?
" "	Segeneiti	350	kg	?	?	?
Ethiopia	?	25,717	kg	?	?	?
Madagascar	Antananarivo	450	kg	?	?	?
Malawi	Kawlazi Est. Nkhtabay	15	kg	?	?	?
Mauritania	H. Chargul/Aloun	850	kg	?	?	?
" "	Kiffa	1,500	kg	?	?	?
Morocco	?	77,485	kg	?	?	?
Niger	Ouallam	3,275	kg	?	?	?
" "	Niamey	400	kg	?	?	?
Senegal	Dakar	17,522	kg	?	?	?
Togo	Sokode	3,915	kg	?	?	?
	TOTAL	229,276	kg			
TOTAL		229	Tonnes			

N.B. Question marks indicate either unspecified or unknown

## RISKS ANALYSIS OF SOIL AND WATER POLLUTION FROM USE AND STORAGE OF PESTICIDES

**Ketil HAARSTAD**

### Introduction

This paper mainly discusses normal use of pesticides applied to the topsoil vegetative layer. The general principles will however apply to storage of pesticides with the exception of course for levels and uncertainty of storage technical facilities and so on.

A risk analysis is according to Norwegian Standard no. 5814 (1991) a systematic description of the probability that a pollution will affect humans, animals, ecosystems, buildings etc. together with the consequences of this pollution. A risk evaluation is a comparison of one or more risk analyses with local and general environmental criteria. Generally, pollution of soil including physical and biological compartments can be considered in three parts; (i) source of pollution, (ii) spreading and (iii) receiving, uptake and effect. Each case should start with a description of the problem based on existing data. Final conclusions will often be based on (iii), while the targets for action against pollution should be based on (i).

Studies have shown that use of pesticides can give high occurrence of pesticide residues in water. In Denmark 1500 analyses of 825 showed 8.6 % findings of pesticides according to Jacobsen (1994). A study of 284 drinking water wells showed 14 % findings. Similarly in the UK, an analysis of nearly 30 000 samples of drinking water showed residues in nearly 30 %, and about 7 % in samples from groundwater (Mardsen, 1992). According to On Tap (1995) a study of tap water from 29 communities showed residues in 62 % of the samples.

### Case study

JORDFORSK has made a risk assessment to study the vulnerability of a groundwater aquifer used for local drinking water supply serving approx. 1000 people. A short list of descriptive data is given in Table 1. Names of applied pesticides are listed in Table 2.

Norwegian standards for pesticides in drinking water allow max 0.1 ppb of individual compounds, and 0.5 ppb for the total content of pesticides.

We have compared three methods for the assessment; (i) risk class, (ii) partition coefficient and (iii) model simulation. The first 2 methods are simple, the third can be anything from simplified to extremely complicated depending on the model chosen.

Table 1. Groundwater recharge and well area

Parameter	Value	Unit
Saturated hydraulic cond.	0.1	cm/sec
Bulk density	1.60	cm <sup>3</sup> /cm <sup>3</sup>
Porosity	0.395	cm <sup>3</sup> /cm <sup>3</sup>
Groundwater depth below surface	12	m
Recharge area	103	decares
Agricultural area	50	decares
No. of pesticide applications	1	
Simulation period	20	years

Table 2. Pesticides applied in the recharge area of a groundwater well (grain crops and strawberries)

N o.	Trade Name	Substance	Use against	Risk class <sup>a</sup>
1	Betanal	Phenmedipham	Herbicide	C
2	Finale	Glufosinate-NH <sub>4</sub>	Herbicide	C
3	Focus ultra	Cycloxydim	Herbicide	C
4	Gesatop	Simazine	Herbicide	C
5	Klevamol	Mekoprop	Herbicide	B
6	Goltix	Metamitron	Herbicide	C
7	Optica Combi	Meko+MCPA	Herbicide	B
8	Preglone	Di-+Paraquat	Herbicide	B
9	Roundup	Glyphosate	Herbicide	C
10	Venzar	Lenacil	Herbicide	C
11	Weedar	2,4-D	Herbicide	B
12	Weedex	MCPA	Herbicide	B
13	Ambush	Permethrin	Insecticide	C
14	Apollo	Clorfentezine	Insecticide	C
15	Gusathion	Azinphos- methyl	Insecticide	A
16	Lebaycid	Fenthion	Insecticide	B
17	Meta- systox	Demeton-s-methyl	Insecticide	A
18	Sumicidin	Fenvalerate	Insecticide	C
19	Bayleton	Triadimefon	Fungicide	C
20	Bravo 500	Chlorothalonil	Fungicide	B
21	Euparen	Tolyfluanid	Fungicide	C
22	Recoprop	Copper oxychloride	Fungicide	B
23	Morestan	Quinomethionate	Fungicide	C
24	Ronilan	Vinclozolin	Fungicide	C

<sup>a</sup> Risk class: A=Toxic, B=health risk, C=minor health risk

#### Method (i) Risk class.

Distribution and use of pesticides in Norway are regulated by the authorities. The pesticides are classified as follows, based on occupational hazard:

X=Highly toxic

A=Toxic

B=health risk

C=minor health risk

Suggested acceptance criteria:

Pesticides accepted for use in recharge area are assumed to be in class C (Norwegian Institute for public health (folkehelsa)).

Limitations:

Risk class is defined only by occupational risk, environmental risk is not evaluated.

A listing in guidelines (from 1987) for protection of groundwater resources includes 21 pesticides given as examples accepted for use, of which 10 % were in class A, 43 % in class B and only 29 % in class C.

20 % of the pesticides from the example have been removed from the list of legal pesticides.

Method (ii). Partition coefficient

Transport of pesticides through a soil column will besides the amount, quality and speed of water, depend on the sorption to soil particles.

The sorption is given by the partition coefficient,  $K_d$ , which is the ratio between the concentration of the substance in the soil and in the aqueous phase at the end of an adsorption test (Kuhnt & Muntau, 1994), and can be calculated by:

$$\log K_d = \log f_{OC} + a \cdot \log S + b$$

$K_d$ =partition coefficient,  $f_{OC}$ = soil organic fraction, a and b = parameters,

S = pesticide solubility in (local) water sample (mg/litre)

Pesticide residence time relative to water is given by:

$$T = t_i/t = 1 + r/n \cdot K_d$$

Suggested acceptance criteria:

Application OK for  $T > 100$

Limitations:

Linear assumption between solubility and partition coefficient.

Based on tests with 106 compounds with a limited range of concentrations, only 8 of the relevant compounds were included (Kenaga & Goring, 1980).

Assume normal distribution of several variables not tested for normality.

Adsorption can depend on water chemistry, highly soluble compounds can have high particle affinity (eg. Glyphosate).

Several basic assumptions are expected not to be met.

Method (iii). Model simulation

Based on the fact that the underlying data was rather limited we used a simple model:

Pestam

Pesticide Analytical Model 4.0

(Ravi & Johnson, undated)

Includes:

decay of pesticide in soil and water, actual precipitation, soil depth and geology, amount of pesticides applied.

Assumptions:

Simulation period 20 years, 1 day between application and the beginning of water infiltration.

Limit for acceptable infiltration dept 480 cm. Limit for acceptable concentration at 480 cm or lower: 0.0001 mg/l. Net annual groundwater recharge on an average basis.

Limitations:

No additional pesticide application within simulation period

Limit on background data on pesticides

Limit on data on local soil and hydrogeology



Figure 1a shows an example of a compound, Meta-systox that does not reach the groundwater level in 20 years, and thus it is accepted in the recharge area. Figure 1b shows a compound that reaches the groundwater table in about 2000 days at a level above the accepted limit and thus it is not allowed to be used in the recharge area.

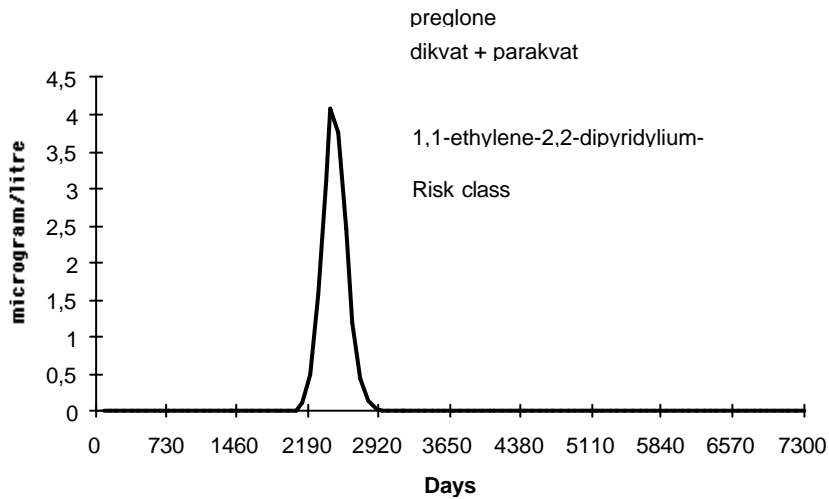
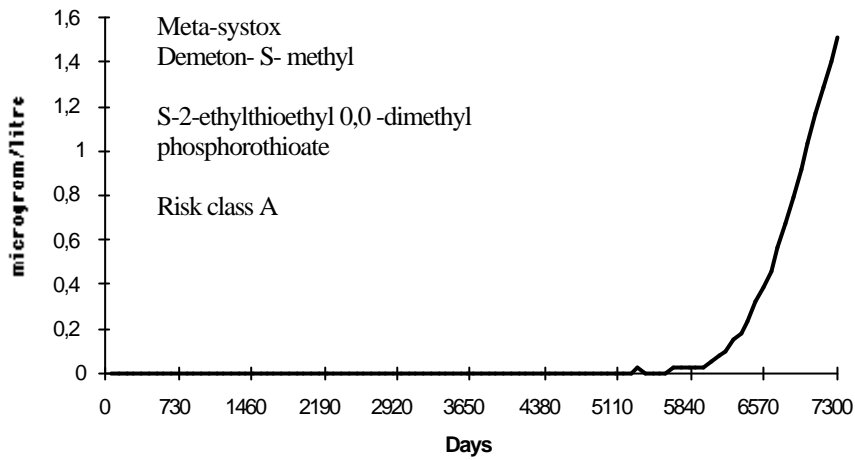


Fig. 1. Concentration of (a) Demeton-s-methyl at depth 3.6 m and (b) Di- +Paraquat at 12 m below surface

## Landfill with DDT - Gvarv

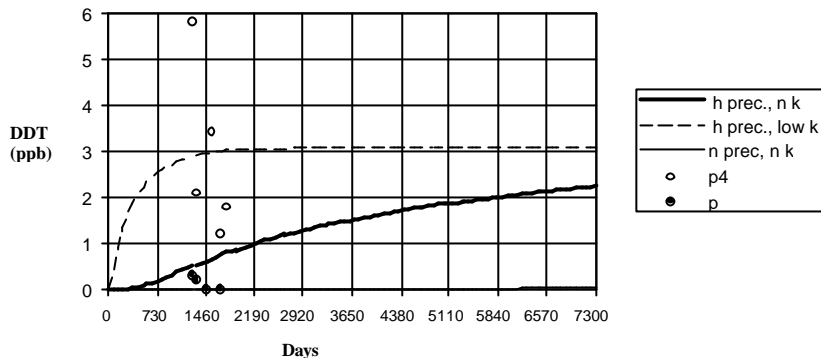


Fig.2. Simulated «Breakthrough curve» from Pestan; DDT in groundwater 0.1 cm

from polluted point in soil based on net groundwater recharge:

high 60 mm/day = episodic event 5 years max.

annual normal = 1.3

partition coefficient;

normal high  $k_d = 140\,000\text{ cm}^3/\text{g}$

low  $k_d = 10\,000\text{ cm}^3/\text{g}$

Other pesticides found: Tolyfluanid, Fenvalerate, Lindane

Groundwater data:

TDS = 70 mg/l

El. cond.= 12 mS/m

TOC= 1 mg/l

HCO<sub>3</sub>=22 mg/l

pH= 6

## Landfill with DDT - Sonsterud

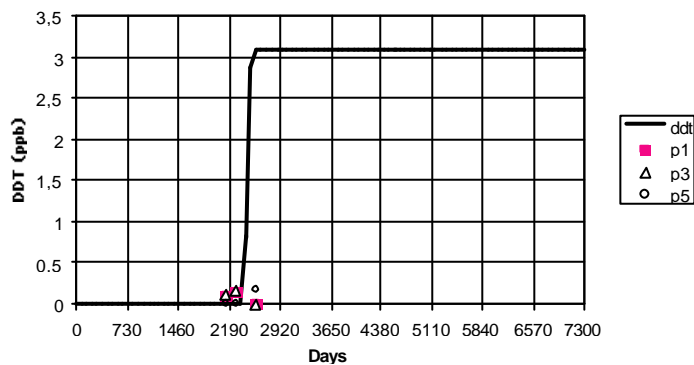


Fig. 3. Breakthrough curve in gw for DDT 150 cm below surface based on net groundwater recharge: 40 mm/day (annual normal = 1.1) partition coefficient,  $k_d = 500\text{ cm}^3/\text{g}$  (normal =  $140\,000\text{ cm}^3/\text{g}$ )

Other pesticides found: Fenvalerate, Propiconazole

Groundwater data:  
 TDS = 415 mg/l  
 El. cond.= 87 mS/m  
 TOC=17 mg/l  
 HCO<sub>3</sub>=15 mg/l  
 pH=5.1

#### Method (iv). GUS

According to Gustafson (1989), the most relevant physical variables on leaching of pesticides in soils are  $K_{OC}$ , which are the soil partition coefficient  $K_D$  adjusted for soil organic content, and the half-life value which is the average time it takes (preferably measured in the field) for soil residues of the parent molecule to decline by 50 %. The other one is preferred because much of the variability of leaching of pesticides is assumed to relate to the variability of the soil organic content. In the case of pesticides, mostly ionic substances, that don't relate strongly to organic content, but have more affinity to clay particles such as eg. Glyphosphate, the average value is divided by the global amount of organic content in soils.

$$GUS = \log_{10}(t_{0.5}^{\text{soil}}) \times (4 - \log_{10}(K_{OC}))$$

Limitations:

Little account of variability in hydrogeology and climate.

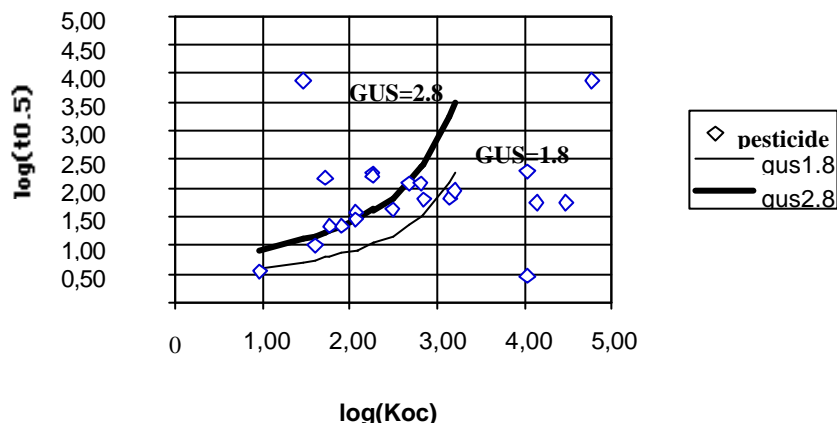


Fig. 4. Application of GUS-method.

## Results

Table 3 shows the results from the risk evaluation of the case study with the specified application rates.

Table 3. Risk assessment of selected pesticides and groundwater pollution

METHOD						
No.	Name	Appl. a	(i) Risk class	(ii) Partition	(iii) Pestan	(iv)GUS
1	Phenmedipham	6	OK <sup>b</sup>	OK	OK	L
2	Glufosinate-NH <sub>4</sub>	10	OK	L <sup>b</sup>	L	OK
3	Cycloxydim	6	OK	OK	L	L
4	Simazine	3	OK	OK	L	L
5	Mecoprop	6	L	OK	L	L
6	Metamitron	8	OK	L	OK	L
7	Mecoprop+MCPA	3	L	L	OK	L
8	Di- +Paraquat	24	L	L	L	OK
9	Glyphosate	8	OK	L	OK	OK
10	Lenacil	2.5	OK	OK	OK	OK
11	2,4- D	1.5	L	OK	OK	L
12	MCPA	1.5	L	L	OK	L
13	Permethrin	0.35	OK	OK	OK	OK
14	Clorfentezine	0.6	OK	OK	OK	L
15	Azinphos-methyl	2.3	L	OK	OK	L
16	Fenthion	3	L	OK	OK	L
17	Demeton-s-methyl	0.5	L	L	OK	L
18	Fenvalerate	0.75	OK	OK	OK	OK
19	Triadimefon	4	OK	OK	OK	L
20	Chlorothalonil	2	-	OK	OK	OK
21	Tolyfluanid	10	OK	L	L	L
22	Copper oxychloride	7	L	L	OK	no data
23	Quinomethionate	0.5	OK	OK	OK	OK
24	Vinclozolin	1.2	OK	L	OK	L

<sup>a</sup> Amount of pesticides applied [kg/hectare],

<sup>b</sup> OK= non-leacher, L = leacher or transition pesticide

### Conclusions

Of the 24 compounds given in the case study, method (i) accepted 14, method (ii) accepted 14 and method (iii) accepted 18. Methods (i) and (ii) disagreed in 50 % of the compounds, methods (ii) and (iii) in 33 % and method (i) and (iii) also in 50 % of the compounds. Only 4 of the 24 compounds (17 %) had same conclusion with all 4 methods.

A risk analysis can be made on many levels from the simple to the complicated. This example show that choosing too simple approach can give unacceptable discrepancy compared to more sophisticated methods. Care should be taken that the input values chosen are representative for the local problem. This is especially important when considering climate over time. Generally it is not desirable to use complicated models without a detailed knowledge of the critical variables in the systems, ie. their distribution and uncertainty.

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**HEALTH RISK ASSESSMENT: LESSONS FROM THE PAST  
AND POINTERS FOR THE FUTURE**

**Colin C. Ferguson**

By convention risk assessment is often treated as comprising three mutually dependent fields: hazard identification and dose-response assessment; exposure assessment; and risk characterisation. Some of the lessons learned from the experience in risk assessment over the past 15 years or so are summarised below.

**Hazard Identification and Dose-Response Assessment**

- Low-dose extrapolation models may be used to rank carcinogens objectively but should not be expected to predict cancer occurrence rates accurately
- Theoretical risk estimates should be derived from several low-dose models, not just from the most conservative model
- Biological differences between species can be adjusted using physiologically-based pharmacokinetic (PB-PK) models
- Best estimates of theoretical risk should be presented as well as upper bound estimates
- Theoretical risk estimates should be checked using epidemiological data whenever possible
- Traditional dose-response methods for threshold compounds suffer from bias towards the absence-of-effect hypothesis

**Exposure Assessment**

- Too much emphasis should not be put on exposure estimates for the maximally exposed individual
- Repeated use of worst case assumptions can lead to very unrealistic exposure assessment
  - Indirect pathways of exposure should not be neglected
  - Exposure estimates should be validated whenever possible
  - Realistic exposure estimates require an understanding of environmental partitioning and environmental fate
  - Sensitivity analyses will help to focus effort on the most important exposure pathways
  - Probabilistic techniques (e.g. Monte Carlo) help to provide a formal way of handling variability and uncertainty
  - The quality of an exposure assessment depends on data quality objectives for sampling design; taking storage and transport of samples; sample preparation and laboratory analysis; as well as rigorous data interpretation.

**Risk Characterisation**

- Low-dose modelling should not be represented as indicating realistic risk estimates
- Background levels of exposure should be taken into account when characterising incremental risk
- Monte Carlo analysis can be useful to indicate realistic risk ranges
- Risk estimates should be put in perspective, especially in the light of uncertainty and sensitivity analyses

- 
- Trying to fix a problem can sometimes create more risk than doing nothing.  
In the future, it is expected that health risk assessment will improve primarily through better data on exposure parameters and bioavailability, and through improved mechanistic understanding of health impacts from low-dose exposure to chemicals. There will also be increased emphasis on risk-reduction strategies driven by cost-benefit analyses.

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## **OVERVIEW STATE OF THE ART OF CLEANING TECHNOLOGIES FOR SOILS CONTAMINATED WITH HCH**

### **1. INTRODUCTION**

Soil and groundwater, contaminated with HCH, and uncontrolled dumps of HCH waste cause a serious risk for human beings and ecosystems. To reduce these risks remedial actions are necessary. Two types of remedial actions are possible. One type is aimed at the removal or destruction/conversion of the HCH from the soil (or groundwater, or waste), the other is aimed at the isolation or immobilisation of the polluted site or dump. What type of remediation technique is environmentally, technically and financially most optimal strongly depends on the specific situation of the pollution, which can vary very strongly. With respect to clean-up of a polluted soil, it can be stated that at present the number of techniques which can be applied in practice are limited while the costs are sometimes substantial. There is a strong need for improvement of existing techniques, broadening the field of application of existing techniques and the development of new alternative techniques. A tailor made approach is necessary.

The aim of this paper is to give a brief overview of the state of the art with respect to existing clean up techniques, techniques which are still in the development phase, and possible new future techniques which might be of interest. Preceding this overview first the type of HCH problems encountered will be discussed briefly. Also some attention is paid to the basic principles of clean-up and the factors which are of major relevancy in the choice and the application of a clean-up technique .

As already mentioned this paper intends to present a brief overview. For more detailed information reference is made to the previous HCH forums.

### **2. TYPE OF HCH PROBLEMS**

The type of HCH problem can vary strongly. This also means that the remedial approach of the problem will be different. The various problems can be classified in the following categories.

- a) Excavated polluted soils
- b) Polluted sites which cannot be excavated due to environmental, technical, or financial reasons and which therefore need an in-situ clean-up
- c) Large diffuse polluted areas
- d) Wastes, characterised by a high percentage of HCH
- e) Polluted groundwater

### **3. REMOVAL PRINCIPLES OF POLLUTANTS FROM SOIL, GROUNDWATER OR WASTE**

Basically there are four different principles to remove a pollutant from a soil, waste water or waste. These basic processes are:

- \* Molecular separation
- \* Phase separation
- \* Chemical conversion
- \* Biodegradation

A removal principle is not always based on one principle. Very often more than one basic process is involved in a treatment. All types of treatment systems make use of the specific differences in properties between the pollutants or polluted particles and the non-polluted substances. In soil clean-up the major factors governing the removal possibility of a contaminant from soil are:



- \* The type and concentration of the pollutant
- \* The physical state of the pollutant
- \* The chemical, physical and (micro)biological properties of the pollutant
- \* The type of soil (sand, clay, loam, peat)
- \* The size and history of the polluted site.

Regarding the history of the polluted site, three factors have relevancy for soil clean-up, especially for in-situ clean-up of soil: the way the site has been polluted, the way the site has been used after it has been polluted and the time interval between the moment of pollution and clean-up.

#### **4. CLEAN-UP TECHNIQUES FOR EXCAVATED SOIL**

##### **A.THERMAL TREATMENT**

Thermal decontamination of soil consists, in general, of two treatment steps. The first step is aimed at removal of the contaminants from the soil by evaporation and chemical destruction (500 - 700 °C). The organic pollutants in the waste gas are completely oxidized in a separate incineration step (1000 - 1200 °C). This method has been developed to full scale and can be applied in practice. Special attention has to be paid to the prevention of the emission of dioxines. The conditions of the treatment process have to be chosen very carefully. Destruction of dioxines in the waste gases requires specific process conditions, such as high temperature, surplus of oxygen, a minimal residence time of a few seconds and an appropriate mixing in the afterburner.

General features:

- \* The method is intensively applied on FULL SCALE. (both mobile and permanent installations)
- \* Removal of HCH below the standard for clean soil is possible. Demonstrated at full scale.
- \* Firms/institutes: Boehringer-Ingelheim/Dekonta (Germany), NBM Bodemsanering BV (Netherlands), Ecotechniek BV (Netherlands)New developments/alternative developments
- \* Thermal Hydro-Dehalogenation of gasphase at about 850 °C
  - Investigated for treating waste streams containing halogenated hydrocarbons
  - In development stage (lab scale)
  - Also interesting for treating waste gas from thermal treatment of HCH contaminated soils
  - Firms/institutes involved: Universities of Leiden and Delft, Koninklijke Schelde Groep, TAUW Milieu (Netherlands)
  - Similar developments in USA for HCH related compounds such as PCB's
- \* Low Thermal Volatilization
  - Evaporation of HCH from soil at about 200 °C
  - In development stage (lab scale)
  - Lab scale results with respect to residual HCH content are very promising
  - Long treatment time
  - Process has to be combined with a waste gas treatment system
  - Firms/institutes involved: Mourik-Groot Ammers/TAUW Milieu (Netherlands)
- \* Thermolytic Dechlorination with Organic Peroxides at elevated temperatures (60 to 80 °C) in a slurry reactor
  - Lab scale investigation

- Removal efficiency strongly depends on the type of HCH-isomer
- Firms/institutes involved: TAUW Milieu (Netherlands), University of Halle (Germany)
- \* Use of techniques developed for treatment of halogenated organic waste
- Base Catalysed Detoxification process (BCD)
- Decomposition of HCH and HCB in liquid alkali media
- Decomposition of chlorinated waste with the KPEG and NaPEG process

More information about these processes is given in paragraph 6.

## **B.WET CLASSIFICATION**

Wet classification is a treatment method consisting of three treatment steps. The first step is an intensive mixing of soil with the aqueous extracting agent, intended to break up conglomerates of polluted and non-polluted particles and to disperse pollutants in the extracting phase. The second step is a selective separation of the clean soil particles from the extracting agent. For sandy soil classification techniques based on hydrocyclones and fluidized bed columns can be used in combination with the use of detergents or other surface active compounds. In the case of the presence of large amounts of clay particles in the soil, it has been pointed out that flotation processes are very suitable for the selective removal of the HCH-containing small clay particles. The third step is the treatment of the polluted extracting agent.

General features:

- \* The method is intensively applied on FULL SCALE
- \* Removal of HCH in general below the standard for clean soil is possible (Dutch standard)
- \* Sludge polluted with HCH is produced during the treatment process
- \* The process can only be applied to soils with no or only a relatively small amount of clay particles and humic substances.
- \* The presence of Hg and lime in the soil can be a problem.
- \* Firms/institutes involved: Heijmans Milieutechniek (Netherlands), Heidemij Realisatie BV (Netherlands).

## **C. EXTRACTION WITH AN AQUEOUS EXTRACTING AGENT**

Extraction is a treatment method intended to dissolve the pollutants present in the soil particles or adsorbed to the surface of the soil particles, or present as pure pollutant particles, into the extracting agent. After the dissolving step clean soil particles can be separated from the soil. The waste extracting agent has to be treated. Water as such is in general not suitable for the extraction process. The dissolving process has to be enhanced by adding such chemicals as organic and inorganic acids (sometimes necessary to dissolve lime components), bases, complexing agents, surfactants, detergents, small amounts of organic solvents and so on. Also increase of temperature can enhance the dissolving process.

General features:

- \* All methods are still in the development phase (lab scale).
- \* Research is mainly focused on loamy sand.
- \* Results with respect to the total HCH removal and to the removal of the various isomers vary strongly.
- \* Best results are obtained using sodium hydroxide (up to 98% removal)

efficiency).

- \* Results are also of interest to wet classification processes and to in-situ treatment processes, especially in-situ extraction and bioremediation.
- \* In general improvement of the extraction process is necessary with respect to removal efficiency, amount of chemicals to be used and treatment time.
- \* Firms/institutes involved: TAUW Milieu (Netherlands).

#### **D. EXTRACTION WITH ORGANIC EXTRACTING AGENTS (AND SUPERCRITICAL CO<sub>2</sub>)**

Extraction with organic solvents (and supercritical CO<sub>2</sub>) is based on the same principle as extraction with aqueous extracting agents. However the solubility of HCH in most organic solvents is very much higher than the solubility in water. This means that with organic solvents the dissolving process is much more effective. An additional advantage is that clayey and loamy soil particles can more effectively separated from an organic solvent than from an aqueous extracting agent. However, the removal of residual amounts of organic solvents from the cleaned soil, the treatment of the waste organic solvent for reuse and the costs of organic solvents are a disadvantage. Also the safety aspects related to large scale application of solvents may be a disadvantage.

General features:

- \* A lot of research into the removal of HCH or related compounds (such as PCB's and PAH's) from polluted soil or dredged sediments has been carried out. In general high removal efficiencies for organic pollutants are observed.
- \* Up to now the organic solvent extraction process is not applied in practice for soil or sediment clean-up.
- \* Pilot plant and full scale experience is obtained with, among others, the following processes:
  - Basic Extraction Sludge Treatment (BEST). Triethylamine is used as extracting agent.
  - Carver Greenfield process. Isopar is used as extracting agent.
  - CF-systems. Liquefied propane is used as extracting agent.
- \* Labscale experience with the extraction of HCH or related compounds from soil and/or sediments is obtained with, among others, the following types of extracting agents
  - Supercritical CO<sub>2</sub>
  - Acetone
  - Hexane (also in combination with steamstripping)
  - Light petroleum
  - Kerosine
  - Methanol
  - Liquefied butane
  - Methanol
  - Combinations of organic solvents
- \* Practical application of organic solvents is most promising in case of clayey and loamy soils and sediments.
- \* Costs data of the organic solvent extraction processes, given in literature,

vary strongly. Probably due to lack on reliable information about practical application of the treatment process.

- \* Firms/institutes involved: TAUW Milieu (Netherlands), Twente University (Netherlands), Wageningen Agricultural University (Netherlands), US EPA

## E. BIOLOGICAL TREATMENT

Biological treatment is intended to mineralise the pollutants biologically. This may be a basis for practical application. Four systems are available:

- \* Slurry reactors (bioreactors) in which the soil is intensively mixed in order to stimulate the microbiological conversion process. Because process control is easy, optimal conditions can be applied resulting in high conversion rates and high removal efficiencies. To a certain extent this treatment system is comparable with the activated sludge system for waste water treatment. Aerobic and anaerobic process conditions can be applied in slurry reactor systems.
- \* Composting systems. These systems are comparable with composting systems used for treatment of organic solid wastes. Compared with slurry reactors substantially lower reaction rates are expected.
- \* Landfarming systems. In landfarming the polluted soil is spread out in a thin layer on top of a specially constructed impermeable layer provided with a drainage system. Aerobic biological degradation of the pollutants in this layer is stimulated by regularly cultivating the layer.
- \* Extensive microbiological treatment (or posttreatment) of soil placed on heaps in controlled soil disposal sites. This treatment system can be applied to non pretreated soil or to soil already pretreated in a bioreactor, in a composting system, or in a landfarm. Extensive treatment of soil placed on heaps may also be an interesting option for soils that are not fully cleaned after an extractive treatment process.

A problem of the biological treatment of HCH contaminated soil is that the conditions for optimal biological degradation of the various isomers are different and that some of the isomers (specially beta HCH) are hardly biodegradable.

### General features

- \* Up to now research has been limited to lab scale experiments both with HCH polluted groundwater and with HCH polluted soil.
- \* In general it is observed that alpha-HCH and gamma-HCH are much better biodegradable than beta HCH and delta HCH.
- \* From the results obtained with HCH-contaminated water (waste water or polluted ground water), the impression is that all isomers are biodegradable, however the conditions for biodegradation (aerobic/anaerobic, temperature, redox potential and so on) are strongly different.
- \* From the results obtained with HCH-contaminated soil it appears that beta and delta HCH are not or not fully biodegradable in soil.
- \* During the biodegradation process of HCH toxic intermediates may be formed.
- \* The limited biodegradation rate of HCH in polluted soil may probably caused by the low bioavailability, probably due to the strong sorption properties of the soil, or the low solubility of the HCH compounds in water or the presence of HCH in the form of particulate pollutants.
- \* As far as known from lab scale experiments also white rot fungi are not

successful in the biodegradation process.

- \* Firms/institutes involved: TAUW Milieu (Netherlands), Wageningen Agricultural University (Netherlands), TNO (Netherlands), Rathenower Anlagenbau GmbH (Germany)

## **5. IN-SITU TREATMENT OF SOIL**

For in-situ treatment of contaminated soil four systems are available:

- \* In-situ extraction with an aqueous extracting agent
- \* In-situ extraction with an organic solvent
- \* In-situ biological treatment (bioremediation)
- \* Combination of in-situ extraction and bioremediation

In-situ treatment is in fact based on the same processes and process conditions already mentioned for treatment of excavated soil. Three aspects are different.

\* The pollutant to be removed in-situ is often relatively mobile and more easily available for dissolving, transportation or biodegradation than the pollutant present in excavated soil.

- \* The permeability of the soil is a very important process factor.
- \* Control of the clean-up process is much more complicated.
- \* Treatment times are much longer, however this is in fact no principal problem.

General features:

\* Bioremediation has been investigated on a full scale. Results with respect to the removal of HCH were disappointing.

\* On lab scale the extraction of HCH with an aqueous extracting agent has been investigated. Among others the effect of the use of sodium hydroxide, sodium chloride, and surfactants on the removal efficiency has been studied. Results vary strongly.

- \* Firms/institutes involved: TAUW Milieu (Netherlands)

## **6. TREATMENT TECHNIQUES FOR HCH CONTAMINATED WASTES.**

### **A. BASE CATALYSED DETOXIFICATION PROCESS.**

In this process HCH or related chlorinated organic compounds, like PCB's are partially or completely dechlorinated. The dechlorination process is achieved at high temperatures (250 °C to 350 °C) in a suitable medium and a reducing atmosphere. A proper catalyst and sodium hydroxide as base have to be added to the system.

General features:

- \* The process has been developed and successfully demonstrated for destruction of PCB's in waste transformer oil at 350 °C.
- \* The process has also been investigated for the treatment of HCH-waste. It was demonstrated that HCH could be converted nearly completely to trichlorobenzene. The final reaction products are free of dioxines.
- \* In combination with a Low Thermal Desorption process for HCH contaminated soil it can be expected that the Base Catalysed Dechlorination process (BSD-process) can also be applied in treating soils or sediments polluted with HCH. In the USA and Australia this process has already been tested for soils and sediments contaminated with PCB's.

- \* Firms/institutes involved: US EPA, IHOBE (Spain), Australian Defence Industries Ltd (Australia/Germany)

## **B. DECOMPOSITION OF HCH AND HCB IN HIGH TEMPERATURE LIQUID ALKALI MEDIA**

In this process a gases stream (air) containing HCH and HCB (hexachlorobenzene) is treated in a liquid alkali bed reactor. The reactor contains sodium hydroxide and sodium carbonate. The temperature of the reactor is about 500 to 900 °C.

General features:

- \* The process has been successfully demonstrated on lab scale. More than 99 % of the HCH and HCB has decomposed.
- \* In combination with a Low Thermal Desorption Process for HCH contaminated soil it may be expected that the process can also be used for treating soil contaminated with HCH or other halogenated organic pollutants. The liquid alkali reactor has to be used as the treatment process for the waste gases.
- Firms/institutes involved: Institute of Plant Protection Sosnowice Branch (Poland)

## **C. DECONTAMINATION OF CHLORINATED WASTE WITH THE KPEG AND NaPEG PROCESS.**

This process uses potassium or sodium polyethylene glycol oxide (KPEG or NaPEG) which are obtained from the reaction between polyethylene glycol (PEG-400) and respectively potassium hydroxide and sodium hydroxide. Halogenated organic waste streams or soil contaminated with these pollutants are mixed up with the reagent (KPEG or NaPEG) at a temperature of approximately 150 °C. The result is a dechlorination of the pollutants.

General features

- \* The process has been demonstrated at pilot plant scale and full scale for treating soil contaminated with PCB.
- \* Removal efficiencies up to 99 % were obtained.
- \* It can be expected that the process can also be applied to HCH wastes and soils contaminated with HCH.
- \* Firms/Institutes involved: US EPA

## **7. TREATMENT OF LARGE DIFFUSE POLLUTED AREA**

The clean-up techniques for soil mentioned in the foregoing are especially intended to treat strongly polluted areas of limited size. In general these techniques are aimed at complete or nearly complete removal of the pollutants. The costs of these techniques are relatively high. For a large number of contaminated sites of limited size these treatment techniques can often be used to clean-up the site within the constraints of acceptable treatment costs.

In several regions, both in highly industrialized Western countries and in Eastern and Central Europe, there are large areas at which the top layer of the soil is diffuse polluted with inorganic and/or organic pollutants. Excavation of the soil by means of the usual excavation techniques, followed by intensive treatment in a treatment installation or intensive in-situ treatment (using the usual expensive

treatment techniques developed for small sites) is not possible. For these areas a completely different clean-up approach is necessary. The following constraints for such a clean-up techniques have to be considered:

- \* Relatively simple
- \* Treatment time of several years
- \* Extensive process with no negative environmental impacts
- \* Relatively cheap
- \* Not always necessary to achieve the standards for completely clean soil.

Basically there are several clean-up principles that might satisfy the above-mentioned constraints. Some are directly derived from the experience obtained from intensive treatment techniques for excavated soil or from in-situ treatment. The following potential clean-up methods for large areas may be considered:

- \* The use of green plants which can accumulate the pollutants. After harvesting, these plants have to be treated in order to concentrate or destruct the pollutants. It is known that some plants can accumulate heavy metals to a very high concentration. If this is also the case with HCH is not known.

- \* The use of plants with a root structure making controlled removal of the plant roots as plant sods possible. The layer removed, containing the plants and the contaminated soil, has to be treated in order to concentrate or destruct the pollutants.

- \* The use of small amounts of chemicals which may directly promote microbiological degradation of pollutants or isomerisation of non-biodegradable pollutants to biodegradable pollutants.

- \* Cultivating the top layer of the soil to promote natural photochemical conversion and/or biological degradation.

The principles of these methods are known: however, whether these principles can be developed for practicable application is yet unclear.

## **8. TREATMENT OF HCH POLLUTED WASTE WATER AND POLLUTED GROUNDWATER**

For treating HCH contaminated wastewater or groundwater several techniques are available:

- \* Physical treatment techniques (e.g. adsorption)
- \* Biological treatment techniques (biodegradation)
- \* Chemical treatment techniques (UV, ozone/H<sub>2</sub>O<sub>2</sub>, High Energy Electron Beam Irradiation)
- \* Combination of biological and physical/chemical treatment techniques.

In general with these techniques (or combinations of these techniques) it is possible to

satisfy the standards set for the effluent (treated waste water). The future challenge is

to improve these systems and to reduce the treatment costs.

Firms/institutes involved: TAUW Milieu (Netherlands), Wageningen Agricultural University (Netherlands), Rathenower Anlagenbau GmbH (Germany), High Voltage Environmental Applications, Inc. (USA).

## **9. CONCLUSIONS**

From the previous discussion about treatment techniques for HCH contaminated soils, waste water, groundwater and liquid or solid wastes the following conclusions can be drawn.

a. Treatment of excavated soil

\* Clean-up is possible with the use of thermal techniques or wet lamination techniques (the latter only for sandy soils). Some optimization of these techniques is probably possible.

\* Alternative techniques, which are still in the development stage, are:

– Solvent extraction

– Low Temperature Desorption followed by a gas phase treatment system.

Several possibilities can be mentioned: Thermal Hydro Dehalogenation, Base Catalysed Detoxification, High Temperature Liquid Alkali Media.

– Biological treatment. Up to now no real breakthrough

– Combination of biological and physical/chemical techniques

\* With respect to the alternatives more research is necessary.

b. In-situ treatment

\* Still in the development phase.

\* Up to now no real break through

\* More research is necessary

c. Treatment of HCH contaminated wastes

\* Several techniques available. Non of them can still be applied reliable on a large scale.

\* Most techniques are based on detoxification with an alkali component at low, moderate or high temperature.

\* More research is necessary, aimed at

– further development of the technique

– improvement of the technique

– demonstration of the technique

– lowering the costs

\* Some of the techniques for treating wastes can be modified to treat contaminated soil.

d. Treatment of HCH polluted groundwater

\* Several techniques are available. Some can be applied already on a practical scale.

\* Research has to be aimed at further optimisation of the techniques.

e. Treatment of large diffuse polluted area.

\* Has not obtained much attention up to now.

\* Study into possible treatment options is recommended

f. It may be expected that techniques aimed at solving the HCH problem have also spin off to other problems caused by HCH related halogenated organic compounds.



**HCH ISOMERS IN HUMAN TISSUES IN POLAND****Jan K. Ludwicki, Katarzyna Góralczyk, Katarzyna Czaja**

Most of the persistent organochlorine pesticides, excluding lindane, were banned in Poland before 1975/76. The first restrictions concerning use and marketing of lindane (gamma-HCH) became effective in 1980 and were gradually extended until its agricultural use was ultimately banned in 1989. The long-term effects of this ban can either be assessed on basis of concentrations of HCH isomers in food products, or basing on biological monitoring of HCH in human tissues.

The aim of this work was to provide information on present concentrations of hexachlorocyclohexane isomers in human adipose tissues basing on biological monitoring performed by the National Institute of Hygiene. The monitoring of organochlorine compounds in human adipose tissues started in 1988 and had been continued until the end of 1991. Moreover, in 1991 we decided to extend this monitoring activity to human milk to assess the exposure of infants to HCH and other organochlorine compounds, including PCBs.

**Quality control:** The laboratory in the National Institute of Hygiene for several years participates in the international interlaboratory proficiency trials for organochlorine pesticides organized by the Ministry of Agriculture, Food and Fisheries in England with the satisfactory results.

In the monitoring of HCH isomers 277 samples of human subcutaneous adipose tissues were taken from surgically treated patients in hospitals in Warsaw. 142 specimens were taken from men and 135 from women aged from 10 to 80 years old. For the analysis the generally accepted extraction and cleanup procedures were used followed by gas-liquid chromatography. The results of the determination of HCH isomers are shown in the Table 1.

Table 1.: Concentrations of HCH isomers in human adipose tissues

HCH isomer	Mean concentration (mg/kg)	90th percentile (mg/kg)	Maximum concentration (mg/kg)
a-HCH	0.016	0.020	0.160
b-HCH	0.228	0.500	5.098
g-HCH	0.074	0.120	2.727

It is clear from the results shown in the Table 1 that despite of very low concentrations of b-isomer in lindane preparations, the b-HCH remains at greatest concentrations in human fat tissue, which can be attributed to its extraordinary persistency and resistance to metabolic activity.

Some additional information on persistency of HCH isomers can be derived from analysis of correlation between age and concentrations of these isomers in human adipose tissue. For this reason the levels of g and b-HCH have been arranged in age groups, and the mean concentrations of HCH isomers for each age group are presented in the Table 2.

Table 2.: Mean concentrations of g- and b-HCH in human adipose tissue as function of age

Age group (years)	Number of samples	g-HCH Mean concentration (mg/kg)	b-HCH Mean concentration (mg/kg)
<25	25	0.078	0.132
>25 - 35	40	0.035	0.133
>35 - 45	48	0.062	0.312
>45 - 55	49	0.069	0.234
>55 - 65	36	0.078	0.393
>65	30	0.049	0.238

The positive trends showing the increase of HCH concentrations with the age are evident in case of b-HCH, but not in case of g-isomer. For better illustration of this trend all results for b-HCH were arranged in three categories: low, medium and high concentrations, and then the percentage of the results falling in these categories for each age group were displayed in the Table 3.

Table 3.:The frequency of low, medium and high concentrations of b-HCH in adipose tissues of people from different age groups (%)

Category (mg/kg)	Age groups (years)					
	<25	>25-35	>35-45	>45-55	>55-65	>65
<b>Low</b> nd.*-0.120	72%	54.8%	33.3%	28.6%	19.4%	30.0%
<b>Medium</b> 0.121-0.230	20%	26.2%	39.6%	46.9%	50.0%	30.0%
<b>High</b> >0.230	8%	19%	27.1%	24.5%	30.6%	40.0%

\* nd. - below the limit of determination

It is clearly visible from the Table 3 that young people were exposed to smaller amounts of b-HCH during their life, and that the percentage of high results increased together with length of age.

During the next stage of the monitoring the human milk was analyzed for organochlorine compounds to evaluate the exposure of breast fed infants. However, the results of this monitoring, together with the data on organochlorine levels in human fat tissues, can be useful in describing the overall situation concerning HCH levels in man.

The samples of breast milk had been taken in 7 regions of Poland between 1992 and 1994. The total number of samples taken for analysis of organochlorine compounds was 365. In several cases parallel to breast milk samples also the samples of placenta were taken to compare concentrations with those found in milk from the same donors.

The results of monitoring are presented in the

Table 4.: Concentrations of HCH isomers in breast milk and placenta

HCH isomer	Breast milk (mg/l of milk) (n = 365)	Placenta (mg/kg wet tissue) (n = 27)
a-HCH	0.0005	0.0050
b-HCH	0.0033	0.1280
g-HCH	0.0004	0.0051

As it can be seen from the Table 4 the mean concentration of b-HCH in breast milk was still highest as compared to the concentrations of the remaining isomers, although the levels of all HCH isomers found in breast milk are much lower than those reported in human adipose tissues. This difference is remarkable even when the levels in milk are expressed on the fat basis. The unexpectedly high levels of HCH isomers, similar to those found in human fat tissue, were found in the placenta. This is even more surprising if one takes into account rather low fat content in placental tissue. This finding demands more detailed studies to find out if there are some "filtering" mechanisms in placenta preventing fetus against high concentrations of organochlorine compounds.

Independently, we managed to observe eight lactations by analyzing samples taken once a week during the whole lactation periods lasting from 15 to 80 weeks.

Analysis of the obtained results showed no correlation between the length of lactation in the individual mothers and the concentrations of b isomer in the consecutive milk samples which could lead to supposition that the presence of b-HCH in the milk was due to dietary intake rather than from mobilisation of body deposits. On the other hand, there were substantial differences in b-HCH concentrations in the milk samples from two consecutive lactations in the same woman when the interval between the end of first lactation and the beginning of the second was 8 months. In this case the levels of b-HCH were higher in the milk from first lactation. In another case, when the levels of b-HCH were observed in two lactations with the 24 months interval no significant differences were found in the milk samples from both lactations. This last findings might mean that even when the body deposits are diminished due to lactation, they are restored during 2 years, but the period of 8 months between lactations is not sufficient to rebuild the former levels of b-HCH. It is also obvious that the dietary intake plays the major role in building body deposits of HCH isomers, as well as is responsible for the levels of these compounds in human milk.

From the presented results of HCH levels in human adipose tissues and in breast milk it can be concluded that the levels of HCH isomers are similar to those found by other authors in European countries. Analysis of the concentrations *versus* age allow to show that the exposure to HCH isomers decreases. However, despite of ban of lindane in agriculture in Poland the HCH isomers still circulate in the environment entering various trophic levels and eventually reaching the man.

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**HANDLING THE REMAINDERS OF A FORMER HCH -PLANT****Ekkehard AMADORI****1. Introduction**

The paper will describe the situation in the surroundings of a lindane plant in the years after shutdown and how the remainders have been handled. The plant itself was only part of a larger chemical works, where still other items were produced. As it was intended to enlarge the latter capacities, measures had to be taken to make possible further use of the area without any restrictions.

My objective is not to discuss the removal of the technical installations and their further use. We will focus mainly on the ecological effects and how they are controlled on-site and in the surrounding areas.

**2. Starting situation**

At first let us recall how HCH or lindane was produced. Reacting benzene with chlorine gives a mixture of HCH-isomers, which contains about 10 - 15 % of the insecticidal gamma-isomer, usually known as Lindane. In the beginning the whole mixture was used as a pesticide, but soon it was possible to separate lindane from the other isomers. This was a large progress with respect to some problems, e.g. bad smell or taste of the foods treated with this pesticide could be avoided. On the other hand new problems arose. But they were not realized at once. The unwanted portions then were thought to be absolutely harmless. With pleasure they were used as landfill, and they were dumped nearly everywhere.

Later on it was realized that the inert portions were not as inert as assumed in the beginning. Progress in analytical techniques showed a certain but small water solubility as well as the evidence of transfer into the whole ecosphere, the atmosphere included. Though we here deal with traces only, from today's point of view they are undesired, should be removed immediately or at least hindered from further spreading.

The following chapters deal with the site and its deposits, with contaminated ground water and the contaminations in the surrounding agricultural area.

**3. Handling the contaminations present****3.1 on the site**

The intended further use set the data for the remediation or reconstitution of the site. But these data as well as the measures to be taken were strictly focused on the intended use as part of a chemical works and not as a kindergarten.

So only heavily contaminated materials were dumped on a special dump site. The biggest business however was to prevent the contaminations present from further spreading. This includes also the landfills which had been realized to equalize the ground in some parts of the site. Fortunately, they are well documented and make it possible to take care of them when work has to be done underground.

As these landfills could not be taken away they had to be stabilized in situ. This meant coverage with macadam or concrete at the surface in order to hinder contaminated particles from being carried out as well as to avoid the infiltration of rain and other surface water, thus transferring contaminants into the ground water.

### 3.2 in the ground water

Special attention must be drawn to the ground water as HCH in the meantime was recognized to be water soluble, in traces, however. Fortunately, the toxicological evaluation of this material did not follow these findings in the same scale. But in accordance with the present opinion we are sure that HCH and other xenobiotics, also in traces, should not be present in the ecosphere and also be hindered from further intrusion.

As already mentioned, water impermeable layers were placed on the surface. Furthermore, care had to be taken to hinder the ground water itself from contact with the dumped materials. This is achieved by lowering the ground water level by pumping out sufficient amounts.

Here the question arose what to do with the water taken out from the underground. It was contaminated by foregoing contact with the dump and /or water from the surface. There was no doubt that this water had to be cleaned. In the meantime a rather simple procedure which also allows the use of this water for further applications, could be established.

### 3.3 in the surroundings

Calling back to our mind how HCH was handled in the fifties or sixties, we cannot be astonished about the following observations. Nearly ten years after the closure of the plant there was found HCH in food grown in the neighbourhood. At first, no obvious reason could be perceived. Actions taken for investigation and compensation will be discussed later.

### 4. Removal of HCH from the ground water

As mentioned above the ground water had to be cleaned before further use. State of the art was (and is) a technique using activated charcoal. This is a rather easy procedure, also when large quantities of water have to be handled. But in our case the coal was rapidly exhausted, causing very high costs. In addition, there was no suitable procedure for the regeneration of the coal at hand, so always fresh coal had to be taken.

In the meantime some experiments in our lab had shown HCH-isomers to be biologically degradable. This was not the common opinion then. But technical realisation failed because of poor results.

So our attention was focussed back on the installation in use which consisted of three parts:

1. elimination of iron and manganese
2. elimination of hardness
3. charcoal filter

Iron and manganese were precipitated by oxidation to the corresponding hydroxides using chlorine, filtration is accomplished by flushable gravel filters.

During the analytical characterisation of the contaminants present in the ground water also chlorobenzene had been found. At first we believed in a generation from traces of benzene during the chlorine treatment, because this compound had never been produced. But afterwards, when chlorine had to be replaced by air for mainly technical reasons, the level of chlorobenzene still increased. Simultaneously the level of the contaminants in the effluent of the charcoal filters reached nearly a steady state. This led us to the conclusion that we had initiated biological degradation by bacteria present in the ground water.

Only the use of chlorine had hindered them from working properly. Afterwards we learned from the literature that the biological degradation of HCH affords anaerobic steps as well as aerobic ones and that chlorobenzene is one of the platforms where anaerobic reductive dehalogenation comes to an end and aerobic mineralisation will start. So lack of oxygen in the ground gives rise of reasonable concentrations of chlorobenzene, and surplus of oxygen let us fail in our first attempts.

The method described takes out about 97 % of the initial contamination, but we are confident to be able to increase it further.

### 5. Measures in the surroundings

As mentioned above about ten years after the shutdown and dismantling of the lindane plant a certain contamination of food and feed from the surrounding fields was detected. One soon came to the conclusion that a constantly blowing wind must have drifted traces of the residues - formerly stored in large heaps before their removal - into the adjacent fields.

Analytical investigations then defined the extension of the contamination and proofed the drift theory. After this the contaminated areas were divided into three parts:

1. „red“ area: HCH > 500 ppb
2. „yellow“ area: HCH 50 - 500 ppb
3. „green“ area: HCH < 50 ppb

Then recommendations were given for the fruits to be grown. These proposals were derived from tests which had been performed immediately. They allowed the growth of cereals in the „red“ zone, recommended not to grow carrots or onions in the „yellow“ part, but did not give any restrictions for the „green“ fields. In addition, the farmers concerned also got or get financial compensation still up till now.

But we are hopeful to stop these compensations in the near future because the contamination steadily decreased over the years. Best effects are shown on intensively cultivated fields, those left uncultivated show a significantly lower decrease. Today most parts of the „yellow“ region may be declared „green“, but also the „red“ areas turned „yellow“ or lost about 80 % of their initial contamination.

In order to verify these findings and to make them believable to the public, we also initiated a research programme with the Agricultural Department of Gießen University. This programme focusses on the transfer of HCH into plants, the results of the last year tests will be available in the near future.

### 6. Evaluation and outlook

From our point of view we come to the conclusion that a final solution of the obvious problems encountered with the remainders of the late lindane production is under way. This is also the opinion of most of the authorities engaged with this problem.

Here some more general remarks shall be added. When starting a remediation one has to talk about limits - tolerable upper limits for the contaminants as well as background levels. As we know the ecosphere in the meantime shows a certain but low level of a lot of contaminants. Also HCH-isomers must be listed here. Japanese researchers showed about 20 years ago that these compounds had been transported across the Yellow Sea from China to

Japan by rain clouds. Similar observations are also known from Europe, here an annual entry of 1 - 5 g of HCH per hectare from the atmosphere is stated.

This HCH-pool in the atmosphere obviously stems from the application of HCH and lindane in agriculture. These compounds were not only biodegraded or fixed in the soil but also partially evaporated.

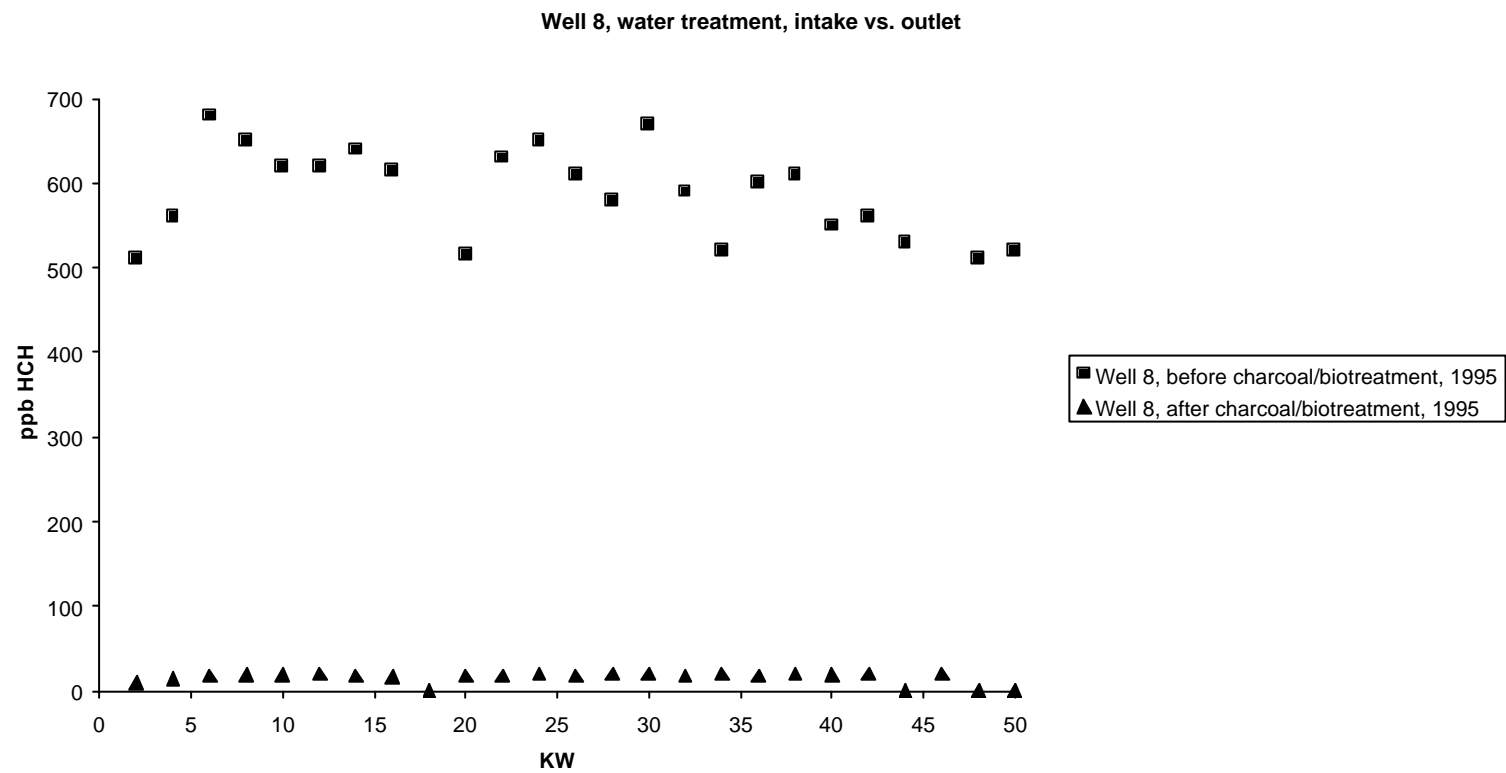
During our own experiments we likewise analyzed „background“ samples. They also prove that HCH in the meantime can be found nearly everywhere. So some soil souvenirs from a (private) bus tour through the Canadian Rockies show HCH in reasonable concentrations - if 2 ppb is thought to be reasonable. Other samples from German agricultural areas contain 5 - 25 ppb. These concentrations can also be found in forests or in the upper soil layers of meadows. All these samples show a rather identical composition of the contaminants with lindane dominating, telling us their agricultural origin. On the other hand, the isomer pattern in the surroundings of the HCH-plant shows  $\beta$ -HCH as the main component thus clearly leading to the source. The reason for the findings long years after the application is clearly to be seen in the fixation of HCH in the soil. It is well known that especially clay and loam really capture these molecules inside their mineral structure, thus preventing solubilisation and degradation. In the same way, no or only slow transfer into plants will occur.

### **7. Final remarks**

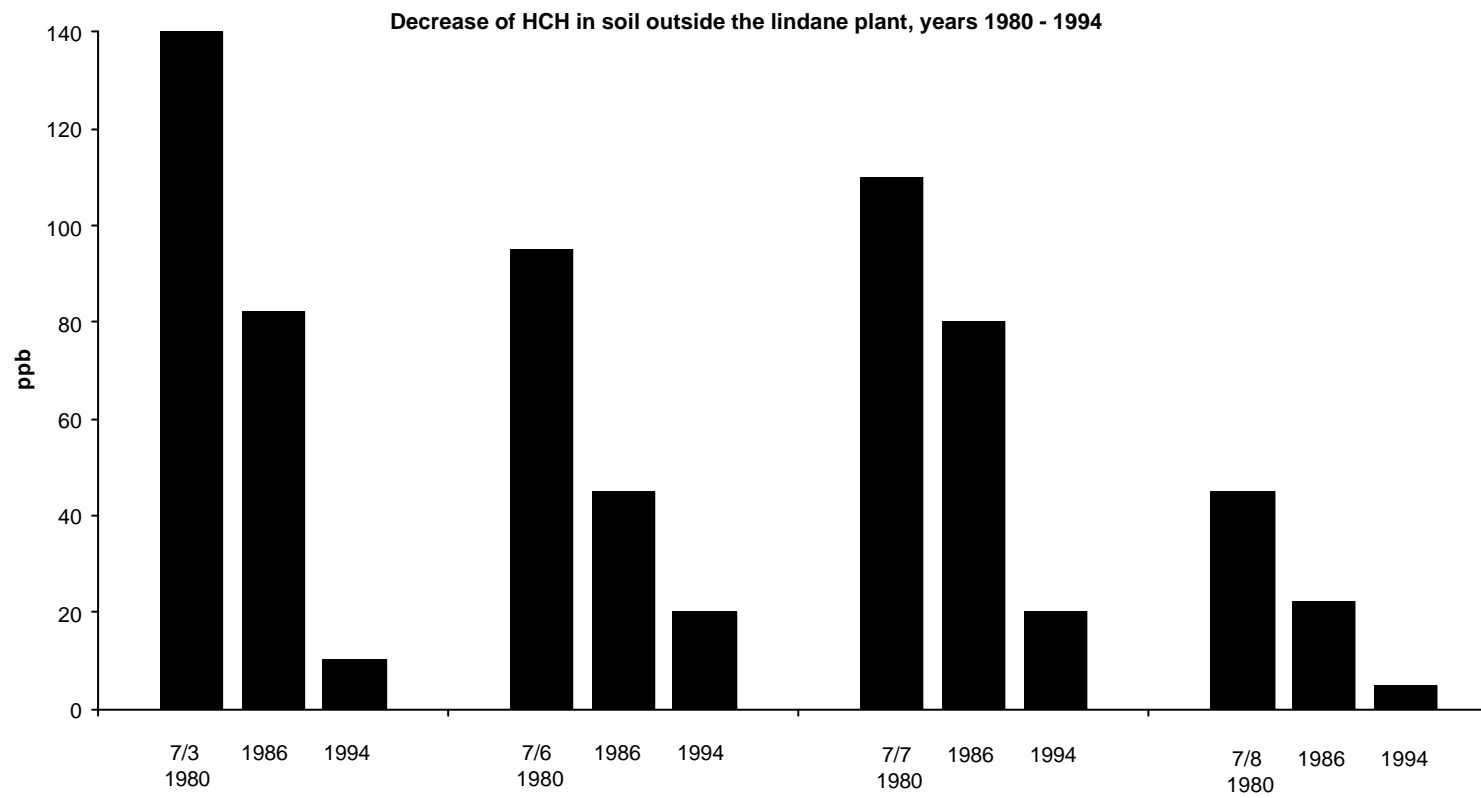
Having learned about the overall presence of HCH in the ecosphere we must keep this fact in mind when evaluating remaining contaminations. These findings must also be considered when limits are to be set. In some cases this will lead to a withdrawal from desirable but unrealistic figures.

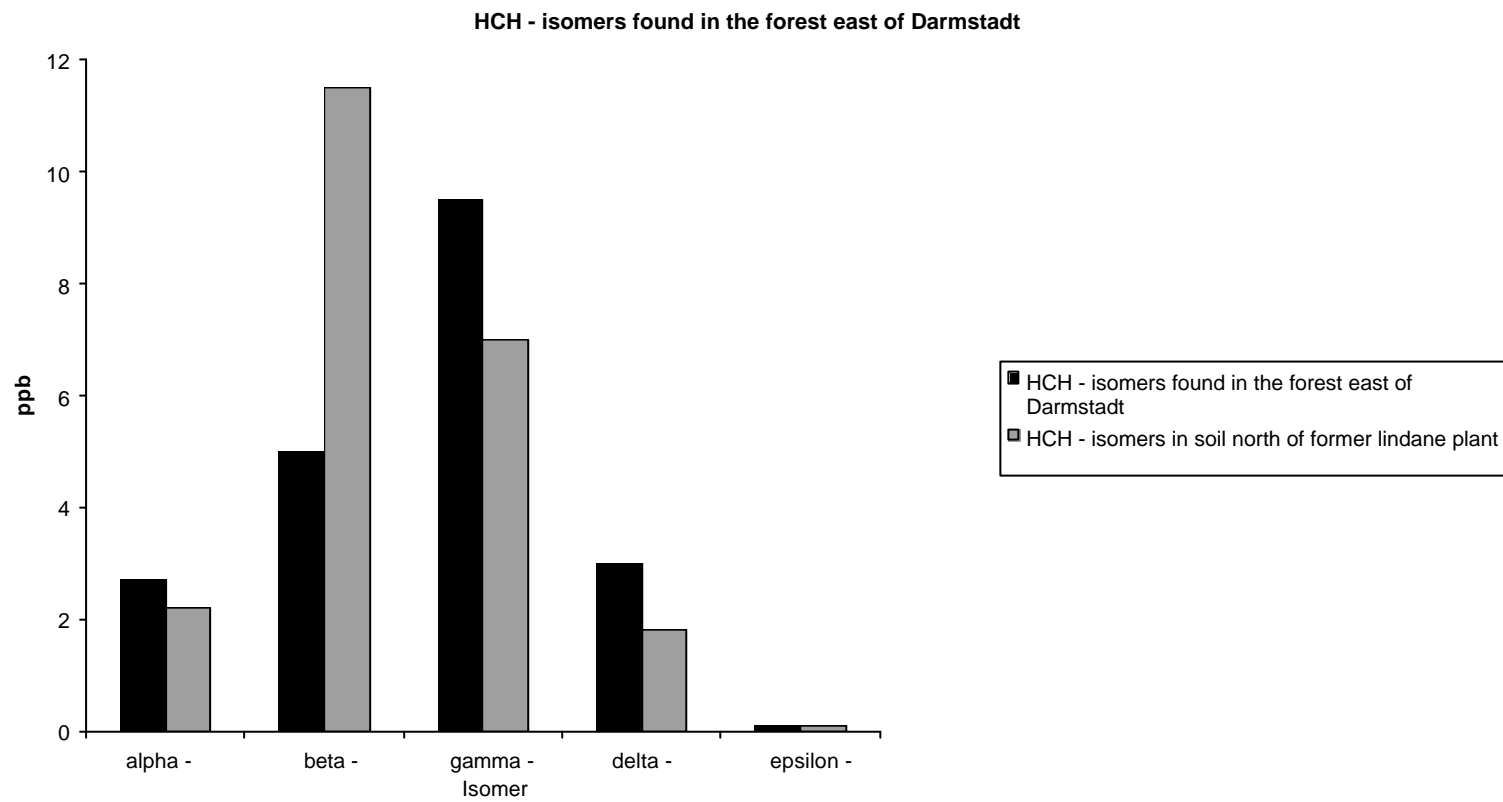
On the other hand we ourselves may be satisfied when realizing that some of the limits set for our surrounding fields now can be found in quasi official standards. This also shows us that we are on a good way and should proceed on it.

(Literature available from the author)

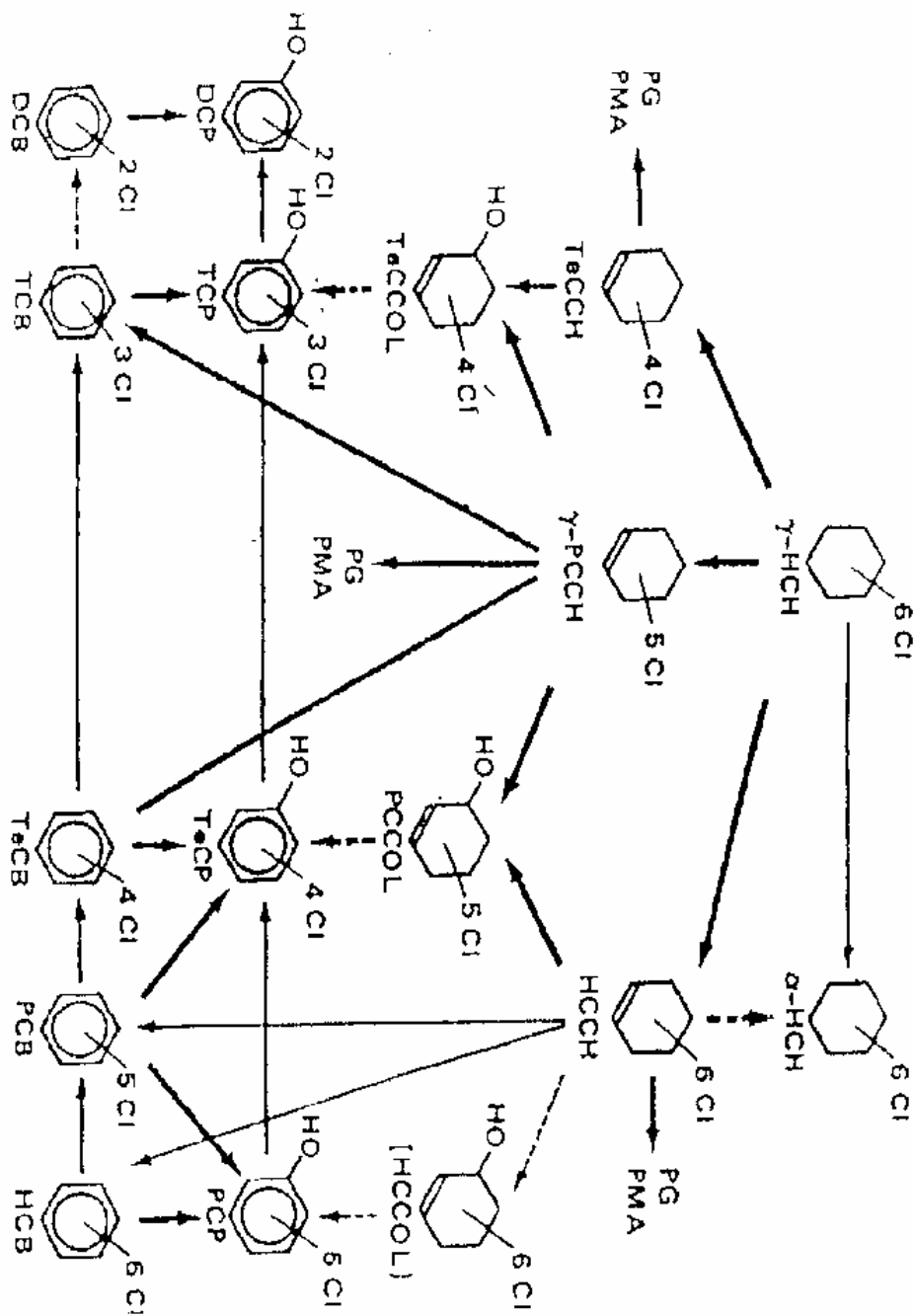








Pathways of Biodegradation of HCH (R.Engst et al.)



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**DISPOSAL AND PROBLEMS OF UNWANTED PESTICIDES STOCKS IN  
REPUBLIC OF LITHUANIA**

**Arunas CEPELE**

Lithuania faces the problems of utilization of pesticides that are unsuitable and prohibited from use as well as purification of soil from the territories of their storage. In 954 storages of former collective farms, about 2.200 tonnes of such pesticides have been accumulated. These chemicals vary in both quantity and toxicity. 20 cases of spontaneous fires have been recorded in such storages. The ground on the territories of the storages is contaminated mainly with pesticides. After the fall of collective-farm system, most of the stores became unnecessary because farmers buy pesticides in small quantities for immediate use.

Lack of funds prevents us from acquiring mobile pesticide burning facilities or building of a special plant for hazardous waste utilization. So, in 1995 the "Unsuitable and Prohibited from Use Pesticide Regulation Program" prepared by the Ministry of Environmental Protection was adopted by the Government and a Group for the Program coordination and control was established. This group consist of 19 specialists from all interested institutions such as the Ministry of Agriculture, State Plant Protection Station, Environmental Protection Ministry, State Public Health Center, Fire Department and others.

The Program consists of 4 activities:

1. Stock-taking and control of all pesticide storages.
2. Establishing of central storages for hazardous waste in each of the 10 Lithuanian districts.
3. Sorting, identification, repackaging and transportation of pesticides to central storages or for utilization.

Utilization of pesticides in Akmene Cement Plant (powdered pesticides) and in

Kedainiai Fertilizer Plant (liquid pesticides).

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**DEALING WITH UNWANTED PESTICIDES IN DENMARK  
- A PRACTICAL SOLUTION OF THE PROBLEM.****Sven Hansen and Cecilie Schwartz****ABSTRACT**

Unwanted pesticides, stored in bunkers or sheds of varying quality and condition, is one of the biggest environmental problem today - especially in eastern Europe and the Baltic countries.

Pesticides, which have been stored for more than 10 - 20 years in various (often very bad) conditions, are now leaking from bunkers to the surrounding areas, whereby soil, surface and ground water are exposed to toxic pesticides. This leaking pesticides can cause enormous environmental damages and disturb the ecological balance.

This paper is about the Danish solution to the pesticide problem.

Due to the "Danish System of Hazardous Waste Management", treatment and disposal of unwanted pesticides (e.g. empty pesticide containers or old pesticides) in Denmark is an integrated part of the Danish hazardous waste management, whereby unwanted pesticides in Denmark cause very limited problems.

The Danish System is built upon one central hazardous waste treatment plant, Kommunekemi, and a waste collecting network of transfer and collection stations placed throughout Denmark.. The transfer stations (18 in all), receive hazardous waste, including pesticides, from industries and small collection stations. The industry must pay a treatment fee to the transfer station depending on the amount and content of waste. In addition to the large transfer stations, each municipality has one or more collection stations (375 in all), which receive hazardous waste from local and private households free of charge. The waste is then transported to the transfer stations, which then collect the waste and forward it to Kommunekemi for treatment and disposal.

In Denmark, the sale of pesticides, and also the number of active ingredients in the different pesticide products, have been decreasing since 1984. The reduction is primarily caused by the use of more active pesticides, but generally there is a tendency to a decreased use of pesticide products. The average dosage per pesticide treatment is reduced from 0,97 kg of active ingredient/hectare in 1983 to 0.68 in 1993.

At Kommunekemi, the amount of received pesticide waste has been reasonably stable since 1985. The amount received varies from 800 to 1300 ton/year. A part of this amount is empty pesticide containers, but mainly solid and liquid pesticide waste is received. At Kommunekemi, the treatment technology is based on incineration of all pesticides which do not contain mercury. Pesticide waste with mercury can not be treated and it is sent to Germany to be deposited there.

Incineration of pesticides is the Danish alternative to storage, and has the advantages of disposing the pesticides once and for all, with only very low effect on the environment.

### **THE DANISH SYSTEM**

The background for initiation of the "Danish System of Hazardous Waste Management" can be found in the growing awareness of environmental problems arising from the increasing industrial pollution all over the world. In this respect, the situation in Denmark was not different from other countries, and in the late sixties, the situation was ripe for promoting some kind of action. The Danish municipalities, being the responsible bodies for the local environmental conditions, were facing growing criticism, as they were not in position to handle the hazardous waste problems in a satisfactory manner. In general it could be said that the municipalities were not in possession of the necessary expertise for handling the very complex problems of waste management. As a result of this, a lot of incorrect dumping and disposal took place.

In 1971 it was decided to create a centralized hazardous waste treatment plant in Denmark, named Kommunekemi, to deal with the above mentioned problems. Together with construction of the plant, a collective system for hazardous waste was created, as well as the necessary legislation, being the authorities who categorize the waste.

The system is build up with the philosophy in mind, that in order to use the system, it should be as easy as practically possible and it should meet the demands of the largest as well as the smallest waste generator. Furthermore, the distance to the disposal point should be as short as possible, and the cost of transport from the waste generator should be as cheap as possible.

As a consequence of this philosophy, a fine masked network of collection centres was built, with at least one centre in each municipality. In Denmark there are now over 300 of these collection stations in operation. The centres are designed to receive small portions of hazardous waste from private households. It is free of charge for private households to deliver hazardous waste to the collection centres . At the centres, the waste is packed into larger units (drums) and shipped off to a network of transfer stations (18 in total), from where the waste is transported to the centralized treatment facility, Kommunekemi.

At the transfer stations waste from larger waste generators (e.g. industry, pharmacies) is received, repacked and shipped off in whole loads for final treatment at Kommunekemi. When waste is delivered to the transfer stations, the waste producers must pay a fee, depending of the amount, quality and content of the waste.

### **THE HAZARDOUS WASTE TREATMENT PLANT KOMMUNEKEMI**

Considering the foundation and legislation of the central treatment plant, Kommunekemi must accept all types of waste, except the following categories:

- Explosives
- Radioactive waste
- Infectious waste

The capacity of treatment at Kommunekemi is 140,000 tons/year, but about 100,000 tons is received each year.

#### Treatment processes

The main treatment processes at Kommunekemi are:

- Incineration in rotary kiln incinerators
- Physical / chemical treatment in batch reactors

• Oil / water separation in heated stripping and separation vessels.

In addition there are:

- Laboratories
- Reception facilities
- Tank farms
- Drum storage buildings (capacity 100,000 barrels)
- Solid waste bunkers
- Electrical power plant
- District heating facilities

#### Power production

Through the different treatment processes, Kommunekemi recovers power and hot water for district heating.

amount of power produced:35,000 MWh.

produced district heating:95,000 Gcal.

The utilization is 49%.

#### Flue gas and waste water

The flue gas emission is checked continuously for the following elements:

Dust, HCl, HF, SO<sub>2</sub>, odour, TOC, NO<sub>x</sub>, lead, Hg, halogens, hydrogen halogens, CO, CO<sub>2</sub>, O<sub>2</sub>, temperature, speed and dioxin.

Waste water at Kommunekemi is divided into 2 categories: process water and rain water, collected from paved areas.

The water is analyzed for several elements, e.g.: metals, phenols, COD, cyanide, BOD, sludge, phosphate, ammonia, fluoride, sulphate, free chlorine, detergents, mineral oil, temperature, pH, chloride.

#### Residues

The total amount of residues in 1994 was: 30,000 tons, and the main residues are divided into: fly ash, slag and filter cakes.

These residuals are deposited at Kommunekemi's secure landfill, Klintholm, situated 20 kilometres from Kommunekemi. The secure landfill is provided with both top and bottom membranes (partly artificial [plastic], and partly by clay and sand). Presuming the amount of residues is stable, Klintholm can receive and deposit residues for the next 30 years.

Some waste groups, which can not be treated at Kommunekemi, are sent directly to the secure landfill (e.g. batteries and asbestos) or to an external depot (e.g. waste containing heavy metals).

### **THE PESTICIDE SITUATION IN DENMARK**

The sale of pesticides in Denmark, related to active ingredient, has been decreasing since 1984, according to the following Figure 1. The major use of pesticides has been for plant protection purposes.

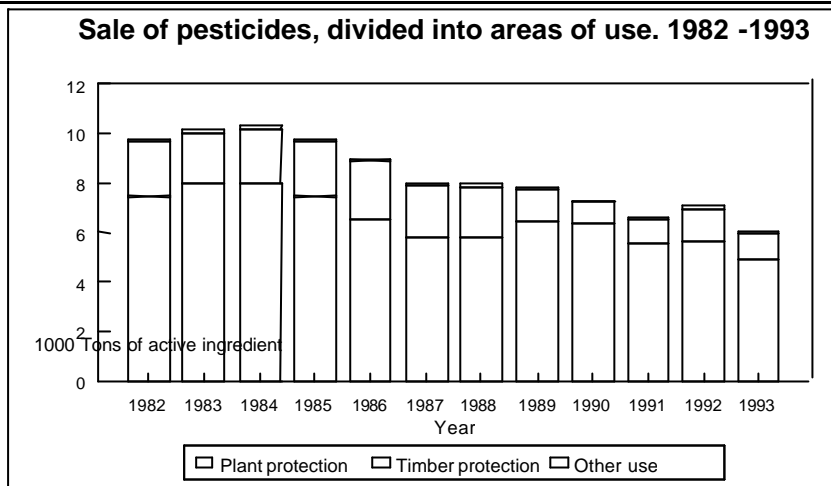


Figure 1. Sale of pesticides, divided into areas of use. 1982 - 1993.

In accordance with the decreasing sale of pesticides, the number of pesticide products and active ingredients have also been decreasing, whereby the amount of pesticide products in 1993 was 1058, and the amount of active ingredients was 243 in 1993.

#### Pesticide use in the plant protection field.

In 1986 The Minister of Environment has made an action plan for reducing the use of plant protection products, which describes that the total use of pesticides must be reduced by 25% before January 1990, measured in relation to the average use in the period 1981-1985. This reduction is valid both for amount of active ingredients and treatment frequency. Before January 1997, the total use of pesticides must be reduced by 50%.

In 1993, the amount of sold pesticides was reduced by 41%, which means that the pesticide action plan has been fulfilled so far.

The reduction is primarily caused by use of high active pesticides. The change of average dosage per pesticide treatment is reduced from 0,97 kg active ingredient/hectare in 1983 to 0,68 kg in 1993. The average pesticide dosage from 1983 - 1993 can be seen on figure 2.

	1983	1985	1987	1989	1991	1993
Kilo active ingredient per hectare per treatment						
<b>Pesticides in all</b>	<b>0,97</b>	<b>0,86</b>	<b>0,86</b>	<b>0,69</b>	<b>0,63</b>	<b>0,68</b>
Herbicides	1,41	1,19	1,12	0,96	0,89	0,90
Growth regulators	0,60	0,68	0,73	0,77	0,86	0,91
Fungicides	0,76	0,87	0,81	0,68	0,68	0,77
Insecticides	0,29	0,17	0,15	0,12	0,08	0,07

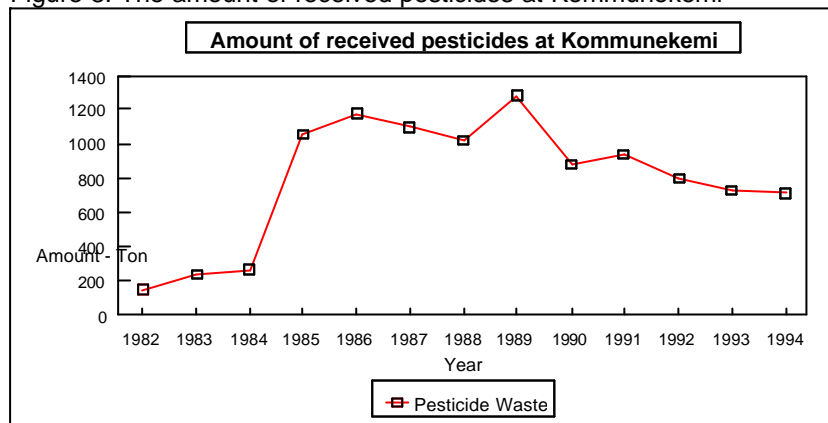
Note: The average dosage is based on the standard dosage, which is made on the basis of the sold pesticides usage.

Figure 2. The average dosage of pesticides, 1983 - 1993



Kommunekemi receives pesticide waste, and on figure 3, the amount of pesticides received from 1982 to 1994 can be seen.

Figure 3. The amount of received pesticides at Kommunekemi



The figures of amount of pesticides used in Denmark and the amount of pesticide waste received at Kommunekemi is not completely comparable, because Kommunekemi also records old empty pesticide bags as pesticide waste. But anyway the figures give an idea of what amount of pesticides is used and how much pesticide waste is treated and disposed.

#### **PESTICIDE HANDLING AT A TRANSFER STATION AND AT KOMMUNEKEMI**

Pesticides are received at the different transfer stations. When the waste arrives it has already been categorized by the waste generator. Pesticides which have been collected from private households will be categorized by the trained staff on the collection stations.

Pesticides which contain mercury are not classified as pesticide waste, but as mercury waste, and are kept together with other mercury containing compounds. When waste contains mercury, it is not possible to be incinerated at Kommunekemi, and they are transported to a special deposit in German salt mines.

The pesticide waste is kept in special poison storage at the transfer stations before the waste is transported together with other waste categories to be treated at Kommunekemi.

The handling of pesticide waste received at Kommunekemi is divided into 3 different parts:

- 1) solid pesticides
- 2) liquid pesticides and
- 3) empty pesticide containers.

Both solid and liquid pesticides are stored in a special closed store, only for pesticides, before they are treated.

The pesticide waste is treated in a special pesticide handling section, where the necessary safety and security precautions are taken, e.g. protective clothing, gloves, safety rubber boots and breathing apparatus with fresh air supply.

Solid pesticides are divided into smaller amounts and repacked into drums. The weight of these drums must not exceed 100 kg each. When the repacking of the drums is completed, they are transported and placed on a conveyor system, which leads to the incinerator. Maximum 100 kilo of pesticide waste can be incinerated per hour in order to be able to keep the emission limits (especially with regard to the content of chlorine).

A small amount of the different liquid pesticides are mixed and tested for reaction in a small test mixing tank. If the temperature rise do not exceed 5° C, it is assumed that the pesticides do not react, and the total amount of liquids are mixed in a special mixing tank (1,5 m<sup>3</sup>) and stored till the next day.

When the mixing tank is filled, the gasses are let through a tank containing water. In this tank, the water soluble gasses are collected. If a reaction should take place in the mixing tank, and the volume increases, an overflow tank will collect the excess liquid. Vapours from the reaction will also pass through the overflow tank and will be absorbed in the water tank.

When the mixing tank has been stored for 1 day, it is weighed, transported to the special pesticide inlet dosage area close to the incinerator. The liquid waste is then transferred to the incinerator by increasing the pressure in the tank by means of compressed N<sub>2</sub>. The flow is adjusted in accordance with the other waste to be incinerated in order to keep the emission limit. Maximum flow is 100 litre/hour, like for solid pesticide waste.

When the tank is empty, it is weighed again in order to check the amount which has been incinerated, and the empty tank is transported back to the pesticide handling place. Both solid and liquid pesticide waste can be incinerated at the same time, if only the other waste streams are adjusted so the total waste will not cause too high emissions.

The empty pesticide containers come to Kommunekemi in special pesticide bags. The weight of these bags must not exceed 25 kilos. The bags are deposited at the "waste pit", together with other kinds of waste e.g. paint buckets etc. The pesticide containers are fed to the rotary kiln by means of a crane, which takes a portion of the various waste types from the pit and transfers it to the incinerator.

### **CONCLUSION**

Incineration of unwanted pesticides is a possible solution to the pesticide problem. When handled safely and according to the regulations (with regard to personal security precautions and handling of the waste), the pesticide waste do not form any specific danger to the workers handling the pesticide waste and the environment, when the emission limit values are kept.

Incineration of pesticides is the Danish alternative to storage, and has the advantages of disposing the pesticides once and for all, with only very low effect on the environment.

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**INVESTIGATIONS ON  $\beta$ -HCH DECOMPOSITION  
IN HEAVY POLLUTED SOILS IN THE RIVERINE AREA  
OF THE RIVER MULDE IN THE REGION OF DESSAU**

**Elke Schulz, Eva-Maria Klimanek, Karsten Kalbitz, Kathrin Heinrich**

**Structure of the presentation**

1. Background
2. Results of investigations on the behaviour of  $\beta$ -HCH in soil
  - 2.1 Transport in soil
  - 2.2 Uptake of HCH by plants
3. Object of the project (knowledge, working hypotheses, experimental basis)
4. First results
5. Conclusions

**1. Background**

The investigations on this topic are supported by the Ministry for Environmental Protection, Protection of Nature and Arrangement of Area of Saxonia-Anhalt in Germany.

Why?

Environmental protection includes the protection and sustainable use of areas such as riverine areas in their characteristic composition. That means a use in a different way for relaxing, as pasture or for agricultural use. That is why these regions are of large interest for scientists of various branches. In 1992 the newly founded Centre for Environmental Research Leipzig-Halle appointed a special scientific committee working on this field from different points of view.

In the Section of Soil Sciences there's a dissertation on the relative mobility of pollutants influenced by dissolved organic substances in the riverine area of the river Mulde near Dessau and Bitterfeld. The results showed that there were areas more or less polluted with heavy metals but in particular there were found areas with a very high concentration of  $\beta$ -HCH. The source of this substance is the former production of Lindane, the  $\gamma$ -isomer of HCH, used in different ways as a plant or wood protection reagent. During the production process the  $\alpha$ -,  $\beta$ -,  $\delta$ - and  $\epsilon$ -HCH were developed as by-products. Together with the production waste water or solid like filter cakes these by-products arrived the river Mulde and the surrounding areas. As a result of various natural flooding situations these substances were spread in the riverine regions and caused contamination of soil in different areas to a different degree.

There is very little information about the behaviour of  $\beta$ -HCH in soil but it seems to be a problematical substance because of its hydrophobic properties and high persistence in soil.

Until now it was supposed that because of its hydrophobic properties there are minimum risks for transport of  $\beta$ -HCH to deeper soil layers and contamination of ground water and also minimum risks for coming into the food chain.

Investigations within a dissertation in our Section showed that  $\beta$ -HCH could be found also in deeper soil layers.

In the frame of another dissertation on the plant uptake of organics we found that  $\beta$ -HCH was taken up from contaminated soil up to a larger extent by carrots, broad beans and maize

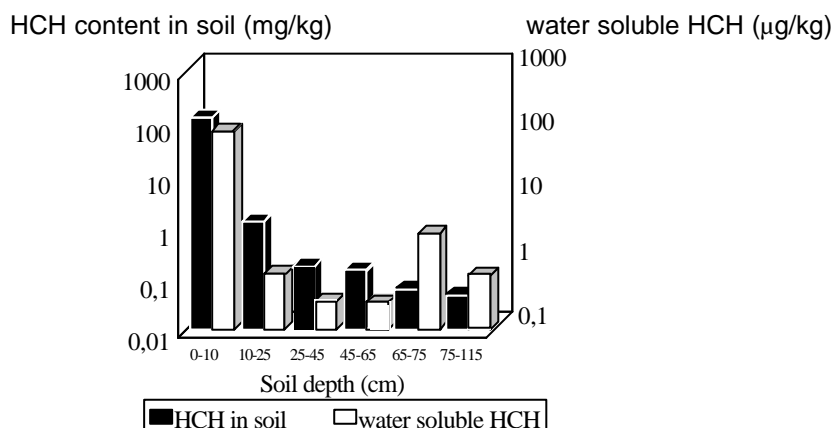
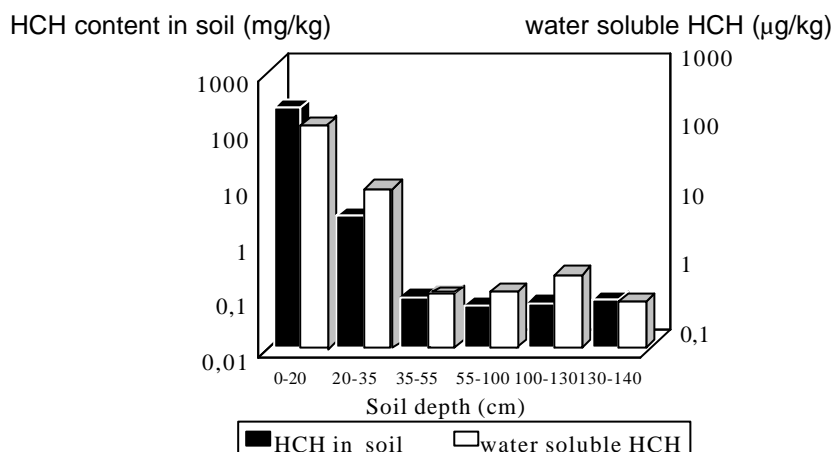
Further on in the recent years some agriculturally used areas in the riverine areas of the river Mulde had to be excluded from use as pastures or for the feed-stuff production. This was the consequence of the presence of  $\beta$ -HCH in cow milk.

So there's an actual demand for handling the problem and this is also the real background for our project.

## 2. Results of investigations on the behaviour of $\beta$ -HCH in soil

### 2.1. Transport in soil

In the riverine area of the river Mulde in the Bitterfeld region on two sites (Spittel, Keller) soil profiles were prepared and sampled for a further analysis of organic pollutants as a total and their water soluble parts. The major contamination component was  $\beta$ -HCH



(site Keller)

(site Spittel)

Fig. 1:  $\beta$ -HCH concentration in soil and water soluble  $\beta$ -HCH content in various depths of a soil profile in the riverine area of the river Mulde

From Fig. 1 it is visible that there's an increase in water soluble parts of  $\beta$ -HCH in deeper soil layers of two soil profiles in the riverine area of the river Mulde. As shown in Fig. 2 the percentage of water soluble  $\beta$ -HCH in the total content of  $\beta$ -HCH increased in deeper soil layers. This may be caused by two different factors. One hypothesis could be that it is a peak of a  $\beta$ -HCH front dislocating

along the soil profile

/1/. It is also possible that there's an influence of groundwater in case of some flooding situations. However, there must have been a contamination of the groundwater by whatever occurring transport process of  $\beta$ -HCH into the direction of groundwater

Water soluble HCH parts of the total (%)

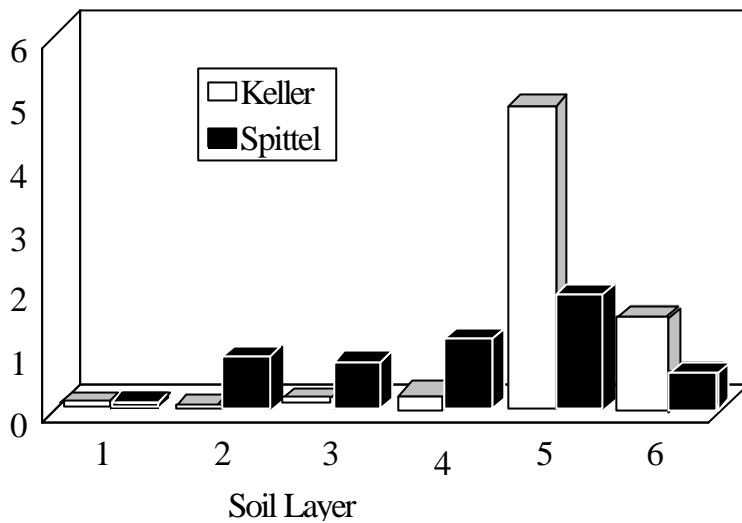


Fig. 2: Water soluble  $\beta$ -HCH parts of the total  $\beta$ -HCH content in two soil profiles (Keller, Spittel) in the riverine area of the river Mulde (Bitterfeld region)

**2.2. Uptake of  $\beta$ -HCH by plants**

In a green-house experiment with soils differing in their contamination level of chlorinated pesticides three different plant species were tested in regard of an uptake of organic pollutants from the soil.

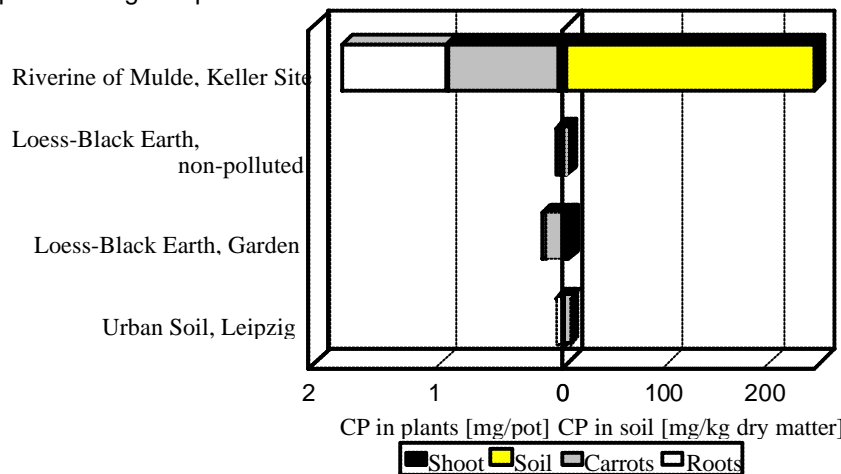


Fig. 3: Content of chlorinated pesticides (CP) in plant parts of carrots and in soil (site Keller) coming from a riverine area of the river Mulde near Bitterfeld

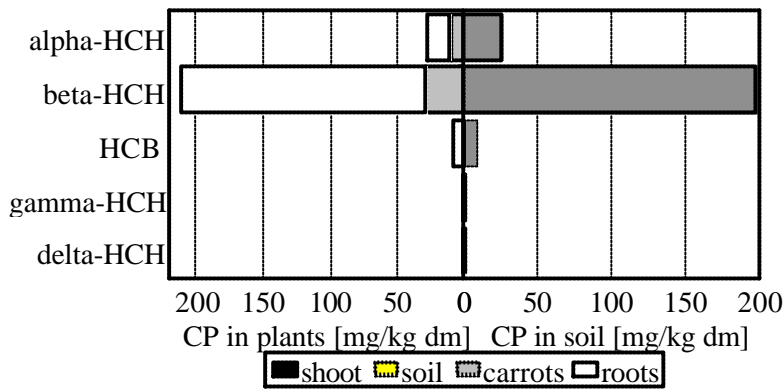


Fig. 4: Content of chlorinated pesticides (CP) in plant parts of carrots and in soil (site Keller) coming from a riverine area of the river Mulde near Bitterfeld

The  $\beta$ -HCH isomer is the mayor pollutant of the relatively high contaminated riverine area of the river Mulde in this region. This substance is also the mayor contamination component in the plant (Fig. 3, 4). From Fig. 5, 6 it is visible that there was a considerable uptake of  $\beta$ -HCH by all tested plants /2/. A comparison of the  $\beta$ -HCH uptake of the different plant species resulted in a higher bioaccumulation factor of  $\beta$ -HCH in carrots because of its oil-cells.

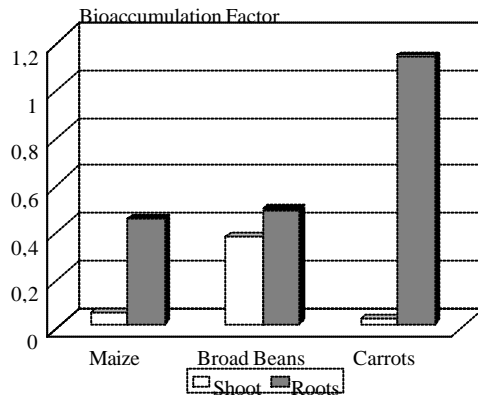


Fig. 5: Uptake of chlorinated pesticides by various plants from a soil (Keller) coming from a riverine area of the river Mulde near Bitterfeld

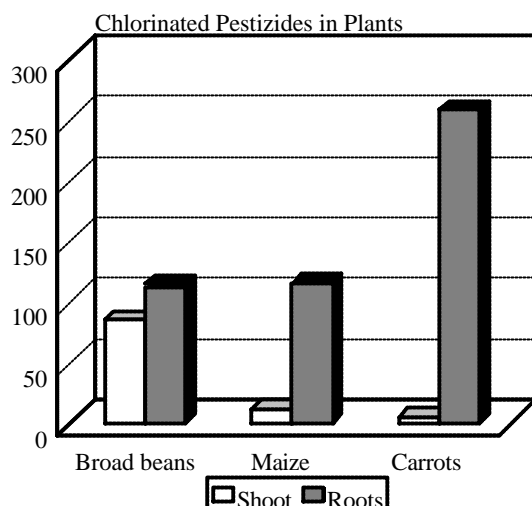


Fig. 6: Bio-accumulation factors of chlorinated pesticides of various plants from a soil (Keller) coming from a riverine area of the river Mulde near Bitterfeld

### 3. Object of the project

It is the task carrying out basic investigations for developing a concept for the use or remediation of heavy  $\beta$ -HCH polluted sites in the riverine areas of the river Mulde near Dessau. One possibility could be an „*in situ-remediation*“ using biological procedures e.g. biological degradation of  $\beta$ -HCH with the help of special microbial strains. This could be one possibility for remediation of sites without disturbing the character of the wetlands.

There is a lot of information on influencing the degradation of the  $\gamma$ -isomer of HCH, the Lindane, and its effects on microorganisms and their activity. But this is not so for the  $\beta$ -HCH. The use of pure microbial strains accelerating the degradation HCH is also described for Lindane mostly. However, it is found that the degradation of the  $\alpha$ -,  $\beta$ - and  $\delta$ -HCH proceeds very slowly /3/. In latest investigations on a  $\beta$ -HCH degradation the use of co-substrates and also a combination of degradation conditions (anaerob followed by aerob ones) is described as presented at the Maastricht Conference on Contaminated Soils in November 1995 /4/.

Because of the very high demand for finding solutions for a further of use of these sites there are a lot of firms dealing with various products and methods for doing this. Some of them offer special microbial strains which would be capable of causing a relatively quick degradation of  $\beta$ -HCH.

Within this project some of the microbial strains will be tested in laboratories, plot and field experiments combining biological and chemical investigations as well as management systems.

The check up of microbial strains for an „*in situ-remediation*“ should include the influence on the autochthone microflora and vegetation. An increase of a  $\beta$ -HCH degradation by adding nutrients for microorganisms could lead to changed nutrient relations in soil and in soil chemical properties.

There is not much information on the effect of  $\beta$ -HCH on the biological activity of soil. A first step will be measuring the biological activity of contaminated sites

compared with noncontaminated ones for conclusions on the influence of the  $\beta$ -HCH contamination on transformation processes in soil. In the next step it is to be tested which factors cause or increase a degradation of  $\beta$ -HCH and lead at least to a mobilization and transport of  $\beta$ -HCH in soil.

In addition in greenhouse experiments the transfer of  $\beta$ -HCH from soil to plants should be tested with contaminated soil of the site and with plants which are characteristic for the site. This is for the evaluation of the existing natural potential for a remediation.

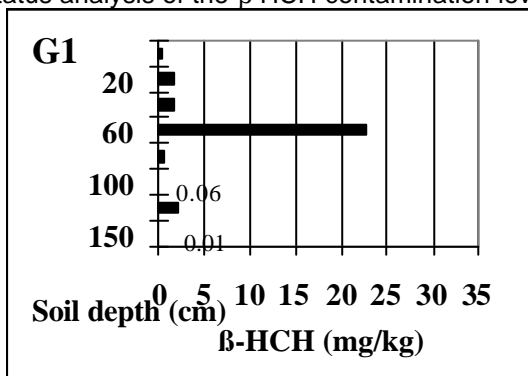
In a small plot experiment under field conditions agricultural arrangements and variants of use respectively will be tested for diminishing the contamination level. For these investigations an agricultural area and a „long term observation“ area will be selected as references. Further on test plots differing in their exposure to natural floods will be selected. So we try to estimate the influence of different moisture conditions on the  $\beta$ -HCH contamination on the natural site.

#### Hypotheses

- ◆ Remediation/decontamination of polluted sites depends on the availability and degradability of a pollutant.
- ◆ The availability is determined by the solubility and mobility of the substance in soil that means also by the tendency of adsorption on humine substances of soil.
- ◆ The degradability is determined by the presence of specific microorganisms or populations being capable of degradation.
- ◆ Different agricultural arrangements can increase the degradation of pollutants and accelerate the decontamination of a site.
- ◆ A controlled cultivation of riverine area specific plants with a (possibly) high affinity to  $\beta$ -HCH could contribute to an acceleration of a remediation process.

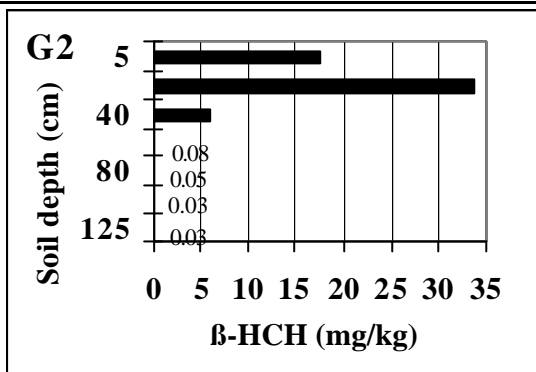
#### 4. First results within the project

In November 1995 we started our work under the supported project preparing some soil profiles from various sites in the wetlands of the river Mulde in the Dessau region. The sites were selected in accordance with the Geological Office of Saxonia-Anhalt. The sites differ in their exposure to natural floods and distance from the bank of the river (grass-land G1, G2, G3; agriculturally used area A1, A2, A3). Soil samples along the soil profile and samples of the specific vegetation of the grasslands were taken for a characteristics of the sites and an status analysis of the  $\beta$ -HCH contamination level.

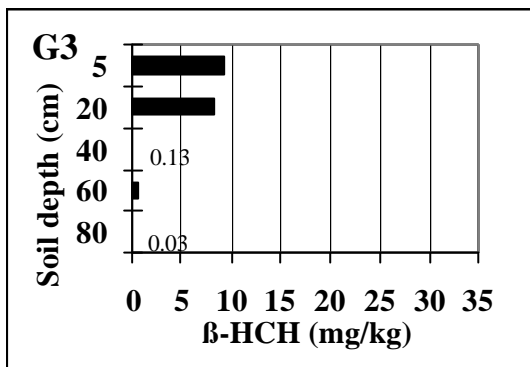


G1: Grassland near the bank of the river Mulde (flooded area in case of natural floods)





G2: Grassland, 150m from the bank of the river Mulde (ground water affected in case of natural floods)



G3: Grassland, 300 m from the bank of the river Mulde (no influence of ground water in case of natural floods)

Fig.7: beta-HCH content in soil profiles at different sampling points in the grassland of the river Mulde near the town of Kleutsch (Dessau region)

In the first layer of the site G1 there was only up to 2 mg/kg of beta-HCH. In the 40-60 cm layer we found a large amount of beta-HCH of more than 20 mg/kg. In spite of this the major contamination of the site G2 of about 30 - 40 mg/kg beta-HCH is up to 40 cm. In deeper soil layers very small contents of beta-HCH were found whereas in site G3 there's a contamination level of about 10 mg/kg only in the layer up to 20 cm. The interpretation of these results (Fig. 7) is difficult and requires an analysis of both the groundwater and the surface water of the river Mulde. However, there must have been some dislocation of the beta-HCH in soil.

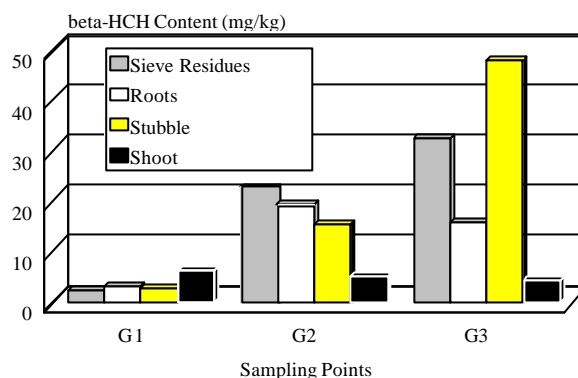


Fig. 8:  $\beta$ -HCH content from different parts of grass from sampling points in the riverine of the river Mulde near the town of Kleutsch (Dessau region)

Fig. 8 the  $\beta$ -HCH content of different parts of grass of the three sampling sites is presented. The varying soil contamination levels of the three sites have no influence on the considerable content of  $\beta$ -HCH in the shoots of about 3 to 5 mg/kg of dry matter. The  $\beta$ -HCH content of the stubble, sieve residues and roots respectively follow the degree of contamination.

### Conclusions

The results of the investigation on the mobility and the uptake of  $\beta$ -HCH by various plant species and the first results of the research project started in November 1995 allow for the following conclusions:

- ◆ There are some heavy polluted sites in the wetlands of the river Mulde in the Dessau region. The major organic contamination component is the  $\beta$ -HCH isomer.
- ◆ The contamination level is influenced by the location of the sites and their exposition for natural floods.
- ◆  $\beta$ -HCH was found also in deeper soil layers. However there must have been a dislocation of  $\beta$ -HCH along the soil profile.
- ◆ Investigations on water soluble parts of  $\beta$ -HCH showed higher percentages of this substance also in deeper soil layers.
- ◆  $\beta$ -HCH can be taken up by various plants up to a considerable level.

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**PROGRESS AND DEVELOPMENT AT THE BILBAO SITE IN SPAIN****Ignacio QUINTANA****INTRODUCTION**

The action being taken in the Basque Country with regard to HCH has been reported to the public on various occasions. Recently, however, the Basque Government Minister for Land Use, Housing and the Environment presented to the parliament the final proposal for an overall solution to this serious problem.

The basic points of the proposal are:

- 4500 t of HCH waste stored at the former Bilbao Chemical Factory;
- 35 inventoried dumps containing approximately 500,000 m<sup>2</sup> of waste and soil contaminated by HCH.

The strategy adopted by the Basque Government is to destroy HCH waste by means of a chemical process in an alkaline medium and to control and store waste and soil contaminated by HCH.

**CASES STUDIED TO DATE AND RESULTS**

Over the last two years work has been carried out at 12 sites, with around 111 hectares being investigated. Investigation priorities have been established fundamentally on the basis of the potential effect on human health or ecosystems and the hindrance of economic development due to limitation of land use in certain areas intended for the construction of infrastructures, industrial sites and recreational areas.

In most cases HCH has been detected on uncontrolled industrial waste tips where waste has been dumped in a disordered fashion in tiers, almost always in an attempt to fill in depressions in the ground

**HCH CONTAMINATED SOIL WHERE RESEARCH PROJECTS HAVE BEEN CARRIED OUT**

	Amounts detected (tonnes)			HCH	Soil type	Present risks
	N°	< 1000 ppm	> 1000 ppm			
Barakaldo	4	35,000	94,000	1,600	Uncontrolled industrial waste tips on marsh land	Human health; dispersal of contaminants; effects on ecosystem through water (implications for clean-up schemes) Limitation of land use
Lemoa	1	2,000	71	300	Uncontrolled joint disposal tip in quarry	Dispersal of contaminants; effects on ecosystem through water, limited use
Galdames	1	2,000	712	300	Uncontrolled tip (HCH only) on a hillside with mine deads	Dispersal of contaminants; effects on ecosystem through water, limited use
Ortuella	1		5,115	100	Uncontrolled tip (HCH only) at mine entrance	Dispersal of contaminants; effects on ecosystem through water; limitation of land use
Asua-Erandio	1		100	88	Industrial waste tip on flood plain	Dispersal of contaminants; effects on ecosystem through water; limitation of land use
Loiu	4	70,200	9,800	4,873	Industrial waste tip on land classified as industrial but used as arable land & cattle farming	Human health: - swallowing - inhalation - contact Dispersal of contaminants; effects on ecosystem through water; limitation of land use
<b>TOTAL</b>	<b>12</b>	<b>109,200</b>	<b>109,798</b>	<b>7,173</b>		

Twelve of the total of 35 sites have been investigated in detail with respect to the presence of waste from lindane manufacturing. In the cases studied this problem affects around 30 hectares. Due to the enormous complexity of the work, some investigations were not exhaustive enough to detect all the HCH deposited at the sites in question, and gaps in historical research which must be corrected mean that not all the HCH on these 35 sites has yet been localized.

The tips at Barakaldo and Loiu present similar problems, as they contain a wide range of organic and inorganic industrial waste products. Human health and ecosystems are at risk in both cases, and there are implications for the schemes to clean up river courses. Indeed contaminants are already being exported into the Galindo and Asua rivers. Finally, land use at both these sites is also limited by the high concentrations of HCH in the soil. Two large-scale development projects are planned for these areas, one industrial and the other involving infrastructure, so they need to be cleaned up.

The HCH-contaminated soil logged so far is classified in three levels as follows, according to HCH concentrations:

- 110,000 t with 1,000 ppm or less of HCH
- 60,000 t with between 1,000 and 10,000 ppm of HCH
- 50,000 t with more than 10,000 ppm of HCH.

An analysis of the cases studied shows that there is no sense in trying to extrapolate these figures for contaminated soil areas on the basis of a ratio of total HCH tonnage deposited in the BAC (Basque Autonomous Community) to tonnage logged in the investigations carried out so far.

The largest areas of contaminated soil were polluted by dispersal, due to incorrect handling of pure HCH which appeared when excavation work was carried out. This is not expected to recur, so the volume of land contaminated by dumping not yet detected is likely to be much less than that detected to date.

Economically and technically proven technology now exists for the treatment of pure HCH. This technology could be used after a separation process to solve the problem of HCH-contaminated land. The proposal for treatment technology is as follows:

- construction of a demonstration plant for treating pure HCH;
  - treatment of HCH stored at the former lindane plant;
- choice of adopting or developing the most suitable preliminary treatment technology (separation) to decontaminate HCH-contaminated land.

### **PROPOSAL FOR ACTION**

Action on HCH-contaminated sites will be taken step by step, initially in response to the need to use the sites in question. However preliminary investigations should clearly be extended to all the suspect sites immediately to obtain a more accurate fix on where HCH is located, how widespread the problems of soil contamination are and what risks these sites pose in terms of dispersal and effects on human health and ecosystems. The following action is therefore proposed:

- preliminary investigation of the 6 suspect sites where the presence of HCH has not yet been confirmed so that they can be included in one of the groups below;
- characterization and check on leaching at 9 points where it will be very hard to find a solution;

- construction of two safe deposit areas, one on the right bank of the river Nervión for waste from 4 tips, and the other on the left bank for HCH-contaminated soil from 12 sites;
- selective excavation according to the levels of concentration indicated and transfer under suitable conditions of the soil from the sites to the safe deposit areas;
- future treatment of contaminated soil stored at the deposit areas when this is technically and economically viable;
- checks on the 4 safety cells set up by private companies which have undertaken schemes on HCH-contaminated sites.

#### TIMING AND BUDGET

Three infrastructure elements are needed to deal with HCH: a treatment plant, the Bilbao Airport safety cell and the left bank safety cell.

ACTION					
TIMING					
ACTION	1995	1996	1997	1998	1999
Pure HCH					
Bilbao Airport safety cell					
Left bank safety cell					
Control and treatment of leaching					
R&D					

The chart shows the timing envisaged for each scheme.

ENVISAGED FUNDING REQUIREMENTS FOR 1995-97 COSTS (thousands of pesetas)	
Pure HCH	720
Bilbao Airport safety cell	820
Left bank safety cell	1,295
R&D	271
Checking measures	371
<b>TOTAL</b>	<b>3,487</b>

The total cost of these operations will be approximately 3,500 million pesetas, around 20% of which will be contributed by the Department.

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**CHLORINATED HYDROCARBONS CONTENT IN TOMBS  
IN POLAND**

**Edward CZAPLICKI, Barbara PODGÓRSKA,  
Malgorzata ROGALINSKA**

**INTRODUCTION**

As the result of so called 'planned economy' high amounts of unwanted and expired pesticides were collected in various stores and other places of storage. Aiming at the solution of this situation at the beginning of the seventies a decision on high level was taken to deposit these chemicals in the tombs.

It was recommended that the tombs should be made of concrete rings or rectangles isolated with tar. Part of tombs was made according to these recommendations, some of them were constructed in a simpler way, unfortunately many of tombs were just holes in ground.

The capacity of tombs containing unwanted pesticides and empty containers was unknown and amounted from 50 kg to several hundreds tons. They were covered with thin layer of soil and completely forgotten.

After approximately 20 years it was found out that some tombs lost their tightness. As a result of this situation there were observed cases of water and soil contamination.

Four years ago first studies concerning the tombs, their content and the effect on the surrounding environment were undertaken in the Plant Protection Institute. More detailed data on the projects already performed and ongoing will be presented by S. STOBIECKI, A. SILOWIECKI and A. KRAUSE in their lectures.

**MATERIAL AND METHODS**

The first report in which the problem of tombs was officially announced on the background of general plant protection situation in Poland was published in 1992 in a sectorial study entitled 'Production and distribution of plant protection chemicals'. This study was financed by the Ministry of Agriculture and Food Economy within a PHARE project.

It has been estimated that the tombs, without owners are presently a kind of 'ecological bomb', which poses a risk for soil, ground water and other components the environment.

In further studies the database concerning all the pesticides authorized in Poland in 1965-1994 has been developed.

The data introduced into the database consist of:

- trade names of pesticides,
- common names of active ingredients,
- chemical groups to which the active ingredients belong,
- classes of toxicity according to Polish classification,
- types of formulations,
- names and countries of manufacturers,
- years of authorization in Poland.

The database contains the data of approximately 1000 products and almost 500 active ingredients and it can be used, among others, for the estimation of tomb contents.

Presently there are 96 tombs with more or less detailed data concerning their contents.

Moreover for each active ingredient chemical and physical properties (solubility in water, solubility in aromatic solvents, persistence in soil) as well as toxicological properties were determined and divided into 4 groups within each property.

From the data concerning all the active ingredients, the data on chlorinated hydrocarbons were selected to determine their contents in the tombs, which is the aim of the present paper.

## RESULTS

Evaluating the content of 32 tombs which was published earlier (1995) and 96 tombs (1995) the ranking of 10 chemical groups occurring most frequently was made (Table 1).

Chlorinated hydrocarbons amount to approximately 30%, phenoxyacids to approximately 13% and inorganic compounds to approximately 15%.

Among other important active ingredients the following ones should be mentioned: dithiocarbamates (approximately 13%), organophosphorous compounds (almost 10%), nitroderivatives (above 7%), tar (near 4%), carbamates (almost 4%), amines (above 2%) and ftalimides (approximately 1%).

On the basis of the materials and documents concerning separate tombs it may be stated that the tombs contain almost all the products used in Poland, mainly in years 1960-1980. It should be added that the tombs contain also other chemicals such as fertilizers, laboratory reagents including potassium cyanide, brucine etc., industrial chemical waste (waste after metal galvanization) and others.

The differences between the estimation of 32 and 96 tombs are inconsiderable with respect to some chemical groups, but there are cases in which they are more distinct.

As it was mentioned earlier chlorinated hydrocarbons were the chemical group representing the highest volume. This is easy to understand taking into consideration that in the sixties and seventies, when 30% of Polish farms belonged to the state, the highest volume of pesticides was directed to these big farms while for the small private owners they were often unavailable.

This period in Poland was characterized by a mass occurrence of Colorado potato beetle, which was controlled on the acreage of more than 2 millions hectares (1,5 treatments per season). Other very important pest was the pollen beetle on oilseed rape, controlled on 500 thousands hectares.

In general, for the control of the above mentioned pests various formulations of the products containing chlorinated hydrocarbons were applied.

Among chlorinated hydrocarbons DDT amounts to approximately 50%, chlorinated camphenes to above 11%, DMDT to approximately 12%, HCH + lindane to approximately 10%, diene compounds to approximately 5% (Figure 1).

Other compounds belonging to that group amount to approximately 12% and they are identified as kelevan, endosulfan, tetradifon and other (Figure 2).

After analyses of the types of formulations of the products containing chlorinated hydrocarbons deposited in 96 tombs it was found out that liquid formulations amount to 20%, dusty formulations to 75% and other formulations to 5%.

In order to further estimate the risk posed by separate tombs, the physical, chemical and toxicological properties of active ingredients were taken into account. Table 2 presents the properties expressed in indicators determined in one of earlier projects (1995) concerning chlorinated hydrocarbons.



It can be seen from this Table that the risk posed by these compounds results primarily from their persistence in the soil, estimated as very high (3) and in the majority of cases from their toxicological properties (cancerogenity, teratogenity, mutagenity, neurotoxicity).

Table 3 shows the ranking of the tombs containing the highest volume of chlorinated hydrocarbons. The highest content of these compounds was found in the tomb localized at Kolonia Krupe, Chelm voievodeship, in the south-eastern part of Poland.

### CONCLUSIONS

1. Among approximately 480 active ingredients occurring in the tombs, chlorinated hydrocarbons are the most important group of chemicals, considering both the volume (27%) and the risk for the environment.
2. Among chlorinated hydrocarbons, DDT amounts to approximately 50%, HCH and lindane to approximately 10%.
3. 75% of the total amount of chemicals deposited in the tombs are solid formulations, 25% liquid formulations.
4. From more or less detailed data for 96 tombs the highest amount of chlorinated hydrocarbons (approximately 10 tons) was determined for the tomb localized at Kolonia Krupe, which really can be called a 'pesticide ecological bomb'.
5. Using the collected and computerized data it is possible to estimate to a high degree of probability the contents of each unknown tomb.

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6.

## CHLORINATED HYDROCARBONS CONTENT IN TOMBS IN POLAND



- Plant Protection Institute
- Poznan , Poland
- Dr Edward CZAPLICKI
- M.Sc. Barbara PODGORSKA
- M.Sc. Malgorzata ROGALINSKA

- brief history

- detailed data described by:

- A.Krause, A. Silowiecki  
Risk assessment for dumping places  
containing unwanted pesticides in Poland,  
Tuesday 9:40 - 10:00
- S.Stobiecki  
Progress and developments on unwanted  
pesticides in Poland,  
Tuesday 10:55 - 11:15

**Database containing all the pesticides authorized in Poland:**

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- common names of active ingredients
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- types of formulations
- names and countries of manufacturers
- years of authorization in Poland

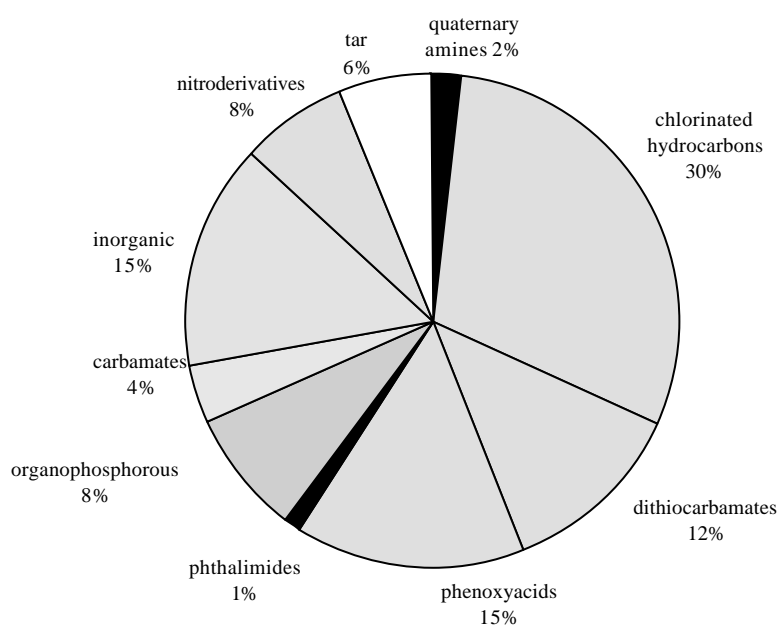
available more or less detailed  
data from 32 and later 96 tombs

ranking of chemical groups most  
frequently occurring in the tombs

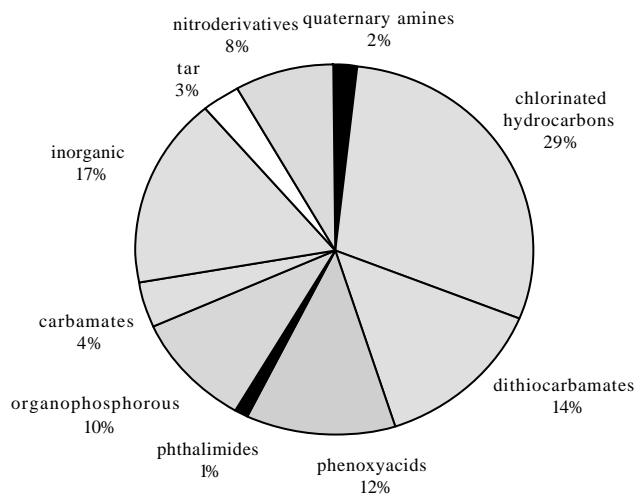
## The most important chemical groups in the toms

CHEMICAL GROUP	MOST FREQUENT ACTIVE INGREDIENTS
*quaternary amines	*chlormequat
*carbamates	*barban, carbaryl
*chlorinated hydrocarbons	*DDT, HCH, DMDT, lindane, chlorinated camphenes, diene derivatives
*dithiocarbamates	*maneb, zineb
*inorganic	*copper oxide, sulfur, calcium polysulfide, zinc phosphide
*nitroderivates	*DNOC, dinocap
*organophosphorous	*disulfoton, dimethoate, fenitrothion
*phenoxyacids	*2,4-D, 2,4,5-T, MCPA, TCA
*phthalimides	*captan
*tar	*tar oil

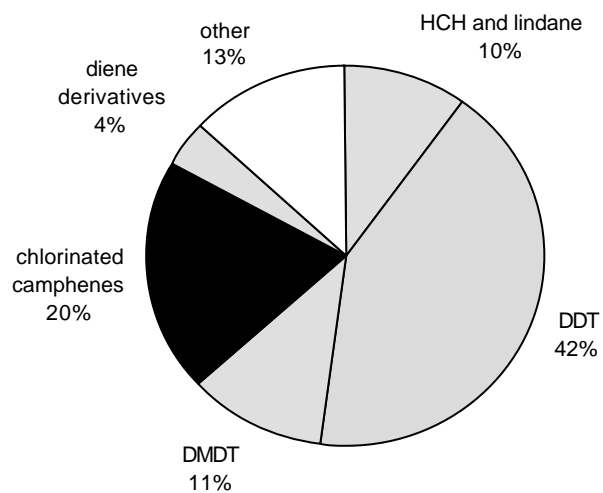
**Fig. 1 Content of the most important chemical groups in 32 toms in %**



**Fig.2 Content of the most important chemical groups in 96 tombs in %**



**Fig.3 CHLORINATED HYDROCARBONS in 96 tombs in %**



## other

- hexachlorobenzene
- tetradifon
- kelevan
- ovotran
- endosulfan

**Solubility in water:**

- 1 - <10 mg in 1 l  
2 - 10 mg -1g in 1 l  
3 - 1-100g in 1 l  
4 - > 100g in 1 l

**Solubility in aromatic solvents:**

- 1 - < 1g in 1 l  
2 - 1-10g in 1 l  
3 - 10-100g in 1 l  
4 - > 100g in 1 l

**Persistence in soil:**

- 1 - neutral for environment  
1.3 - not persistent  
2 - moderately persistent  
3 - persistent

**Toxicological properties:**

- 1 - neutral  
3 - moderately dangerous  
9 - dangerous  
27 - extremely dangerous

### SOME PROPERTIES OF CHLORINATED HYDROCARBONS

Active ingredient	Solubility in water	Solubility in aromatic solvents	Persistence in soil	Toxicological properties
DDT	1	4	3	9
chlorinated camphenes	1	4	3	27*
DMDT	1	4	3	9
HCH	1	3	3	27
lindane	2	3	3	27*
dieldrin	1	4	3	27*
heptachlor	1	4	3	27*
aldrin	1	4	3	27*
tetradifon	1	4	3	3
kelevan	1	4	3	27*
endosulfan	1	4	3	9

solid formulations      75 %

liquid formulations      25%

ranking of the volume  
chlorinated hydrocarbon in tons:

<b>Tomb - location</b>	<b>Product (t)</b>	<b>a.i. (t)</b>	<b>chl.hv. (t)</b>
Kol. Krupe	138	17	9.77
Rywoczyny	82	26	9.11
Ostrowiec	84	29	8.35
Hiszpania	76	30	7.45
Ocieka	16	7	5.59
Makoszyn	50	16	4.88
Biskupice	44	12	4.51
Anusin	35	11	4.40
Korolowka	48	19	4.12
Niedzwiady	29	12	3.69
Kol. Gucin Korolowka	16	6	3.61
Iwiny	45	14	3.48
Cierzpiety	40	14	3.45

## CONCLUSIONS

- Among approximately 480 active ingredients occurring in the tombs, chlorinated hydrocarbons present the most important group of chemicals considering both from the volume (29%) and the risk for the environment
- Among chlorinated hydrocarbons DDT amounts to approximately 42%, HCH and lindane to approximately 10%
- 75% of total amount of chemicals deposited in the tombs are solid formulations, 25 % liquid formulations



## CONCLUSIONS

- From the more or less detailed data for 96 tombs the highest amount of chlorinated hydrocarbons (approximately 10 tons) was determined in the tomb located at Kolonia Krupe, which really can be called a “pesticide ecological bomb”
- Using the collected and computerized data it is possible to estimate to a high degree probability contents of each unknown tomb.

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**USING GEOLOGICAL AND GEOPHYSICAL METHODS IN INVESTIGATIONS OF THE INFLUENCE OF THE TOMBS ON THE NATURAL ENVIRONMENT****Stanislaw WOLKOWICZ****INTRODUCTION**

Tens or even hundreds of repositories of already expired pesticides exist in Poland. They were built in the 70-ies and located at random. No studies of geological structure of areas in the regions of storage were performed prior to the location of the places of storage.

Since 1995 Polish Geological Institute in cooperation with the Plant Protection Institute have begun research on the influence of the unused pesticide repositories on the natural environment.

The studies have the following aims:

- to determine a geological structure of the area around the repository,
- to determine hydrogeological conditions, i.e. first of all,
- to estimate flow direction and velocity of the waters from the first water horizon, that is mostly dependent on pollutions emitted from the repository,
- to check the tightness of the repository construction due to studies of the pollution halo around the repository by means of geophysical and geochemical methods.

After interpretation of the results of the field geophysical works, piezometric wells were drilled. Soil and water samples were taken during drilling. Also the already existing wells localized at the direction of fluids flow from the first water horizon were sampled for research. Samples of soil and water were analysed for pesticide residues and for heavy metals content (Hg, Pb, Cu, Zn).

**STUDIES ON THE GEOLOGICAL STRUCTURE BY MEANS OF GEPHYSICS**

The method of geoelectric sounding (SGE) has been applied during the studies on the geological structure of the basement of the are of accumulation in question. Measurements of the layer impedance with an increasing depth of penetration of the current lines of the electric field are crucial in this analytical method. Results of the sounding correspond to a diagram (a curve) of impedance  $\rho_k$  plotted against the different distance of the supplying electrodes A and B. It is, therefore, the diagram of the function  $\rho_k=F(AB/2)$  presented at the logarithmic coordinates with a scale module of 6.25 cm.

Sounding (field works) was performed according to the Schlumberger's symmetric pattern, in which successive measurements of the impedance were done in relation to different distance between the current electrodes (AB) and the potential (MN) electrodes ranging from 3 to  $\infty$ . The most often sounding applied was that with a distance of 160-320 meters between the electrodes AB.

Multi-layer curves determined as the curves of the type KQ, HKH, KHK in the geophysical nomenclature result from the hitherto performed studies. The types correspond to the number and the sequence of the layers. All the curves were quantitatively interpreted using the computer package "INCEL" developed at Geological Faculty of Warsaw University,.

The results of geoelectric measurements were interpreted in relation to known lithological profile from the area of the repository. Usually profiles of the piezometric drills and the neighbouring archive boreholes were used.

Due to the ways of interpretation, a relatively precise information has been obtained on the lithological variability of the repository basement. Usually 10-20 geoelectric soundings were done at one repository.

## **STUDIES OF POLLUTION AUREOLE BY MEANS OF GEOPHYSICAL METHODS**

### **Electric sounding and electric profiling**

As in results from the interpretation of the geoelectric sounding measurements, the resistance of the layer polluted with pesticides shows a decrease. It is most evident when we observe a change in the impedance resistance value at the depth close to the occurrence of the first water horizon. That results from the fact that pollutions from the repository are laterally transported by water while part of them is absorbed by sediments forming a water-bearing horizon.

The geoelectric sounding may be used in the studies, however for better resolution of the image electric profiling focusing onto impedance variability of only one selected depth horizon was applied. The latter method is also quicker and approximately ten times cheaper than the former one.

Studies of the pollution aureole by means of the electric methods do not give satisfactory results in the following cases:

- when the repository basement is built of rocks either not sorbing the migrating pesticides or sorbing them only to a very low degree.
- when the repository is high above the water-bearing horizon and the pollution occurs within the interval of several tens of meters vertically downwards and the shallowly located aureoles of soil pollution have reduced dimensions,
- when the repository is located close to another object which also emits pollution, e.g., communal dumping site. The results registered represent a total effect of both of the objects.

### **Atmogeochemical studies**

Atmogeochemical studies correspond to the determinations of the content of one component of the soil-air by use of the adequately calibrated equipment. For many years this method has been used to study content of mercury vapours (mercurometry) and radon concentration (emanometry). For determination of the organic matter vapours a photoionizing detector (PID) is used, and it might be equipped with different ionization lamps detecting different gases.

For the study on the influence of pesticides repositories on the environment - the version PID 580S of the apparatus was used, and calibrated for the compounds from the xylene group (the compounds which are commonly used in pesticides). The measurement results are directly obtained in the field, so immediately a proper distribution of the measurement points makes it possible to trace an anomaly. The measurement itself is short and lasts about 15 seconds. Soil air is sampled from the hole at the depth of about 80 cm. It is important to cut down the access of the atmospheric air during the soil-air sampling.

The method is really quick. It is possible to make about 200 measurements per day, in favourable conditions.

The method does not give good results when:

- the basement is built of the soils characterized by low porosity and low emanation strength (clays, tills, very fine-grained clayey sands, residual watering clays),
- ground waters horizon lies very shallow (more shallow than the depth required for sampling).

- Two main conditions must be fulfilled to get the proper result:
- the air temperature must be higher than 10° C,
- the measurement may be done at least 4 hours after a rain fall.

Thanks to the atmogeochemical studies, it is possible to assess if the repository is tight, while the shape of the anomaly points to the direction of pollution migration.

In case of the soil-covered repositories the method discussed allows to localize places of emission (e.g., Biskupice repository, the Lublin voivodship). Also unknown areas of pesticides burial might be localized (e.g., NiedŹwiady repository, The Kalisz voivodship).

The atmogeochemical method is more sensitive than that of geoelectric sounding and profiling (e.g., Tomaszów Lubelski repository, The Lublin voivodship), although the limitations of the method should be taken into account.

In general, therefore, both methods should be applied together.

In case of several sources of the pollution emission, the atmogeochemical studies, thanks to the medium measured, result in separation of the individual sources.

### **HYDROGEOLOGICAL STUDIES**

Since the ground water represent the main transport medium and the object of pollution with pesticides, it is really important to analyze water relations in the neighbourhood of the repository.

At the initial stage the studies are conducted on the basis of the regional data from the regional hydrological maps. In many cases, in the places where the geological structure of the first meters from over tens to several tens does not vary, such an analysis supported by measurements in the surrounding wells, seems to be sufficient to a relatively precise determinations of the water flow direction. In many cases, however, flow direction of waters in the first water horizon may strongly differ from the regional one. The repository in Góry Opolskie (the Lublin voivodship) is a good example here. The repository mentioned lies on the small Quaternary structure implaced into the Upper Cretaceous carbonate sediments. The local water flow is perpendicular to the regional direction.

### **Relation between the geological structure of the repository basement and migration of the pollution in sediment and waters**

The process of repository influence on the surrounding natural environment depends in a great degree on the lithological character, lithological variability of the layers and the depth of the water horizon.

The repositories are, therefore, located in the following geological-hydrogeological conditions:

- the repository located in sand sediments of small thickness with the non-permeable deposits underneath (clays, tills) - the water horizon lies shallowly. The repository is dipped in water and continuously leached which results in a constant emission of the substances into the natural environment. The vertical spread of pollution is limited whereas the horizontal expansion may correspond to the distance ranging from hundreds of meters to a few kilometres. In that case the residues of pesticides occurs mainly in the whole profile of the sand layer, in the top part of the non-permeable layer, as well as (of course) in water,
- the repository placed in sand sediments of significant thickness (some tens of meters) - the water horizon lies relatively deep. The repository is, therefore,

"hanged" over the water horizon being washed only by the rainfalls. In case of a leaking repository the pollution has only a limited spread on the surface, whereas its vertical expansion corresponds to the whole depth interval between the surface and the water horizon. The most intensive pollution occurs at the depth of the water horizon. This part of the profile, where the sediments are dry, displays a minimum pesticide pollution. The geological material collected from the repositories in such a position shows a distinct regularity of pesticide residues at the depth of 7-11 meters, the fact most probably connected with the zone of capillary hanging waters. On contact with water horizon, the pollution is further transported by underground waters. The lateral spread is similar to the one discussed previously, although it should be smaller. The case described is quite common in Polish geological conditions and, therefore, it's a real threat to underground waters, which in turn, often are the basic source of water supply for the settlements of the area,

- the repository placed on the compact fissured sediments (e.g., structures like carbonate platforms). Several hanging water horizons and the regional water horizon may occur in that area. The last horizon mentioned may lie at the depth of several tens of meters and may gather infiltrating waters from the hanging levels. The repositories are washed by the rainfall waters. They create a real danger for underground waters since although the rock environment is either non-active or low-active in relation to the migrating pollution, the flows through fissure paths are very quick, their direction being strongly variable. Waters of the regional water horizon are often the main source of local water-supplying services. The extent of pollution may reach even several kilometres. In the samples from rocks under the repository no pesticides were detected.
- the repository located in non-sealing sediments (as clays, tills and residual clayey sediments) of a significant thickness. The water horizon (in general strained) occurs below and is well protected by the overlying sediments. The spread of the pollution is limited: vertically it extends only to some meters, while horizontally - to some tens of meters. Pollution is transported mainly by the surficial rainfall and melting waters. The repositories placed in such geological conditions are relatively safe.

## CONCLUSIONS

Aiming at the proper evaluation of the threat for the natural environment caused by the repository of expired pesticides it is crucial to know the geological structure of the repository basement, especially the lithological character, the depth of the first water horizon as well as direction and velocity of the water flow in that horizon.

To achieve this goal geoelectric sounding was used, then it was further interpreted on the basis of the known drilling profile. These studies, together with hydrogeological measurements in the wells from the adjacent area, lead to the recognition of the hydrogeological situation in the neighbourhood of the repository.

Field geophysical methods (geoelectric and atmogeochemical ones) were applied aiming at the determination of the tightness of the repository, the extent of emission as well as the spread of the pollution halo. When used directly in the field and directly controlling the extent of an anomaly those methods have a great advantage.

The pollution spread together with the depth was determined on the basis of soil samples taken during sinking of the observatory wells.

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The content of minerals and substances sorbing the pesticides transported as solutions has the significant influence on the migration velocity of the pollution halo. Clay minerals, iron hydroxides and the organic matter seem to play the most important role here.

The problem of the influence of the sediment components onto the migrating pollution demands a further research.

Taking into account the geological structure of the repository basement - the most dangerous for the natural environment are the repositories located on the fissured rocks and in sands of the significant thickness, with a water horizon underneath important from the economical point of view.

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**CURRENT SITUATION OF UNUSED PESTICIDES IN LATVIA AND STATE STRATEGY FOR SOLVING THE PROBLEM**

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**Ilgonis STRAUSS**

The problem of unwanted pesticides in the Republic of Latvia is considered an important part of the common hazardous waste problem. Therefore I would like to begin with very short description of hazardous waste problem in my country.

Solution of the hazardous waste problem is one of the main priorities in the area of the environmental protection in our country. Hitherto Latvia had no formalised system for the proper management of hazardous waste on national level. It means that there does not exist a system of collection, storage and treatment of hazardous waste. In addition to that — there are no suitable storage places for hazardous waste. For that reason hazardous waste accumulates in the territories of enterprises. Large amounts of hazardous waste is kept in poor storage conditions and often some of it gets finally into the household landfills.

Last year together with the Danish company Chemcontrol A/S we proved that at present time in Latvia there are accumulated approximately 1.2 mil. m<sup>3</sup> of hazardous waste. This study also demonstrated that among different kinds of hazardous waste we can point out a special sort - old unwanted pesticides from former collective farms. There were determined approximately 1400 m<sup>3</sup> of old unwanted pesticides. The classes of expired pesticides were not identified. However we suppose there are all classes of pesticides that were used on our territory for a very long time, including those which were forbidden many years ago, for example DDT, Hexachloran (Lindane), CC and many others (approximately 110 names).

The problem of unwanted pesticides is extremely serious because this kind of hazardous waste is stored in very poor conditions in more than 120 sites throughout all Latvia which cause threat to human health and to the environment. Storage conditions are more or less acceptable only at two sites and there are collected approximately 800 m<sup>3</sup> old pesticides. I have to mention that in some sites there were accidents and fires due to bad conditions of storage of unwanted pesticides.

The main reason of such situation is some shortcomings in process of privatisation in the rural areas. When former landowners or their heirs got back their lands according to the Law of land reform, most of Soviet collective farms collapsed and their property was privatised. However privatised were only those attractive and useful, whereas the rest of properties actually became unclaimed property. Those were mainly urban style multiflat houses, several infrastructure units, as well as pesticide storage sites with some amount of useful pesticides, however the main part of them is just unwanted (forbiden, spoiled etc.) pesticides collected for tens of years. At present time all this property including unwanted pesticide storage sites formally are under the authority of local Municipalities. But the financial situation of most local Municipalities does not allow to manage properly this property, including storage, treatment or diposal of unwanted pesticides. Probably local Municipalities will not be able to solve this problem for a long time and therefore it is necessary to solve the historical hazardous waste problem (including old pesticides) on state level.

For this reason at present time Latvia has updated the National Hazardous Waste Management Strategy (NHWMS), which is divided into two phases (the implementation phase 1 and the current, operative phase 2). Implementation of

the strategy will be financed by national and international (European Union and Danish Government) means.

Phase 1 - the Implementation phase - is planned to be carried out within the next two years. During this time we will develop the central hazardous waste storage facility. We have chosen the former Russian Army base - the tank garages in the central part of Latvia, which will be rebuilt for the central storage facility. Danish side assisted us to prepare detailed design for reconstruction of this military base and right now started the rebuilding works.

In the nearest future we will also form a special hazardous waste management company, which will deal with collection, transportation, storage and treatment of hazardous waste. During the Phase 1 this company will mainly deal with unwanted pesticides. Collection and repacking will be made on the separate already located sites and then transported to the central storage facility. In phase 1 the storage facility will be developed for storage of approximately 600 m<sup>3</sup> solid and liquid pesticides in total.

We are working towards future elimination of collected hazardous waste as well. We have a plan to prepare the kiln in a cement plant for incineration of hazardous waste including the part of expired pesticides in an environmentally safe way. Hazardous waste, which can not to be burnt due to a very low calorific value or due to some other reasons, for example high amount of heavy metals, will be stabilised or solidified on the cement base in order to avoid leaching of components which could harm the environment. In the near future we have to establish also a controlled secure landfill for permanent disposal of solidified waste.

Thanks to the planned activities we expect to solve completely the unwanted pesticide problem as a part of Latvian Hazardous Waste Project during the next two years. However as it was mentioned above the first steps will be repacking, collection and transportation of unwanted pesticides to the central storage facility. We suppose to have finished this part of job by the beginning of the next year.

Phase 2 (Operative phase) - it will be continuous collection, transport and treatment of currently produced hazardous waste with gradual transition on the principle „waste producer pays”. We anticipate that at this stage the amounts of unwanted pesticides will be minimal.



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**ECOLOGICAL ASPECTS OF USE OF PESTICIDES IN BELARUS**

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**Yilor F. SAMERSON, Aleiz F. SKURIAT**

In crop farming of Belarus, plant protection against pests, diseases and weeds is an important element of the technology for the majority of agricultural crops, since the natural and climatic conditions of the Republic of Belarus with damp and lukewarm climate are favourable for the spread of more than 65 harmful species of pests, 100 types of diseases, 40 species of weeds and the potential yield losses due to the absence of the effective protection constitute 25–30 %.

In connection with this, to avoid yield losses and deterioration of its quality due to the harmful influence, in the Republic, along with the agrotechnical methods, the chemical and biological means of plant protection are widely used.

Depending on the phytosanitary situation and the assortment of products within 1985–1990, annually on the fields of Belarus more than 100 different pesticides with the total tonnage of up to 16–20 thousand tons were used or, on the average, 3.0–3.5 kg per ha of arable land. In 1991–1993 because of the change in the assortment of preparations in the aspect of application rates decrease, the volume of pesticides in use decreased, constituting 11.3–14.7 thousand tons, making up 2.04–2.6 kg/ha of arable land. The change of the economic situation in the agricultural production in 1993–1995 led to the unjustified decrease of pesticides in use.

Therefore, in 1994, 6.7 thousand tons were used or 1.12 kg per one hectare of arable land. Among plant protection products judged by tonnage, 50–55 % are herbicides, 6–10 % — insecticides, 20–25 % — fungicides and dressers, 6–7 % — growth regulators, 1.5–2 % — defoliators and desiccants, 0.7–1 % biological preparations. In our opinion the potential range of the influence on the environment with respect to each functional group of the preparations will depend on the volumes of their use taking into account the individual characteristics and peculiarities of the behaviour of particular preparations in the environment.

In view of this, for Belarus the ecological problem may be caused by herbicides, fungicides, dressers and insecticides the share of which constitutes 70–90 % of the total volume of the products in use.

In connection with deterioration of the ecological situation in the Republic after the accident at the Chernobyl power station, a complicated problem arose in relation to health of men and surroundings protection against the negative complex action of radionuclides and plant protection products.

Taking into account the level of radioactive contaminants within the territory, two lists of admitted for use pesticides have been made and accepted. For the first zone with the level of radiation from 0–16 curie/km<sup>2</sup> all the products allowed to be used on the territory of the Republic by the Ministry of Health of Belarus have been agreed upon to be included in the list. For the second zone with the level of radiation from 16–40 curie/km<sup>2</sup>, the products of the first group of toxicological danger have been excluded from the list, the use of the II group products have been restricted along with the products persistent in soil with the expressed delayed post effect, carcinogenic, or influencing the thyroid gland. In this zone the preference is given to the III and IV groups judged by the toxicological classification of used products.

To control the most harmful species of pests depending of the phytosanitary situation, annually eradication measures have to be applied on the acreage of 1.6 mln ha in re-counting for a single treatment. As a result of a retrospective analysis we should emphasise that for these purposes in 1971–1975, the

average of 3630 tons were used annually; in 1976–1981 — 2360 tons; in 1981–1985 — 2000 tons; in 1986–1988 — 1450 tons; 1988–1994 — 200–250 tons of insecticides were used.

Among the assortment of the insecticides used in the agricultural production in 1971–1975 the dominant ones were hexachlorocyclohexane and DDT. So, in 1974 on the territory of Belarus 2097 tons of 12 %–dust of hexachlorocyclohexane were used what constituted 57.7 % from the whole amount of insecticides used at that time for pest control.

The use of DDT on the territory of Belarus was decreased at the beginning of the 70s. So, in 1970 in agriculture some more than 570 tons were used, in 1971 — 128 tons, in 1973 82.2 tons. Since 1974 DDT hasn't been used in agriculture of the Republic.

Starting from 1975, for the last 18 years, we have been able to observe a gradual decrease in the volumes of products based on gamma–isomer of hexachlorocyclohexane in the agricultural production and their practical decline in 1993–1994.

At the same time it is necessary to notice that the decrease in use of products based on HCH, was accompanied by the increase of chlorinated terpenes and camphenes, used widely for 10–15 years.

In Belarus there is no production of pesticides, including hexachlorocyclohexane and other products containing chlorinated hydrocarbons.

That's why the source of the environmental pollution can be the use of HCH and other stable pesticides containing chlorinated hydrocarbons used for agricultural crop pest control, forest and ornamental plantings as well as burial of some expired pesticides.

The disposal of expired pesticides in the Republic of Belarus was carried out in 1974–1985 by means of burring them in special places located in seven regions of Belarus (Brest, Gorodok, Gorots, Verkhnedvinsk, Slonim, Postav, Petyrikov). During this period by means of this method 3776 tons of different products have been disposed of.

The many years of use of hexachlorocyclohexane and other insecticides with chlorinated hydrocarbons (DDT, polychlorpinen, polychlorcamphen) couldn't but influenced the contamination of the environment by their residues.

Based on the results of a study by the Geochemistry and Geophysics Research Institute of the Academy of Sciences of Belarus (Lukashev K.N., Nikitin L.B., 1983) conducted in 1981–1982 it was found out that the majority of soil samples and ground waters contained the residues of HCH and DDT.

The survey of soils, done by the laboratories at chemization stations of agriculture, controlling the ploughing soils contamination with the residues of pesticides in 1974–1978 on the acreage of 169.5 ha showed, that on the average in Belarus the residues of DDT and the products of its decomposition were found in 30 % of the analysed samples and 7 % of HCH in the quantity of 0.01–0.2 mg/kg.

The level of HCH and DDT residues in the majority of the samples did not exceed the maximum permissible concentrations determined in Belarus for soil, for both of the products at 0.10 mg/kg and for water at 0.02 and 0.10 mg/l, respectively.

However, taking into account the ability of chlorinated hydrocarbon insecticides to accumulate in the links of food chains, the presence in water and soil of residues of pesticides from this group is not wanted.

As it was mentioned on the territory of Belarus during 1970–1985, along with the insecticides containing HCH and DDT used for pest control, chlorinated terpenes

and camphenes were widely used, in particular the polychlorpiperin, which in certain years (1973,1976) was used in the quantity of more than 1200 tons.

The research done at the Byelorussian Scientific–Research Institute of Plant Protection showed, that polychlorpiperin was characterised by a significant persistence in the environment, it can be preserved in soil for more than a year, it can accumulate through its multiple use on one and the same field, and it contaminates surface flow of water.

The annual survey of fields (not less than 60-65) done by the State Administration on Hydrometeorology and the Control of the Environment showed that in some cases the soil contamination by polychlorpiperin is up to the level of 0.371 mg/kg with the maximum permissible concentration of 0.5 mg/kg in Belarus.

Having in mind the conservation of wildlife and preventing the negative post effect on agricultural crops, besides the problem of the insecticides containing chlorinated hydrocarbons, there exists the problem of soil contamination by sim-triazine herbicides used for growing maize monoculture. Among the other preparations widely used in agricultural production in the recent past we should mention sodium trichloroacetate, which was capable of migration through the soil profile due its good solubility, causing the contamination of surface and ground waters.

Moreover, there are more than 20 thousand rivers and lakes on the territory of Belarus. That's why the use of plant protection products easily soluble in water is not advised as it may lead to the contamination of water resources and the negative influence on ichthyofauna and water–storage reservoir fauna on the whole.

Among the recent assortment of pesticides, special attention should be drawn to a group of sulphonyl–area herbicides preserved in soil for a long time.

With respect to decrease in the level of wildlife contamination by unwanted pesticides, an important issue is the development of their devaluation methods. Taking it into account, the research on soil cleaning against the polychlorpiperin residues has been accomplished at the Byelorussian Scientific–Research Institute of Plant Protection using the method of biological detoxification.

In laboratory and field experiments with the dosed product application in soil and the analytical fixation of polychlorpiperin product in soil before and on the completion of the experiment, the high activity of the bacterium *Serratia marcescens* in the detoxification of polychlorpiperin was observed, as well as the activity of the bacteria *Bacillus mesentericus*, *Pseudomonas denitrificans*.

Therefore, in the Republic of Belarus the source of the environmental contamination by hexachlorocyclohexane and other insecticides containing chlorinated hydrocarbons lies in their wide use in the course of the previous 15–20 years and the places of burial useless products.

Despite the limitation and full cessation of the products from this group (DDT from 1974, PCP from 1985, HCH from 1993) their residues are still found in soil and in water.

Bacteria *Serratia marcescens* proved highly effective in cleaning of soil and removing the residues of the insecticide polychlorpiperin (chlorten) from the group of chlorinated piperines.

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**REMEDIAL TREATMENT OF LINDANE (HCH)  
AND MERCURY CONTAMINATED SOIL****Hans STRUIJK****Introduction**

Rapid industrial development after World War II resulted in fast growing quantities of industrial waste. Huge amounts of waste have been dumped without exception in distant areas. Afterwards these sites have been covered with sand and clay-layers to realise new developments as residential, recreational and new industrial areas. Soil pollution became a political topic in the Netherlands in 1979 with the so called "Lekkerkerk"-case. Toxic substances were found in a new urban quarter, which had serious risks for the inhabitants and therefore had to be cleaned up. "Lekkerkerk" led to a national investigation of more 'hidden' polluted sites. This investigation has led to more than 100.000 contaminated sites.

In Hengelo the production of the insecticide lindane (HCH) has led to serious contamination of the soil. The waste resulting from the production of lindane out of benzene was often dumped on the industrial production sites. Apart from HCH the soil in the vicinity of Hengelo is sometimes also polluted with mercury caused by a chlorine-alkali-production process. At the time of discovery (1977) there was no effective soil-remediation-technique available for the treatment of this type of contamination. Because a break-through was expected the soil contaminated with HCH/mercury was temporary stored in special depots. In total approximately 400.000 m<sup>3</sup> of soil is contaminated with HCH and/or mercury. Because of the seriousness of the contamination and the associated risks approximately 160.000 tons of HCH-contaminated soil was excavated and stored in special depots in Hengelo. In the nineties the space of the contaminated sites and the space used for the storage of the contaminated soil was needed for building purposes. Since it was not permitted to dump this contaminated soil in land fills the only solution left was remediation.

**Dutch Association of Soil Cleansing Companies (NVPG)**

Immediately after the "Lekkerkerk"-case contractors applied for the sanitation of contaminated sites. They developed soil cleansing techniques which linked with their existing business activities. In 1984 the Dutch Association of Soil Cleansing Companies (NVPG) was founded. Their most important objective is the promotion of soil and groundwater cleansing in an economically and environmentally sound manner. Anno 1996 sixteen Dutch companies are affiliated to the NVPG. Generally the companies have one or more medium to large-scale treatment installations with an annual joint soil cleansing capacity of 1,5 million ton of contaminated soil.

In need of building space the local government of Hengelo asked the soil cleansing companies to develop a remedial technique with which their problem of the contaminated soil could be effectively tackled in an environmentally responsible manner. Some companies have accepted the challenge and specialised in the remediation of HCH/Mercury-contaminated soil. Ecotechniek B.V. and NBM B.V. use a thermal treatment installation. Heijmans Milieutechniek B.V. uses physical/chemical treatment processes. In his lecture Mr. Struijk will only present the thermal treatment of contaminated soil with halogenated hydrocarbons. Physical/chemical remediation will be presented by a representative of Heijmans Milieutechniek B.V.

### **Thermal treatment**

Soil contaminated with hydrocarbons and cyanides has been successfully treated in thermal treatment facilities since the eighties. Many batches of soil however are also contaminated with halogenated hydrocarbons such as volatile solvents (tri, per), halogenated pesticides (drins, HCH, DDT), PCB's and dioxins (PCDD) and furans (PCDF). These contaminants are highly toxic and were difficult to treat because of the emissions to air. In order to be able to treat this kind of contaminated soils Ecotechniek B.V. and NBM B.V. decided to rebuild their installations in such a way that the very stringent emission demands could be met. After this an extensive test program took place. The tests were considered to be successful when the end concentration of the contaminants was within the legislative limits (i.e. target values for the quality of soil) and the emission into the air of the polluting components (in particular dioxins and furans) within the Emission Guideline for waste incineration.

In the adapted thermal facility three types of contaminated soil have been treated:

- soil contaminated with drins;
- soil contaminated with HCH, dioxins and furans;
- soil contaminated with dioxins and furans.

The contaminated soil is heated to evaporate the volatile components in a rotary klin. This process results in a clean soil flow and a contaminated gas flow. The contaminated gas flow is treated in a waste gas facility. The process gas flow is led through a series of multi-cyclones for dust removal and fed to an afterburner for additional treatment. More dust is removed from the gas by means of a dust filter. The acid exhaust gases (SO<sub>2</sub>, HCL) and any organic components (furans, dioxins) are removed in an absorbent unit. Finally the gas flow is led through a gas washer and then exhausted through a smokestack.

The test results led to the following conclusions:

- soil contaminated with halogenated hydrocarbons (drins, HCH, dioxins, furan, etc.) can be successfully treated in an environmentally responsible way with a thermal treatment facility;
- soil contaminated with halogenated hydrocarbons can be cleaned to values lower than the detection limits of the analysis equipment (when the level of halogenated hydrocarbons is very high, the soil can be cleaned to extremely low concentrations).
- the emission of dioxins and furans is considerably lower than the target value. Low values were also measured for other components in the gas flow (CO, SO<sub>2</sub>, HCL, HF, organic C and dust).

The test program showed that oil contaminated halogenated hydrocarbons can be processed in an environmentally responsible way with a thermal remediation facility. Ecotechniek B.V. and NBM B.V. have applied for permits. Based on the positive test results both installations now have a permit to treat the most polluted soils.

### **Physical/chemical treatment**

When the soil is also contaminated with heavy metals cleaning below target values for these components with a thermal remediation technique is often not achievable. In this respect physical/chemical techniques appear to have better possibilities. Heijmans Milieutechniek B.V. has used the physical/chemical technique successfully for the treatment of soil contaminated with heavy metals,

oil and polycyclic aromatic hydrocarbons. In 1990 Heijmans Milieutechniek B.V. and other contractors with a physical/chemical treatment facility were asked to carry out a test on soil contaminated with HCH and Mercury. The test result with the existing facility of Heijmans Milieutechniek B.V. was promising (performance >97%), but the end concentration of the contaminants was still above target values. Since then Heijmans Milieutechniek B.V. has optimised their physical/chemical treatment facility. The production process and circumstances were stabilised due to a more constant input and a counter current system. Furthermore they used new cleansing and separation techniques such as carbon/metal spirals, magnetic separators and foam flotation.

These technological innovations and additional testing resulted in better overall performance (>99%) and end concentrations. The optimised facility not only proved to be able to successfully clean soil contaminated with HCH and Mercury but also other complex contaminated soils.

### **Conclusion**

In the Netherlands there are two operational techniques available for environmentally responsible treatment of soil contaminated with halogenated hydrocarbons; a thermal and a physical/chemical technique. Soil contaminated with halogenated hydrocarbons only can be successfully cleaned below target values with both techniques. When the soil is also contaminated with other contaminants such as heavy metals, the physical/chemical technique will lead to the best cleaning results. Due to technological innovations and testing it is now possible to successfully clean up contaminated soil in an environmentally responsible manner which was not possible at the time of discovery.

## RISK ASSESSMENT AND SITE RANKING - AN INTEGRATED APPROACH

K. Theo VON DER TRENCK

### 1. Priority and Need of Action

About 40,000 contaminated sites can be expected in the state of Baden-Wuerttemberg. Since not all of these sites can be dealt with at the same time, the state administration follows a procedure of 5 steps to systematically collect data and increase the knowledge about every single site. Each investigative step is followed by an assessment at a specific level of evidence ("Beweisniveau". BN). Four levels of evidence have been defined depending on the preceding investigation (BN 1 after the historical investigation, BN 2 after the preliminary technical investigation, BN 3 after the deeper investigation, and BN 4 after the in-depth investigation).

The assessment yields a risk index ( $r$ ) that serves to rank the sites and to determine the action that is to follow. The uncritical sites are sites to be screened out as early as possible.

A so-called "action matrix" determines the consequences for the site as a result of the risk index and the level of evidence as one of the following:

#### Action categories

- a) Eliminate the case from the procedure and transfer it to the archive;
- b) Retain the case in the data base and reassess, if the site use changes;
- c) Monitor the site and its emissions periodically;
- d) Test possibilities for remedial actions (containment and/or decontamination)
- e) Investigate the site further with technical methods.

About 34,000 cases have been registered by now, and around 6000 have been formally assessed at least once. The stepwise procedure of sequential data collection and assessment allowed to drop 2075 sites from the procedure so far (need of action: A or B).

The risk index is composed of:

1. the **hazard** of the material deposited or spilt ( $r_0$ ),
2. a modifier ( $m_I$ ) to assess the possibility of emissions from the site ( $m_I \cdot r_0 = r_I$ )
3. another factor ( $m_{II}$ ) to assess the emissions entering environmental resources like the groundwater ( $m_{II} \cdot r_I = r_{II}$ ),
4. third factor ( $m_{III}$ ) to assess concentration changes during migration of contaminants to possible human receptors ( $m_{III} \cdot r_I = r_{III}$ ),
5. and fourth factor ( $m_{IV}$ ) to assess the importance of the resource at risk ( $m_{IV} \cdot r_{III} = r_{IV}$ ).

The index  $r_{II}$  is entered into the action matrix and determines the kind of action to be taken, and the final index  $r_{IV}$  determines the urgency of the action and the priority. Indices ( $r_{III}$ ) greater than 4 always entail a further investigation or remedial considerations of the site.

### 2. Risk Assessments

One can recognize that the site assessment procedure follows the general principles of risk assessment with  $r_0$  **describing the hazard** of a site relative to a standard dump site, and  $m_I \cdot m_{II} = m_{III}$  **describing the effectiveness of a given exposure pathway**.

The product  $r_{III} = r_0 * m_I * m_{II} * m_{III}$ , thus describes the risk posed by the site, whereas  $r_{IV} = r_{III} * m_{IV}$  corresponds to a weighed risk or a priority, and has effect on finding further measures.

The above procedure was implemented before contaminant concentrations were known. For an updated assessment procedure a substance-specific risk index ( $r_c$ ) is calculated based on the guide values directive previously described (UM & SM B-W, 1993; v.d. Trenck et al., 1993a, b). The directive contains assessment values that were toxicologically derived from chronic toxicity/carcinogenicity criteria and exposure assumptions for realistic worst case scenarios of direct soil ingestion (P-M) and drinking water consumption (P-W).

Since risk assessment for all relevant contaminants has been incorporated into the guide values, the updated procedure can serve to assess and rank all sites with known contaminant concentrations.

### 3. Concentrations-Based Ranking

The guide values H (negligible risk) and P (tolerable risk) are markers of environmental hygiene that characterize any substance. Combined with a third marker for extreme risk, the concentration that would exert a lethal effect in the worst case scenario (LC), they form a characteristic triple that may serve to rank sites on the basis of contaminant concentrations.

The tree markers H, P, and LC can be regarded as equivalent over the whole spectrum of contaminants (v.d. Trenck et al., 1993; v.d. Trenck and Ruf, 1994). For the purpose of ranking, the marker concentrations were assigned to the risk indices  $r_c=0$ ,  $r_c=4$ , and  $r_c=16$ , and thus span a characteristic curve: the evaluative function [ $r_c=f(c)$ ]. This function integrates the criteria for the necessity and the objective of a remediation into the ranking system, which determines the priority and the need of action (UM B-W, 1988; Hillmert, 1990).

The effect-related markers (P and LC) are based on the worst case scenario without consideration of site-specific alleviations. Often the actual risk is lower because of restricted site use and limited spreading of the contaminants. The guideline provides that on the site-specific level 3 of the hierarchy, the actual conditions determine the remediation goal. Therefore the residual contamination ( $c_{eM}$ ) will be higher than the P-values in cases for which level-3 remediation goals are chosen. For such concentrations the risk index ( $r_c$ ) is greater than 4 in the worst case scenario (P-scenario).

The restricted use and reduced exposure of the actual case are expressed by the ratio of the site-specific clean-up goal and the assessment value ( $c_{eM}/P$ ). The measured concentration ( $c$ ) is therefore divided by this ration resulting in a "reduced" concentration ( $C = c * P / c_{eM}$ ) for the purpose of ranking. Entered in the evaluative function, the reduced concentration yields the relevant concentration-based risk index  $R_C$  [ $R_C = f(C)$ ]. By definition,  $R_C$  always equals 4 when the clean-up objective has been achieved. This procedure allows a realistic incorporation into the relevant risk index ( $R_C$ ) of all results of the site investigation and of all decisions of the assessment committee (use and exposure information).

The teoretical basis of the slope of the evaluative function will be explained and its significance for the  $P_{max}$  - W values for site demarcation will be shown.

### 4. HCH Example

The contribution is made by the guide values (H-W, HB, P-W, P-M1) presently used for the three isomers  $\alpha$ -HCH,  $\beta$ -HCH and gamma-HCH and the risk indices

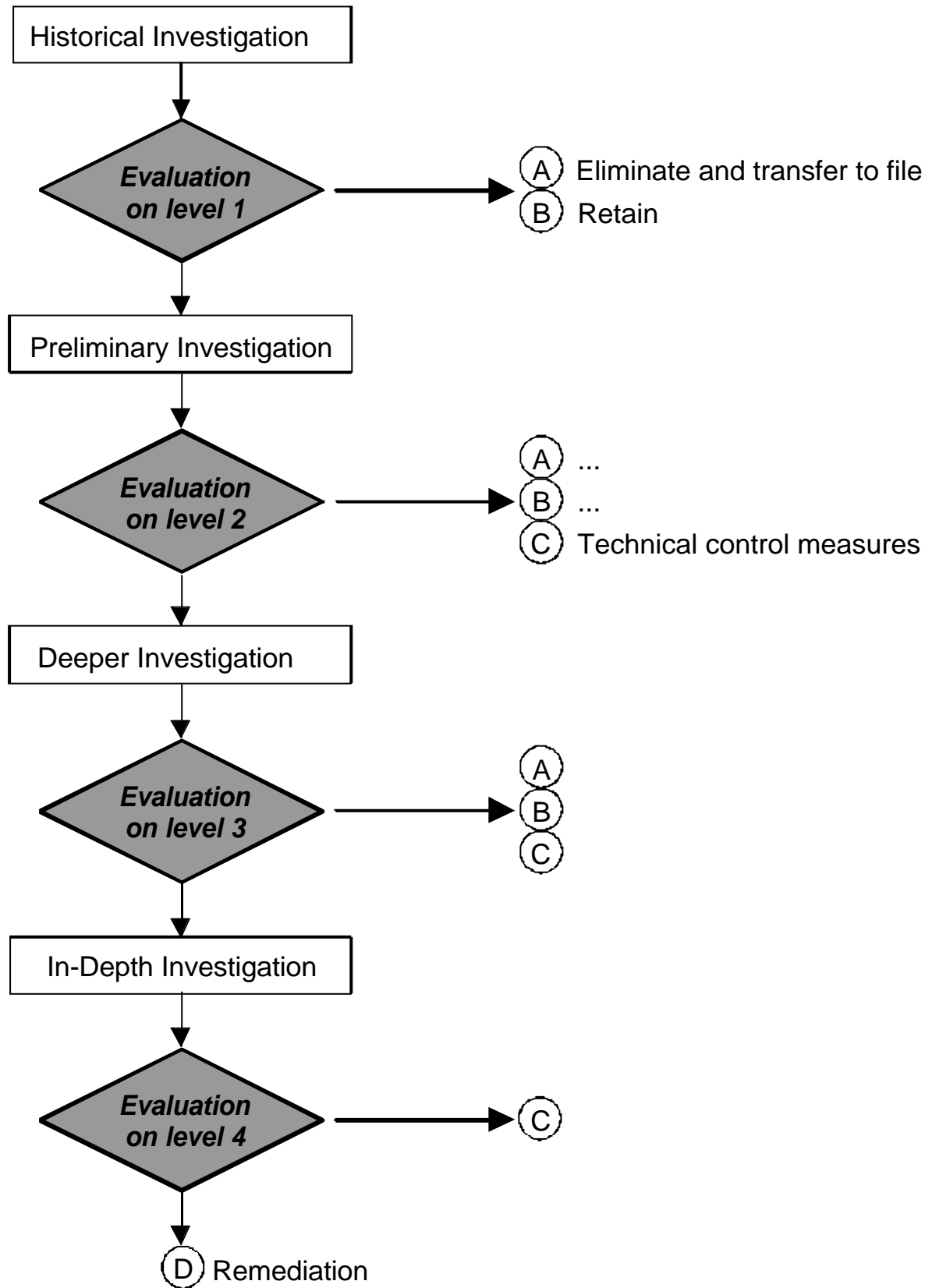


for sites contaminated with different concentrations of these isomers. New P-M1 values are proposed based on updated toxicological information. The effects on the ranking results of the proposed changes are demonstrated to validate the approach and to give a feeling for its sensitivity.

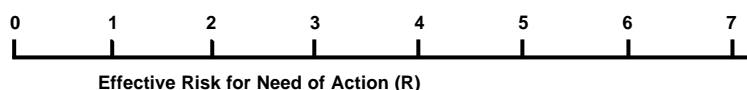
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## Stepwise Investigation and Evaluation



## Action Matrix



Poll. Potential	1	A	B	E <sub>1-2</sub>	
	2			E <sub>2-3</sub>	
	3			C	E <sub>3-4</sub>
	4				D

- A: Eliminate from procedure  
 B: Retain in data base; reassess before change of use  
 C: Monitor emissions periodically  
 D: Test possibilities for remedial action  
 E: Investigate

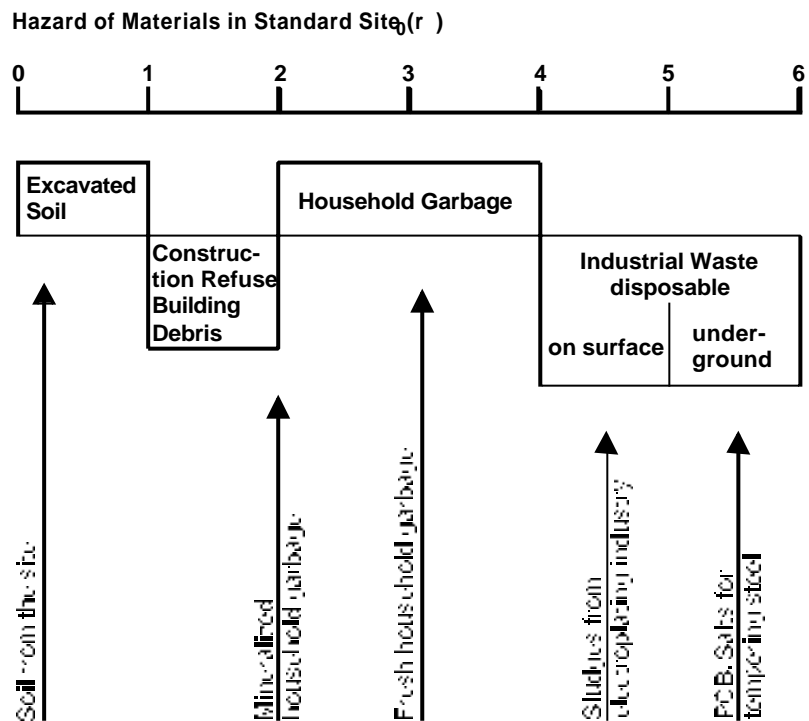
## Composite Risk of a Dump Site

sections of exposure route

$$R = r_0 * m_I * m_{II} * m_{III} * m_{IV}$$

*effective risk*  
*hazard of material*  
*emission*  
*in-mission*  
*migration*  
*importance of resource*

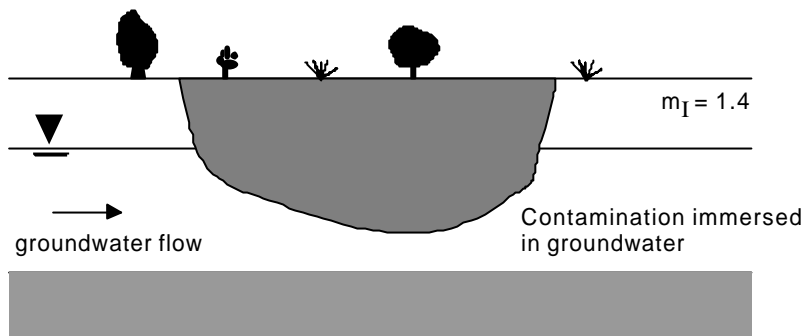
## Hazard of Materials in Standard Household Garbage Dump Site



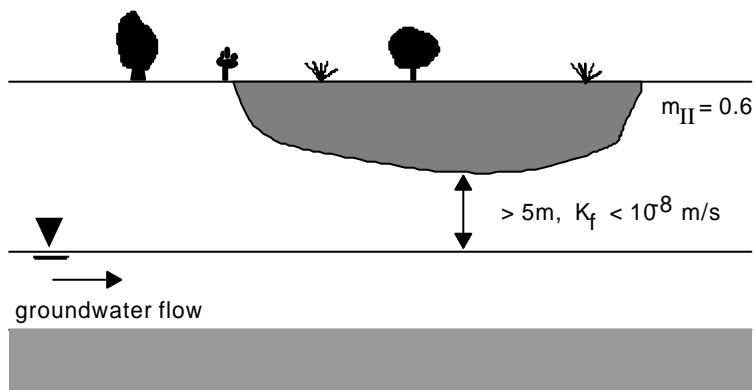


# Illustration of m-Factors

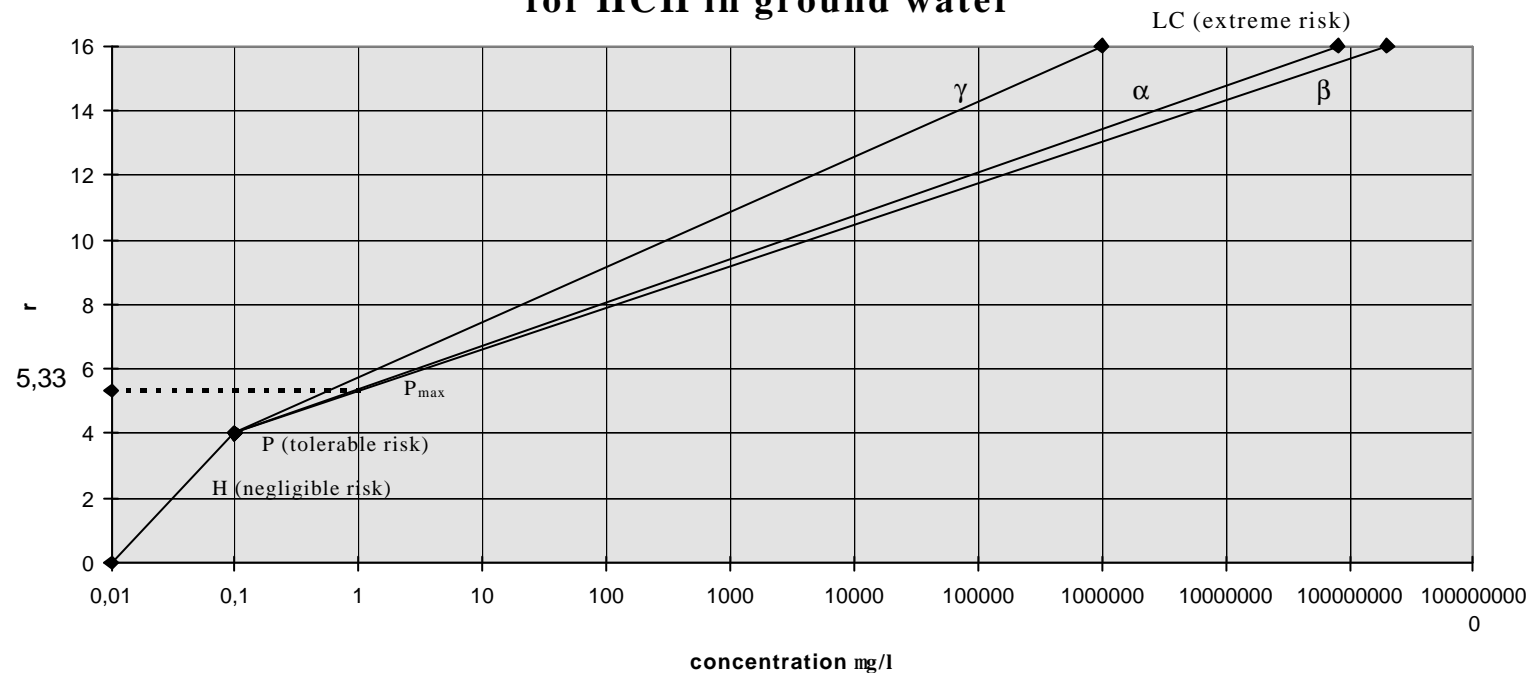
## $m_I$ : Factors affecting the quantity of the emission



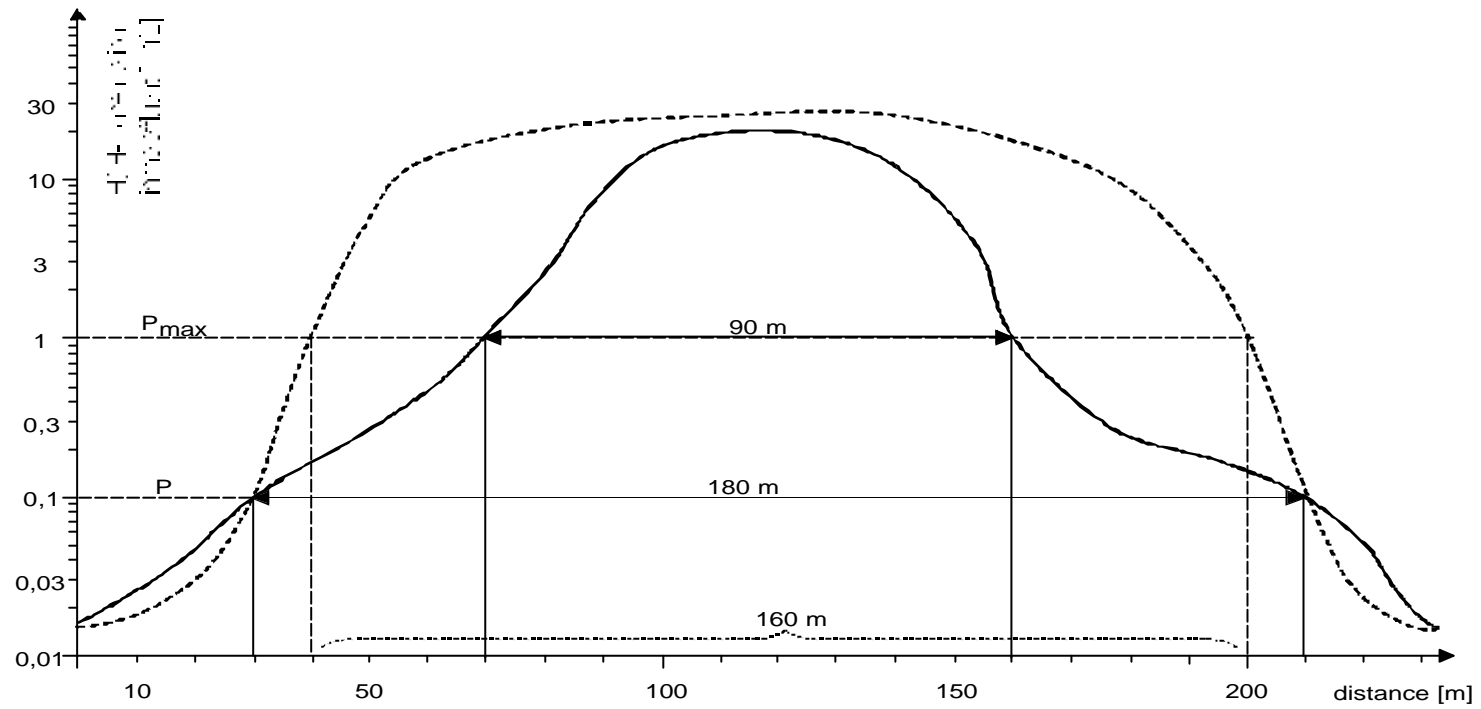
## $m_{II}$ : Factors affecting the emission efficiency



### The evaluative function $r_c = f(c)$ for HCH in ground water



## Site Demarcation by $P_{max}$ -W

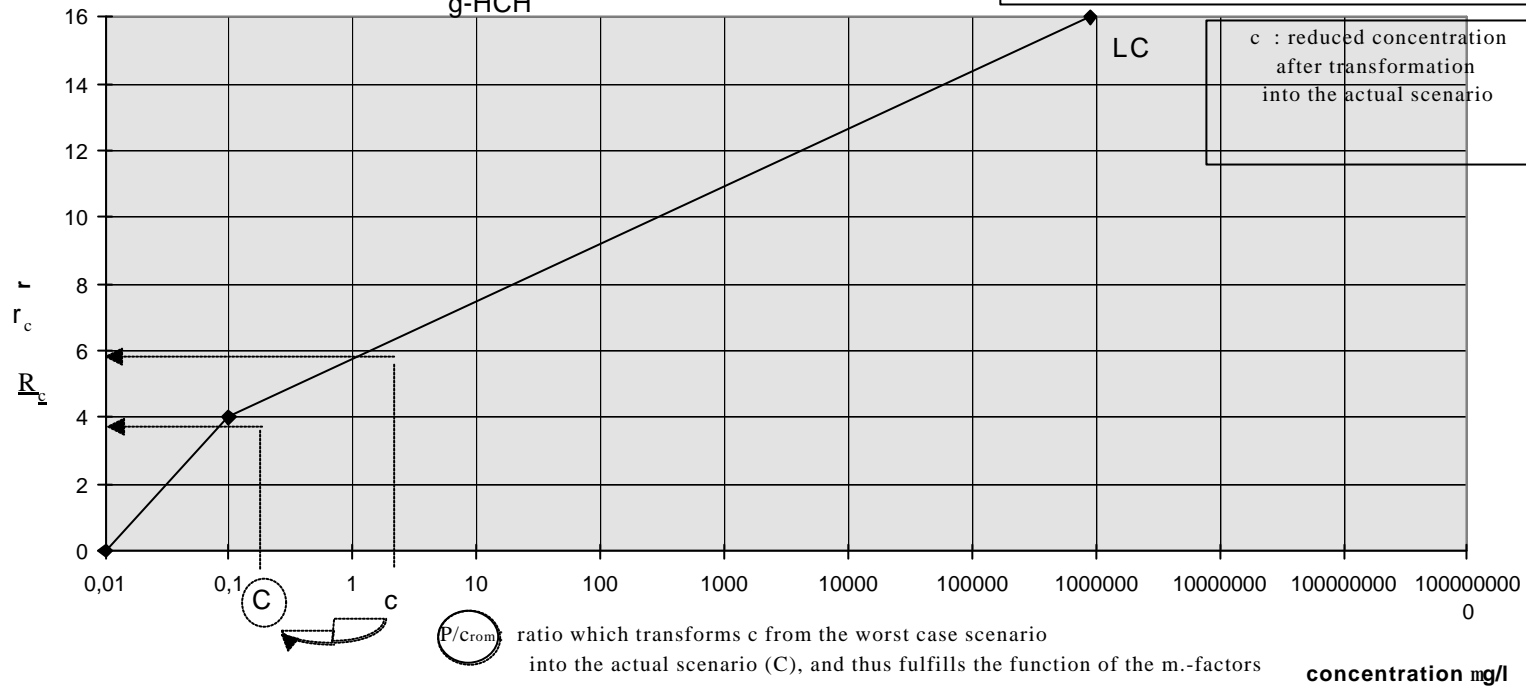




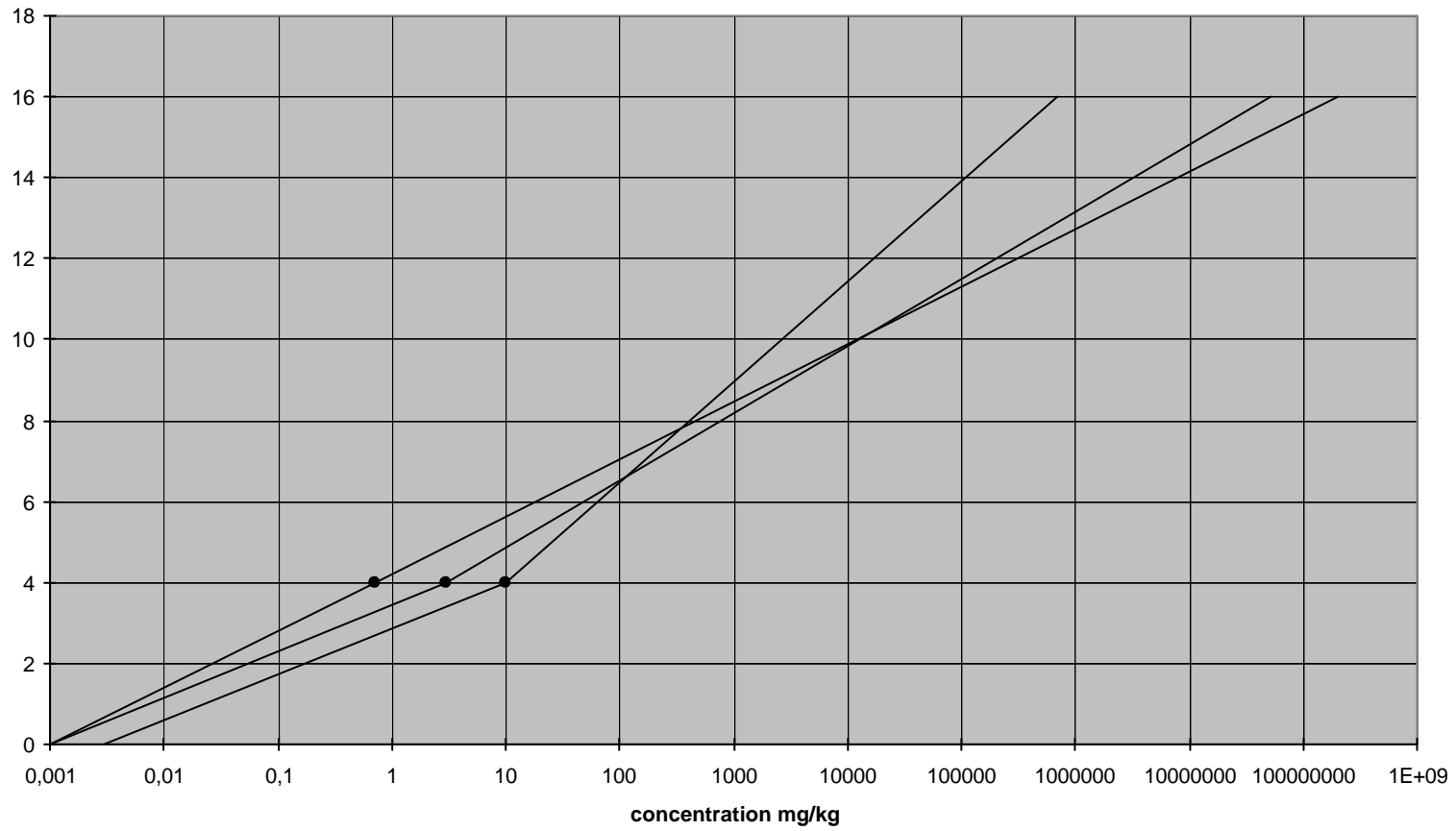
### Transformation of Concentrations from the P-Scenario into the Actual Scenario

g-HCH

c: concentration measured (2 µg/l seepage)  
 c<sub>rem</sub>: residual concentration after clean-up (1 µg/l)  
 P: assessment value (0,1 mg/l)



Characteristic curves for HCH  
in playground soil



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**TOXICITY OF PHENYLUREA AND ACETANILIDE HERBICIDES  
IN GRAM-NEGATIVE CELLS AND PERSISTENCE  
IN SURFACE WATERS**

**Anolda Cetkauskaite  
Janina Berzinskiene**

**Application**

The chlororganic herbicides of older classes (phenylureas and acetanilides) were intensively used in agriculture in Lithuania till 1990 (Sukyte J. et.al., 1990). Some of them (as propanil, pronamide) are used in mixtures (basagran, etc) or together with herbicides of new generation as sulfonylureas (Valionis S. et. al, 1992). the acetanilides (panadol, niclosamide, pantogamum, bromisovalum) and phenylsulfonylureas (clopamidum, clocyclamidum, chlorpropamidum) are also widely used in pharmacy (Mashkovskij M.D., 1993).

**Biodegradation.**

During the period of 1981-1990 the non-standard experiments of the biodegradation of organic compounds (phenols, derivatives of dichlorophenoxyacetic acid, aniline derivatives, acetanilides) by surface waters microorganisms were performed by Paris et. al., (1981, 1983, 1986, 1987) Steen et. al. , (1989), Vasiljeva et. al. (1989). In these experiments low concentrations (0.1-1 ppm) of compounds were used. The standart tests (ISO and OECD) of biodegradation recommend to use much higher concentration of test compounds, namely, 5-40 and 100 ppm (ISO, 1994). Thus, we analysed biodegradation and toxicity of phenylurea and acetanilide herbicides in higher concentration range, namely 2-10 ppm. The microbial transformation kinetics were measured for two acetanilide (propanil and propachlor) and three phenylurea (fenuron, monuron, and diuron) herbicides in surface water samples of Neris River upstream and downstream Vilnius city. A second - order reaction rate constants were used to describe the microbial transformation of chlorinated herbicides (Paris D.F. et. al., 1981). The initial concentration of microorganisms varied from  $4.7 \times 10^5$  to  $2.7 \times 10^6$  cells/L and from  $1.4 \times 10^8$  to  $5.3 \times 10^8$  cells/L for water samples of Neris River upstream and downstream Vilnius, respectively. The values of second-order biodegradation rate constants (Kb) revealed the following order for decreasing transformation rates of compounds tested: propanil > propachlor > monuron = diuron > fenuron. The first order constants (Ka) did not changed significantly, although the total numbers of bacteria in water samples varied in two orders.

**Toxicity.**

The effects of chlororganic herbicides on the light production of bioluminescent bacteria were measured (method described in Bulich A.A., 1984). Exposure of *Photobacterium phosphoreum* 430 cells with the chlororganic herbicides (concentration 2-40 ppm) during 2 hours inhibited the bioluminescence in the following order for the phenylureas: chloroxuron > diuron > monuron > fenuron and for acetanilides: propanil >> monalide > propachlor. The aforementioned compounds (at the same concentration) had no effects on bioluminescence of luciferase reaction in cell-free extracts of *Photobacterium phosphoreum*. The uptake of lipophilic cations of tetraphenylphosphonium ( $TTP^+$ ) (indicator of cell membrane voltage, see Kamo et al. , 1979) by intact *Photobacterium* cells were measured during cell exposure to herbicides. During first 10 minutes the accumulation of  $TTP^+$  in cells was enhanced by acetanilide herbicides (50 ppm) in the following order : propanil > pronamide > monalide >

propachlor. The accumulation of TTP<sup>+</sup> caused by acetanilides decreased after 10 minutes of cell exposure; the effect was similar to the effect of antibiotic polymyxin B, and was sensitive to ionophore gramicidin D.

The acetanilides (at the same concentration) caused a slow potassium ion (K<sup>+</sup>) efflux from *Photobacterium* cells with the lag period of 10 - 20 minutes in the following order : propanil >> monalide > propachlor. Polymyxin B and gramicidin D induced a stronger K<sup>+</sup> efflux from cells. This work can help to understand the phenomenon of membranotoxicity of phenylurea and acetanilide herbicides to gram-negative cells during short exposure in a long-term processes.

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**CONTAMINATION OF THE MULDE RIVERSIDE WITH  $\beta$ -HCH  
AND HEAVY METALS-FACING THIS PROBLEM DAILY**

**Petra SCHMIDT, Wolfram SCHÖLL, Ulrich FACH,  
Joachim HÖLTKEMEIER**

As already reported at 3rd HCH forum in Bilbao, the sediments of the Mulde river in the region of Dessau/ Bitterfeld in the Land of Saxony-Anhalt are in part highly contaminated with  $\beta$ -HCH. This is because of the fact that, for many years, insufficiently purified industrial sewage has been drained into the river. Furthermore, loading with heavy metals has occurred owing to centuries of ore mining in Southern Saxony and because of chemical industry.

Due to periodical high waters of the Mulde river many many years, floating sediments have been flooded from the fields and meadows in the Mulde riverside areas of the regional country of Bitterfeld and the town of Dessau. Hence, contamination with  $\beta$ -HCH has occurred and, in certain locations, with heavy metals as well.

The area of the affected region totals about 2000 hectares of which approximately 500 hectares are „highly contaminated”.

Initial analyses conducted for the region of Dessau/Bitterfeld, while providing evidence of other contaminants, revealed in part very high  $\beta$ -HCH and heavy metal concentrations in soil, plant and foodstuff samples of animal origin which were taken in this region. The Presidency of Dessau being the higher-level administrative authority established a task force, the Mulde Meadowland Working Group, to co-ordinate all relevant issues resulting from contamination of the areas in the Mulde meadowland region, such as sampling, decisions, and recommendations. I take the liberty to report here on further activities relating to this problem.

As customer protection is highly desirable the Presidency of Dessau issued a hazard prevention order taking into account the territorial distribution of the concentrations of harmful substances as determined in upgrowth and in animal-based foodstuffs in the flood plain. This regulation entirely prohibits agricultural use for all areas within the main dykes on the Lower Mulde as well as for defined areas of individual bounds of the affected region. For particular areas outside the dykes, the regulation provides for restricted use with respect to growing and harvesting of forage and litter for domestic animals.

A problem is incurred in classifying the areas in that they do not represent a steady-state system as repeated flooding may cause changes in  $\beta$ -HCH levels in the upgrowth at any time. Therefore, even after issuing this hazard prevention order, further samples are being continually examined for foodstuff and forage produced in the region. Typically, some 800 forage samples were analysed in the 1993-1994 period, and in the year 1995 a total of 107 samples were examined. In 1993/1994, about 50 percent of the areas within the entire flood plain for which samples have been examined - and these included areas beyond those previously prohibited - were classified useable without any limitation, and approximately twenty percent were found to be suitable for use with certain limitations. For thirty percent, however, utilization had to be prohibited. The studies and examinations conducted in 1995 provided further important information. While confirming in the part the findings obtained in 1993-1994, they also revealed changes in the load situation.

In the light of the investigations conducted, the hazard prevention order was updated in September 1995. For part of the area within the main dykes for which agricultural use had been initially prohibited, the general ban for use was lifted owing to the topographic location and since it had been demonstrated in detail that there were no harmful substances present.

Under the scheme of monitoring, samples of produce from allotments in this region have also been continuously analysed.

In 1994, for example, fifty random sampling campaigns were carried out in plots of allotment holders in the region of Bitterfeld/Dessau. The fruit and vegetables examined included rhubarb, kohlrabi, potatoes, and lettuce. The distance between the allotments from which samples were taken, and the Mulde river was in the range from about 10 to 700 metres.

On the whole, the findings revealed only a minor  $\beta$ -HCH load, if any.

The German Regulation for Maximum Acceptable Residues and its Annex 2 B stipulate a limit of 0.02 ppm for HCH isomers including  $\beta$ -HCH in vegetable foodstuffs. Thus, in none of the samples analysed, the maximum limit was exceeded. In contrast, in view of experience gathered by the analysing board, in particular under the foodstuffs monitoring conducted on the Federal scale, the  $\beta$ -HCH levels determined were assessed to be within the normal range for Germany. This is attributed to annual intensive soil cultivation on the allotments as well as to rinsing the produce prior to consumption.

Evaluation of the heavy metal levels in these samples was based on the recommended maximum levels of harmful substances in foodstuffs as published by the Central Recording and Evaluation Board for Environmental Chemicals of the Federal Institute for Consumer Health Protection and Veterinary Medicine. Lead and mercury levels did not exceed the maximum recommended limits in any of the samples.

Higher cadmium levels were noted, for example, in lettuce, carrots and beetroots. Much higher cadmium levels, that is two times higher than the recommended limit, were found in celery only.

Also, the levels of copper, zinc, cobalt, nickel and chromium determined in these samples did not substantially differ from empirical findings obtained from scheduled investigations or surveys made in the course of foodstuffs monitoring in Germany.

In addition to the produce from allotment holders, specimens of various wild mushrooms picked up in the flood plain of the Mulde river were analysed for  $\beta$ -HCH and heavy metal levels.

Again the German Regulation for Maximum Acceptable Residues was used as a reference in assessing the  $\beta$ -HCH concentrations found. This Regulation stipulates a maximum limit of 0.02 ppm „for other vegetable foodstuffs”. In none of the mushroom samples studied were the maximum levels exceeded. The  $\beta$ -HCH levels ranged from ‘not detectable’ to 0.007 ppm. This is attributed to the extremely short above-ground growing time of mushrooms.

Evaluation of the heavy metals in the mushrooms samples analysed was based on empirical figures from the 1993 mushroom monitoring in addition to the data reported in the literature. References in the literature have mainly reported data on the toxically relevant elements of lead, cadmium and mercury. Little information is available on arsenic, nickel or chromium in wild mushrooms.

For the samples analysed, the levels of heavy metals did not substantially differ from those mushroom species studied already during the 1993 mushroom monitoring in Saxony-Anhalt.

Referring to cadmium, *Agaricus arvensis*, for example exhibited higher levels than those determined in 1993. It should be pointed out however that, according to data reported in the literature and experience gathered by the analysing board, it is just this mushroom species which is specifically classified as 'accumulating heavy metals'.

Analysis of samples of vegetable foodstuffs from the flood plain was continued in 1995 in order to further substantiate the results obtained.

Moreover, in 1995 specimens of the game in this region, that is roedeer and wild boars, were analysed for organochlorine compounds and heavy metals.

The areas to be surveyed were co-ordinated with the forestry offices, the lower -level gamekeeping authorities and hunters. Due to the mobility of game, these areas are somewhat larger than those stipulated in the hazard prevention order. Hunters were advised by official publication that shot game may be consumed after the negative result of the residue analysis has been presented.

Results obtained from the game survey are continually evaluated among the hunters concerned by veterinary officers.

Apparently that roedeer were contaminated with  $\beta$ -HCH only. Twenty-three of the 98 animals examined had levels higher than the acceptable limit. In wild boars, DDT was found in addition to  $\beta$ -HCH and, hence, 26 of 49 wild boards examined had to be discarded because of the presence of  $\beta$ -HCH, and seven because of DDT. Five wild-boar samples exhibited levels of both  $\beta$ -HCH and DDT that were higher than tolerated limits. Heavy metals in the livers and kidneys of the game in this region varied; on the whole, however, they were too high and, thus livers and kidneys were not suited for consumption by man. Hunters were basically discouraged by the competent authority from eating such innards of shot game.

To determine the actual background loads in game and thus facilitate interpretation of the findings, further sampling was initiated for roedeer and wild boards from two region that had been officially reported to be non-contaminated. The results hitherto obtained indicate that these animals were not contaminated.

Irrespective of the above, a game monitoring scheme is currently pursued throughout the Land of Saxony-Anhalt.

In the long term, the working group is facing the task of preparing proposals for landscaping and further use of these Mulde riverside and meadowlands. Since, because of the locally high contamination levels and the well-known long half-lives of the contaminants, unrestricted agricultural use does not appear to be likely for the years to come, conceptual approaches are being prepared jointly with Saxony-Anhalt's Office of Environment and Conservation of Nature as to how specific fields or coupes can be used to permit different outlets.

- 1) Purposeful attention including disposal of upgrowth, to areas which are intended to be maintained in their current 'shape' for reasons of preservation of land.
- 2) Forestation of individual areas (approximately 140 hectares). In 1995, initial forestation of deciduous hardwood trees began on 3.4 hectares of land owned by Saxony-Anhalt. More forestation is scheduled for autumn.
- 3) Disuse of areas (40 hectares)
- 4) Changing the modes of cultivation, for example turning grassland areas into arable land
- 5) Small-scale 'rehabilitation' scheme trails.

However, these modes of use are required to be co-ordinated with the owners

of the areas who, in view of the altered political conditions in East Germany, need to be established, and such investigations have turned out to involve much time and cost.

Since, while in the light of the problems incurred the afore-mentioned measures cannot be implemented at short notice, attendance to and maintaining the disused areas are absolutely necessary, the following schemes are currently adopted:

- 1) Chopping and removing upgrowth in selected greenland areas that are rich in species
- 2) Mulching, at least twice a year, areas the overall view of which is required to be maintained for reasons of preservation and landscaping.

This will be carried out for a total of about 450 hectares. Currently, the areas are tended by mulching on the basis of agreements reached between the farmers and the lower-level authorities for preservation of nature. Under these agreements, the farmers receive financial compensation for tending the areas which amounts to about DM 500,000 per year. Moreover, taxation was lifted for the contaminated areas.

Because of the cost involved, culturing of such areas by mulching may be a temporary solution only. These areas require close scientific investigation into changes observed in flora and fauna when the mulching approach is adopted. Large-area action to clear such areas had to be dismissed as the cost involved is too high:

- Single mowing costs about 300 DM/hectare
- Clearing costs about 500 DM/hectare
- Discarding costs 500 DM/hectare or more, depending on the amount of greenstuff collected

To summarize, restructuring, revamping and partial closure of the chemical industry based in the Bitterfeld/Dassau region have resulted in significant improvements as for the quality of air and the water in the Mulde river. However, the contaminated sediments and sludges of the upstream waters are still present. In order to rule out further contamination of the Mulde river and its adjacent areas it is highly desirable that (i) the contaminants be removed from the sewer system of the former Chemie AG and (ii) measures be taken to prevent contaminants from draining into the ditches and the river.

As a first step, a sewage works was commissioned in Bitterfeld on May 11, 1995. Thus, only clean water which is sewage that does not require further treatment is drained into the ditch system. In this context, it is noteworthy that the amount of water drained into the ditch system was reduced by about 30,000 m<sup>3</sup>/day and, hence, the proportion of contaminated sludge carried along because of whirling up was diminished as well.

Removing the remaining contaminant deposits from the ditch system would cost a tremendous amount of money. Typically, the cost of rehabilitation of the most affected section is estimated at about 120 million DM.

As the current hazard prevention order merely provides for agricultural use of the flood plains of the Mulde meadowlands, the Presidency of Dessau commissioned a study for the ditch system such that the hazards can be evaluated and action may be initiated as necessary for further prevention of hazards. The findings obtained were surprising :

- 1) Direct hazards to the population because of the current load of contaminated sediments on agricultural areas had already been counteracted by issuing the hazard prevention order for the flood plains of the Mulde river.



- 2) Removal of contaminated sediments from the ditch system, even though desirable, cannot be afforded according to the principle of proportionality, especially that there is no urgent need and in view of the finding that, even after the ditch system had been cleared, the load remained on the originally contaminated areas and, hence, the upgrowth could not be utilised or used within certain limitations only.
- 3) As a consequence, the hazard prevention order is required to be maintained in effect for the flood plains for an indefinite period.

With a view to justify the precautions in the immediate area of the ditch system the regional county of Bitterfeld has instituted further specialist and legal investigations.

Application of various large-area field rehabilitation schemes has not yet been attempted for agricultural areas; it is not justifiable for reasons of preservation of nature and mainly because of the cost impact involved. Therefore, attempts should be made to develop different approaches that can be implemented at short notice. These, however, call for further expert opinions and/or investigations such as:

- Study the uptake or the migration path of contaminants in the plant. Elucidate which useful plants take up which harmful substances and along which route, and which plants accumulate harmful substances.
- Utilization of contaminated biomass, e.g. by composting, silage, thermal treatment, etc.
- Institute a field trial to investigate into the effect of ploughing or deep ploughing on areas contaminated with  $\beta$ -HCH.
- Carry out pilot projects on large-area microbial in-situ rehabilitation of the Mulde meadowlands.

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**RISK ASSESSMENT FOR DUMPING SITES OF UNWANTED PESTICIDES**

**Adam Krause**  
**Andrzej Silowiecki**

The risk for ground water quality, posed by 15 dumping sites of unwanted pesticides, was assessed by Leaching Potential, Leaching Index, and Ground water Ubiquity Score screening, as well as PRZM and LEACHM mathematical models based on the information on site qualitative and quantitative inventory, hydrogeological setting, and physico - chemical data on individual active ingredients.

Due to foundation in either fissured rocks or aquifer 7 sites were classified into the highest risk category without simulation. The inventories of the remaining 10 sites were filtered in order to select items disposed of in significant quantities, and screened with respect to their potential for ground water contamination (LP, LI and GUS indices). The total concentration of active ingredients released from the site, which theoretically reached the ground water level, ranged from  $6.16E+00 - 0.00E+00$  mg/L, for the studied sites. Based on such calculation 10 sites were ranked according to the decreasing risk for groundwater quality.

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**EXPERIENCES WITH DECONTAMINATION OF SOIL WITH HCH**

**John A. Fairweather**

ADI (Deutschland) GmbH has obtained the license rights to a process for destroying chlorinated hydrocarbons. This process was developed in the laboratories of US-EPA. ADI has developed the process further. Chlorinated hydrocarbons such as HCH, PCB, other pesticides, dioxins can be eliminated from different media such as solid and liquid wastes, river and harbour sludges, contaminated soil and waste dumps.

The process is a chemical one under inert gas conditions thus avoiding the production of dioxins as occurs in incineration processes.

ADI has built 2 industrial scale pilot units and has begun operating on various contaminated media. Planning is underway for a 5 t/h unit for treatment of contaminated soil later this year.

Results of the test programmes to date are presented.

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**PROGRESS AND DEVELOPMENTS ON UNWANTED PESTICIDES  
IN POLAND**

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**Stanislaw STOBIECKI**

Unwanted pesticides stored in tombs, stores, other places of storage, small handy closets and specially assigned rooms on farms pose the greatest danger to the natural environment and people. This is caused about by chemization of agriculture in Poland. The problem of unwanted and expired pesticides results from many years of errors in pesticide management and especially in their distribution. Mainly in 1950–70 low prices and central distribution of the supply led to gathering of large amounts of pesticides that could not be used later on. Historical changes in our country caused that, together with the advent of market economy the problem of storing expired pesticides ceased to exist. Nevertheless we still have not solved the problem of containers for chemicals classified as poisons and we do not know what to do with large amounts of pesticide waste. In Poland there are no sites for dangerous materials that would accept pesticides neither are there incinerators in which pesticides could be safely burnt. Existing storage facilities, mainly so called tombs pose more and more danger to the environment due to their progressing untightening and still increasing emission of toxic substances. First of all, drinking water reservoirs are in danger. There are many places all over Poland where it is necessary to stop emission of pesticides from leaking tombs immediately.

The range of the problem in Poland is considerable. The amount of substances stored in the tombs is estimated at 10.000 tonnes, in storage facilities at 25.000 tonnes, at farms at 25.000 tonnes. This makes up a total of about 60.000 tonnes of unwanted pesticides.

In 1992 studies were commenced in order to solve the problem on the scale of the whole country. It was pointed out that both the range of the issue and the high level of technical and organizational difficulties indicate that all activities should be coordinated by the Main Inspectorate of Environmental Protection whereas executive coordination should lie within the responsibilities of one institution. This role is fulfilled by the Institute of Plant Protection. Polish experts made numerous studies, projects and programmes of recognitive and preparatory character. In the second half of 1995 technical preparations were also made to stop the emission of toxic substances from two leaking storage sites: one in Soœnicowice, voivodship of Katowice and the other one in NiedŸwiady, voivodship of Kalisz. The main studies carried out are the following:

1. Under the PHARE programme in 1993 we performed the project „Acquisition of the output data concerning the problem of disposal of unwanted pesticides and empty containers”. The project aimed at recognition of the issue and indication of methodology for future procedures.
2. The Main Inspectorate for Environmental Protection from the funds provided by the National Fund for Environmental Protection and Water Management ordered the Institute of Plant Protection to make the study „An analysis of identified hazards with development of a conception of activities for 1996–2000 and implementation recommendations for the facilities that underwent expertises and are planned to be disposed of tombs containing expired pesticides”. This extensive and comprehensive study was completed in August 1995 and it included the following main parts:
  - Quality analysis of the substances stored in the tombs for 100 selected places.

- Estimation of hazards posed by the substances stored in the 100 tombs.
  - Making an analysis of the contamination level of the area around 15 selected tombs.
  - Making a collective analysis for 15 tombs with a computer hazard assessment model.
  - Recognition, analysis and assessment of methods of disposal and other ways of handling pesticide waste.
  - Development of a factual and financial conception of work on the solution to the problem of unwanted pesticides in Poland for 1996–2000.
3. From the PHARE funds in 1995 three projects were started and they aim at technical and organizational preparation for remediation of two tombs and also at a pilot implementation of the developed method to stop spreading of toxic substances from leaking tombs by means of repacking the tomb contents to tight containers and storing them in special safe storage facilities located near the tombs. This pilot action, prepared according to the standards set out by EC countries, will be performed in spring in 1996.
  4. At the preparatory stage are projects aiming at a definitive disposal of unwanted pesticides and decontamination of soil from around the untight tombs.

Future strategy for Poland will in a great degree depend on the impact that the places of storage have on the environment. A theoretical ranking of the tombs to be disposed of will determine priorities of future remediation activities and also of detailed studies on contamination of the area around the tombs which will precede remediation. The choice of methods of disposal will depend on local conditions and the level of danger that a given tomb may pose to the environment.

It is planned to use mobile and semi-mobile installations for incineration and decontamination of soil. A possibility is being concerned to gradually dispose of the tombs within the chosen areas of the country. With appropriate financial support and good organization the process of cleaning up the entire country should not last longer than 8 years.

We realise how difficult a task it is to dispose of the pesticides from the whole Poland. Every day of work brings new experience, new possibilities of practical solutions. Studies and programmes executed so far are a good basis for a practical physical disposal of unwanted pesticides and, at the same time, eradication of the danger.

Now it is only good organization and money. I stress the word "only" because optimistic view in this case is obligatory.

I would like to draw your attention to the fact that the area around the tombs is poorly protected. However, the wells containing unwanted pesticides are mostly underground, so there is no direct danger for people. A decision on a possible disposal of tombs has to be taken individually on the basis of detailed studies.

We realise how difficult a task it is to dispose of the pesticides from the whole country. Every day of work brings new experience, new possibilities of practical solutions. Studies and programmes executed so far are a good basis for a practical physical disposal of unwanted pesticides and, at the same time, eradication of the danger.

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**IN SITU REMEDIATION OF HCH CONTAMINATED SOILS  
BY LEACHING WITH SODIUMHYDROXIDE  
(AN INTERIM SUMMARY)**

**Hennie van VREE, Marc LEIJENDECKERS  
Leon URLINGS, Charles PIJLS**

### **1. Introduction**

Up to today, remediation of soil contaminated with hexachlorocyclohexane (HCH), mainly has focused on ex-situ treatment (physico-chemical, biological and thermal treatment). Remediation of HCH contaminated sites mostly takes place at highly contaminated industrial sites or diffusely contaminated agricultural areas. There is much interest in full scale application of in situ treatment of soil and groundwater at these sites, since the only alternative is often containment, which is expensive.

This presentation summarizes the preliminary results of current research project carried out by Tauw Milieu bv. The objective of this laboratory study was to determine the feasibility of in situ remediation of HCH contaminated soil by leaching with sodiumhydroxide.

The project was partially funded by NOVEM (Dutch Organization for Energy and Environment) and the Province of Overijssel.

### **2. Background**

At certain part of the Province of Overijssel low permeable sandy loam soils turned out to be heavily contaminated with HCH. At those sites where the concentration levels exceeded the Intervention values, the soil was excavated, but just up to 3m bgl. Residual HCH levels of < 0.4 mg / kg are still found here. To remediate these sites there is a need for low cost suitable remediation techniques. This project investigates an in situ remedial option, aimed to convert HCH to possible intermediates such as chlorobenzenes and chlorophenols and simultaneously leach these contaminants out of the soil and groundwater.

Previous experiments and literature describe that at a high pH, conversion of HCH to trichlorobenzenes (TCB) and monochlorobenzenes (MCB) takes place. These conversion products are more leachable than HCH. This would indicate that after a complete conversion of HCH to TCB and MCB, a simultaneous leaching step can remove these intermediates. On site groundwater treatment and neutralization of the treated soil by this system are aspects to be studied. At this moment little is known about its full scale feasibility. Specially the desired pH, final levels of the soil, remediation time, control and management of such a remediation are not totally clear yet.

### **3. Objectives and methodology**

The objectives of the feasibility study are:

- to determine the technical and economic feasibility of an in situ remediation in low permeable soils (sandy loam) by conversion of HCH and/or flushing with sodiumhydroxide;
- to investigate the influence of NaOH on permeability (duration of remediation);
- to gain insight into the formation of intermediates during conversion of HCH, and neutralization processes.

The study consisted of three phases:

**Phase 1:**

Batch test were carried out in order to determine the optimal pH and exposure time (hydrolyse kinetics). Twenty batches were installed, each containing 100 g of soil diluted in 1 l water (L/S = 10). Extraction and conversion rates of HCH were measured for the pH range 9-12 and mixing times 1.5, 15 and 30 days. The pH was adjusted by adding NaOH (1N).

**Phase 2:**

Two column test were performed to investigate soil permeability at two pH regimes; one column had a fixed pH value of 11; the pH of the second column varied between 11-13. Parameters like pH, conductivity and permeability were investigated. Conversion and extraction rates were determined. Clogging due to precipitation of humic acids and transport of organic matter was studied as well.

Two other column tests were performed to study the conversion of HCH and formation of intermediates.

**Phase 3:**

In a desk study applications on full scale are studied. Results of the batch and column tests will be used to determine the feasibility of the full scale application. The emphasis should be on remediation duration time (flushing), monitoring and controlling, final concentrations and remediation costs.

#### **4. Preliminary conclusions and recommendations**

Batch tests proved that a high pH ( > 11) will be needed to create optimal flushing and conversion conditions in the column tests. The permeability was however negatively influenced at high pHs by precipitation of humic acids, and flushing and clogging afterwards of organic matter in the columns.

The batch tests showed that overall reductions of HCH of 85-95% can be achieved at pH 12. A lower pH decreases the reductions efficiency of all isomers. Conversion of the individual HCH isomers follows the sequence:

alpha, gamma > delta > epsilon > beta

Full scale applications will only be of interest if the investigated option and technically and economically feasible. As discussed above, the permeability is negatively influenced, thus indicating long remediation times. Cost estimates for such a remedial option revealed that for each ton of contaminated soil about US \$25 to US \$50 worth of chemicals would be needed (sodiumhydroxide). Cost of chemical to neutralize the soil afterwards are estimated to be in the range of US \$ 0.50/ton of soil.

Preliminary conclusions:

Due to the clogging of loamy sand at higher pH, this remediation technique may not be feasible. However, for soil with low organic matter contents (e.g. highly permeable sandy soils) it could be an interesting option. Treatment of soil contaminated with HCH in the order of several mg / kg of soil seems to be feasible.

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**DECONTAMINATION OF HCH AND MERCURY CONTAMINATED  
SOIL USING EXTRACTIVE SOIL WASHING TECHNIQUES**

**Henricus N. DE GROOT**

All over the world numerous production sites of insecticides and pesticides are known to be contaminated with products and process residues. One of the most persistent and widely spread insecticides is HCH (Lindane).

Soils contaminated with insecticides and/or pesticides are usually co-contaminated with mercury, other heavy metals, mineral oils and PAH's. Due to high toxicity, the risk for groundwater contamination and possible carcinogenic properties of HCH, many of these polluted sites must be cleaned up or made less hazardous.

In the past decade several techniques were tested to clean or decontaminate these soils. On-site techniques as well as off-site treatment was investigated, even biological testing was performed. Thermal treatment proved to be difficult due to the presence of heavy metals like mercury. After thermal treatment the soil can not always be used without restrictions due to the heavy metal concentrations. Up till some years ago the extractive soil washing techniques were also not adequate to treat these kind of heavily polluted soils. The remaining concentrations in the treated soil, mainly the organic compounds, were too high for reusing.

End of 1994 Heijmans Milieutechnik B.V. in Rosmalen (NL) successfully adjusted one of her soil washing plants allowing for cleaning soil heavily polluted with HCH and mercury. The mercury, other heavy metals, oil and the PAH's were removed in the same washing process. This soilwashing strategy consists of a number of physico/chemical cleaning and separation steps in a special order to ensure that both the HCH and the other contaminants are effectively removed. The treatment of soil contaminated otherwise is also possible with this treatment system.

Cleanup results depend on the initial concentrations, the chemical properties of the pollutants and the requirements for reuse of the cleaned material.

In 1995 Heijmans contracted the treatment of 22.000 tons of HCH and mercury contaminated soil. All 22.000 tons have been cleaned and reused as a construction material leaving about 20 % (DS) to be disposed of as treatment residue. Soils with high contents of DDT have been successfully treated this way as well. Other contaminated soils have been treated in the soil washing plant by means of this cleaning system resulting in high decontamination effectiveness.

New developments are on the way with respect to testing systems capable to treat the soilwashing residue. The most promising is smelting the residue and cooling it in a mould to basalt.

Facts about the cleaning and new developments including actual processing results will be presented in the presentation of Heijmans Milieutechniek B.V. during 4th Forum on HCH and Unwanted Pesticides.

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## **Processing:**

- 1. Homogenising**
- 2. Screening off coarse material**
- 3. Desliming of the sand fraction**
- 4. Attritioning sand fraction with chemicals**
- 5. Separating sand and process water**
- 6. Removing light particles like coal**
- 7. Removing heavy particles like slacks and metals**
- 8. Removing metal particles using a wet magnet**
- 9. Contaminant specific froth – flotation  
(HCH, PAH's and Mercury)**
- 10. Dewatering of the clean sand**

Parameters	Mean input concentration	Mean output concentration	Requirements
Alpha HCH	126,425	<2.5	10 µg/kg
Beta HCH	67,385	4.8	10 µg/kg
Gamma HCH	5,215	<2.5	10 µg/kg
Delta HCH	102,285	<2.5	10 µg/kg
Epsilon HCH	18,680	<2.5	10 µg/kg
Total HCH	319,990	<15	
Chromium	15	1.7	50 mg/kg
Cadmium	0.13	0.1	0.4 mg/kg
Lead	46	2.8	50 mg/kg
Coper	15	1.0	15 mg/kg
Zinc	40	9.7	50 mg/kg
Mercury	0.74	0.1	0.2 mg/kg
Nickel	4.7	1.0	10 mg/kg
PAH's (10)	1.23	0.2	1.0 mg/kg

- **With the Heijmans process many other hazardous chemicals can be removed from contaminated soil**
- **Depending on input concentrations, legislation and cleaning requirements the process can be simplified**
- **Prices vary between USD 50 and USD 150 per ton contaminated soil to be treated including disposal costs of residues**

## **Mass Balance:**

**100% input generates after treatment:**

**80% reusable material**

**20% process residue to be treated or to  
be disposed of**

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**THE ELTRONDEC<sup>®</sup> – BEAM TREATMENT SYSTEM  
FOR DESTROYING HCH****Heidrun LORENZL****1. The Innovative Technique ELTRONDEC<sup>®</sup>**

This new innovative technique uses high-energy electrons for treating water, wastewater and sludge.

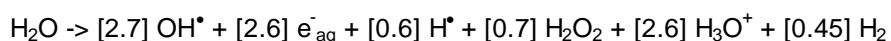
The application of electron accelerators is widespread in industry: for example in polymer-industry, in surface treatment of metals, for welding, and in medical technique for disinfection. But the HVEA company is the only one worldwide that treats liquid fluids by means of e-beam-system. The technique was developed by an interdisciplinary team of scientists and engineers who have studied the effect of high-energy electron irradiation on the removal of toxic organic chemicals in aqueous solutions. The system is economical, 100 % functional and treats all organics unselectively. The amount of contaminants does not interfere with the treatability result of the system.

The results are several wastewater treatment systems of different sizes:

1. The mobile E-beam is used for tests, feasibility studies and demonstrations, there is no problem with its transport to different facilities.
2. The permanent system contains an electron accelerator, which regenerates high-energy electrons up to 1.5 MeV rated up to 50 mA.

**2. Chemical Reactions**

High energy electron beam irradiation of aqueous solutions results in formation of free radicals shown in the following equation (absorbing 100eV of energy):



Of the products formed in Equation the most reactive are the oxidizing, hydroxyl radicals ( $\text{OH}^\bullet$ ), the aqueous electrons ( $\text{e}^-_{\text{aq}}$ ) and hydrogen radicals ( $\text{H}^\bullet$ ). The presence of both  $\text{e}^-_{\text{aq}}$  and  $\text{OH}^\bullet$  in aqueous solutions at similar steady state concentrations is unique in this process and distinguishes it from other advanced oxidation processes like UV. These reactive species initiate chemical reactions capable of destroying organic compounds in aqueous solution, for example lindane, to carbon dioxide, water, and salt. The by-products are non-toxic. This process, therefore, represents a new ultimate technology for the remediation of contaminated water, soil, and sludge.

Tests in the United States and Germany have shown the effective treatment of complex mixtures that contain hazardous chemicals in drinking water, wastewater, and water with up to 8 % suspended solids. The process has been shown to be effective in destroying compounds listed in the following table. Chemicals which are studied mixed with other chemicals for example in landfill-leachate or processwater are marked with a star.

**TABLE 1****List of chemicals studied by HVEA**

<b>Acenaphthene*</b>	<b>p-Dihydroxyphenol*</b>	<b>Toluene*</b>
Acenaphthylene*	Diisopropylbenzol	1,2,4-Trichlorobenzene*
Acetic Acid*	Diisopropylmethylphosphonate (DIMP)	1,1,1-Trichloroethane*
Acetone*	Dimethylmethylphosphonate (DMMP)	1,1,2-Trichloroethane*
Acetaldehyde*	2,4-Dimethylphenol	Trichloroethylene (TCE)*
Anthracene*	1,4-Dioxane	Trichloromethane*
Aroclor	Ethylbenzene*	Trinitrotoluene (TNT)
Benzene*	Endrin	Vinyl Chloride
Biphenyl*	Fluoranthene*	m-Xylene*
Bromodichloromethane*	Fomaldehede*	o-Xylene*
Bromoform	Formic Acid*	p-Xylene*
2-Butanone (MEK)*	Glyoxal*	
Carbazole		
Chlorobenzene*	Hexachlorbenzene*	
2-Chlorobiphenyl	Hexachloro-1,3-butadiene	
3-Chlorobiphenyl	Hexachloroethane	
4-Chlorobiphenyl		
Chloroform*	Lindane*	
2-Chlorophenol		
3-Chlorophenol	Methanol*	
4-Chlorophenol	Methylene Chloride*	
o-Cresol	Methylglyoxal	
Cumolhydroperoxide*	Methylhydroperoxide*	
	4-Methylphenol*	
Dibromochloromethane*	Methylphosphonic acid	
1,2-Dibromo-3-chloropropane (DBCP)	MKW*	
1,2-Dibromoethane (EDB)		
1,2-Dichlorobenzene*	Naphthalene*	
1,3-Dichlorobenzene*	Nitrobenzene*	
1,4-Dichlorobenzene*	Nitrocellulose	
2,2'-Dichlorobiphenyl	Nitroguanidine	
4,4'-Dichlorobiphenyl	2-Nitrophenol	
1,1-Dichloroethane*	3-Nitrophenol	
1,2-Dichloroethane*	4-Nitrophenol	
1,1-Dichloroethylene*		
cis-1,2-Dichloroethylene	Phenanthrene*	
trans-1,2-Dichloroethylene*	Pentachlorophenol	
2,4-Dichlorophenol	Phenol*	
2,6-Dichlorophenol		
2,4-Dichlorophenoxyacetic acid (2,4-D)	RDX	
1,2-Dichloropropane*		
cis-1,3-Dichloropropene	1,2,3,5-	

trans-1,3-Dichloropropene	Tetrachlorobenzene* 1,2,4,5-	
Dieldrin	Tetrachlorobenzene* 1,1,1,2-	
Diethylmethylphosphonate (DEMP)	Tetrachloroethane* 1,1,2,2-	
m-Dihydroxyphenol	Tetrachloroethane* Tetrachloroethylene (PCE)*	
o-Dihydroxyphenol	Tetrachloro Carbon*	Stand: 18.10.95

### 3. Treatment of HCH-contaminated water

To prove our experience in treating pesticides we were looking for a highly contaminated water for studying the treatment of HCH by E-beam. During the demonstration at Espenhain last year we had the possibility of treating what we call the „lindane-water“.

We solved the HCH-contaminated solids and treated the solution with E beam.

The initial concentrations and the results are shown in table

**Table 2: Analysis of the „lindane water“**

parameter [mg/l]	series of test				removal (%)
	0	0,6	3	5	
COD	8260			6144	74,38
BOD	2660			3490	131,20
AOX	39,1			20,1	51,41
alpha-HCH	3,919	-	0,710	0,501	12,78
beta-HCH	1,141	0,5923	0,128	0,1057	9,26
gamma-HCH (Lindan)	0,7296	0,4297	0,0398	0,0453	6,21
delta-HCH	0,349	0,2673	0,0224	0,0293	8,40
Summe HCH	7,5679	1,6648	1,0388	0,5477	7,24
pH-Wert:	6,9			6,4	

We removed about 92.7 % in a demonstration with the mobile system of 500 kV. The demonstration certified that HCH is well treatable by E-Beam. With our stationary system we can guarantee to clean water to drinking water quality.

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**PESTICIDES IN THE REPUBLIC OF MOLDOVA**

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**Anatol Tarita**

The Republic of Moldova is an independent state and has been a rightful UNO member since 1992.

The Republic is in the South- Eastern part of the European continent. In the West, it is bounded by Romania, in the North, East and South by Ukraine.

The territory of the country from the North to the South is 350 km, and from the West to the East - 150 km. The republic area is 33,7 thousand km<sup>2</sup>. The capital of the republic is Chisinau. The country population is approximately 4,4 million inhabitants, the average density of the population is 129 people per km<sup>2</sup>. The quota of the urban population is 47%.

The territory of the Republic of Moldova includes three natural zones: forests, forest steppe and steppe. It represents a component part of the Eastern European plain and 90% of the country lies between the Dniester and Prut rivers.

The territory of Moldova is exposed to some intensive exogenous processes: soil erosion, landslide, karstic phenomena and suffusions. The climate in Moldova is temperate - continental. The average annual air temperature across the territory of the republic is +8, +10 °C. The average annual precipitation is 380 mm in the South and 560 mm in the North of the republic. In Moldova, 3 years out of 10 are droughty. The geo-climatic conditions of the republic are very suitable for agricultural production.

Moldova's soils according to their qualities, surface, time stability, energetic capacity and chemical potential are the most precious natural resource.

Black - earths, the most fertile and structurally organized soils in the world, occupy 3/4 of the Republic's territory.

Moldova's soils, down to one meter below the ground level, have accumulated about one million tons of nitrogen, 60 mln tons of phosphorous and 700 mln tons of potassium.

We consider with a great regret that within the last 25 years the productivity of our soils has decreased considerably. The ratio between arable fields and the population has also decreased from 0,53 up to 0,42 hectares per one inhabitant. From the end of the 50s till the middle of the 70s, Moldova's agriculture was under the pressure of agrochemical ambitions and then it was considered that with the help of mineral fertilizers it was possible to considerably increase the harvest of the plants as well as rise soil fertility after humus degradation.

Later on the "all - territory irrigation" was carried out and this was considered the only positive action.

At the same time there appeared absolutely negative changes such as: soil and underground water salinization, chemical pollution of many agricultural products, contamination of soil with pesticides and theirs derivatives, heavy metals and fluorine, soil **suprphotation**, ect. Cases of salinization and soil contamination occurred as the result of irrigation with untreated water.

It is very important for our Republic to solve the problem of microelements, especially of Cu, which is of **anthropeic** character after its using in wine - growing. Accumulation of this element in soil is observed. There are cases where the content of Cu in vineyard is five times higher than in the fields nearby.

Another important problem is high concentration of F in soils.

Water erosion brings great damages to our soils. Now, endangered by erosion are 1,86 mln. ha of soil. As a result of water erosion and so-called

"industrial", "intensive" technologies in agriculture the soil slopes are also suffering and become more eroded.

As a result of growing ravines and microdales the upper layer of soil has deformed and became heterogeneous .

There are 250 complexes and animal farms in Moldova (now only 93 are working) having thousands heads of swines and horned cattle. Through hydraulic elimination of animal waste, mineralized and alkaline waters are creating an enormous mass (anually 13 mln tons ) of contaminated waste waters, highly mineralized and containing sodium bicarbonate, ammonia, nitrates, sometimes pathogenic.

Together with other factors that have caused degradation of soil fertility, a big contribution was also made by application of pesticides in the 1970s and 1980s .

In the last years (see the diagram) the use of all pesticides in Moldova has been greatly reduced . The application of pesticides in total per republic in 1985 was nearly 22,8 kg of active substance /ha, but in 1993 only 3,98 kg/ha. According to the diagram of annual application of pesticides, the highest level of pesticide use was obtained in the middle of 1980s (approxim. 40 thousand tons). Now the spectrum in use contains 114 active substances and 139 formulations. the majority of them comes from the herbicide group (53 formulations) insecticides and acaricides (42 formulations) and fungicides (25 formulations). Together, these three groups of substances make up over 85% of the number of the pesticides in use. About 10% out of used pesticides fall under the first class of toxicity, they are very toxic for the mammals, birds, insects and fish. The following preparations are parts of this group: cooper sulphate 3277 tones was used, metaphos 332,56 t, phosphamid 232,52 t,treflan 213,48 t,chlorophos 139,75 t, decis 115,78 t, HCH 59,12 t, DNOC 40,2 t (all of them contain active substances). An important part of the spectrum of the used preparation falls under the second class of toxicity. It poses a real danger for the ground and aquatic bioecosystems. The preparations from this group, which were used on a large scale, were 2,4 DA(208,62 t), cooper chlorohyd (205,66 t), carbonophos (94,0 t), karate (42,3 t), reglon (22,63 t) and phosalon (22,73 t). According to the structure of agriculture of Moldova ( see the diagram) the multiannual plantations (orchards, vineyards) occupy about 26% of the total arable lands. For a long period of time these plantations were contaminated with their derivatives and metabolites. As a result of abuse utilization of pesticides, the majority of agricultural soils,especially in the central districts of the republic, became contaminated. In order to determine the degree of the soil contamination with pesticide residues, the Institute of Research and Technologies for the agrochemical service has organized a monitoring agroecotoxicological system on the territory of the Republic since 1988.

The data collected so far show a decrease in the quantity of pesticide residues (DDT,HCH,symitriazin) in the soil, underground waters, plants and agricultural products, but there are still places where the amount of DDT and HCH is very high (for example the storage, graveyards of the chemicals). We must mention here, that in 1993 the agricultural sector of the republic had 620 t of prohibited pesticides and 254 t of expired pesticides .

Now, the intensive agriculture remains the main source of pollution with the organic and nutritive substances of the surface and underground waters. In the last years its polluting potential was reduced, also due to the decrease in quantity of used fertilizer. In 1993, 36187 tones of mineral fertilizers (active subst.) were used in the agriculture of the Republic of Moldova, out of this quantity 20219 tones of nitrogen fertilizer, 10,581 tones with phosphorus, 5387 tones with

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potasium. The whole quantity was applied on an agricultural land of 362 thousand ha. As a result the total quantity of nutritive elements which penetrated into the aquatic basins in 1993 is estimated to be 7-8 thousand tones of nitrogen and over 900 tones of phosphorus. These are the problems of restoration, improvement, conservation of the soil cover in the Republic of Moldova.

Taken into consideration the difficult economic situation in our country and lack of funds we rely on the Western help to cooperate with us to resolve these important ecological problems.

THANK YOU.



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