DEPARTAMENTO
DE URBANISMO,
VIVIENDA Y
MEDIO AMBIENTE
DEL GOBIERNO
VASCO

IHOBE
Sociedad Pública
Gestión Ambiental

3 RD INTERNATIONAL

HCH & HALOGENATED PESTICIDES FORUM

19-20 SEPTEMBER 1994

BILBAO

EUSKO JAURLARITZA
GOBIERNO VASCO

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Agenda

AGENDA

3rd International HCH & Halogenated Pesticides Forum
September 19-20, 1994
BILBAO

Monday September 19, 1994

8.00 Leave from Hotel Abando with bus to Castillo de Butrón

8.30 Registration

9.00 Welcome and official opening
Mr. José Antonio Maturana, Minister for Town Planning, Housing and the Environment, Basque Country

9.15 Opening of technical proceedings by Chairman Mr. Bram de Borst

Inventory/risk assessment

9.30 Low volatile Chlorinated Hydrocarbons in aquatic sedements in Berlin and Environs
Mr. Konstantin Terytze, Germany

10.00 Studies of pesticide contamination of areas adjacent to the chosen places of storage of unwanted pesticides
Mr. Stanislaw Stobiecki, Poland

10.30 The HCH-Situation in the Russian Federation
Mr. Andrei Pokarzherskii, Russian Federation

11.00 Guide values for dealing with contaminated sites in Baden Württemberg, example of an HCH location
Mr. Karl von der Trenck, Germany

11.30 Coffee Break

11.45 Problems arising with pesticides use in Belarus
Mr. Vilor Fridmanovich Samersov, Byelorussia

12.15 Use and analysis of pesticides in Lithuania
Mrs. Milda-Zita Vosyliene, Lithuania

12.45	The Muldeau problem: a typical example of the middle European industrial heritage and promises for temporary remedial **Mrs. Petra Schmidt, Germany**
13.15	<u>Lunch</u>
14.15	Departure for bus trip to former Production Plant Bilbao Chemicals and Landfills near Sondika Airport **Explanation by Mr. Ignacio Quintana**
18.30	Return at Hotel Abando
20.00	Reception at Town Hall Welcome by Mr. Josu Ortuondo, Mayor of Bilbao City
21.00	Dinner at Sociedad Bilbaina (Remember costume and tie are prescribed!)

Due to illness the presentation of Mr. Colin Ferguson is cancelled.

Risk assessment of contaminated sites: science, public policy and social justice?
Mr. Colin Ferguson, United Kingdom

Tuesday September 20, 1994

8.00 Departure from Hotel Abando with bus to Castillo de Butrón

Technical Solutions

9.00 Biotransformation of ß-HCH to monoclorobenzene under methanogenic culture conditions
Mr. Peter Middeldorp, The Netherlands

9.30 Works on the project Handelskade, video
Mrs. Annemarieke Grinwis, The Netherlands

10.00 Solvent stripping experiments of packed HCH and mercury contaminated soil
Mr. Jos Brouwers, The Netherlands

10.30 Coffee Break

11.00 Thermal hydro dehalogenation
Mr. Wouter van der Meer, The Netherlands

11.30 Biological purification of HCH contaminated waters by mixed cultures under aerobic and anaerobic conditions
Mr. Steffen Heinrich, Germany

12.00 Lunch and Filling in the questionnaires

13.30 Wet (classification/flotation) and thermal (desorption) treatment of HCH, drins and dioxin/furan-containing soils - operational experience in the Netherlands
Mr. Ton Honders, The Netherlands

14.00 Effect of desorption, temperature and soil moisture content on the aerobic bioconversion of α- and ß-HCH in soil
Mr. Huub Rijnaarts, The Netherlands

14.30 Tea/Coffee break

15.00 Overview of remediation techniques
Mr. Wim Rulkens, The Netherlands

15.30 Conclusions and statements of the 3rd Forum
Mr. John Vijgen

16.00 Announcement 4th Forum

16.30 Closure by Chairman Mr. Bram de Borst

16.45 Official Closure
Mr. José Antonio Maturana, Minister for Town Planning, Housing and the Environment, Basque Country

Poster presentation

During the coffee breaks and lunches a poster presentation will be held to the conference room by:

Mr. Anatol Tarita, Moldavian Republic on the item:

Pesticides in the Moldavian Republic

APPENDIX OF WRITTEN INFORMATION

Water resources pollution with halogenated pesticides in Romania
From: Mrs. Marioara Ionescu,
Environmental Engineering Research Institute, Bucharest, Romania

BHC Soil contamination in Sao Paulo metropolitan region
From: Mr. Renato Pizzi Rossetti
CETESB, Sao Paulo, Brazil

3rd HCH INTERNATIONAL FORUM

INAUGURAL ADDRESS

Date: Monday, 19 September 1994
Time:
Place: Castillo de Butrón (Butrón Castle)

Ladies and Gentlemen,

To this Third International Forum on HCH and Halogenated Pesticides it is my pleasure to welcome representatives from industry, from the universities, from technology centres, from the scientific community, and from the environmental administrations. The object you have in common is to take a close look at what we know about the effects on human beings and on the environment of pesticides, whether or not they are used as intended. This is knowledge built up in response not only to purely scientific interest but also to the necessity, steadily more urgent, to lay down strategies and lines of action for the elimination of these effects, if not ultimately of the problem itself.

The First International Forum, held in Zwolle, Holland in 1992, opened with a rapprochement and an unrestrained discussion of the problems concerning mainly the European countries. It concluded with a serious commitment to progress further in the years following. There was a firm desire to enlarge the group by the admission of representatives from all those countries that in one form or another are affected by the problem of tips containing halogenated pesticide wastes.

In the second encounter, held in Magdeburg, Germany, a first estimate was made of the number of sites affected by HCH tips. Those in Europe were set at between four hundred and five hundred, while for the world generally the figure was thought to lie somewhere between one thousand and five thousand. The cost of recovering these sites was estimated, in light of current technological achievement, at between one and five hundred billion marks, while in the case of the European Union the figure was put at between ten and fifty billion.

Another of the conclusions of this Second Forum referred to the variety of ways in which soils were contaminated with HCH in the various countries affected. These involved land bearing lindane plants, or toxic waste tips that had not been not monitored, or tips that were scattered. They involved soil in which contaminants were of low concentration. And so on. Yet another conclusion referred to the various solutions now glimpsed as feasible in a future not too far ahead, solutions that are still being looked into by the various task forces set up at that forum. In short, the most important observations made on the occasion of the second encounter were the high incidence of contaminated sites, the severity of the risks that this posed, and the technical complexity involved in tackling specific solutions at reasonable cost.

As host I am obliged to make some reference to those particular problems that affect the Basque Country. They are not, as might be expected, very different from the problems acknowledged in other parts of the world. I would begin by mentioning the Master Plan for the Protection of Soil in the Autonomous Community of the Basque Country, which will be made public in Vitoria on September 21st and 22nd. At this Congress, which will provide a setting for the presentation of the conclusions of the Third Forum, and which you are all invited to attend, a proposal will be made for a solution to the problem of industrial sites and tips contaminated with HCH. Such contamination is one of the most serious problems in the context of soil areas within the Basque Country.

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As many of you know from previous fora, lindane production is no longer carried out in the Basque Country. Over a number of decades, however, two firms generated approximately 82,000 metric tons of HCH waste. This sizeable quantity was dumped at thirty-five points within our Autonomous Community, giving rise, as we have said, to one of the main environmental problems now confronting us.

The strategy contemplated for the solution of this problem has been set down following an in-depth discussion, outcome of which is indeed the level of public consensus essential for the undertaking of a task of such magnitude. It is a clearly defined, straightforward strategy, but also one that is sufficiently flexible to permit revision in the light of further research in treatment technology. It defines the various lines of action to be undertaken over the next few years.

On the one hand it is planned to conclude studies initiated in 1993 into the risk associated with points inventoried as HCH-infected. At the same time there are two major research projects under way, the dechlorination of pure HCH waste and the separation of residues in the soil. The first of these projects is being undertaken with BCD, or basic catalytic dechlorination. Separation of HCH from soil will be by means of such technologies as soil washing and thermal desorption.

The final aim is to have each of these projects taken up by industry. Before such a development can occur, however, it is essential to undertake action of some sort to eliminate the risk to public health and ecosystems at the points in question. Over the short term the solution opted for, the aim being to avoid the negative implications of contaminated soil for urban and economic development in the Basque Country, is excavation, followed by storage in two secure but temporary depositories. These are strategically situated on the banks of the River Nervión. In those cases in which no other solution would be technically and economically viable, excavation will be followed not by such storage but by isolation on site.

According to the first economic assessment, which is part of the Master Plan for Contaminated Soil in the Autonomous Community of the Basque Country, the clean-up costs thus entailed over the forthcoming years, to be borne by our Autonomous Community, amount to more than 5000 million pesetas. The same assessment puts the cost of an outright solution at 13,300 million.

Only a few days ago, the North American Environmental Agency published a study carried out into the toxicity of dioxins. You are all familiar with these compounds, which derive from the production of HCH and of halogenated pesticides. The conclusions of the report are disquieting. Every day there appear new data to occasion serious doubts about certain activities carried out in the past, activities in which production and consumption were the priorities and other factors were left out of account. This Forum has recognized the hard legacy of thousands of soil areas contaminated by HCH and halogenated pesticides, and it is the inquietude they feel that has brought all the participants here to our country.

Ladies and gentlemen, you represent sectors committed to the preservation of the environment and of modern society. I allude to universities and research centres, the sources of our concern while at the same time the depositories of knowledge; to industry, which is the necessary force behind the technological and economic development of a people; and finally to the public administrations, of which the endeavour is to channel human energy toward the goals that society has set for itself. It is my hope that this Forum, by availing of science, of the practical experience of manufacturing centres, and of the open and collaborative work of public administrations, will bring us a little closer to a form of day-by-day development compatible with the health of the environment. In the meantime it is indeed encouraging to see how a problem common to various peoples has led to solidarity in the quest for solutions.

Low volatile Chlorinated Hydrocarbons in aquatic sedements in Berlin and Environs

Mr. Konstantin Terytze
Germany

Low Volatile Chlorinated Hydrocarbons in Aquatic Sediments in Berlin and Environs

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ABSTRACT

Low volatile chlorinated hydrocarbons, especially DDT, HCH and PCB have been used as indicators for the level of pollution in aquatic sediments.

These compounds are present in all the sediment samples analysed by gas chromotography. Enrichment factors between water and sediment are high (K_d = 85,108 in the case of DDT), documenting the strong geoaccumulation tendency of toxic chlorinated hydrocarbons.

No linear relationship showed between the concentration of contaminants (HCH and PCB) and the amount of organic matter in the sediments. The application of the EVOLON model to determine the kinetics of sorption showed clearly a value of saturation. The sorbed amount of low volatile chlorinated hydrocarbons is to a large extent dependent upon the portion of organic matter on the surface of the sediment particles.

1. Introduction

Sediments act as natural buffer and filtration systems in the terrestrial-limnological cycle, in particular.

The sorption, enrichment or degradation of introduced substances is not unlimited.

The aquatic sediments represent an integration of the contaminants emitted over time and may be used as an indicator of local and short-term inputs.

The main emphasis of the article is:

- the investigation of the enrichment of DDT, HCH and PCB in aquatic sediments and
- the modelling of the sorption of HCH and PCB as function of sediment organic matter.

2. Areas subject to investigation and methods used

2.1 Locations of sampling

For the purpose of the present work sediment samples were taken once a month, beginning in April 1987, to analyse them for low volatile chlorinated hydrocarbons (LVCH): lake *Grosser Müggelsee, Strandbad Oberspree* (bathing resort at the river Spree), *Spree-Abzweig Britzer Zweigkanal* (Britz canal at the river Spree), *Dahme-Abzweig Teltowkanal* (point where the river Dahme flows in the Teltow canal), bridge *Altglienicker Brücke, Teltow-Seehof (Zehnrutengraben)*, bridge *Teltow-Ramrathbrücke*, lake *Machnower See* near the lock, motorway bridge *Stahnsdorf* as well as *Teltowkanal-Griebnitzsee* (place where the Teltow canal flows into the lake Griebnitzsee) in the Potsdam area (end of Teltow canal). The location of the waters investigated and of the samplings is shown in Figure 1.
Sediment samples were taken up to a maximum depth of 10 cm using a similar grab to Van-Veen whose flaps and grabs shells are closed by a falling weight (ROTHE, 1986). The samples taken from the upper sediment layer represent the living anthrophogenic substance input in question.

2.2 Preparation of samples and methods of analysis

Glass bottles washed out with bidistilled water were used to transport and store the sediment samples subject to LVCH-analysis. In case it was not possible to investigate the sediment extracted immediately after sampling, the sample was stored at -18 °C to avoid biological activities and chemical transformations.
The sediment samples intended for LVCH-analysis were dried at 30 °C and a relative humidity of 40 % in a climatic cabinet, in porcelain basins, and subsequently homogenized. The following preparation method has been proved advantageously for gas-chromatographic determination of sediment samples: An originally weight-in quantity of 1.5 g dried sediment was filled into a round flask and mixed with 20 ml of perchloric acid ($HClO_4$) and 10 ml of crystalline acid (CH_3COOH). The suspension was boiled for 4 hours at 70 °C at

the recycle and, following this, cooled to room temperature and mixed with 40 ml of n-hexane for ultraviolet spectroscopy. After shaking the mixture for 5 minutes and settling it for 15 minutes the organic extract was separated from the aquatic suspension by a separator and the n-hexane subsequently filled in a 100 ml separating funnel. After adding 40 ml of H_2SO_4, five minute-long shaking and a settling time of 20 minutes the acid phase was rejected.

Depending on the quality of the sediment's material the hexane extract was then each time purified with 20 ml of concentrated H_2SO_4. Following this procedure which took place several times (3 to 6 times) the extract was washed twice with 50 ml of bidistilled water.

The hexane extract was filled in a pointing soldering stick with ampule neck and at a temperature of 40 °C concentrated to 0.3 - 0.5 ml at the rotary evaporator. For gas-chromatographic analysis the volume was topped-up to 0.85 ml.

The verification of the accuracy of the method used for acid digestion is discussed in the works of HUSCHEK and GIESE (1989). Since the elementary sulphur and some sulfans are present in almost all oxidizing as well as reducing sediments the determination of metabolites and isomers is disturbed by LVCH. Elementary sulphur is effectively eliminated from sediment extracts by adding copper chips newly activated with HNO_3 (EDER et al., 1987). Identification and quantification of low volatile hydrocarbons took place in each total sample by means of gas-chromatography.

2.3 Separation and Identification

For separation were used: gas-phase chromatograph: Hewlett Packard 5890, Series II
Column: quartz capillary 50 m-column; internal diameter 0.2 mm; silicon-methyl-coating (0.2 μm) (HP 1; homopolar)
Temperature program: 90 °C (1 minute); up to 190 °C (8 °C/min.);
up to 247 °C (1 °C/min.); up to 260 °C (20 °C/min.) 15 min.
Injector: 7673 automatic samplers of Hewlett Packard; Splittless 150 °C
Detector: electron capture detector (ECD) ^{63}Ni; 300 °C
Injection volume: 2 μl
Detection limit: 10 pg/μl

Identification of the components only through the comparison of the retention times is not possible since a number of peaks show very similar retentions.

The sample was therefore increased by a standard consisting of the single components α-HCH, HCB, β-HCH, Y-HCH, δ-HCH, pp-DDE, pp-DDD, pp-DDT at a concentration of 100 pg/μl. This way the intensities will be changed. The absence of compounds which are looked for but not contained in the sample is confirmed by the occurrence of additional peaks.

Another question of the sample cleaning and analysis for LVCH is described in detail by TERYTZE and GOSCHIN (1991).

3. Concentrations and enrichment fators of LVCH in the Berlin area

The measured degrees of contamination with DDT, HCH and PCB for the Teltow Canal, Lake Müggelsee and the Spree River are illustrated in Figures 2 - 5.

Differential-diagnostic analysis of individual metabolites of DDT and isomers of HCH not only shows their bearing paterns due to direct input but also reveals information about their current, environment-induced states of metabolism.

The distribution coefficient (Kd) for the Teltow Canal, Lake Müggelsee and Spree River are given in Tables 1 and 2.

Table 1: Concentration profiles and enrichment factors (K_d) of DDT and HCH in the Teltow Canal (concentrations based on dry sediment weight)

Sampling points	Water Σ DDT	(ng/ml) Σ HCH	Sediment Σ DDT	(ng/g) Σ HCH	K_d Σ DDT	 Σ HCH
Dahme, Abzweig Teltowkanal	0.037	0.090	3,149	1,180	85,108	13,111
Altglienicker Brücke	0.230	0.292	7,324	1,305	31,844	4,469
Teltow-Seehof "Zehnruthengraben"	0.094	0.163	906	481	9,638	2,951
Teltow Ramrathbrücke	0.042	0.091	151	89	3,595	978
Machnowersee nahe Schleuse	0.054	0.108	913	484	16,907	4,481
Autobahnbrücke Stahnsdorf	0.071	0.093	168	131	2,366	1,408
Teltowkanal-Ende	0.022	0.067	139	95	6,318	1,418

Table 2: Concentration profiles and enrichment factors (K_d) of DDT and HCH in Lake Müggelsee and Spree River (concentrations based on dry sediment weight)

Sampling points	Water	(ng/ml)	Sediment	(ng/g)	K_d	
	pp-DDE	Y-HCH	pp-DDE	Y-HCH	pp-DDE	Y-HCH
Spree, Abzweig Britzer Zweigkanal	0.016	0.068	38	34	2,375	500
Strandbad Oberspree	0.012	0.062	12	35	1,000	500
Mueggelsee kurz vor den Bänken	0.011	0.024	203	212	18,455	8,833

The size of the distribution coefficient K_d, which reflects the interaction of the concentration of a substance in solution C_1 with that fixed in the sediment C_f ($K_d = C_f/C_1$), is an indicator of the magnitude of transfer between the compartments.

K_d can be regarded as an enrichment factor and provides important information about geoaccumulation.

The high enrichment factors of DDT and HCH at the beginning of the Teltow Canal indicate the direct input of contaminated waters by the chemical industry in the past.

On the plant's site, DDT contents of 1,249 ng/g and HCH contents of 4,312 ng/g have even been registered at a depth of 40-44 m below ground.

4. HCH and PCB Sorption as Function of Sediment Organic Matter

The sorption process for HCH and PCBs were modelled by a phenomenological approach, the socalled EVOLON model (MENDE, 1989), which can be used to model complex interactions of two factors without a knowledge of the physicochemical relationship between them. The model describes a monotonous transition process between two stationary levels and can be interpreted as a dose-effect relationship.

It depends on only five parameters, three of which are simple scale parameters, which adapt the model to the measured data and the chosen units. These parameters can be removed by simple linear scale transformation. The other two parameters represent exponents which reflect characteristic units and scale independent system qualities. They are measures of the deviation from a linear growth or linear saturation (logistic model), respectively.

The EVOLON model consists of two terms, one representing no linear growth and one no linear saturation.

The exponents represent the deviation from an exponential base process (k, l = 1) and they build a highly aggregated measure for stimulating or hampering co-operative processes in the system. The model can be described by the following differential equation:

$$\frac{d_y}{d_x} = Cy^{k(B-y)1} \tag{1}$$

where C is a velocity parameter; B represents the upper stationary level, and k and l are real exponents.

The fifth parameter is the initial value $y_0 = y(to)$ of the process of parameter fitting. This initial parameter should be in the center of the interval.

In the figures y_0 always corresponds to the abscissa value x_0. In our case B = Y and y > 0. The EVOLON approach in equation (1) is used with the lower limit Y = 0. Such an approach is justified if a simple monotone correlation is expected. The mode used here is sufficiently universal and may be simplified later if a linear relationship between B and 1 is found in various fits with similar regression coefficients. Thus it is possible to conclude for the socalled logarhythmic bordercase

$$\frac{d_y}{d_x} = Cy^{k^{*}\exp(B-y)} \tag{2}$$

In some instances, only a simple concave or convex process occurs, which can be described by a growth and saturation term. Thus k or l become very small when using the complete EVOLON model. In this instance no differential equation is given, but the explicit solution can be given in terms of parabolic or a hyperbolic equation to describe the growth or saturation process.

If the process must be described as a combined growth and saturation process, then the model cannot be explicitly solved, a differential equation must be integrated numerically:

$$y\,(X0) + \int_{X_0}^{x} \frac{dv}{C_y{}^{k^{*}(B-y)1}} = Fx\,(C,B,k,l,y(x0)) \tag{3}$$

For the identification of the parameters the following equation must be integrated to find the minimum solution:

$$\sum_{i=1}^{n} (F_{xi} - y_{idat})^2 = \text{Min!}$$

This cannot be solved by a linear equation. A combined process for the identification of the parameters was developed, which uses the following steps.

In the initial step the initial combination of the initial values is calculated from the logistic equation k = l = 1 using a linear regression model. These initial parameters are improved by using the Simplex Method by Nelder and Mead (MENDE, 1989). A cluster procedure is used to identify the agglomeration of values. These are fitted by the Marquardt gradient procedure, thereby dissolving the clusters. As a convergence for the end of this process: MARQUARDT's gradient is $< 10^{-4}$.

Thus at least four successful iteration steps must follow, without subiteration, and the square sum of the relative changes of the parameters is lower than 10^{-3}. This formal stipulation criteria could not be achieved due to the large scatter of the data. As an indication of the quality of the data fitting, with each fitting the mean relative deviation (MRD) is given:

$$\text{MRD:} \sum_{i} \left| \frac{F_{xi} - y_{idat}}{F_{xi}} \right| \Big/ \; n. \qquad (4)$$

The Figures 6 - 9 illustrate the sorption of HCH and its isomers as a function of the organic matter content in the sediments. The isomers show a clear saturation value. The figures illustrate the raw data (abscissa: organic matter and ordinate: concentration of contaminants) and the modelled fits.

The description of the sorption of PCB (Figure 10) as a function of the organic matter content represented by the loss on ignition, was realised by application of a hyperbolic saturation function. It expresses the solution of the EVOLON differential equation for a disappearing growth exponent k (Evolon) = 0. The corresponding saturation exponent is l (Evolon) = 1/C + 1; l = 1.3455.

This weak hyperbolic saturation indicates a complex process rather than a simple molecular reaction.

The saturation value is 2,378.9 ng g^{-1}. The limit of y for x = 0 is zero in an adequate approximation (4 %) 0. The sorption is totally based on the organic matter content. MRD value of the model (27 percent) reflects the precision of the analysis of the contaminants.

The existence of this saturation value leads to the following interpretation: The organic matter is predominantly fixed to the sediment matrix and the content depends linearly on the thickness of the sediment layer. Thick sediment layers overlap each other and the sorption positions are partly blocked.

Following this hypothesis, the amount of the LVCH's sorbed is dominantly controlled by the organic matter at the sediment surface. This hypothesis agrees with MÜLLER-WEGENER & ZIECHMANN (1984), who observed similar sorption behaviours of some herbicides in terrestrial soils.

The destruction of the surface sediment by the navigation traffic and excavation activities may have serious consequences for the underlaying groundwater aquifers. The analysed sediments of the investigation area may be subdivided into three groups based on loss on ignition < 1 %, 1 - 20 % and > 20 %.

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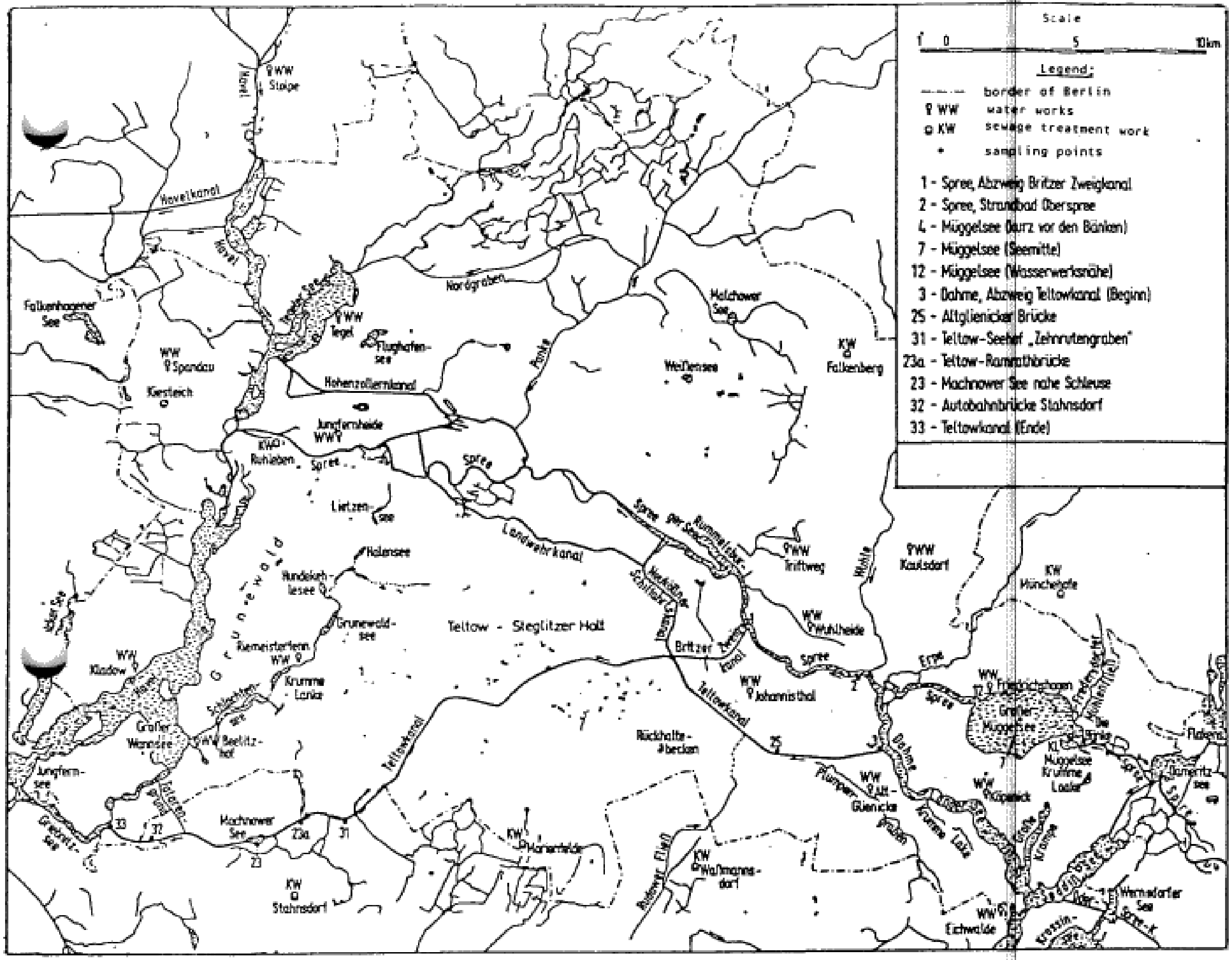


Figure 1: Survey of the field of investigation and position of the sampling points

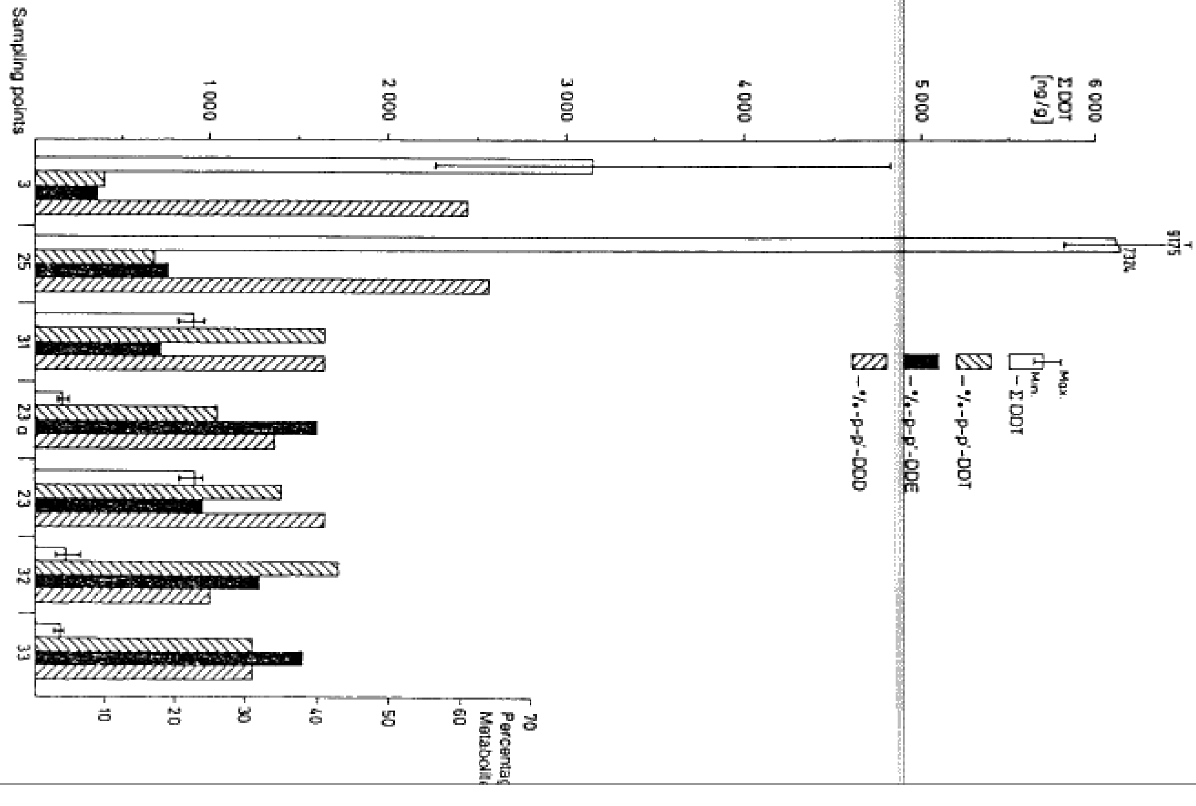


Figure 2: Concentrations of total DDT and percentage of p-p'-DDT, -DDE and -DDD in sediment of Teltowkanal

3 - Dahme, Abzweig Teltowkanal (Beginn); 25 - Altglienicker Brücke, 31 - Teltow-Seehof „Zehnrutengraben"; 23 a - Teltow Ramrathbrücke, 23 - Machnowersee nahe Schleuse, 32 - Autobahnbrücke Stahnsdorf; 33 - Teltowkanal (Ende)

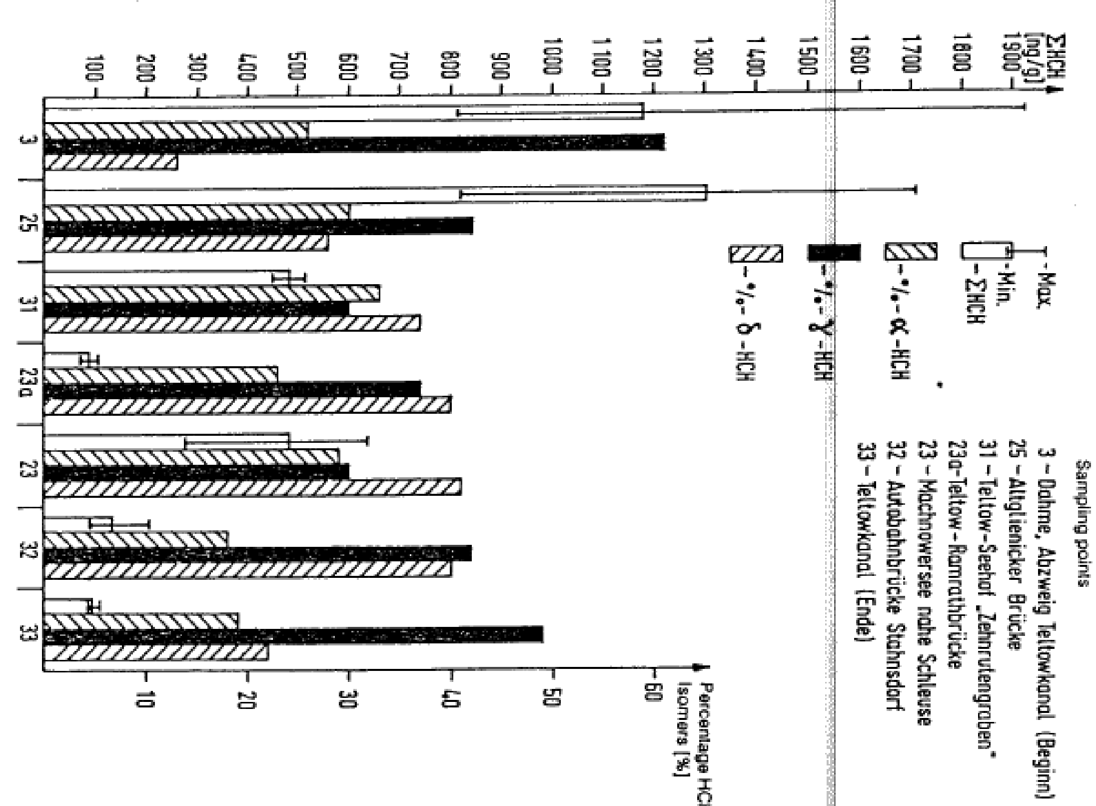
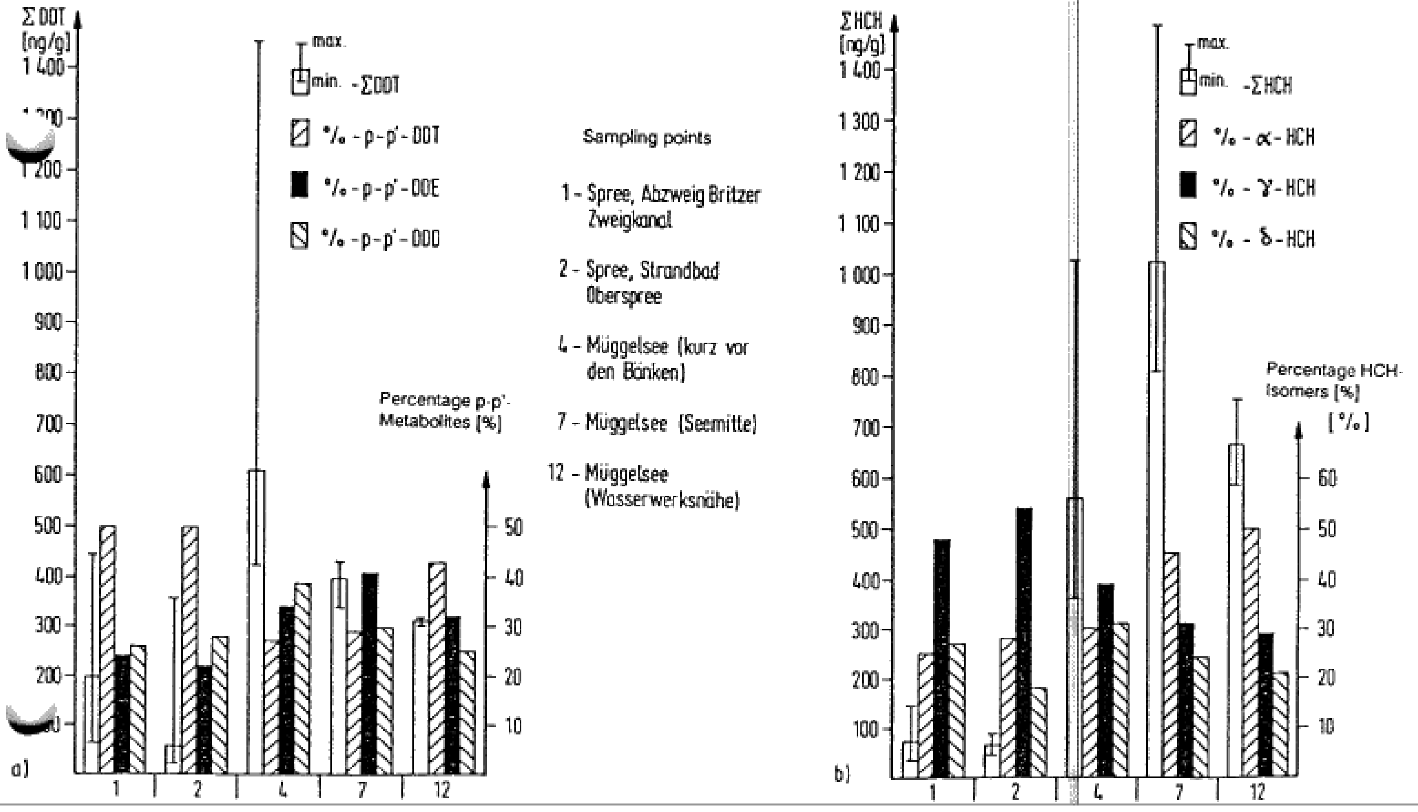


Figure 3: Concentrations of total HCH and percentage of alpha-, gamma- and delta-HCH in sediment of Teltowkanal



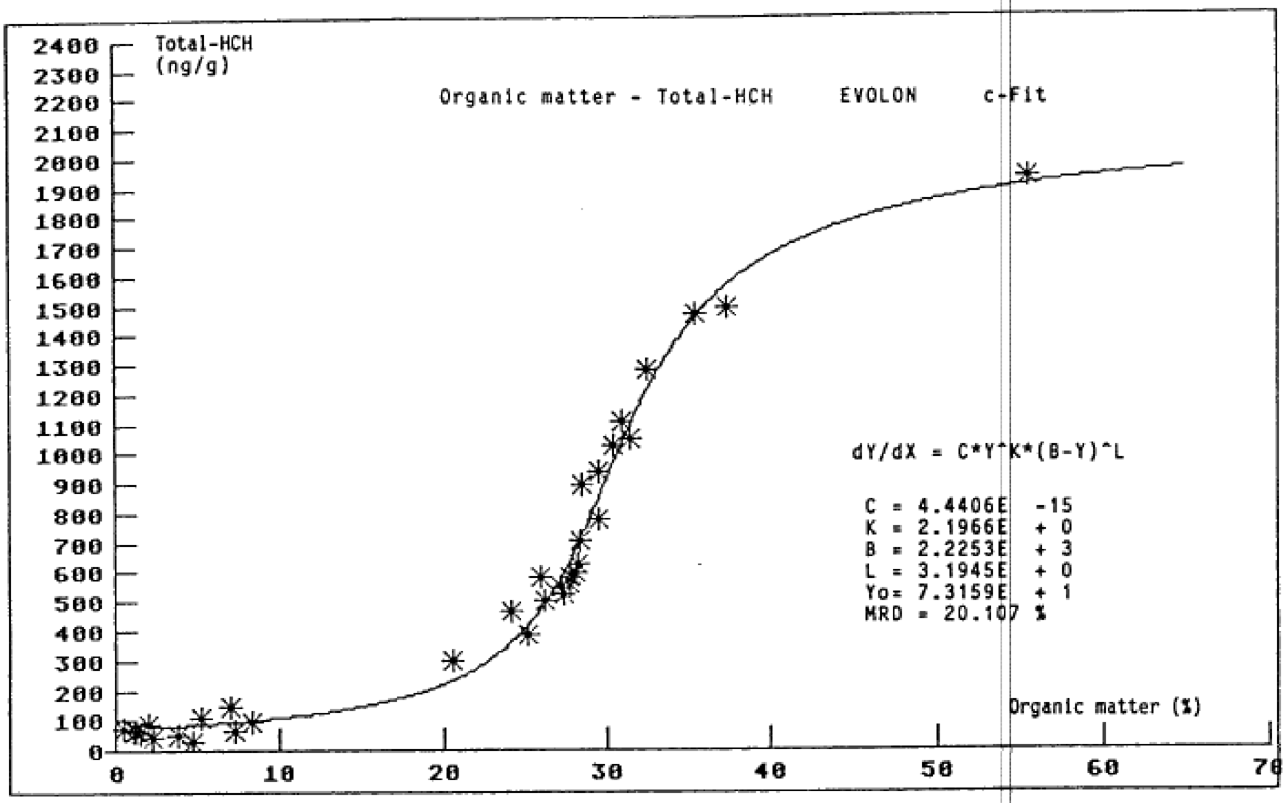


Figure 6: Sorption of Total-HCH as a function of organic matter in the sediments

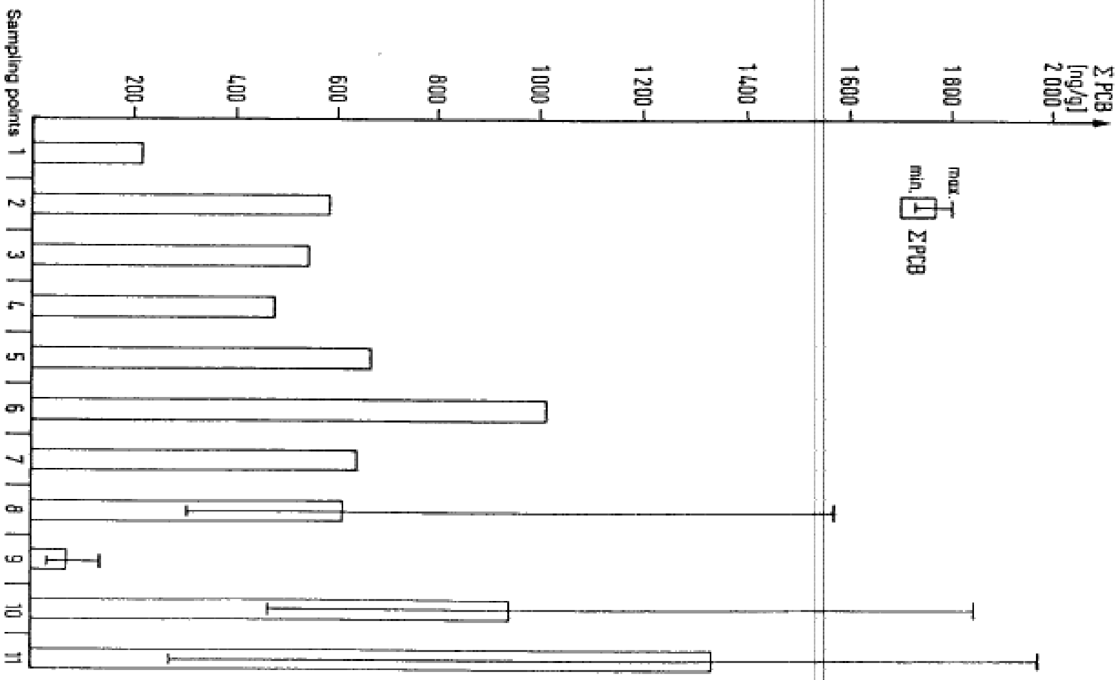


Figure 5: Concentrations of total PCB (Arochlor 1254) in sediments

1–Neuendorfer See; 2–Alt-Schadow; 3–Beeskow; 4–Ögelsee; 5–Altarm Oder-Spree-Kanal; 6–Fürstenwalde; 7–Mönchwinkel; 8–Müggelsee (kurz vor den Bänken); 9–Strandbad Oberspree; 10–Britzer Zweigkanal; 11–Dahme, Abzweig Teltowkanal

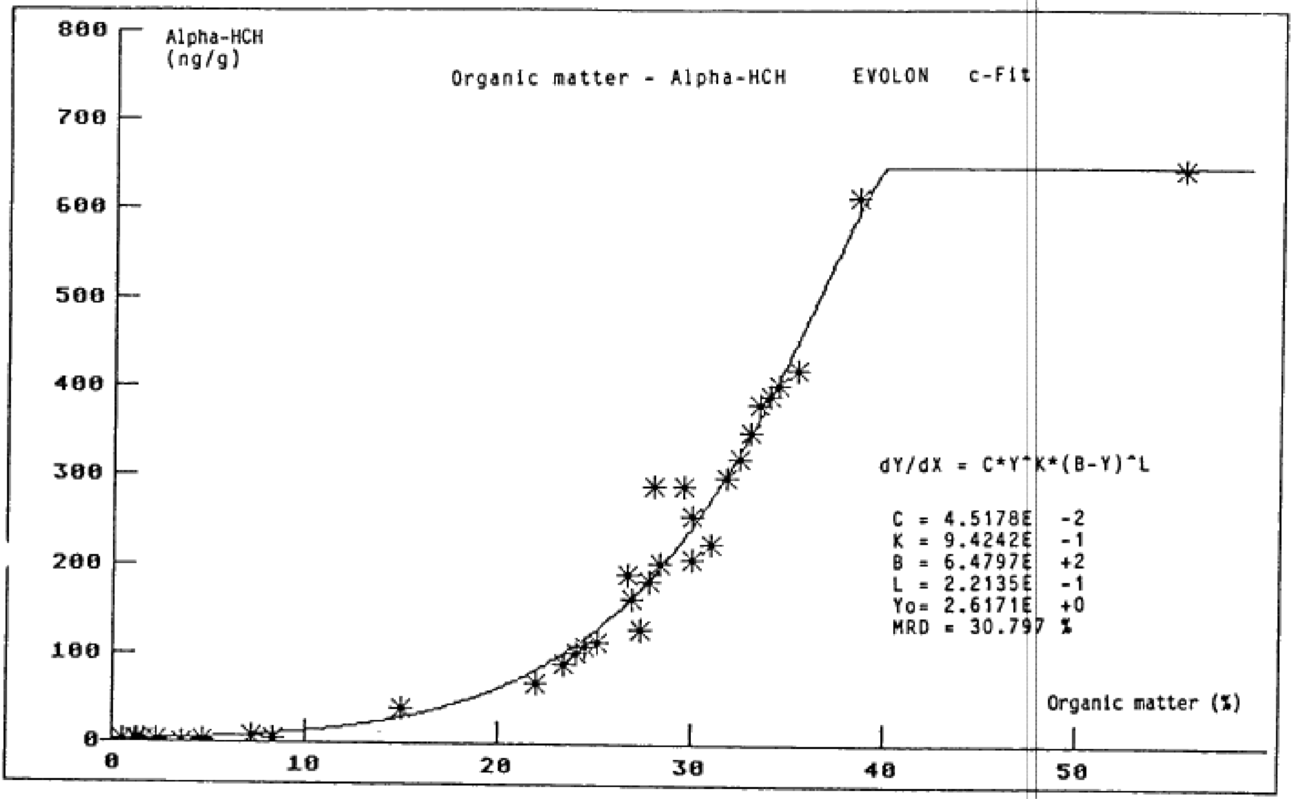
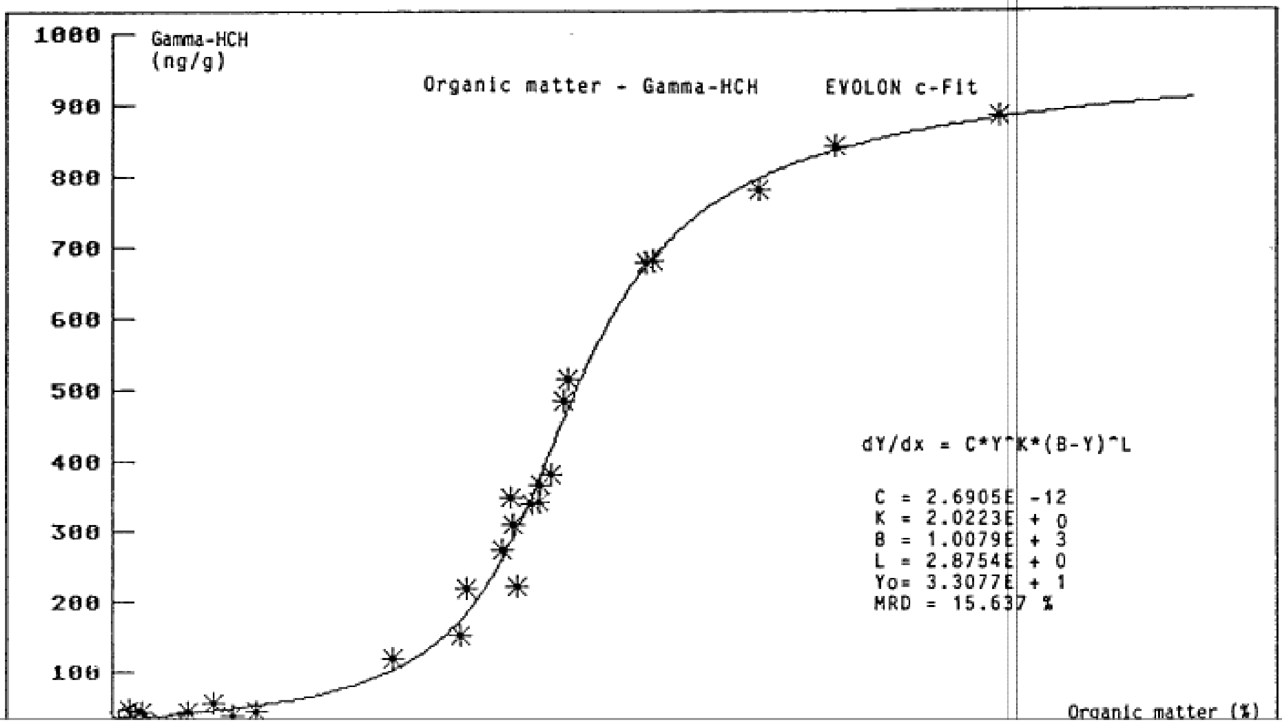


Figure 7: Sorption of Alpha-HCH as a function of organic matter in the sediments



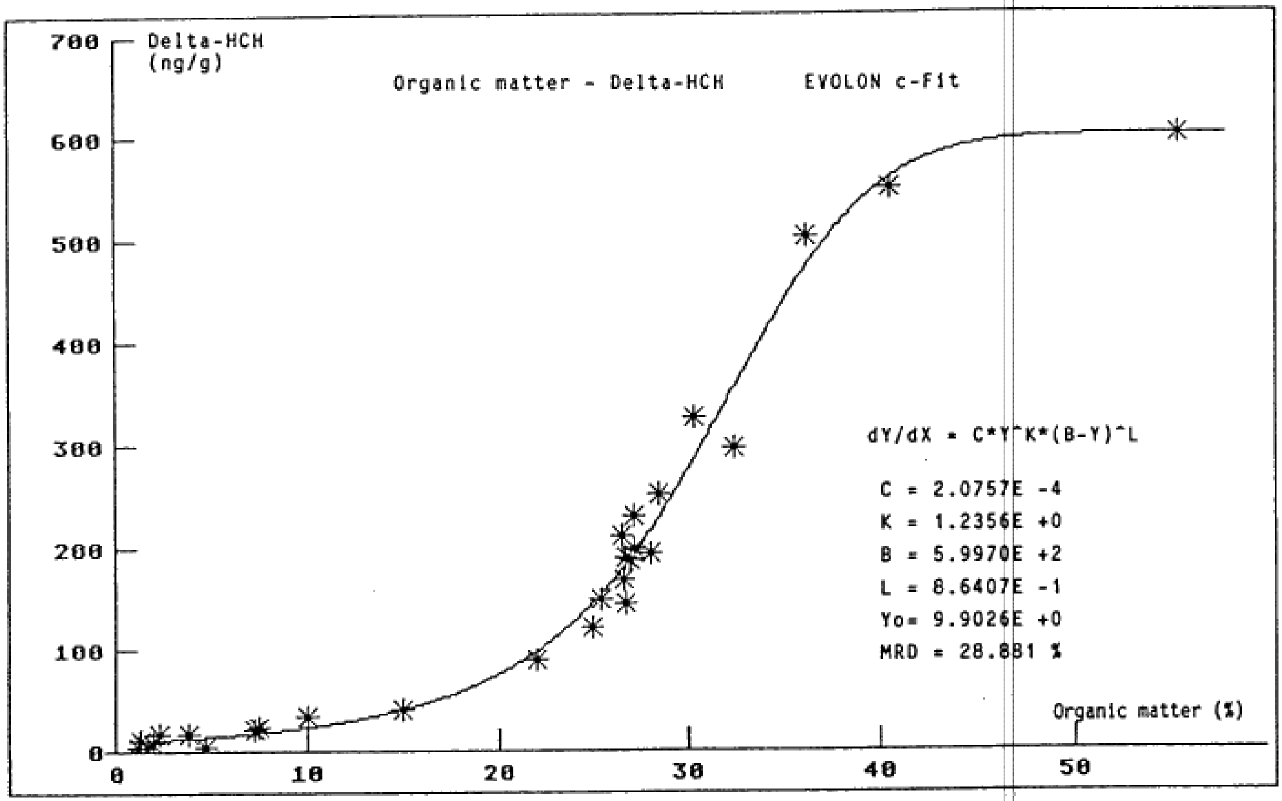
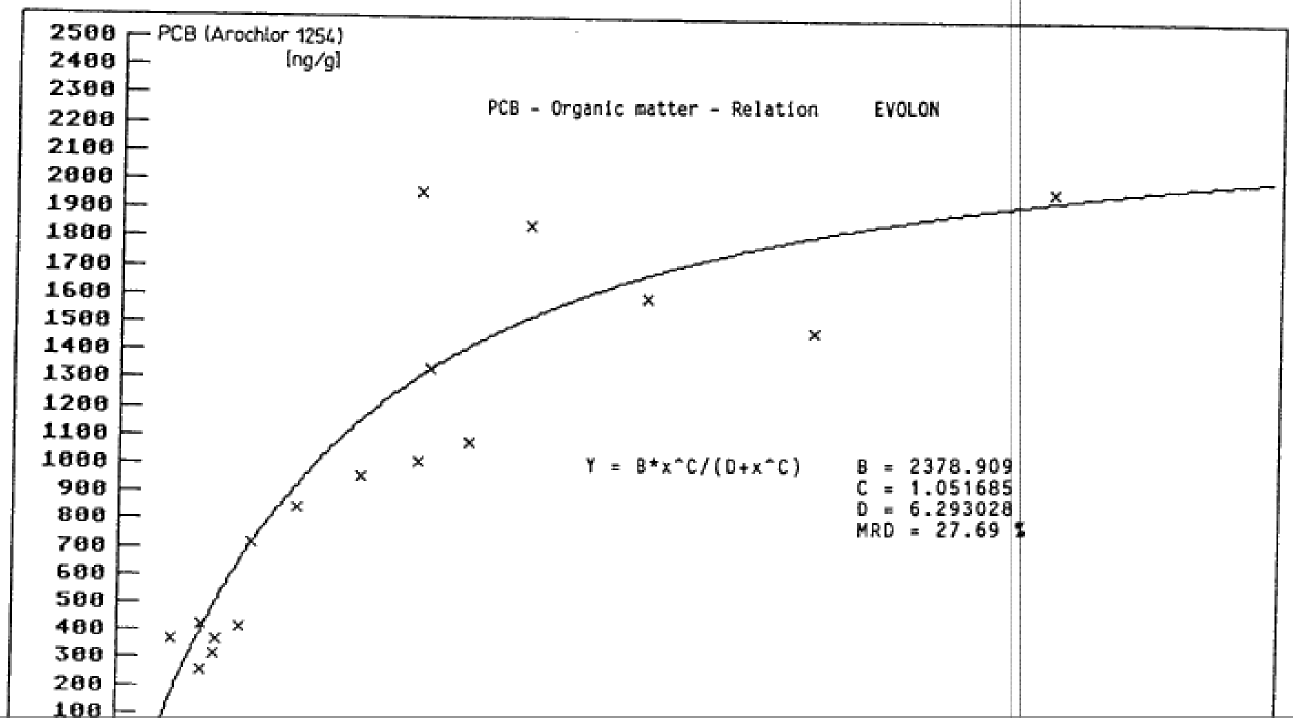


Figure 9: Sorption of Delta-HCH as a function of organic matter in the sediments



Studies of pesticide contamination of area adjacent to the chosen places of storage of unwanted pesticides

Mr. Stanislaw Stobiecki
Poland

STUDIES OF PESTICIDE CONTAMINATION OF AREAS ADJACENT TO THE CHOSEN PLACES OF STORAGE OF UNWANTED PESTICIDES

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The quality of pesticides produced nowadays continously improves and there are more and more new and better pesticides on the market. This creates a serious problem which is the gathering of useless materials which are of bad quality or were banned from usage. Another reason for the present unwanted stocks was bad distribution and price policy that was realised in Poland for more than 40 years.

Unwanted pesticides are a serious problem. Their disposal is technically a very difficult issue. For years some provisional solutions have been applied. Unwanted pesticides have been gathered in so called "tombs". Mostly the tombs are built of concrete circles with a diameter of 1-2 meters and they are 1-3 meters high. They have concrete lids on the top and at the bottom. Both the inside and outside of a tomb are insulated with tar. Tombs are situated underground. The capacity of each is 1-10 m3 and 1-10 tonnes of materials can be stored in it.

Apart from the tombs, unwanted pesticides are gathered in stores, sheds or put directly into ground pits. The stored substances are of the older generation hence they have higher toxicity and greater stability. The state of the majority of the tombs is unknown. Any loss of tightness can result in a considerable danger of soil, surface and groundwater contamination.

Since 1992 the Institute of Plant Protection has tried to solve the Polish problem of unwanted pesticides. During II HCH Forum in Magdeburg we presented our introductory actions which allowed us to estimate the range of the problem and its vital importance for the envirоment. Now we present the next stage of our work in which on the basis of chemical analyses we want to find out whether the places of storage are tight and if they are not, how great the contamination of soil with pesticides is.

A few tombs from the provinces of Poznan, Katowice and Radom were chosen for our studies. Soil samples were taken from the areas adjacent to the tombs. Amounts of 30-50 g soil were dried to constant mass in the air and then extracted with chloroform and methyl chloride.
The procedure of preparing a sample for quantitative determination by means of the GC method was chosen in such a way that 1 microlitre of extract corresponded to 2 mg of soil. The samples were analysed with the GC method (detectors ECD and NPD) and the GC-MS method.

The results of the analyses are presented in the table:

MAXIMUM AMOUNTS OF DETECTED PESTICIDES in mg/kg					
Pesticide	Detectability limit	Niedzwiady	Socnicowice	Libiaz	Nagorniki Wlk.
Lindane	0,01	47,0	0,139	0,032	0,339
DDT	0,010	500,0	0,041	0,120	0,256
Metoxychlor	0,010	320,0	3,400	-	-
Chlorfenson	0,010	10,0	-	0,146	-
Malathion	0,030	45,0	-	-	-
Butyl, Phthalate	0,500	681,0	100,0	18,0	10,0

Note "-" means levels below the detection limit.

In one case out of the tombs that were studied great amounts of pesticides like DDT, HCH, metoxychlor, chlorofenson and malathion were detected. The detected amounts e.g 500 ppm of DDT point to a considerable untighten-pesticides in the amount below 1 ppm also shows evidence of loss of tomb tightness.

The results make it necessary to control all the places of storage and they clearly show the importance of the problem.

We have developed a general plan of solving the problem of unwanted pesticides in Poland considering the substance, organisation and economic issues of the whole enterprise.

Elements of general a plan of solving the problem of unwanted pesticides in Poland

1. Exact inventory all over Poland.
2. Technical inspections.
3. Selections of the most dangerous places.
4. Analysis of contamination level within the area.
5. Protective actions:
   - civil engineering isolation method
   - method of transfer to safe depots
6. Studies on indentification and incineration of mixtures.
7. Organisation of a system for collection of pesticides from stores.
8. Building an incineration plant.

The program implemenation is an important ecological action

The local authorities of the areas where the pesticide depots are located have no technical and finance possibilities to solve the problem.
The inventory of unwanted pesticides and empty containers will become the basis for further steps i.e.:
-analysis of the level of danger;
-protective operations;
-disposal through incineration .

The HCH-Situation in the Russian Federation

Mr.Andrei D. Pokarzherskii
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THE HCH-SITUATION IN THE RUSSIAN FEDERATION

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Presented by: Andrei D. Pokarzherskii

The problem of real estimation of HCH impact, content or food chain migration in agricultural and "natural" ecosystems in the former Soviet Union (not only the Russian Federation) is complicated due to marked differences in formal and real situations of HCH application in agriculture, forestry and other sectors within the former USSR.

The first problem of HCH estimation is the failure of data on HCH production and distribution in former USSR republics. In any case, the HCH production was within limits of some per cents of the total production of pesticides in the USSR. But it is relatively difficult to determine the real share of every republic in HCH consumption for agrochemical and other needs. It is known that in the southern republics HCH was used for cotton production, in the European part of the USSR for corn, barley and wheat production and in the taiga forest regions against parasites. But it is very difficult tot estimate the actual pesticide doses applied which varied as factor 2-10 for recommended technologies.

The next problem of the estimation of the HCH situation in Russian Federation is the problem of the correct application of HCH in the technologies. For the Russian Federation it is a common thing that some elaborated technologies were modified for concrete conditions. They could be simplified, could be changed, especially in cases of private farms. But in state and collective farms HCH was used in doses significantly higher than the recommended ones. Private farmers used very high doses of HCH (and other pesticides) up to the end of the 80-ies. Such contrasts in applied and recommended doses do not allowe extrapolation of the dates received in one situation to an other one. Bad tools and machines for pesticide application and the use of aerospraying made assessment more difficult. At last, the decrease of pesticide production, increase of costs, destruction of the state system of pesticide supply have led to the re-use of outdated compounds. These compounds accumulated at pesticide landfills which are now a source of contamination and the compounds are a source of applications out of consideration.

Moreover the compounds found in landfills are a mixture of transformed pesticides and their application may induce other effects in the comparison of initial components. Another source of contamination are the former storage sites of pesticides at collective and state farms. All these local sources of pollution can change a picture of soil and water contamination, and may have caused a relatively permanent pesticide level in soil and waters. All these features of pesticide application in the former Soviet Union and Russian Federation complicate the estimation of the HCH (and other pesticide situation in the Russian Federation.

The next problem is the problem of pesticide content control in soils, waters and foodstuffs. There are no analytical problems since gas-liquid chromatography is widely distributed in the system of research stations in the former USSR. But the costs for analysis are high, possibilities for control are limited and the main source of foodstuffs contamination - private farms-are out of control. The features of pesticide application mentioned in the previous paragraph create complications for correct conclusions about contamination levels in forage and food. There are few published data on soil, water, forage and foodstuffs contamination in the former USSR and all of them show a noticeable variation of HCH concentration. The data of published studies can be used as preliminary ones for consideration of ecological or health hazards in concrete regions but not for a wide extrapolation. The reason for the small amount real data on pesticide contamination of the environment is a lack of interest in the problem. Among the 861 themes of the Federal science-technical program :Ecological Safety of Russia" there are only 8 concerned with pesticides and only 1- with chloro-organic pesticides (determination in water). There is no such theme as the evaluation of coupled effects of different types of pollutants, although pesticides (HCH among them) sharply influence bacteria characters in soil contaminated with heavy metals.

It is obvious that the territory of the Russian Federation is poorly studied and described with regard to levels of HCH and other pesticides in soils, waters and foodstuffs. The state Hydro Meteorological Committee carried out studies at territories of 11 biosphere research stations (5 at the territory of the Russian Federation). There has not been found any surplus of HCH content in waters and soils in the comparison with NOEL (The USSR standard NOEL for HCH is 0.1-1 mg/kg for soil., 0.03 mg/cub.m (maximal) for air (0.05 for gamma-HCH) and 0.02 mg/l for water). In studies carried out in agricultural ecosystems, a surplus of pesticide (including HCH) content in soils and foodstuffs in comparison with NOEL of a factor of 3-50 (up to 5 mg/kg for HCH in soil) was encountered.

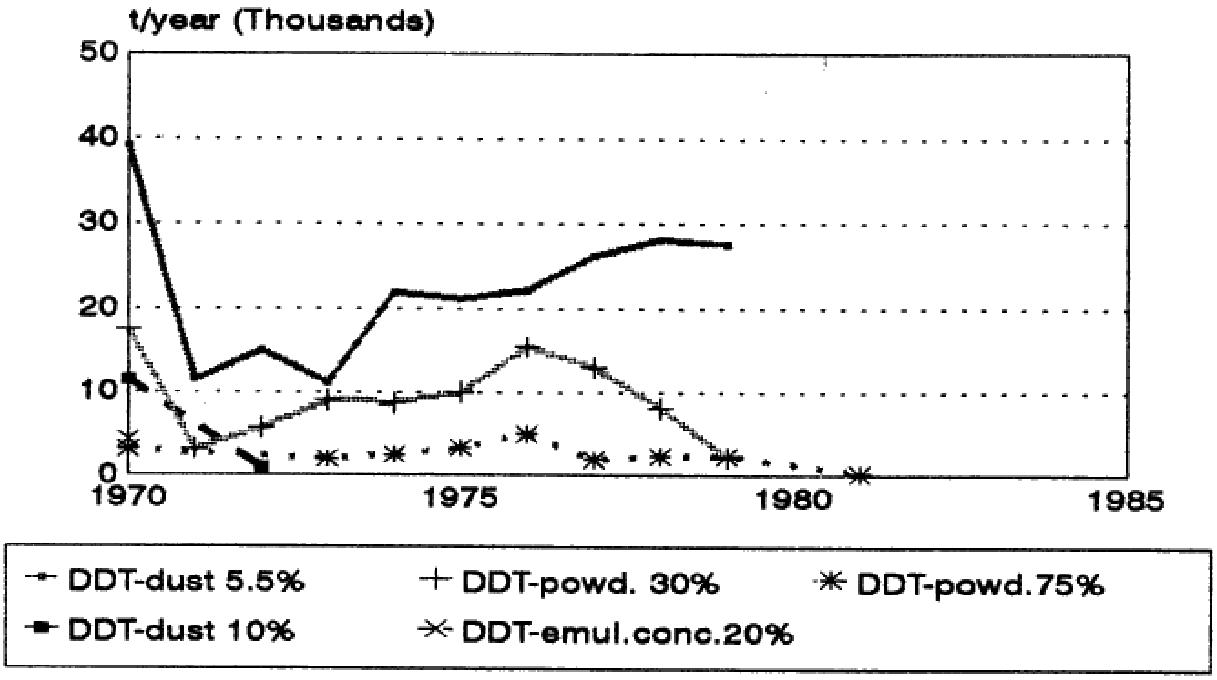
But the amount of available data for estimation is limited and methods of data collection are often unsatisfactorily described. Many data are obtained in experimental studies and not during observation of actual ecosystems. The failure of data results in the underestimation of pesticide impact on the environment and the overestimation of effects of other pollutants (heavy metals and radionuclides).

On the other hand pilot studies of agrochemical services in the northern part of central Russia showed that soils and waters in the region may be relatively clean with regard to pesticides and heavy metals but a failure of data limits the possibilities of extensive extrapolations.

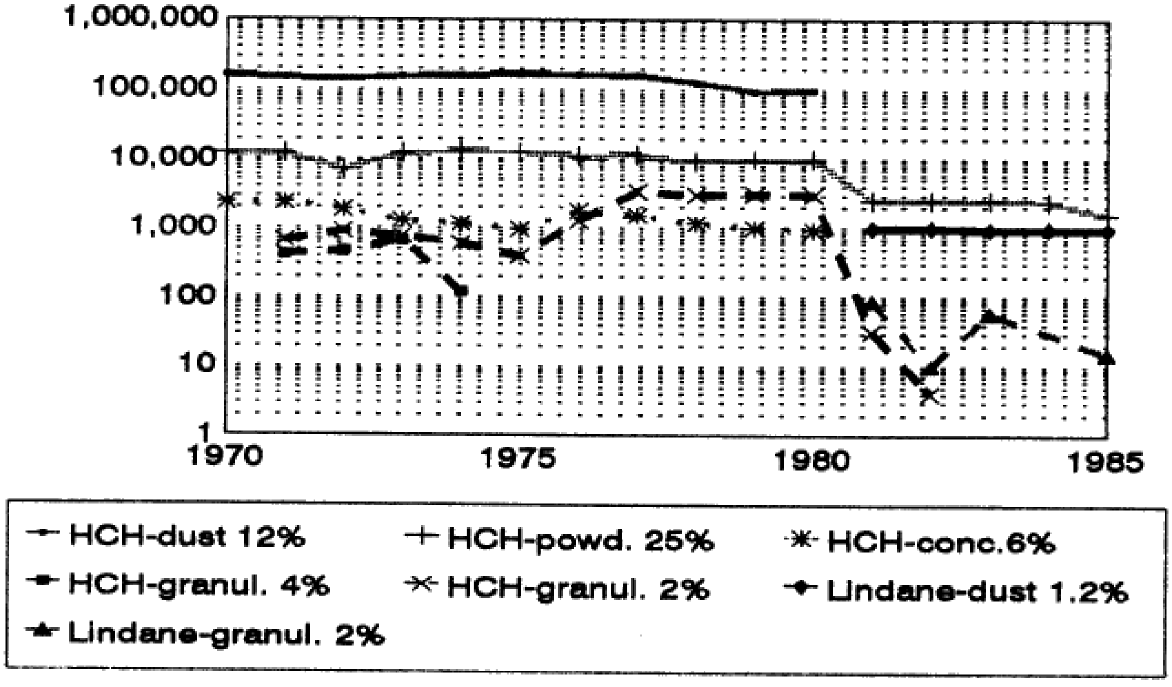
To estimate the real HCH situation (and other persistent pesticides in Russian Federation) it is important to create a system of research sites in the Russian Federation, to carry out studies of HCH (and other pesticides) content in agricultural and natural ecosystems in Central Russia and to continue monitoring studies of pesticide content in environmental compartments.

It is very important to develop a system of restoration and remediation of hightly contaminated sites and fields in urbanized and industrial regions of Russia with a high population density.

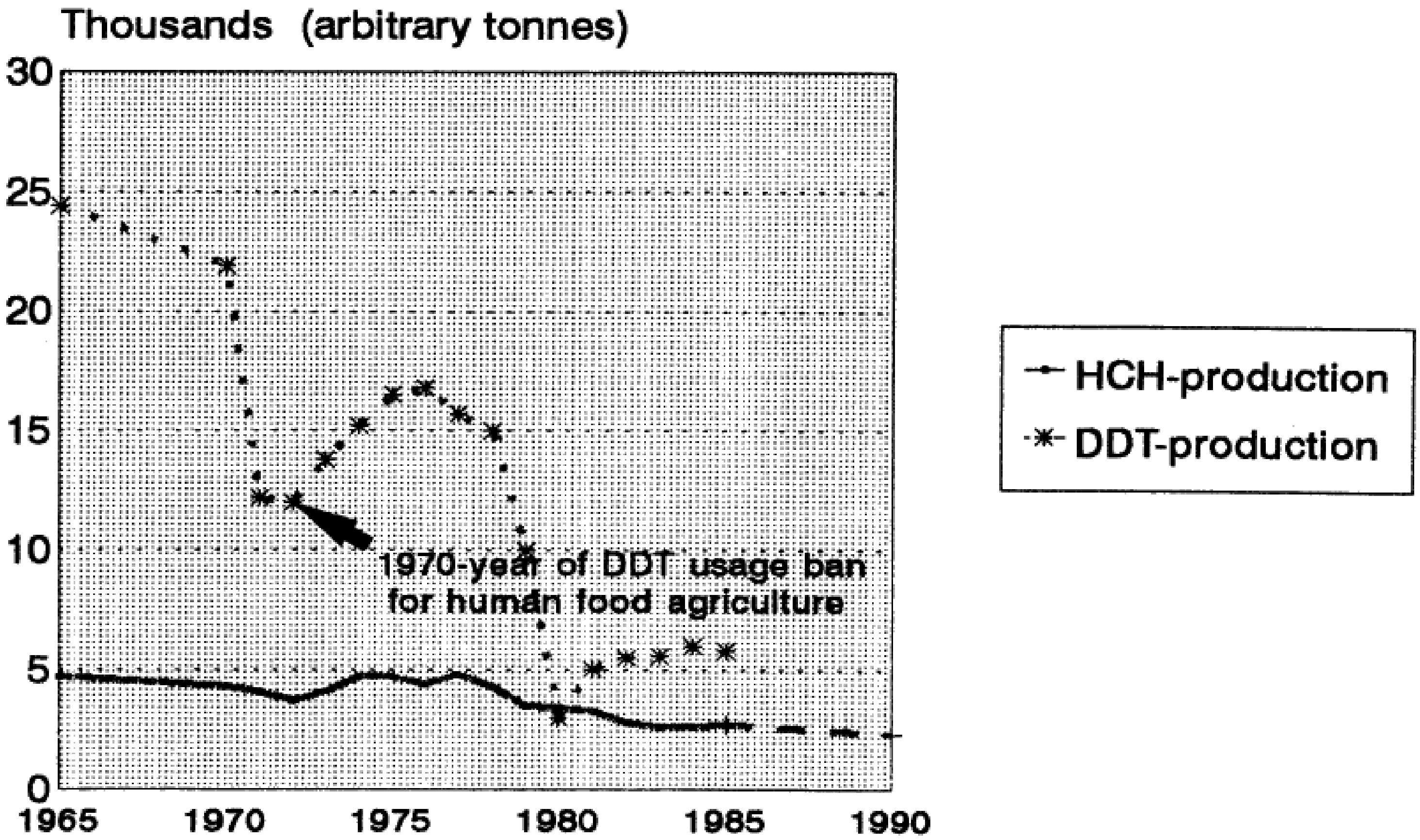
Agriculture supplies by DDT in the USSR (tonnes)



Agriculture supplies by HCH in the USSR (tonnes)



HCH & DDT-production in the USSR



1970-year of DDT usage ban for human food agriculture

Guide values for dealing with contaminated sites in Baden Würtemberg

Mr. Karl von der Trenck
Germany

Paper for presentation on the 3rd HCH-FORUM 19-20 September 1994, Bilbao, Spain

GUIDE VALUES FOR DEALING WITH CONTAMINATED SITES IN BADEN-WÜRTTEMBERG

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1. Description of the Guideline

An estimated number of about 35,000 contaminated sites in Baden-Württemberg necessitated the implementation of guide values and a standardized procedure to deal with these sites in a uniform and yet site-specific manner. The procedure as well as the guide values were issued one year ago as a joint directive by the Ministry of Labor, Health and Social Affairs and the Ministry of the Environment of the state of Baden-Württemberg (*UM & SM B-W, 1993*).

The directive contains a **three-level hierarchy** of numerical criteria and rules which serve as both **screening levels** during the investigation and as **remediation objectives.** The decision for the appropriate level of remediation is based on <u>feasibility and environmental balance</u> considerations. The levels are ordered as follows:

*** Level 1 (Background-Values - Comprehensive Protection)**
On principle, all remediations have to aim first for background levels. These level-1 criteria describe the natural composition of the uncontaminated environmental media soil (**H-B values**) and groundwater (**H-W values**). Use is not considered at this background level, and therefore no health effects have to be taken into account. It turns out that the corresponding contaminant concentrations are generally very low and **permit all uses.** Thus, level-1 criteria are the most protective of the resources soil and water. In the case of lack of feasibility or negative environmental balance for level-1 objectives use-specific requirements are considered next:

*** Level 2 (Assessment-Values for Worst Case Exposure Conditions)**
Level two introduces toxicological effect data combined with conservative exposure assumptions. It was designed to **protect the most sensitive but still plausible human uses** of a site (i.e. drinking water consumption [P-W] and the playground scenario with soil ingestion [P-M1]). The corresponding numerical

criteria constitute general requirements, which are use-specific but not site-specific. At least four resources are considered on this level: Groundwater as such (**a. P-W values as initial effluent concentrations**) and its use (**b. P-W values as final groundwater concentrations**), the health of humans on contaminated sites (**c. P-M1 values**), and soil with respect to growth and quality of plants (**d. P-P values**). Barriers against migration of the contaminants, the effect of dilution, and abandonment of certain uses, etc., are not taken into consideration on level 2.

*** Level 3 (Site-Specific Requirements)**

Lack of feasibility or a negative environmental balance of level-2 objectives lead to consideration of site-specific circumstances which may alleviate the requirements (definition of specified uses of soil or water). With respect to groundwater, the distinction is again necessary between groundwater as a resource (a) and the use of groundwater (b). On level 3 the guideline gives **rules** of how to derive site-specific remediation objectives for groundwater in the form of fluxes and concentrations of contaminants after taking into account barriers, dilution, and the abandonment of uses.

a. For the protection of **groundwater as a resource** both of the following requirements are to be met :

a1. Limit of Effluent Flux Discharged from the Site (E_{max})

The daily **effluent** (E) of contaminants emitted from the contaminated zone into the groundwater must not exceed the E_{max} values [g/d] tabulated in the appendix. The E_{max} values were designed as amounts of substance sufficient to contaminate 25 L of clean water per second ($= 2.16 * 10^6$ L/d) up to the P-W concentration. They limit the extent to which the diluting capacity of the groundwater present at the site may be used.

a2. Limit Concentration of Groundwater Affected by the Site

In usable groundwater no contamination (averaged over the width of the site and the depth of the directly involved aquifer) is admitted above the **P-W** values. Thus on level 3 the P-values limit the **final groundwater concentration** instead of the effluent concentration, which is regulated by the P-values on level 2.

These requirements are site-specific, since the flux and the concentration of contaminants depend on the fluxes of water through the site, on the mobility of the contaminants and their accessibility to the water as well as on the adsorptive capability of the underground.

b. The Use of Groundwater

If drinking water quality (P-W) is not attainable the use of groundwater may be abandoned on level 3, or the water may be decontaminated before its distribution as drinking water to the consumers.

c. & d. Human Health & Growth and Quality of Plants

The guideline provides residential **(P-M2)** and industrial **(P-M3)** assessment levels, based on two standard scenarios, to protect human activities on contaminated sites. These levels serve as benchmarks enabling the State Health Administration to define site-specific remediation objectives. In cases where the situation is the same as the standard scenario of this guideline, these values can be used directly as remediation objectives. Otherwise further investigations are necessary to explore the site-specific scenario and/or specifically restrict the use of the site.

The same applies to soil with respect to plant production: If the P-P values cannot be adopted as goals, further studies and/or exclusion of certain crops are necessary.

Restriction of Uses

P-values are only binding as remediation objectives, if the respective uses (b, c & d) are desired in future. On level 3 the use of already contaminated groundwater (b) may be abandoned, the access of humans to a site (c) may be blocked, or the consumption of plants (d) from a contaminated site may be restricted. In these cases the respective P-values can be disregarded.

Partial restriction of these uses (b, c & d) requires the administration to issue **site-specific remediation objectives.** In all cases with use restrictions, the uses possible in the future are to be legally defined and recorded.

However, the pertinent law (*§25 LAbfG, 1990*) requires that usable groundwater be protected against polluting effluents without exception. The maximal alleviation possible concerning **groundwater as a resource (a)** has been formulated above as a combination of the effluent flux limit (E_{max}) and the limit concentration (P-W).

Necessity of Remediation

The guideline does not contain intervention values. Remediation is rather triggered by the residual contaminant levels that have been adopted as remediation objectives for a specific site.

The decision concerning the remediation objectives is made by the assessment committee of each county (KommissionsVO, 1990). The committee consists of specialists of the relevant branches of the public administration including one representative of the state environmental protection agency. It is headed by an officer of the county magistrate.

Remediation of a contaminated site is necessary, if the concentration of at least one contaminant surpasses the remediation objective set by the committee. Therefore, the remediation objectives have to be set first and compared with the actual state of the site.

Site Demarcation

In the case of **level-2 remediations** (P-W values as objectives), a contour line of a slightly higher concentration can function as the "practical" boundary of the area that is to be remedied. This possibility exists for the resource groundwater (case a) only, and the demarcation of the zone to be remedied can be done with the aid of the P_{max}-W values. The P_{max}-W values are based on the same scenario as the P-W values (i.e. lifelong consumption of 2L/d by a person weighing 60 kg) but pose a slightly increased toxicological risk.

The P_{max}-W values were derived by combining toxicological criteria (*such as acute toxicity without a safety factor* ***and*** *the tolerable daily intake [TDI] which does contain a margin of safety large enough to allow lifetime exposure under worst case conditions*) with the risk index system that is used for ranking sites and for deriving the resulting need of action (*Hillmert, 1990; UM B-W, 1988. The procedure is explained in detail in a previous publication: v.d. Trenck et al., 1993*). The decision about the extent of the use of the P_{max}-margin is based on a qualitative appreciation of the relevant case-specific details.

For instance, in case of a sharply confined contamination nothing is gained by making use of the P_{max}-margin. In such a case the amount of material that has to be treated will not decrease significantly by using P_{max}-W instead of P-W as the boundary of the area that is to be remedied. But with a more diffuse contamination that is slowly tapering off into the surrounding area, it may make a great difference in cost to tolerate a ring of slightly contaminated material around the center that is to be cleaned up.

A more extensive presentation of the guideline in English has been submitted for publication (*v.d. Trenck et al., 1994*).

2. Example for the Groundwater Pathway

A fictitious example that somewhat resembles the "Deventer Handelskade" project (*Grinwis, 1993; TAUW, 1993*) is used to illustrate the functioning of the directive. The Deventer example was chosen because it provides a basis for direct comparison of the Dutch regulations with those in Baden-Württemberg. It is hoped that this comparison will spur a fruitful discussion at the present HCH-FORUM.

A pesticide factory caused a massive soil and groundwater contamination with waste products of gamma-HCH that may have been buried or dumped on the site. The core of the contamination extends 6 m down into the soil and the uppermost (freatic) groundwater layer with a mean HCH concentration of 880 µg/L water. The groundwater table is at 3 m below the surface. The freatic zone consists of sand and clay intermittent. The pore-water of this zone is not considered as usable groundwater. Its flow is directed downward. A water-bearing layer follows from 6 m to 30 m with groundwater moving at 0.2 m/d towards the river Ijssel. The water of this layer is polluted with approximately 40 µg HCH/L. The hydrogeological situation of the site can be described as:

- no horizontal flow through the contaminated core ($Q_1 = 0$ m^3/d),
- a horizontal flow underneath the contaminated material ($Q_2 = 270$ m^3/d),
- and a formation of new groundwater on the site of $Q_3 = 12$ m^3/d.

It is assumed that feasibility and environmental balance dictate a groundwater remediation on level 3 for this site. Under these conditions three alternative remediation objectives are derived for groundwater:

1) The permissible effluent concentration can be calculated from the tabulated values for HCH (P-W = 0.1 µg/L and $E_{max} = 0.2$ g/d). The **concentration limit** yields **2.4 µg HCH/L**, and the flux limit 17 µg/L. The concentration limit is stricter and therefore overrides the flux limit.

2) The same site located in the upper Rhine valley with a groundwater velocity of 3 m/d would be characterized by a much larger flow rate underneath the site ($Q_2' = 4032$ m^3/d). As a consequence the permissible concentration of the effluent would increase to 34 µg/L, and the **flux limit of 17 µg HCH/L** would become overriding.

3) Isolation Option
If the surface is sealed by a layer of asphalt, almost no new groundwater is

formed on the site. A small residual flow through the contaminated material (Q_3' = 0.1 m^3/d) remains in the freatic zone via lateral infiltration from the canal ("gracht") nearby. This decrease in flow through the polluted core increases the permissible concentration of the effluent:
Based on the flux limit 2000 µg/L would be allowed, but as a result of the limit of 0.1 µg/L (P-W) for the final concentration the effluent concentration must be kept below **270 µg HCH/L.**

A 100fold reduction of the flow rate Q_3 in option 3 compared with case 1 thus yields a 100fold higher permissible effluent concentration.

3. Conclusion

The State Waste Act of Baden-Württemberg (*LAbfG, 1990*) defines the remediation objective as a condition of the environment that is in accordance with the public welfare. The German Federal Water Act (*WHG, 1986*) declares the maintenance of water quality as one element of the public welfare. Any introduction of substances into the groundwater may therefore interfere with the public welfare, and no harmful pollution of the groundwater may be granted.

The guide values directive introduced by Baden-Württemberg is an attempt at translating these laws into numerical contaminant concentrations taking into account general requirements such as background values and health criteria as well as local conditions. Care must be taken to balance different aspects of public welfare. The guideline is the only directive of its kind in the world that regulates both concentrations and fluxes of contaminants into groundwater, and thus places special emphasis on the protection of large aquifers.

The example demonstrates the effects of changes of the site conditions on the permissible HCH concentrations of the effluent discharged into the groundwater.

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Abbreviations

E = effluent flux

E_{max} = effluent flux limit

H-B (Hintergrundwert für Boden) = background level in soil

H-W (Hintergrundwert für Grundwasser und Bodeneluate) = background level in groundwater or leachate

P (Prüfwert) = assessment value

P-M (Prüfwert für den Aufenthalt von Menschen auf kontaminierten Flächen)
= soil assessment level for humans

P-M1 (Prüfwert für Kinderspielplätze) = soil assessment level based on the playground scenario

P-M2 (Prüfwert für Wohngebiete) = soil assessment level based on the residential area scenario

P-M3 (Prüfwert für Industrie- und Gewerbeflächen) = soil assessment level based on the industrial area scenario

P-P (Bodenprüfwert im Hinblick auf Wachstum und Qualität von Pflanzen)
= soil assessment level for plants

P-W (Prüfwert für Grundwasser und Bodeneluate) = assessment level for groundwater and leachate

P_{max}-W (Toleranzgrenze des P-W-Wertes für die Abgenzung des zu sanierenden Bereiches auf Stufe 2)
= maximal leachate concentration for site demarcation on level 2

TDI = tolerable daily intake as defined by WHO (1993)

VSD = virtually safe dose of initiating carcinogens (Klaassen, 1986)

Appendix

Table of Guide Values

Appendix 1

Substance		Guide Values (UM & SM B-W, 1993)							
		Leachate/Groundwater			Soil				Maximal Flux of Effluents
		H-W µg/l	P-W µg/l	P_{max}-W µg/l	H-B mg/kg	P-P mg/kg	P-M mg/kg		E_{max}-W g/d
Al	aluminum	100	150	750	-[6]	-[6]	P-M1 P-M2 P-M3	-[6, 10] -[6, 10] -[6, 10]	320
As	arsenic	3	10	25	6 - 17[1]	20 (pH≥5, T1[1]) 40 (pH≥5, T2-T6[1])	P-M1 P-M2 P-M3	20[11] 30 130	22
Cd	cadmium	1	3	8	0.2-1.0[1]	1 (T1[1]) 1 (5≤pH≤6) 1.5 (pH≥6, T2-T6[1])	P-M1 P-M2 P-M3	3 15 60	6.5
Cr	chromium (total)	2	40	200	20 - 90[1]	100 (pH≥5)	P-M1 P-M2 P-M3	100 500 -[4]	90
Cr(VI)	chromium (hexavalent)	0.4	8	30	1	-[7]	P-M1 P-M2 P-M3	-[4] -[4] -[4]	18
Cu	copper	5	100	250	10 - 60[1]	60 (pH≥5)	P-M1 P-M2 P-M3	-[3], [10] -[3], [10] -[3], [10]	220
Hg	mercury	0.05	0.7	2	0.05 - 0.2[1]	1 (pH≥5)	P-M1 P-M2 P-M3	2 10 40	1.5
Ni	nickel	3	20	75	15 - 100[1]	50 (pH≥5)	P-M1 P-M2 P-M3	100[11] 100[11] 300	45
Pb	lead	4	10	40	25 - 55[1]	100 (pH≥5)	P-M1 P-M2 P-M3	100 500 4000	20
Se	selenium	4	8	25	1	-[7]	P-M1 P-M2 P-M3	-[7] -[7] -[7]	17.5
Sn	tin	2	10	50	4 - 20[1]	50	P-M1 P-M2 P-M3	-[3], [10] -[3], [10] -[3], [10]	20
Tl	thallium	3	8	25	0.2 - 0.7[1]	0.5 (pH≥5; T1[1]) 1.0 (pH≥5; T2-T6[1])	P-M1 P-M2 P-M3	1[11] 4 15	17.5
Zn	zinc	150	1500	3400	35 - 150[1]	150 (T1[1]) 150 (5≤pH<6;T1-T6[1]) 200 (pH≥6;T2-T6[1])	P-M1 P-M2 P-M3	-[3], [10] -[3], [10] -[3], [10]	3200
CN^-	cyanide (total)	0.2 or n.d.	40	80	n.d.	-[7]	P-M1 P-M2 P-M3	50[16] 150[16] 150[16]	85
F^-	fluoride	250	750	1750	150	250	P-M1 P-M2 P-M3	750 3750 15000	1600
NH_4^+	ammonium	100	500	1600	-[6]	-[6]	P-M1 P-M2 P-M3	-[6]	1100
Total AH[9]	usually benzene, toluene, xylene, ethylbenzene	n.d.	10	50	0.01	-[7]	P-M1 P-M2 P-M3	60[15] 60[15] 60[15]	20
Benzene[9]		n.d.	1	5	0.01		P-M1 P-M2 P-M3	0.01[13] 0.01[13] 0.01[13]	2

Appendix 2

Substance		Guide Values (UM & SM B-W, 1993)						
		Leachate/Groundwater			Soil			Maximal Flux of Effluents
		H-W µg/l	P-W µg/l	P_{max}-W µg/l	H-B mg/kg	P-P mg/kg	P-M mg/kg	E_{max}-W g/d
toluene[9]					0.01	-[7]	P-M1 9 P-M2 9 P-M3 9	
VCH [9]	volatile chlorinated hydrocarbons	0.1 or n.d.	10	50	0.001	-[7]	P-M1 0.2 P-M2 0.2 P-M3 0.2	20
VCH (carc.) [9]	CCl_4; 1,2-dichloroethane, vinyl chloride (sum)	0.1 or n.d.	3	10	0.001 or n.d.	-[7]	P-M1 0.001 [14] P-M2 0.001 [14] P-M3 0.001 [14]	6.5
CHCl etc. [A1] [5] [9]	chloroform etc., boiling below 65°C	0.1 or n.d.	10	40	0.005 or n.d.	-[7]	P-M1 0.02 [17] P-M2 0.02 [17] P-M3 0.02 [17]	
HCH (total)	hexachlorocyclohexane	n.d.	0.1	1	0.004	0.1	1 15 (betaHCH: 2) 2 -[3] 3 -[3]	0.2
HC (IR)	hydrocarbons, mineral oil	10 [A2]	50 [A2]	300	50/100 [12]	400	P-M1 - P-M2 - P-M3 -	100
Naph.	naphthalene	0.05	2 [A2]	10	0.05	-[7]	P-M1 -[7] P-M2 -[7] P-M3 -[7]	4.5
PAH	EPA-PAH without naphthalene [A3]	0.05	0.15	0.8	1.0	10	P-M1 5 (BaP: 0.5) P-M2 25 (BaP: 2.5) P-M3 100 (BaP: 10)	0.32
PCB (LAGA)	polychlor.biphenyls (sum or LAGA = DIN x 5)	n.d.	0.05	0.5	0.05	1.5	P-M1 3 P-M2 -[3] P-M3 -[3]	0.1
PCDD/F	dioxins and furans as 10^{-6} ITE	n.d.	5	15	2	5	P-M1 cf. P-M2 dioxine P-M3 directive	10
PCP	pentachlorophenol	n.d	0.1	0.5	0.004	0.2	P-M1 9 P-M2 -[3] P-M3 -[3]	0.2
Pesticides	without PCP and HCH	n.d.	0.1	1	0.03	0.2	P-M1 -[7] P-M2 -[7] P-M3 -[7]	0.2
Phenols (volatile with water vapor)		10	30 [A2]	100	0.02	-[7]	P-M1 -[7] P-M2 -[7] P-M3 -[7]	65

[A1] Abbreviation designates chloroform, dichloromethane, 1,1-dichloroethene as well as cis- and trans-dichloroethene.

[A2] The assessment level is considered to be exceeded as soon as the substance is sensually perceptible.

[A3] In leachates obtained in vitro from soil or other material contaminated with PAH, part of the contamination may absorb onto lab ware and escape the determination. Therefore, such results should be confirmed by backcalculating groundwater samples or by comparison with leachates formed in situ.

[1] According to the clay content (T1-T6) or the indigenous mineral (cf. directive referring to § 19 chpt. 3 BodSchG, 1991).

[2] pH: pH-value according to DIN 19684, Part 1.

[3] Case by case decision; in spite of the low toxic potential for humans higher levels cannot generally be tolerated because of ecotoxicological relevance.

[4] Case by case decision; consider possible exposure to dust containing carcinogenic Cr(VI)!

[5] This parameter comprises chloroform, dichloromethane, 1,1-dichloroethene as well as cis- and trans-1,2-dichloroethene.

[6] The total soil concentration is not relevant in contaminated sites; the H-W- and P-W-values have to be observed.

[7] Case by case decision.

[8] For anthropogenic substances the practical quantitation level is given as H-B-value.

[9] For volatile contaminants (e.g., aromatic or chlorinated hydrocarbons) the guide combined analysis is allowable only within maximal steps of one meter of the depth profile (UM & SM B-W, 1993, Appendix 3.3).

[10] Toxic for humans only in concentrations of g/kg.

[11] The theoretical value [mg/kg] for As = 6.4, Ni = 15 or 75, respectively, Tl = 0.75 is within the geogenic background of soils in Baden-Württemberg. The table contains the upper rounded background concentration as P-value. According to current knowledge these soil concentrations have not led to elevated burdens in humans.

[12] In upper soil layers with > 1% organic carbon content.

[13] The practical quantitation level is given as P-value.

[14] The value corresponds to the practical quantitation level for CCl_4. It is not attainable for the other substances.
In case of suspected soil contaminations with these substances a special investigation (e.g. soil air content) is advisable.

[15] All the guide values for benzene and toluene and the total AH-value have to be observed.

[16] The acute toxicity dominates the assessment level for cyanide; pica behavior with 10 g single soil ingestion is considered. The P-M1 value is based on 10% of the LOEL of 0.5 mg/kg and 10 kg body weight. The P-M2 and P-M3 values are based on 10% of the LD50 of 1 mg/kg and 15 kg body weight.

Problems arising with pesticides use in Belarus

Dr. Vilor Samersow
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PROBLEMS ARISING IN THE USE OF PESTICIDES IN BELARUS

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Presented by: Mr. Vilor Samersov

The natural and climatic conditions of the Republic of Belarus are favourable for the development of 65 species of pests, 100 types of diseases and 40 species of weeds. The potential agricultural yield losses due to the absence of effective protection is about 25 - 30%.
To avoid yield losses and lower crop quality chemical and biological means of plant protection are widely used in the Republic.
Depending on the phytosanitary situation and the assortment of products used in the course of 1985-1990, over 100 pesticides with a total tonnage of 16-20 ths. tons were used annually, or an average of 3.0 to 3.5 kg per ha of arable land. Judged by tonnage, about 55-60% of these are herbicides; 8-10% insecticides, fungicides and dressers; 20-25% plant growth regulators; 5-7% defoliators and desiccants; 1.5-2% biological preparations.

In connection with the worsening ecological situation in the Republic after the Chernobyl power station accident, a complicated problem arose in relation to the protection of the public health and the surrounding area against the complex negative consequences of radio-activity and plant protection means. According to the level of radio-active contamination, the territory was divided into two zones, for which lists of permissible pesticides were drawn up.
For the first zone with a radiation level of 0-15 curie/km^2, all the products allowed by the Ministry of Health of Belarus to be used on the territory of the Republic were included in the list. For the second zone with a radiation level of 15-40 curie/km^2 the products of group I with regard to the toxicological danger have been excluded from the list, the use of the group II products have been restricted. In this zone the preference is given to the III and IV groups, judged by the toxicological classification of products use.

To control the most harmful species of pests, depending on the phytosanitary situation, controlling measures have to be taken annually, on an acreage of 1.6 mln ha.

For these purposes the following amounts of pesticides were used, yearly and in average:

From 1971 - 1975: 3,630 tons;
from 1976 - 1980: 2,360 tons;
from 1981 - 1985: 2,000 tons;
from 1986 - 1988: 1,450 tons;
from 1989 - 1993: 200 - 250 tons.

Among the range of the insecticides used in agricultural production from 1971 - 1975, the dominating one was hexachlorocyclohexane. This way 2,097 tons of 12% dust-HCH were used on the territory of Belarus in 1974, which made up 57.7% of all pest control insecticides used. The use of DDT on the territory of Belarus was reduced at the beginning of the seventies. In 1970 however, 570 tons of DDT were used in the Republic's agriculture (refer to table 1).

From 1975 onwards, in the course of the last 18 years, there has been a decrease in the agricultural use of products based on the gamma-isomer of HCH, up to its practical cessation in 1993-1994.
At the same time it should be noted that this decrease was accompanied with an increase in the use of chlorinated terpenes and camphenes, which continued during the next 10 - 15 years.

In Belarus there is no production of pesticides, including HCH and other products of the organo-chlorine group.
Consequently, the source of the environmental pollution is the use of HCH and other stable organo-chlorine compounds for agricultural crops, forest and ornamental planting, as well as the storage and dumping of pesticides that have gone out of use.

From 1974 - 1988, the outdated pesticides were mainly buried in so-called "sepulchres" (caves in rock or brick), located in seven regions of Belarus (Brest, Gorodok, Gorets, Verkhne-dvinsk, Slonim, Postav, Petrikov). In the course of this period 3,776 tons of different products were dumped this way.

The frequent, intensive and wide use of HCH and other organo-chlorine compounds (DDT, polychlorpinen, polychlorcamphen) and the residues of the given products have led to a serious and widespread environmental problem.

In 1981-1982, the Research Institute of the Academy of Sciences of Belarus (Lukashev K.N., Budjeko N.N., Nikitin L.B., 1983) conducted geochemical and geophysical research into the effects of the agricultural use of hexane products, DDT and polychlorpinen. The majority of soil and groundwater samples taken from agricultural land and its groundwater, contained residues of HCH and DDT.

The survey of soils conducted by the laboratories of chemical stations of agriculture, controlling the ploughing soils contaminated by the residues of pesticides at an earlier period of time (1974 - 1978) on the acreage of 169.5 thousand ha. showed that about 30% of the samples taken all over Belarus contained residues of DDT and the products of its decomposition and 7% HCH dust in the quantity of 0.01 - 0.2 mg/kg.

Although the HCH and DDT residue content didn't increase in the majority of cases, the highest permissible concentrations determined in Belarus for soil are 0.10 mg/kg for both of these products, and for water 0.02 and 0.10 mg/l respectively. But, taking into account the ability of organo-chlorine insecticides to accumulate in the food chain, the presence of residues and pesticides of this group in water and soil is unwanted.

As mentioned before, besides HCH and DDT, chlorinated terpenes and camphenes were widely used on the territory of Belarus from 1970 to 1985. The product polychlorpinen was in particular widely used during certain years,(1973 - 1976), in a quantity of over 1,200 tons.

Research conducted at the Belorussian Scientific Research Institute of Plant Production showed that polychlorpinen were characterized by a significant persistence in the environmental compartments; it can stay in the soil for over a year, and in case of multiple use on one and the same field it can accumulate and contaminate surface and groundwater. The annual survey of 60 to 65 fields carried out by the State Administration on Hydromethodology and the Control of the Environment, showed that in some cases polychlorpinen with a content value of 0.371 mg/kg were encountered in the soil. This value is below the permissible concentration of 0.5 mg/kg in Belarus. Taking into account the possible danger of soil contamination by polychlorpinen, BelSRIPP conducted research into cleaning up the soil by means of biological detoxication. The application of active strains of the bacteria Serratia marcenscens during a soil clean-up investigation for soil contaminated with polychlorpinen proved to be effective. The activity of the bacteria Bacillus mesentericus and Pseudomonas denetrificans has been noticed as well in this respect.

From the viewpoint of wildlife conservation and the prevention of negative post-effects on agricultural crops, there is also the problem of soil contamination by sim-triazine herbicides, used in the corn mono-culture.

In conclusion we can state that, in the Republic of Belarus, the source of hexachlorcyclohexane and other organo-chlorine compounds contaminations lies in their extensive use during the past 15-20 years, and the dumping of outdated products.

In spite of the limitations imposed upon the use of this group of products and its final cessation (DDT from 1974, PCP from 1985, HCH from 1993), their residues are still found in soil and water. The application of active strains of the bacteria Serratia marcenscens for the clean-up of soil contaminated with the residues of polychlorpinen (chlorten) proved to be very effective.

USE AND ANALYSIS OF THE PESTICIDES IN LITHUANIA: ENVIRONMENTAL ASPECTS

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Presented by: Mrs. Milda-Zita Vosyliene

GENERAL ANALYTICAL SITUATION.

Monitoring, field and model analysis of pesticides in Lithuania is performed by various scientific and governmental organizations, and the main of them are listed below:

1) Lithuanian Agriculture Institute, Voke Branch (Laboratory of Pesticide Analysis) in Vilnius,
2) Central Chemical Laboratories at the Lithuanian Environmental Protection Department in Vilnius and Kaunas,
3) Institutes of Ecology and Geography of Lithuanian Academy of Sciences in Vilnius,
4) Faculty of Nature Sciences of Vilnius University.

PESTICIDES USE IN LITHUANIA

The pesticides in Lithuanian agriculture are used for the protection of the following cultural plants: crop (winter and spring crops), potatoes, flax, mangel and sugar beets, spring and winter rape, corn (maize), vegetables, berry fruit bushes, pasture grass-land.

Table 1 shows most used herbicides in Lithuanian agriculture at present. This information is taken from the recommendations to Lithuanian farmers and reports the herbicides used for crop and beet protection [1].

Two year experience of Lithuanian chemists working in the laboratories of chemical environmental monitoring (i.e. LEPD) revealed that short visits of most foreign specialists are inefficient because of an administrative and general advisory character of arriving staff.

PESTICIDE FATE AND TOXICITY STUDIES IN VILNIUS UNIVERSITY

Analysis of chemical degradation, biodegradation and toxicity of chloraromatic herbicides and their degradation products on microbial cells is carried by the interlaboratory research group of the Department of Biochemistry and Biophysics and Dept. of Botany and Genetics of the Faculty of Nature Sciences, Vilnius University by Dr. Cetkauskaite A.V., Dr. Berzinskiene J.A., D.Sabaliunas and Prof. Lekevicius R. The project is devoted to both fundamental and applied research, i.e. complex characterisation of biodegradation and analysis of toxicity mechanisms of phenylurea herbicides and their degradation products in surface water samples and pure bacterial cultures.

The attempt is being made to carry out a modern research according to satisfactory technical possibilities and understanding requirements of current analysis methods announced in EEC proposals of 1990 on the evaluation and control of environmental risk of existing substances: the requirement for test methods applicable to materials or mixtures of poorly soluble constituents /6/. Understanding the mechanisms and priority sites of action of chloraromatic pollutants in bacterial cells is a basis for the selection of microbiotest methods and characterisation of quantitative structure/activity relationship in ecotoxicology /7/.

The first and second order rate constants have been calculated for acetanilide (propanil, propachlor, etc.) and phenylurea (fen-, mon-, diuron) herbicide biodegradation in surface water samples from the Neris river upstream and downstream Vilnius representing less and more polluted water areas (according to BOD, COD, etc.). Biodegradation of herbicides is analyzed over the concentration range of 1-10 ppm in aerobic conditions. The acetanilide and phenylurea herbicide residues concentration and concentration of their degradation products (aniline, 3,4-dichloraniline, etc.) is measured by HPLC technique.

The main results of biodegradation experiments carried out in 1992-1994 with surface water microflora indicated faster primary biodegradation of acetanilide class herbicides (such as propanil and negligible of such as propachlor /8/), and no significant biodegradation of phenylurea class herbicides.

A comparison of structure/activity correlation or comparison of chloraromatic compounds of one structural class in the non-specific permeabilizing activity on microbial cell membranes and inhibition of enzymes systems is performed in the analysis of the toxicity mechanisms of phenylurea and acetanilide herbicides.

The toxicity of herbicides and/or mixtures of herbicides with their degradation products is analyzed using the bioluminescence quenching test in Photobacterium phosphoreum (Ph.ph.) cells and membrane potential measurements in Ph.ph and Escerichia coli strains. The degree of Photobacterium bioluminescence inhibition by phenylurea herbicides was observed in the following order: fenuron < monuron < diuron < chloroxuron. The results obtained in experiments with Escherichia coli - galactosidase induction confirmed the same order of the inhibitory action of the phenyl urea herbicides. Comparison of these two methods revealed the higher sensitivity of Photobacterium bioluminescence inhibition test compared to the method of E. coli -galactosidase induction. Direct measurement of herbicide effect on bacterial cell membrane was achieved with tetraphenylphosphonium (TPP^+) ion-selective electrode in Photobacterium phosphoreum cell suspension. Results of these measurements indicated an enhancement of Photobacterium cell permeability to TPP^+ ions by phenylurea herbicides in the following order: monuron < diuron < chloroxuron.

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Table 1. The Herbicides Recommended for Protection of Crop, Flax and Potatoes [1,2].

Herbicide, commercial name	Formula & chemical name	Dose, (kg/ha)	
		Active material	Commercial preparation
2,4-D amino salt 40%	Dichlorophenoxy acetic acid	1.0-1.2*	2.5-3.0*
2M-4C1P (MCPP)	2-[(4-Cloro-o-totyl) -oxy]propionic acid		
1) Mecoprop 50% water solution of MCPP		1.0-1.5*	2.0-3.0*
2) Sys-Mecmin 66% water solution of MCPP		1.0-1.5*	1.5-2.3*
2M-4C1P (MCPA) 70% soluble powder or 40% water solution	2-metil,-4-chlorophenoxy acetic acid	1.5-2.0	2.0-2.8
2M-4C1 (MCPB) 80% soluble powder	4-[(4-Cloro-o-tolyl) oxy]-butyric acid	2.5-3.0*	3.0-3.7*
2,4-DS (2,4-DB) 80% soluble powder	4-(2,4-Dichloropheno-xy) butyric acid	2.0-3.0*	2.5-3.7*
Prometrine 50% hygroscopic	2-Methylthio-4,6-bis(isopropylamino-s-triazine	0.6-0.8*	1.2-1.6*
Simazine, 80% hygroscopic powder	2-Chloro-4,6-bis(ethylamino-S-triazine	0.6-0.8*	1.2-1.6*
Granstar 75% purity	Sulfonylurea herbicide	0.020*,****	0.027*,****
Starane (Fluroxipyr)	4-amino-3,5-dichlor-6-fluor-2-p-iridyloxyacetic acid	0.2-0.3*	0.5-0.75*
Basagran (Bentazon) 48% water solution	3-izopropyl-2,1,3-benzotia-diazinon-4,2,2-dioxid	1.5-2.0*	3.0-4.0*
Dialen 40% water solution		0.8-1.0**	2.0-2.5**
Stirine: 50% hygroscopic powder	Simazine, 14% + Prometrrine, 36%	0.7-1.0* 1.0-1.5***	1.4-2.0* 2.0-3.0***
Fiuzilad (Flozifop butyl)	(Mixture of 2 isomers)	0.25-0.4****	2.0-3.0****
Betanal (Burefem, Kemifam) 16% concentr. emulsion		1.0*	6.0*

MIXTURES OF HERBICIDES

	0.5+2.0*	0.7+2.5*
2,4-DS + Basagran	0.5+1.0*	0.7+2.5*
Granstar + Starane	0.01+0.2*	0.013+1.0*
2,4 D amino acid + Lontrel	1.0+0.2*	1.4+0.7*
MCPA + Glean	0.6+0.005*	0.9+0.007*
Lontrel 416 C: MCPP + Lontrel 52.5% concentration emulsion	1.0-1.5*	1.9-2.9*
Acetatrine: 30% acetochlor + 20% prometrine	2.0-3.0***	4.0-6.0***

*- crop, **- corn, ***- potatoes, ****- flax

The "Mulde rue problem", a typical example of the middle europian industrial heritage and promises for a temporary remidial

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THE "MULDE-AUE-PROBLEM", A TYPICAL EXAMPLE OF THE MIDDLE EUROPEAN INDUSTRIAL HERITAGE AND PROMISES FOR A TEMPORARY REMIDIAL

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Since the beginning of this century Central Germany - i.e. the area south of Berlin - has developed into one of the most important industrial areas in Europe for the production of chemical products inside Europe.
One of the chemicals produced in the Bitterfeld administrative district which is situated near Dessau in the state of Saxony-Anhalt was Lindane (γ-HCH). As a by-product ß-HCH is generated which amounts to about 70 to 80 percent of the total outcome. Over the years together with insufficiently treated sewage ß-HCH was introduced via ditches into the river Mulde. As a consequence of this long-lasting introduction ß-HCH-isomers accumulated in the sediments of the ditch-system and the river. Furthermore the river Mulde had been permanently polluted by heavy metals and arsenic dating back to century-old ore-mining activities in southern Saxony.
Because of regular floodings of the river Mulde the sediments were whirled up and subsequently contaminated the fields and pastures in the surroundings of the river Mulde inside the Bitterfeld administrative district and the city of Dessau. The total area affected measures approximately 2000 ha of which 500 must be considered as dangerously contaminated.
Already under the former east German government the pollution of the river Mulde and the surrounding land were well known but any information about the actual extent of the contamination was limited to a select group of people. But no remedial actions were taken.

In 1990 - at first sporadically - official tests into the quality of soils, feed and foodstuffs, i.e. meat and milk, were implemented. These tests showed in some areas extremely high results for ß-HCH (e.g. concentration of ß-HCH in samples of plants: n.d. - 1.0 ppm (limit: 0.01 ppm); concentration of ß-HCH in samples of deposits of fats in cows: n.d. - 1.0 ppm (limit: 0.1 ppm); concentration of ß-HCH in samples of deposits of fats in sheep: 0.3 ppm - 5 ppm) which already in 1991 sorced the authorities to declare the most polluted areas as unsuitable for agricultural use.

As a result of these effects which were supported by further measures and by means of rigorous food quality controls it became possible to reduce the concentration of ß-HCH in the locally produced milk (1990: n.d. - 0.4 ppm (limit:0.3 ppm); 1994: n.d. - 0.06 ppm (limit: 0.075 ppm)). Milk is generally considered as an extremely sensitive indicator for ß-HCH.

To avoid contaminated meat being marketed as food the relevant authority ordered animals for slaughter to be registered before killing. This enables the authorities to carry out tests for ß-HCH and heavy metals which can be used then as a basis for the relevant ratings.
Since then animal and vegetable foodstuffs as well as feed have been tested continuously.

In order to coordinate all the various jobs related to the problem a special task force was formed inside the administration of the Dessau region which it self is part of the state administration. The team has been performing tests, taking decisions about the further use of contaminated land and has been discussing the disposal of contaminated biomass. Moreover its task has been complicated by the fact that the pastures along the river Mulde are listed as a nature reserve. Some areas even form part of the Mittlere Elbe boisphere reserve.
The team directly answerable to both the ministry of environment and the ministry of agriculture of the state of Saxony-Anhalt.
As consumer protection has always been regarded as vital the state administration of the Dessau region prepared a hazard-preventing-decree on the basis of detectable concentrations of ß-HCH and heavy metals in food and feed. Inside the main dyke system of the river Mulde the decree rules out any use of land for the production of food and feed whereas outside the dyke system only certain areas have been affected by the decree. There agricultural use is either restricted or prohibited.
To ensure a high standard of safety food and feed testing is still being carried out. Today part of the program are also local people growing vegetables and fruits or breeding small animals for their own use.

In the long run the team has to determine the future use and shape of the landscape i.e. the meadows and fields along the river Mulde. As high pollution and long half-lives of the contaminants seem to prevent any agricultural use for years to come the team has been developed plans for:
- a possible reforestation
- the lay-out of succession areas
- a possible reorganisation of land use i.e. the use of former meadows for the cultivation of cereals
- the development and testing of processes to decontaminate farmland.

Looked at in the short term decisions must be taken to dispose of contaminated biomass and how to manage the future maintenance of disused farmland.
At the moment there are plans to cut the grass twice a year and leave it lying around on the meadows. But this can only be regarded as a temporary solution. Some areas will require intensive attention and removal of cut grass. Furthermore considering the preservation of plants typical for the area it will be necessary to observe the meadows and fields permanently.

In order to protect the river Mulde from further contamination the causes for the occurrence of contaminants will have to be removed. This means that the ditch system of the once huge state-run but now nearly defunct chemical plants will have to be cleared from sediments which otherwise would be spread over the pastures in the course of the annual floodings. In 1995 the opening of a new sewage plant in Bitterfeld will mark a further improvement for the quality of water.

A lot of time is still needed to find a comprehensive solution for the topic of contaminated pastures along the river Mulde. Apart from economical and ecological aspects financial considerations are vital.