Working Paper

Emissions and Distribution of Hexachlorocyclohexanes in the Rhine Basin Area in the 1980s and Prognoses for 1990-2020

Anja Verschoor
RIVM, The Netherlands

WP-92-31
April 1992

IIASA International Institute for Applied Systems Analysis □ A-2361 Laxenburg □ Austria
Telephone: +43 2236 715210 □ Telex: 079 137 iiasa a □ Telefax: +43 2236 71313

Emissions and Distribution of Hexachlorocyclohexanes in the Rhine Basin Area in the 1980s and Prognoses for 1990-2020

Anja Verschoor
RIVM, The Netherlands

WP-92-31
April 1992

IIASA International Institute for Applied Systems Analysis ◻ A-2361 Laxenburg ◻ Austria
Telephone: +43 2236 715210 ◻ Telex: 079 137 iiasa a ◻ Telefax: +43 2236 71313

Summary

The Rhine Basin project, a cooperative study between the Dutch RIVM (National Institute of Public Health and Environmental Protection) and IIASA, analyzes sources of chemical pollution of the Rhine Basin in order to find relations between pollution and effects. This report deals with sources and distribution of an agricultural chemical: the pesticide lindane. Currently, more than 90% of the composition of lindane is the γ-isomer of hexachlorocyclohexane (HCH), but in the past other isomers were present in larger amounts. All the isomers of HCHS are treated in this report as one group.

In the 1980s about 300 tons of lindane were applied annually in the Rhine Basin. More than 90% of the use was for cereals, beet and maize. About 3.3% was applied to forest soils. Atmospheric deposition is substantial (4.8%). About 23 tons of HCH accumulates in the soil, and another 26 tons in surface waters. Volatilization and biodegradation in the soil are important processes that determine the fate of HCHs.

The effects of four scenarios on future HCH accumulation, erosion and emission to surface waters have been determined. Emissions to surface waters react relatively quickly to changes in lindane use. Levels of lindane in soils and the atmosphere react more slowly to changes in lindane use. A 10% reduction in pesticide use does not affect emissions or accumulation significantly compared with unchanged pesticide use. Prohibition or a voluntary replacement of lindane by alternatives cause a considerable decrease in emissions to surface waters and accumulation in soils. However, even after a prohibition of lindane it has been calculated that it will take more than 4000 years to remove all the lindane residues from the soil.

Contents

Appendices

1 Introduction

As long as civilizations have existed rights to the use of rivers have been a source of human conflict. Rivers function as transport routes, sources of energy and drinking, irrigation and cooling waters, and often as public sewers. With increasing population levels and industrial activities, rivers could not serve all these functions satisfactorily. Laws and regulations were made to protect the use of rivers by groups with opposing interests. Many times the cooperation of different nations was required, which delayed effective regulations. Often rivers became severely polluted owing to activities perceived as essential for the economic well being of populations residing in the rivers' basins.

For example, the Rhine river, flowing through parts of Austria, Switzerland, France, Germany, Luxembourg and the Netherlands, provides drinking water for 20 million people (Friedrich and Müller, 1984). Because of the convenience of transport over the river and the availability of large amounts of water required for various industrial activites, all sorts of industries settled along the Rhine. Moreover, because soils in the basin are quite fertile, intensive agriculture has been a long-standing activity. Today the Rhine Basin is one of the most densely populated areas in the world. All these factors have resulted in an enormous level of pollution of the Rhine (sometimes called the sewer of Europe or Europes cloaca). This pollution has caused numerous deleterious effects on the ecosystem of the river. For example, many fish species indigenous to the Rhine have disappeared, including salmon that were once plentiful.

The species that have survived are dangerous for human consumption owing to high concentrations of toxic chemicals in their edible tissue. Since the environmental awareness in the 1960s, agreements have been made concerning the control of emissions of polluting chemicals into the Rhine:

1963 Berne Convention: Setting up the International Commission for Protection of the Rhine against Pollution;
1972 Chloride Agreement between France, Switzerland, West Germany and the Netherlands;
1976 The First Bonn Convention under the auspices of the Protection of the Rhine against Pollution;
1976 Rhine–Chemistry Agreement of Neighboring States;
1979 The Second Bonn Convention under the auspices of the Protection of the Rhine against Pollution.

A big disadvantage of these international environmental agreements is that the will to limit emissions only exists if the environmental problems are visible and proven to be caused by a particular activity. Generally, a long period of negotiation will follow any agreed upon action, with the country benefiting the most from the existing situation trying to delay the agreement. Finally, after the implementation of the action plan, the improvement of the environmental situation is often slower than expected. Sometimes the environmental quality even continues to deteriorate although emissions have stopped.

For this reason the RIVM/IIASA Rhine Basin Project has undertaken a study of the linkages between the sources of chemical pollution of the basin and related ecological efforts. This project already resulted in a historical reconstruction of emission factors for cadmium (Elgersma, Anderberg & Stigliani, 1991). Reports on other heavy metals such as lead and zinc, fertilizers N and P and organic chemicals such as PCBs and HCHs will follow.

The results described herein pertain to the hexachlorocyclohexanes (HCHs). γ-HCH or lindane is an interesting example because it is typical of numerous agrochemicals applied on a diffuse scale and subsequently ending up in all environmental compartments of the basin. There are no direct sources of HCHs to the river. Rather, they enter the surface waters indirectly by dispersion and transport in the environment.

The contribution of several sources of lindane is quantified in Chapter 3. In order to quantify the emissions in a river basin, the following questions have been used as a guide:

1) What are the uses of the pollutant?
2) Who are the producers and users and how much do they apply?
3) What are the possible pathways for the pollutant to enter the river basin and how are they transported within it?

The following sources of information provided data for the analysis:

1) National governments: national import, export and production data.
2) Regional authorities: monitoring data and land use.
3) Companies: production data, recommended application dose
4) Scientific literature: environmental processes, degradability, volatilization, adsorption and accumulation.

In some respects rough estimations had to be made because insufficient data were available. For example:

- The application rates of lindane on certain crops, which were known for the Netherlands, have been used for the other Rhine Basin countries as well.
- The amount of households connected with sewage treatment plants, which was known for West Germany, has been applied for the other countries also.
- The catchment area of the Rhine in the Netherlands and Austria was estimated visually with a European map 1:4,000,000. Surface area of France and West Germany in the Rhine basin were calculated on the "Department" or "Kreise" level. This method gives a more reliable estimate. The Rhine catchment area of Switzerland was mentioned in the literature (Bundesamt für Statistik, 1982).

As far as possible an historical reconstruction of emissions by several sources has been made for the period 1950–1990 and prediction for HCH emissions for the period 1990–2010 (Chapter 5) have been made with different scenarios:

1) Use of HCHs does not change over the period 1990–2010.
2) Use of HCHs will be prohibited in 1995.
3) Lindane is replaced by alternative pesticides.
4) A reduction of agricultural areas will take place.

In this report HCHs are treated as one group. Based on the available data it was impossible to distinguish between the isomers. Despite the poor availability of data on HCH use, this report gives a rough estimation of the contribution of several sources. Besides, this study can be used as a framework for further studies on pesticides. The estimation can easily be improved if more information becomes available.

2 Hexachlorocyclohexanes

HCH, a man-made organo-chlorine compound has eight stereoisomers. The γ-isomer, also called lindane, is used as an insecticide. The other isomers (α, β, δ, ε, ζ, η, θ) are formed during the production of lindane. The older name for HCH, still used in English literature, is benzenehexachloride (BHC). Lindane is sometimes referred to as gammaxane. In Appendix 6 a list of commercial names of lindane-containing pesticides is given, for tracing data about pesticide use, and calculating active ingredients.

During the usual production processes five isomers are formed. In the environment only α, β- and γ-HCH are found. In the past, the raw reaction product containing 65% α-HCH, 8% β-HCH, 15% γ-HCH, 9% δ-HCH and 3% ε-HCH was used directly in pesticide formulations. Nowadays in most countries only the use of lindane (>99% γ-HCH) is permitted.

Although not as persistent and accumulative as DDT and PCB, there is a growing concern about the use of lindane. Because of its high volatility it has been transported over large distances via the atmosphere; HCHs have been found in plant and animal tissues in very remote areas. In addition, γ-HCH has been discovered in mothers' milk.

In Appendix 5 relevant physical chemical and biological properties are listed. HCHs are quite persistent: halflife in aerobic soil environments have been reported between 88 and 135 days. HCHs have a high adsorption capacity, which implies that the risk of leaching to groundwater is not very high. In the water environmnent it results in binding to particulate organic matter or sediments.

3 The Contribution of Different Sources to the Pollution of the Rhine River with HCHs

3.1 Industries

Industries act as consumers when they use chemicals to support their activities (cleaning agents, carriers, solvents, machines, equipment). If the chemical is a constituent of the final product, the industries are referred to as manufacturers. Furthermore a distinction between primary and secondary producers can be made, the former producing the chemical as a major product, the latter producing it as a by-product.

Their emissions can end up in the river by several pathways:

- effluents from sewage treatment plants;
- direct accidental or deliberate dumps into the river;
- spills directly into the river;
- spills leached through the soil;
- storage in soil (leaching and run-off);
- replacement, weathering or corrosion;
- deposition of atmospheric emissions.

3.1.1 Primary and Secondary Industries

HCHs were first produced in 1942 in France and England. At present there are still four HCH-producing industries in the Rhine Basin countries. Of these, only Shell Agrar GmbH & Co Kg in Ingelheim, Germany is in the catchment area of the Rhine. Except in cases of accidents, direct emissions by primary producers can be neglected because it is very profitable for the producer to prevent losses of his primary product. The HCH-producing industries are listed below:

West Germany:
  BASF Aktiengesellschaft, Ludwigshafen (SRI, 1978)
  Celamerck GmbH&Co Kg., Ingelheim, Rheinland-Pfalz (SRI,1978, 1982 and 1986)
  Shell AgrarGmbH&Co Kg, Ingelheim, Rheinland-Pfalz (SRI, 1990)
France:
  Rhône-Poulenc Agro SA, Le Pont de Claix, Isère (SRI, 1990)
  Saint Auban, Alpes-de Hautes-Provence (SRI, 1982 and 1986)
  Rhône Poulenc Chimie, Basic Chemicals Division, Le Pont de Claix, Isère (SRI, 1990)
  SARPAP SA, Gardonne, Dordogne (SRI, 1986 and 1990)
  PCUK, Produits Chimiques Ugine Kuhlmann SA, Halogen Division, Jarrie, Isère
Austria:
  Chemie Linz AG, Linz (SRI, 1986 and 1990)
The Netherlands:
  until 1952: DAGRA, Bunschoten
  until 1954: CT Stork Chemical Industries Ltd, Hengelo

It is very difficult to find production statistics specific only to HCHs. Usually they are included in aggregated pesticide production statistics, which are too general for this investigation. Better estimates of HCH-emissions to the environment are obtained if sales statistics are used. But also these data are often only available under the header pesticides. In Table 3.1 the available production statistics are assembled.

3.1.2 Manufacturers

Although there are currently four primary producers of lindane in the basin countries, about 100 formulation plants exist in Western Europe (de Bruin, 1979, cited by Slooff & Matthijsen, 1988). Import and sales of lindane by pesticide formulation industries in the Netherlands are given in Table 3.2. By comparing

TABLE 3.1. Production statistics of HCHs.
a. Commercial grade
1. Source: Ministre de la qualité de la vie, 1974.
2. Source: Elskens, 1979.
3. Source: Slooff and Matthijsen, 1988.

	Production of HCHs (ktons)		
Year	FRANCE	WEST GERMANY	AUSTRIA
1972 (1)	2.2 (a) 1.0 export		
1977 (3)	28 HCH-> 3 lindane	15 HCH-> 1.5 lindane	1 HCH -> 0.1 lindane
1979 (2)	36 HCH->4.8 lindane, export 50%		

TABLE 3.2. Import and sales statistics of lindane in the Netherlands 1974-1985.
Source: Slooff & Matthijsen, 1988

Year		Sales	
ton lindane	Import	CBS[1]	NEFYTO[2]
1974			19
1975			21
1976			25
1977			24
1978	205	41	
1979	201	40	
1980	155	31	
1981	181	36	
1982	86	17	
1983	120	24	
1984	106	21	27
1985			28.5

[1] CBS = Central Bureau voor de Statistiek (The Dutch Central Bureau of Statistics).
[2] NEFYTOM = Nederlands Stichting voor Fytofarmacy (The Dutch Association of Phytopharmaceutical Industries).

import and sales statistics one can conclude that approximately 20% is applied in the Netherlands itself. The sales statistics obtained from two sources are not exactly the same. However more important for emission calculations is the trend in sales over a longer time scale (1974–1985). They serve as a check on the reliability of the calculated applied amounts of lindane in agriculture.

About 0.1% of the HCH will reach the water at the formulating plant. The manufacturers control their emission by adsorption methods and filters, so pollution of surface water is negligible. The solid wastes and contaminated packages are usually incinerated at high temperature (Slooff & Matthijsen, 1988).

3.2 Agriculture

Agriculture contributes to emission by the application of pesticides which can end up in the river basin by surface run-off (water-erosion), leaching and atmospheric deposition.

Pesticides, especially the older ones, have a broad spectrum of action. Often several formulations have been used, sometimes in a mixture with other pesticides. In order to quantify the contribution of pesticide application in the river basin the following data have to be traced or estimated:

- Type of crops treated with the pesticide;
- The chance that the pesticide will be applied on the crop (are there alternative treatments or pesticides used);
- Acres of crops in the river basin area;
- Use per crop;
- The soil types in the area under investigation;
- Climatic data (precipitation, temperatures);
- Biological (biodegradability, bioaccumulation) and physico/chemical (solubility, adsorptivity, volatility, photodegradability) properties of the pesticide.

Local high contamination levels can occur through careless rinsing of pesticide spraying equipment and empty containers, and through discharge of sheep-dips (in order to kill parasites in the skin and wool, sheep are dipped lindane-baths) and crop treatment plunge baths.

Lindane is used as an insecticide on many crops. Application of lindane is dependent on whether there is a plant disease and whether there are alternative treatments. Those two factors are included under "chance of application". A list of crops which might recieve lindane treatments and the chances of application are listed in Table 3.3.

Lindane is mainly used as a seed protectant for maize and beet, for which about 0.5-1 kg a.i./ha (active ingredient = lindane) are used (Elskens, 1979). The average application to soil grown with maize is 612-735 g/ha (Slooff & Matthijsen, 1988).

The following estimates have been based on an average dosage of 0.67 kg a.i./ha for cereals, beet, and maize, and application on probability of 0.1 for both cereals and beet, and 0.075 for maize. Calculations for roses and tulips and based on Table 3.4. Trends in lindane use are thus only due to changes in land use.

TABLE 3.3. Crops, maximum dose and chance of lindane application (Van den Berg *et al.*, 1990).

Crop	Max. dose (kg a.i./ha)	Chance of application
Beet	1.1	0.1
Maize	0.4	0.05–0.1
Forest	1.4	0.006
Roses	1.4	0.002
Conifers	0.2	0.002
Conifers	1.4	0.004
Gladiool	1.4	0.03
Tulip	1.4	0.1
Lely	1.4	0.1

TABLE 3.4. Application (tons) of lindane on several agricultural crops. Databases: CROP19XX.WK1, FLOWERS.WK1, AGRI87.WK1 (flop:GERMANY\HCH), AREA.WK1 (flop:FRANCE\HCH). Source: Menke, 1988.

Country	Year	Cereals	Beet	Maize	Tulips $x10^{-3}$	Roses $x10^{-3}$
West Germany	1972				10	0.3
	1975				10	0.3
	1976	142	109	9		
	1978				8	0.3
	1981				10	0.3
	1984				4	0.3
	1985	134	9	17		
	1987	130	9	17		
The Netherlands	1985	33	2	6		
France	1988	44	13			
Switzerland	1975	9	2	1		
	1980	9	3	1		

Because of the large surface area devoted to cereal production, it receives the largest share of HCHs. There is uncertainty, however, as to whether all types of grains receive the same level of application of lindane. Because of the lack of grain-specific data, it was assumed in this analysis that lindane application is applied equally to all types. Cereal areas for Germany are the sum of areas of summer and winter wheat, summer and winter barley, rye, oats, mixed winter corn and corn. French statistics present cereal area without any disaggregation.

During the use of lindane against ecto-parasites and for sheep-dips, an emission of 30% to the soil occurs by dripping. In the Netherlands 2.0 tons a.i. is used for these purposes, resulting in an emission to the soil of 0.6 tons/year. An unknown part evaporates (Slooff & Matthijsen, 1988).

TABLE 3.5. Estimated dripping of HCH for veterinary applications. Sources: Bundesamt für Statistik, 1981; Statistisches Bundesamt, 1991;INSEE, 1989. Databases: LIVESTOC.WK1 (flop: GERMANY\HCH), AREAFR.WK1 and AREASW.WK1 (flop: FRANCE\HCH).

	% of livestock in Rhine basin	livestock*1000		HCH dripped to soil in Rhine basin (ton)	
		1980	1988	1980	1988
West Germany	37.7	39233	39087	0.40	0.40
The Netherlands	50.0	24291	19955	0.33	0.27
France	3.3	50153	43114	0.04	0.04
Belgium/ Luxembourg	8.8	8350	9596	0.02	0.02
Switzerland	89.0	4647[1]	4256[2]	0.11	0.10
Sum		126674	116008	1.01	0.87

[1] Data 1978.

[2] Extrapolated with average decrease in livestock in the other countries.

Based on the extent of the livestock and the percentage of the lifestock in the Rhine basin, HCH dripping is estimated by assuming 0.6 ton dripping/22123*10^3 livestock (extrapolation 1980–1984 data the Netherlands). Included in livestock are horses, cattle, pigs, sheep and goats. The results are listed in Table 3.5.

3.3 Households

The bulk of municipal waste ends up in sewage treatment plants, incinerators or landfills. Households also use pesticides in their homes and gardens. These pesticides enter the soil and the air and finally can cause an emission to rivers. Households are consumers of all types of solvents, paints, cleaning agents, oils etc., most of which formerly ended up in the sewer. Since the end of the 1980s efforts have been made to collect these small amounts of chemical wastes separately. Because the collection system, however, is not yet totally efficient and the public is not well enough informed, a large amount of the chemicals still ends up in the sewer or the dustbin. Although much of the contamination is removed in sewage treatment plants, one has to consider that a part of the households is not connected to such plants, and waste waters from these sources may directly discharge into surface waters. In the Rhine Basin there has been a rapid development of sewage treatment. Currently, perhaps only 10% of the population is unconnected. The contribution of sewage treatment plants to HCH emissions is described in section 3.4.

HCHs are used againts insects in house and garden, and for wood control. In West Germany owners of ***allotment gardens*** have been interviewed about their pesticide use (Neitzel, 1987). Ninety-four percent of the plant diseases in the garden are treated however in a mechanical way or with old household remedies (beer, stinging nettle extracts, etc.). About 6% of the plant diseases are treated with synthetic pesticides. The results of that research suggest that lindane-containing products have not been used for pests in fruits or vegetables. Commercial names of lindane containing products used in allotment gardens in West Germany are listed in Appendix 7. An average application of 0.16–2.25 kg a.i./ha treated surface is used, the chance of application is assumed to be $1.8x10^{-3}$, and the fraction of the allotment gardens grown with roses or summer flowers is 0.29. The average application of lindane containing products is thus $1.93x10^{-4}$ kg a.i./ha (Raw data in Appendix 8).

Data of the Umweltbundesamt (1989) show that the surface area of allotment gardens is dependent on the amount of inhabitants in a settlement. The number of settlements in certain size categories is listed by the Statistisches Bundesamt (1986). Assuming equal distribution of land between the settlements enables us to calculate the surface area of allotment gardens in West Germany (database: GARDEN.WK1 flop:GERMANY\HCH). Thus the total surface area of allotment gardens in the Rhine basin area is estimated at 464043 ha. This results in lindane usage of 90 kg.

TABLE 3.6. Lindane use (kg) in allotment gardens in the Rhine basin area. (Database: GARDEN.WK1 (flop:GERMANY\HCH) and VIEWEMIS.WK1)

Country	Lindane use (kg)
West Germany	90.0
The Netherlands	19.2
France	9.8
Luxembourg	0.7
Switzerland	15.3
Austria	1.0
SUM	121.2

Because data for the other basin countries are absent, pesticide use in allotment gardens is related to the population in the Rhine basin area. Population data are given in Appendix 2. Table 3.6 gives the result of this estimations.

3.4 Municipal sources

Energy use, communication and environmental care are usually organized by (semi) governmental institutions.

The production of *energy* causes emissions of CO, CO_2, NO_x and SO_x. The electricity has to be distributed. Emissions of metals caused by corrosion of high tension wires is also a known source of pollution. Transformers which are used for the distribution of the electricity are cooled by mineral oils, PCB, silicon-oils or other heat transfer chemicals. Although these materials are used in closed systems they have the potential to end up in the environment. For HCH, emissions from this source are unimportant.

Sewage systems can have combined inputs from storm runoff and households/industries, or these sources may be a separately connected. In the recent years industries have increasingly installed their own treatment plants, but before the early 1970s that was certainly not the case. In separate sewage systems there is a direct overflow to surface water in case of heavy rainfall, which can cause episodic high pollution levels. Depending on the technical setup of the treatment plant pollutants are degraded, stripped or adsorbed. After treatment the effluent is discharged to the surface water, and compounds which have not been removed add to the aquifer pollution load. Some persistent chemicals end up in the sewage sludge which is dumped, incinerated or reused as compost, and agricultural fertilizer.

Dumps: Emissions from new dump-sites will be small because in recent years a lot of precautions have been taken to prevent leaching (liners) and run-off (covers) from dumps. Older dumps were not engineered to retain the wastes, and emissions to the ground- and surface waters can be considerable. Besides, in older dumps toxic industrial waste is often mixed with municipal waste (which e.g. was the case in Gouderak, Holland).

Incinerators: Toxic wastes, particularly organic chemicals, may be destroyed at high temperatures. The efficiency of destruction varies. Solid residues, ashes and slags containing heavy metal and toxic organics, must be safely disposed of. Often the slags are used as a foundation material for roads or industrial sites. The ash is used in concrete and bricks. As these materials age and wear, toxic substances may be released, thus posing a threat to ground- and surface waters. The mobility of heavy metals in building materials has been investigated, but the presence and mobility of organic pollutants is yet unknown.

Recycling: Municipal waste can be recycled to compost which is used in gardens and parks to improve the soil structure. In this compost high levels of heavy metals and probably also some persistent organic compounds exist and become distributed in the environment.

Pesticides are not exclusively used by agriculture and households. Also government agencies apply relatively large amounts of these chemicals for the maintainance of parks, railways, canals, road-sides and for pest control. The bulk of the wastes produced by households and industries end up in facilities built to protect the environment against uncontrolled quantities of toxic wastes. Sewage treatment plants, incinerators and dumps are usually run by the authorities whereas recycling is usually a private business.

3.4.1 Sewage Treatment Plants

The purification efficiency for HCHs in sewage treatment plants is 38% (RIZA, 1986, cited by Slooff & Matthijsen, 1988). Domestic waste water in the Netherlands contained 200 kg of HCHs (Feenstra & van der Most, 1985 cited by Slooff & Matthijsen, 1988). About 62% (124 kg) is released in effluents from sewage treatment plants which are generally channeled directly to surface waters.

TABLE 3.7. HCH emission to surface water in the Rhine basin by domestic waste water.

Country	kg HCH in waste water	HCH emission (kg) to Rhine Basin
West Germany	841	228
The Netherlands	200	64
France	745	19
Luxembourg	5	3
Switzerland	90	49
Austria	105	3
TOTAL	1986	367

Because data for other countries are not available, the amount of HCHs in domestic waste water is estimated assuming that the pollution load is linearly related with the population level. (Population data are given in Appendix 2.) The estimates are given in Table 3.7.

Data in Appendix 4 suggests that only 90% of the inhabitants had a connection to the sewage treatment plant in 1985. This means that in addition to the emission of 367 kg HCHs by sewage treatment plants, 367/9*100/62 = 59 kg HCH is directly discharged to surface waters by the unconnected households. **Thus, a total of 391 kg HCHs enters surface waters in the Rhine Basin from domestic waste water.**

The average amount of HCHs in sewage sludge in the Netherlands in 1981 was 94 µg HCH/kg d.m. (dry weight) with a minimum of 3 µg and a maximum of 3600 µg HCHs/kg dry weight (Slooff & Matthijsen, 1988).

Considering sewage sludge production given in Appendix 4, and 46% recycling of the sludge on agricultural land, HCH emissions to the soil in the German part of the Rhine Basin were: 75 kg HCH in 1980 and 89 kg HCH in 1985. The following equation has been used for the HCH emission (kg) in the Rhine basin by reuse of sewage sludge in agriculture:

pop. x sludge/capita/year (kg) x [HCH] (µg/kg) x %agr. reuse x I x 10^{-9} (1)

pop. = population living in the Rhine basin area
%agr. area = % of the agricultural land in the Rhine basin
%agr. reuse = % of sludge which is reused in agriculture
[HCH] = HCH concentraion (=94 µg/kg d.m)
I = concentration factor = % pop./ % agr. area

For the West German situation multiplication by the concentration factor 55/39 is applied, because 55% of the West German population lives in the Rhine basin (and produce sewage), while only 39% of the West German agricultural area is located in the Rhine basin (and available to take up sewage sludge). It is striking that the sewage sludge production per capita per year in West Germany is approximately 3 times higher than in the Netherlands in the beginning of the 1980s: West Germany 36 kg d.m./capita/year in 1980 (UBA, 1984), the Netherlands 13 kg d.m./capita/year in 1981 (CBS, 1987).

TABLE 3.8. HCH emission (kg) to agricultural soil in the Rhine basin from application of sewage sludge in the beginning of the 1980s.

Country	Sludge/capita (kg)	% agricultural reuse of sludge	HCH emission to the soil in Rhine basin (kg)
West Germany	36	46	76.6
The Netherlands	13	31	2.7
France	25	39	5.3
Luxembourg	25	39	0.3
Switzerland	25	39	5.2
Austria	25	39	0.4
SUM			90.0

Using an average sewage sludge production of 25 kg/capita/year for the other basin countries and an average agricultural reuse of 39%, (the mean of West Germany 46% (UBA, 1984) and the Netherlands 31% (CBS, 1987)) Table 3.8 can be completed for all the Rhine Basin countries.

In the Netherlands 2.8 kg of HCH in dry sewage sludge is reused in agriculture. An equal amount is recycled to compost and used in parks and households (CBS, 1987). If this ratio is also valid for other countries another 47 kg HCH will be emitted to the soil (equation 1 without the concentration factor). This totals to an HCH emission of 137 kg due to reuse of sewage sludge.

3.4.2 Dumps

In the Netherlands in 1984, 31% of the sludge is landfilled (CBS, 1987).
Using the following equation:

pop. x sludge/capita (kg) x %dumped x [HCH] (µg/kg) x 10^{-9} (2)

% dumped = % of the sewage sludge dumped
others as in (1)

a HCH emission (kg) to dump sites in the Rhine basin is estimated on 46 kg. The results for the individual countries based on 31% dumping,are presented in Table 3.9.

TABLE 3.9. Amount of HCH (kg) on dump-sites in the Rhine basin area in 1984. (database: VIEWEMIS.WK1)

Country	kg HCH to dump-sites
West Germany	36.0
The Netherlands	3.0
France	3.0
Luxembourg	0.2
Switzerland	4.0
Austria	0.3
SUM	46.5

3.4.3 Incinerators

About 2.8% of the sewage sludge in the Netherlands was incinerated in 1984 (CBS, 1987). Incineration will result in a complete destruction of HCH. In this way 4 kg HCH have been removed from the Rhine basin area, calculated with equation 3.

pop. x sludge/capita (kg) x %incin. x [HCH] (µg/kg) x 10^{-9} (3)

%incin. = % of sewage sludge which is incinerated
others as in (1)

3.4.4 Governmental and Semi-governmental Consumers

Forests

Lindane is used in production forests both for soil and wood treatment. Wulf & Wichmann (1989) have interviewed foresters about the amount of lindane (and other pesticides) they used. Their research shows that the amount of lindane per *treated* area has increased. However, because the treated area as well as the number of treatments decreased, the overall HCH usage decreased 2.6-fold. The dosage for wood treatment has been transformed into a dosage per hectare, because wood production is not mentioned in all the statistics, whereas forest area is.

TABLE 3.10. Trends in lindane use for surface and wood treatment in German forests (Wulf & Wichmann, 1989; SBA, 1986).

Year	response %	kg	ha	no.	dosage (kg/ha)	kg per treatment	kg used in Germany	avg kg/km^2 forest
Soil surface treatment (active compound)								
1976	42.0	3195.0	5263.6	384	0.61	8.32	7607.143	0.105313
1985	87.2	2359.6	2808.1	361	0.84	6.54	2705.963	0.037461
1986	85.2	2461.9	2866.7	376	0.86	6.55	2889.554	0.040003
Wood treatment (active compound)								
1976	47.0	9796.1	1053153	712	9	13.76	20842.77	0.288547
1985	84.7	13783.0	965860	512	14	26.92	16272.73	0.225279
1986	85.2	6680.9	492830	334	14	20.00	7841.432	0.108557

Based upon Table 3.10, 1.6 tons for soil treatments and 4.2 tons for wood treatment were applied in the West German forests of the Rhine basin in 1986. This calculation is based on actual amounts of lindane used, so indirectly the probability of application is included. In 1977 the application rates were 3.9 ton for soil, 10.8 ton for wood.

West German lindane dosages in forest are also used for emission calculations in the other Rhine basin countries. Forest areas are mentioned in Appendix 2. The resulting HCH emissions are listed in Table 3.11.

The estimated HCH emission by forest-use of HCH is 10.5 tons/year in the time-period 1980–1986.

Pest control

Pest control in and near builings is often done by the municipalities or specialized private companies. Only data on lindane use by the Dutch government were available; 85 kg by municipalities, 2 kg by the Ministry of Defense in 1977 (CBS, 1978). As a rough estimate the use of lindane in the other basin countries is

TABLE 3.11. HCH emissions in forests in the Rhine basin area in the 1980s.

	HCH use (tons)	
Country	Soil treatment	Wood treatment
West Germany (1986)	1.6	4.2
The Netherlands		
France (1985–86)	0.2	1.0
Luxembourg	0.04	0.11
Switzerland (1980)	0.7	2.4
Austria	0.1	0.1
SUM	2.64	7.81

TABLE 3.12. HCH (kg) use by municipalities for pest control in the Rhine basin.

Country	HCH Emission in Rhine Basin (kg)
West Germany	199
The Netherlands	43
France	22
Luxembourg	2
Switzerland	34
Austria	2
SUM	302

assumed to be the same, on a per capita basis, as for the Netherlands. Table 3.12 lists the estimated usage in the basin based on this assumption. Use by the army has been neglected because it appears to be of minor importance and because no information was available about the relative shares of military activities related to lindane use.

3.5 Atmospheric deposition

In remote areas such as the arctic a concentration of 0.3-1.15 ng/m^3 α-HCH and 0.02-0.1 ng/m^3 β-HCH has been measured, which can be considered as a global background concentration (UBA, 1983).

Background outdoor air HCH-concentrations in the Rhine basin area are considered to be similar to those measured in Delft, the Netherlands, with exception of the Ruhr area. Atmospheric concentrations were 0.25 (max. 1.2) ng α-HCH/m^3 and 0.36

(max. 3.4) ng γ-HCH/m^3 in Delft in 1979/1980. In the Ruhr area concentrations of 2.1 (max. 7.4) ng α-HCH/m^3 and 0.77 (max. 3.7) ng γ-HCH/m^3 were measured. Dry deposition of HCHs in the Netherlands is estimated to be 0.5-1.5 ton/year (Slooff & Matthijsen, 1988).

Taking 1 ton HCH/year as the average dry deposition in the Netherlands, which is equal to 24 g/km^2, and assuming this figure is valid for the other basin countries also, the dry deposition of HCHs (tons) in the other countries can be calculated with equation 4:

24 g HCH/km^2 x surface area (km^2) x 10^{-6} (4)

Rainwater in the Netherlands has been monitored from 1974-1982 and contained $<$ 10 to 140 ng HCH/l (Slooff & Matthijsen,1988). Average HCH-concentrations in rainwater in de Bilt, the Netherlands were 50 ng/l in 1981 and 40 ng/l in 1982 (Provinciale Waterstaat Zuid-Holland, 1985).

Considering the rainfall statistics of the basin countries on a regional level (appendix 3) the average annual wet deposition of HCH in the German Rhine basin area has been calculated and the results are presented in Table 3.13.

TABLE 3.13. Deposition of HCHs (tons) by rain in the Rhine basin area.

Country	Area in Rhine basin (x10^3 km^2)	Precipitation (mm)	Dry deposition of HCH (tons)	Wet deposition of HCH (tons)
West Germany	109	variable[a]	2.7	4.0
The Netherlands	21	796	0.5	0.8
France	23	712	0.6	0.8
Luxembourg	3	760	0.1	0.1
Switzerland	36.5	1221	0.9	2.2
Austria	4	868	0.1	0.2
SUM	197		4.9	8.1

[a] Appendix xxx and database:RAIN.WK1 (flop:GERMANY\HCH).

Wet deposition of HCH (tons) is calculated with equation 5:

annual precipitation (mm) x surface area (km^2) x [HCH] (ng/l) x 10^{-9} (5)

Assuming that 0.6 ng HCH/m^3 air is a reasonable estimate for the outdoor air concentration, a mixing layer of 100 m and the Rhine basin area being 197x10^3 km^2, an amount on the order of 0.01 ton HCH is estimated to be continuously present in the air shed of the Rhine basin.

3.6 Summary

An overview of the results with more details about the sources in each country, are given in Appendix 9. Figure 1 portrays the shares of lindane emissions from all the various sources, 1985. It can be seen that the agricultural bulk products are responsible for more than 90% of the emissions in the basin. The contribution of wet and dry deposition is considerable (4.8%). The contribution of each country to the HCH emission is strongly correlated with their area% of agricultural land in the Rhine basin ($r^2 = 0.92$).

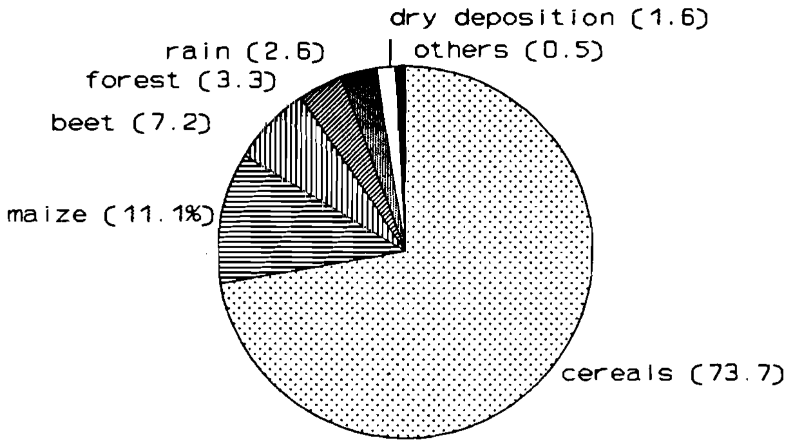

FIGURE 1. Sources of emission of HCHs in the Rhine basin, 1985. Total emission 314 tons HCH. (Database: viewemis.wk1, graph: FL\viewemis.cgm)

The emission by agricultural use in the Netherlands (±83 ton) is four times as high as the statistics in Table 3.2. It is possible that the estimated surface areas of cereals, beet and maize are too high. This means that the assumption that the ratio of crop area/agr. area in the Netherlands is not equal to that in West Germany. More accurate data for the Netherlands can be obtained from the LEI (Institute for Agricultural Economy) in the Hague.

According to Table 3.1 France and West Germany produced 2400 ton lindane for their internal markets in 1979, whereas 1800 ton (GER 160 (agricultural use in the German Rhine Basin)/0.385 (the fraction of the total German agricultural area found in the Rhine Basin), FR 58/0.042) has been applied in the beginning of the 1980s. This is 25% lower than the production statistics allow. In this case the probability of application or the average lindane dosage obtained from Dutch literature might not be valid for the West German and French cases.

The production statistics are very poor and the sales statistics have an uncertainty of at least 25% (Table 3.1 and 3.2). The estimated direct emissions of Figures 1 and

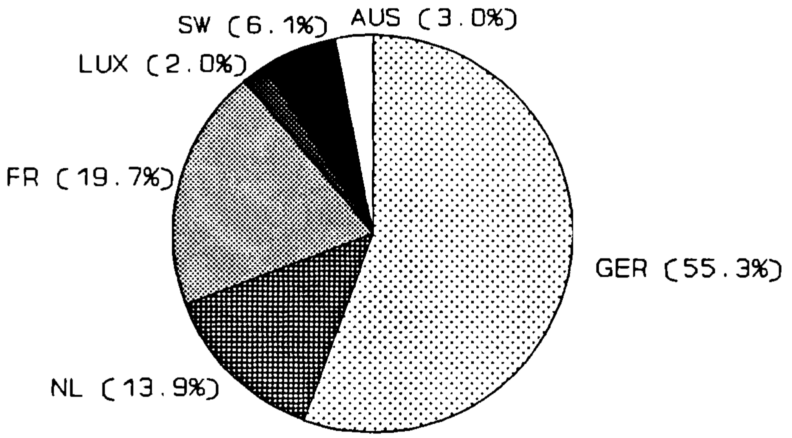

FIGURE 2. Contribution of the Rhine basin countries to HCH emissions in the Rhine basin, 1985. (Database: viewemis.wk1,graph: FL\landemis.cgm)

2 and Appendix 9 are reliable within margins of 25%. So the total direct emissions are estimated at 300 ton HCH/year ± 75 ton. The reliability of the HCH emission by atmospheric deposition is dependent on the reliability of the amount of rain and the HCH concentration. It was not possible to quantify this reliability.

4 Processes of Environmental Dispersion

All the main HCH applications (pesticide for bulk agriculural products) cause an emission directly to the soil and to the air. Lindane is not used as a pesticide in surface waters. Since the Rhine basin project is concerned with emission of HCHs to the surface waters in the basin, environmental dispersion of HCHs must be estimated or calculated in order to fulfill the project goals. Previous chapters have described the sources of HCH emissions, this chapter will describe environmental pathways by which HCHs can enter the surface water. Since no regional approach has been followed for the calculation of the environmental distribution of HCHs, no differentiation between the basin countries will be made.

4.1 Drift and volatilization

If pesticide sprays or dusts are used large quantities can drift to the river, when they are applied under certain weather conditions (strong winds). Volatilization and subsequent precipitation by rainfall can be an important pathway of pesticide loss from agricultural land. In the atmosphere dilution of the concentration occurs and atmospheric movement cause distribution over a larger area. On the one hand this implies a reduced emission in the area under investigation. On the other hand however sources outside the area might also contribute to atmospheric deposition within the area under investigation.

By *drift* of HCHs during pesticide spraying 1-10% of the pesticide can reach the surface water. Menke (1988) based his calculation on 1% drift, resulting in an emission of 15 kg of lindane in the Dutch Rhine basin area.

For the other countries the drift is calculated by assuming 1% drift during application for the agricultural bulk products maize, beet and cereals. Drift for forest application is not considered because the high canopy closure prevents drift over larger distances. The amount of HCH used in other applications is so small that the assumption that drift will not occur, does not give rise to a significant error. These assumptions results in an estimated 2.9 tons of HCHs reaching the surface water by drift.

A quantitative description of lindane *volatilization* is very difficult, because the influence of important factors as soil organic matter content and soil moisture content are not worked out in a model. Volatilization (vapor pressure) is inversely related to the soil organic matter content. Organic matter is the most important adsorbent for hydrophobic pesticides, and are thus of primary importance in describing rates of diffusive movement and volatilization in soils. The humidity of the soil affects volatilization of pesticides. When the water content is reduced below values that correspond to a monomolecular layer (for Gila silt loam <2.8%) adsorption sites of clays become active, on which pesticides are more strongly bound, so that their fugacity decreases 50–00-fold. The effect is reversible in response to changes in water content. Air temperature only has a secondary effect by evaporation and reduction of the soil moisture content.

Field measurements reported by Glotfelty (1981 & 1984) showed a volatilization of 50–90% in six days in a moist fallow silt loam and 12% in 50 hours in a dry fallow silt loam (cited by Taylor and Spencer, 1990). Both options (50 and 90% loss) are worked out for the Rhine basin area.

	tons HCH
Emission into Rhine basin:	314
Drift from agriculture bulk application: 1% =	2.9
Remainder	311
Volatilization 50–90%	157-283
Remainder	28–154

4.2 Degradation

The 25–125 tons of HCH that remain in the soil after drift and volatilization will be subjected to microbiological degradation processes. Half-life times of days to years have been reported (Callahan, 1979; Elskens, 1979; Slooff & Matthijsen, 1988; Howard *et al.*, 1991). The observed half-life times are very dependent on soil type, tempertaure and experimental set-up.

For the estimation of HCH removal by biodegradation in soils two options are estimated:

1) Half-life time of 88 days. This is the fastest aerobic biological half-life time reported (Rao & Davidson cited by Slooff & Matthijsen, 1988).

2) Half-life time of 135 days, the slowest biodegradation rates reported for soil with relevant carbon contents (±3% OC).

Further assumptions:

- Biodegradation takes place during one growth season only (= 183 days). After that period degradation will cease by the poor availabilty of HCH residues.
- During the growth season HCHs are present in the plough layer, where aerobic conditions exist.
- Biodegradation will follow first order kinetics: $C_t = C_0 \times e^{-kt}$

Using half-life times of 88 and 135 days, 76% and 61% of the HCHs, respectively, will be removed in one growth season (183 days). The removal in tons of HCHs degraded for two options at two initial concentrations is summarized in Table 4.1.

The HCHs remaining in the soil after drift, volatilization and biodegradation varies between 7 and 60 tons HCHs.

TABLE 4.1. Removal of HCHs from the soil (tons) by biodegradation, at 2 different initial concentrations and 2 different half-life times.

	DT50 = 88 days	DT50 = 135 days
C_0 = 28 tons HCH	21	17
C_0 = 154 tons HCH	117	94

4.3 Surface run-off and erosion

Background concentrations of HCHs in the upper 20 cm of maize-land in the Netherlands are 80–250 µg/kg (Slooff & Matthijsen, 1988).

Erosion is the transfer of soil particles by wind and water. Since the more fertile components of the soil are taken away (clay, organic matter, fertilizers and seeds) erosion results in a decrease of soil fertility. Deposition of the soil particles damages standing crops, causes siltation of streams and reservoirs and may block ditches and tracks. With the removal of soil particles, pesticides attached to it also are removed and deposited, usually in lower parts of the valley, or in the river basin.

Most vulnerable to erosion are soils with intensive agriculture (esp. maize-culture and vineyards), situated on slopes. Maize is sown very late (end of May), which leaves the soil exposed to wind and rain for a long time. Heavy machinery compacts the soil and encourages surface run-off and erosion.

The CEC (1987) reports soil losses in several areas:

Because the data on erosion are not very detailed, an average erosion of 0.7 tons/ha/year in agricultural areas of the Rhine basin is used in the following calculations. Annual loss of HCHs (tons) from the soil by erosion is calculated with equation 6.

TABLE 4.2. Annual soil loss in parts of the Rhine basin area (tons/ha/year). Source: CEC, 1987.

Region	Annual soil loss (tons/ha)
GERMANY	
Trier	0.2–2
Mosel Valley	0.5–2
Rhine Mosel	0.7
Bayern[a]	2.2
LUXEMBOURG	0.7–1.8

[a] Umweltbundesamt, 1989.

Agr. area (ha) x soil loss (tons/ha/year) x [HCH] (µg/kg) x 10^{-9} (6)

Using the total agricultural surface area and background concentration in soil of 80-250 µg/kg (Slooff & Matthijsen, 1988) annual HCH erosion will vary between 0.5 and 1.6 ton/year.

The total agricultural surface area has been used in equation 6. Due to crop rotation more land is actually contaminated than only the maize areas reported in the statistics. Furthermore cereals and beet land are assumed to accumulate the same amount of HCHs as maize land. Although these crops are bulk products they maximally account for 40% of the agricultural area. Estimation of HCH erosion must be considered as a worst case.

Since lindane is mainly applied directly to the soil, and because of its high adsorption coefficient, the potential for *surface run-off* is very small. Run-off losses are commonly <1% for soil incorporated pesticides or foliar applied pesticides.

4.4 Leaching

Leaching risk is neglectible because of the high adsorption coefficient of HCHs to organic matter (K_{om} = 700 l/kg).

Although HCHs have a high adsorption coefficients, it might leach if crevices in soils or landfills appear. There is a small risk of HCH leaching to groundwater, which is hard to quantify. Model calculations for agricultural applications of HCH revealed that HCH will not leach to groundwater. Assumptions for these calculations were a soil with 5% organic matter, a groundwater level of 1 m, a 74% wet year (74% of the years have less precipitation), no biodegradation, Darcy transport[1] and no volatilization. (Van der Linden & Boesten, 1989.) According to the soil variability

---

[1] Darcy transport also called "flux density equation" describes the transport velocity of water through the soil matrix, determined by the hydraulic permeability and the hydraulic pressure in the soil.

model of Jury, the chance of leaching of 0.01% of the applied lindane to groundwater in a coarse textured soil can be 0.943 (Jury, 1990). However, no reports about HCH in groundwater samples collected under agricultural land have been found. In this investigation leaching will be neglected, because in practice other processes will affect the distribution of HCH at higher rates.

In landfills equipped with liners no distribution of HCH will take place. It is assumed that currently (starting in the beginning of the 1970s) all the dump-sites are equipped with liners.

4.5 Mass balance

In Figure 3 the main sources and distributive pathways for HCHs are schematically represented. Volatilization and biodegradtion from soil are very important processes. Biodegradation is estimated at 22% of the annual dosage. The 206 tons (68%) which undergo atmospheric transboundary movement or photodecomposition are estimated from consideration of mass balance. The photodecomposition rates mentioned by Howard *et al.* (1991) (DT50 < 29.5 hours) are to a high to explain a background air concentration of 10 kg. If the remaining 206 kg would be photodecomposed, a half-life time of 70 days would be valid.

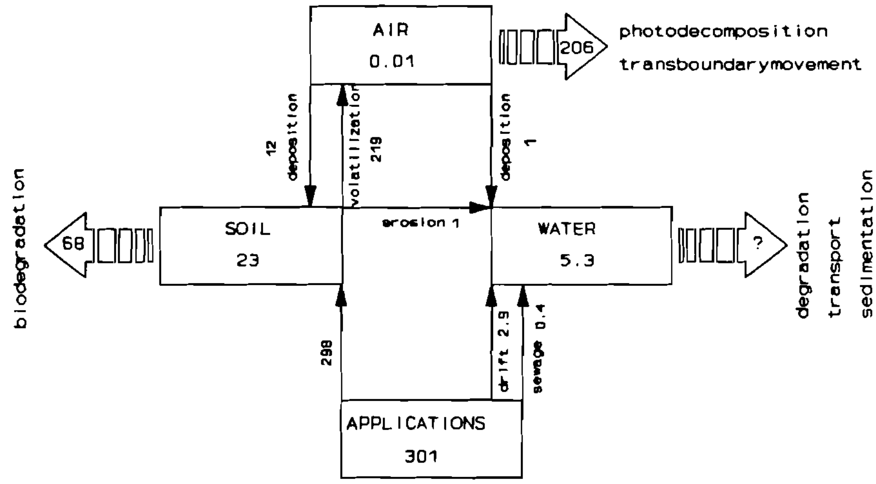

FIGURE 3. HCH flow (tons/year) in the environmental compartments of the Rhine basin area as in the beginning of the 1980s.

About 23 tons of HCH per year accumulate in the soil and 53 in the surface waters of the Rhine basin area. Processes in surface water have not been estimated because of the complex interrelationships between degradation, sedimentation and transport.

With an average discharge of 2000 m^3/sec, the average HCH concentration in water would be 84 ng/l.

The accumulation in the soil results in the increasing importance of erosion as a distributive pathway. This is discussed in more detail in Chapter 5. Degradation and volatilization are processes which are considered to be important after recent pesticide application (degradation, a maximum of one growth season, volatilization, one week), before the HCH-molecules have been captured by adsorption.

5 Prognoses

5.1 Scenario 1: Lindane use is maintained at 1985 level

According to the calculations in Chapters 3 and 4, an accumulation of 23 ton HCH/y will occur if the HCH use is not changed. Assuming that the accumulation only takes place in the upper 20 cm of the soil, with a bulk density of 1500 kg/m^3, the HCH concentration increases by 0.84 μg/kg/year.

The HCH concentration (μg/kg) in the upper 20 cm is described as a function of time in equation 7, where t is the time in years after 1985 (1985 is t=0).

$$\mathbf{C(t) = 160 + 0.84 \times t} \qquad (7)$$

An erosion term of $C(t) \times 700/(1500 \times 89.8 \times 0.2 \times 10^9)$ should be substracted from equation 7 to be correct. This term, however, is only $2.6 \times 10^{-11} \times C(t)$ and is thus negligible.

An erosion of 0.7 ton soil/ha/y is equal with the removal of the upper 47×10^{-6} m of soil in the agricultural areas. The predictions for the concentrations of HCH in the top 20 cm until 2020 and the increasing loss of HCH from soil by erosion is are presented in Figure 4. The HCH (tons) removed by erosion is given by equation 8:

$$\mathbf{E(t) = 0.7\ (ton\ soil/ha/y) \times 89.8 \times 10^5\ (ha) \times C(t)\ (\mu g/kg) \times 10^{-9}} \qquad (8)$$

5.2 Scenario 2: Prohibition of lindane use in 1995

In the case of a prohibition of lindane use in 1995, the accumulation of 0.84 μg/kg/year will continue until 1995, during which the concentration will increase to a value of 87.5 μg/kg.

By ploughing, the HCH concentrion will be distributed homogeneously in the upper 20 cm. Erosion of the top layer (700 ton = 47×10^{-6} m) will thus cause a dilution of the remaining residue with 47×10^{-6} m clean soil.

After 1995 the concentration in the plough layer can be described with equation 9.

$$\mathbf{C(t) = C_{1995} \times (0.2 - 47 \times 10^{-6} \times t)/0.2} \qquad (9)$$

Removal of lindane by erosion alone will take 3723 years to reach a concentration of 10 μg/kg in the plough layer of agricultural areas.

The amount of HCH (tons) removed from the surface by erosion can again be described by equation 8. HCH erosion and HCH residue are graphically represented in Figure 4.

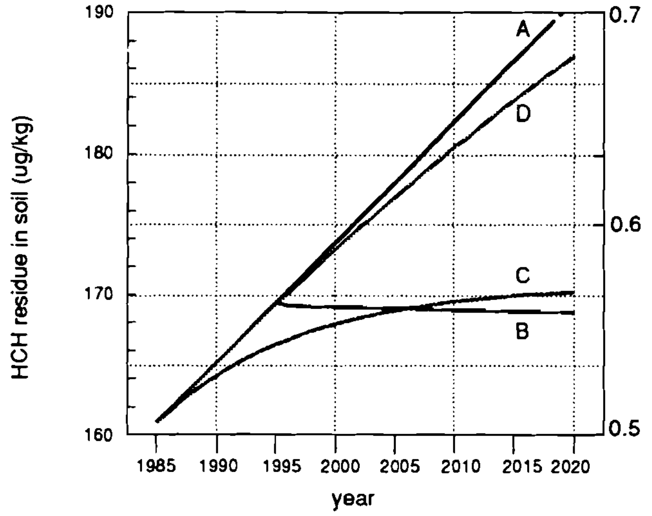

FIGURE 4. Prognoses for HCH emissions (tons) to surface water in the Rhine basin calculated with 4 scenarios: A. Lindane use at 1985 level; B. Prohibition in 1995; C. Voluntary replacement; D. 10% reduction.

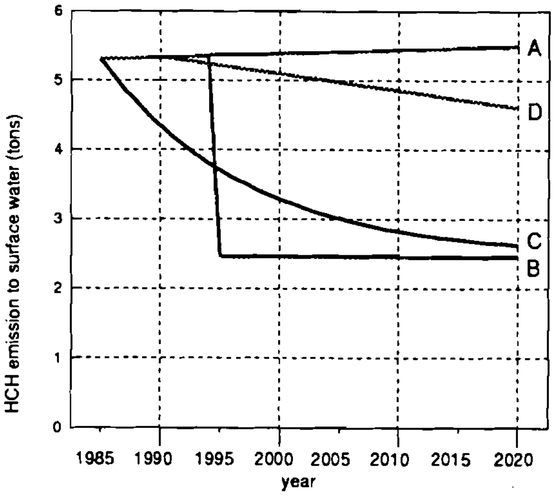

FIGURE 5. Prognoses for HCH emissions (tons) to surface water in the Rhine basin calculated with 4 scenarios: A. Lindane use at 1985 level; B. Prohibition in 1995; C. Voluntary replacement; D. 10% reduction.

Direct contamination of surface water by drift has ceased after 1995; thus decreasing the annual HCH load in surface water by 2.9 tons. Thus, the input to the rivers will increase solely by erosion. The overall effect on the surface water is a decrease of the HCH emission, as given in Figure 5.

5.3 Replacement of lindane by alternatives

Warmenhoven *et al.* (1989) have assumed a voluntary replacement of 40% of the lindane pesticides in 5 years (=8%/y). This means that the use (U) of lindane will decrease according to equation 10.

$$\mathbf{U(t) = U(0) \times 0.92^t} \tag{10}$$

U(0) is the HCH use in 1985, equal to 298 tons.

According to the mass balance in Figure 3, about 8% of the applied HCH will accumulate in the soil, whereas 10% enters the surface water by drift. By voluntary replacement of lindane by alternatives the HCH accumulation will decrease, resulting in a residue C(t) as calculated with equation 11.

$$\mathbf{C(t) = 160 + 0.08x10^{12}/(89.8x10^{9}x0.2x1500) \times U(t_i)} \tag{11}$$

Erosion can again be described by equation 8. The results for HCH erosion, HCH residue in soil and HCH emission to surface water are represented in the Figures 4 and 5.

5.4 Scenario 4: Changes in land-use

If a reduction of 10% in agricultural area is assumed between the years 1990 and 2000, it results in a 10% reduction of HCH-emissions if lindane application is unchanged. The use of lindane between 1990 and 2000 can be described by equation 12.

$$\mathbf{U(t) = 298 - 0.01 \times 298 \times (t-5)} \tag{12}$$

where t=0 in 1985. Until 1990 the data in section 5.1 are valid (unchanged lindane use). After 2000 the use of lindane is assumed to be constant again at the year 2000 level. C(t) can be described with equation 11, erosion with equation 8. The results for HCH erosion, HCH residue in soil and HCH emission to surface water are shown in the Figures 4 and 5.

5.5 Summary

In this section the future HCH accumulation in soil (Figure 4), the HCH erosion (Figure 4, fl\erosion.cgm) as well as the expected HCH emission to surface water (Figure 5, fl\water.cgm) have been calcultated (database: erosion.wk1). Accumulation and erosion show similar trends because the amount of soil lost by erosion is kept constant at 0.7 ton/ha/y. So HCH erosion has a linear relationship to HCH residue in the soil.

For the calculation of the emissions to surface water, atmospheric deposition and sewage effluent have been kept constant, and the contribution of drift and erosion varied dependent on the chosen scenario.

As can be seen, the voluntary replacement of lindane pesticide (since 1985) has almost the same effect on HCH accumulation and erosion as a prohibition. Of crucial importance is the year in which the changes are implemented. For the emission to surface waters prohibition has a strong decreasing effect. This effect is larger than that of a voluntary replacement of lindane.

No changes in lindane use or a reduction of 10% in use causes a rapid increase in HCH concentrations in the soil. A 10% reduction in lindane use has only a very slight decreasing effect on HCH accumulation and erosion.

Comparison of the figures shows that the effect of the scenarios is more visible, and stronger for HCH emissions to surface water. The soil is a large environmental reservoir for HCH. Under changing environmental conditions, however, during which HCH may be mobilized from soils (e.g., due to changes in organic matter, soil salinization and acidification), the sink may be transformed to a source of HCH, thereby causing time-delayed emissions to other environmental compartments.

6 Conclusions

Agricultural bulk products (cereals, beet and maize) are the largest consumers of lindane pesticides. They are responsible for more than 90% of the consumption. Forestry, responsible for 3.3% of the emission of lindane, is the second largest user. More important than the use in forests, however, is the atmospheric deposition, accounting for 4.8% of the annual emissions. Other consumers of lindane pesticide (<0.5% of the emission) are livestock, tulips, roses, allotment gardens and municipal pest control. Lindane also occurs in domestic waste: sewage sludge, waste water and solids, but these sources are only responsible for 0.1% of the emissions. The reliability of the estimated emission is about ±25%.

Volatilization and transboundary movement are very important distributive pathways. About 20% of the applied lindane will be degraded in the soil. At the current application rates 23 tons HCH/y accumulates in the soil. In agricultural areas the HCH concentration will increase by 0.84 µg/kg/y. Erosion of HCH will increase in proportion to the soil concentration.

Without a change in lindane use, the accumulation in soils will increase rapidly, and the emission to surface waters will increase gradually. Changes in lindane use affect the surface water more rapidly than the soil. The soil is the main sink for HCH. After a complete prohibition of lindane use, it will take almost 4000 years to decrease the HCH concentration in the soil to below 10 µg/kg.

The changes in HCH emissions in 2020 (compared to 1985 emissions) to the surface water for 4 different scenarions are as follows:

A.	Lindane use unchanged at 1985 level	+ 4%
B.	Prohibition of lindane in 1985	-60%
C.	Replacement of lindane by alternatives	-58%
D.	Reduction of 10%	- 3%

References

Brockhaus, 1983, Länder und Klima, Brockhaus Texte und Tabellen, Wiesbaden.

Bundesamt für Statistik, 1981, Statistisches Jahrbuch der Schweiz 1981, Birkhäuser Verlag, Basel.

Bundeszentrale für politische Bildung, 1989, Datenreport 1989, Zahlen und Fakten über die Bundesrepublik Deutschland, Band 280, Statisches Bundesamt, Bonn.

Callahan, *et al*, 1979, Water-related environmental fate of 129 priority pollutants, Volume 1, EPA (WH-533), Springfield, USA.

CBS (Centraal Bureau voor de Statistiek), 1978, Gebruik van chemische bestrijdingsmiddelen door overheidsinstellingen. The Hague, The Netherlands.

CBS (Centraal Bureau voor de Statistiek), 1987, Environmental statistics of the Netherlands, Staatuitgeverij, The Haque.

CEC (Commision of the European Communities, Directorate General Environment, Consumer protection and Nuclear Safety), 1987, The state of the environment in the European Community 1986, Office for official Publications of the European Communities, Luxembourg.

Elskens I., 1979, Measurement and surveying methods in the aquatic environment of chlordane, DDT, heptachlor, hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) and PCB's, Commision des communautés européennes.

Elgersma F, Anderberg BS & Stigliani WM, 1991, Aqueous emission factors for the industrial discharges of cadmium in the Rhine River Basin in the period 1979-1990: an inventory, International Institute for Applied Systems Analysis, Laxenburg, Austria.

Friedrich G & Müller D, 1984, Rhine, in: Ecology of European rivers, BA Whitton (ed.), p265-315, Blackwell: Oxford.

Green RE & Karickhoff SW, 1990, Sorption estimates for modeling, in: Pesticides in the soil environment: Processes, Impacts, and Modeling, Cheng HH (ed.), pp. 79-101.

Greve PA, *et al.*, 1989, Organochloorbestrijdingsmiddelen en PCB's in bodemmonsters, RIVM 728709001.

Howard PH *et al.*, 1991, Handbook of environmental degradation rates, Lewis Publishers Inc., USA.

INSEE (Institute nationale de la statistique et des études economique), 1988, Annuaire statistique de la France 1988, Volume 93.

INSEE, 1989, Annuaire statistique de Lorraine 1989.

Leonard RA, 1990, Pesticide movement into surface waters, in: Pesticides in the soil environment: Processes, Impacts, and Modeling, Cheng HH (ed.), pp. 79-101.

Menke MA, 1988, Emissies van bestrijdingsmiddelen, meststoffen en zware metalen. Inventarisatie voor de bronnen landbouw en atmosferische depositie in het kader van het Noordzee aktie programma, Rijkswaterstaat-DBW/RIZA.

Ministre de la qualité de la vie, 1974, Environnement et cadre de vie dossier statistique. Tome 1. Description des milieux, les activités economique et l'environnement gestion des mileiux, pollutions et nuisance, La documentation francaise, Paris.

Neitzel M, 1987, Erhebung über Art und Menge der in Kleingärten eingesetzten Pflanzenbehandlungsmittel, Umweltbundesamt Texte 11/87.

NOOA (National Oceanic and Atmospheric Administration), 1988, A historical reconstruction of major pollutant levels in the Hudson-Raritan basin:1880-1980, Volume III. Chemicals and other wastes., USA.

Provinciale Waterstaat Zuid-Holland afdeling Milieu, 1985, Verslag waterkwaliteitsbehher 1982-1983.

SBA (Statistisches Bundesamt), 1986, Statistisches Jahrbuch 1986 für die Bundesrepubliek Deutschland, Verlag W. Kohlhammer, Stuttgart und Mainz.

SBA (Statisches Bundesamt), 1987, Land- und Forstwirtschaft, Fischerei, Fachserie3, Reihe 3. Bodennutzung und pflanzihe Erzeugung. Verlag W. Kohlhammer, Stuttgart und Mainz.

SBA (Statisches Bundesamt), Statisches Jahrbuch 1990 für das Ausland, metzler-Poeschel, Stuttgart.

Slooff W & Matthijsen AJCM (eds.), 1988, Integrated criteria document hexachlorocyclohexane, RIVM, Bilthoven, the Netherlands.

SRI International, 19XX, Directory of chemical producers, Western Europe, Volume 1 and 2, USA.

Taylor AW & Spencer WF, 1990, Volatilzation and vapor transport processes, in: Pesticides in the soil environment: Processes, Impacts, and Modeling, Cheng HH (ed.), pp. 79-101.

UBA (Umweltbundesamt), 1977, Materialien zum Immisionsschutzbericht 1977 der Bundesregierung und den Deutschen Bundestag, Erich Schmidt Verlag, Berlin.

UBA (Umweltbundesamt), 1984, Daten zur Umwelt 1984, Berlin.

UBA (Umweltbundesamt), 1986, Daten zur Umwelt 1986/87, Erich Schmidt Verlag, Berlin.

UBA (Umweltbundesamt), 1989, Daten zur Umwelt 1989, Erich Schmidt Verlag, Berlin.

Van den Berg R *et al.*, 1990, Verdunning en omzetting van bestrijdingsmiddelen in grondwater, RIVM 725801002.

Van den Berg S, Lagas P & Heusinkveld HAG, 1990, De EG-adsorptie/desorptie-test. Toetsing van de conceptprocedure, RIVM 725701001, Bilthoven, the Netherlands.

Van der Linden AMA & Boesten JJTI, 1989, berekening van de mate van uitspoeling en accumulatie van bestrijdingsmiddelen als funktie van hun sorptiecoëfficiënt en omzettingssnelheid in bouwvoormateriaal, RIVM 73880003, Bilthoven, the Netherlands.

Wagenet RJ & Rao PSC, 1990, Modeling pesticide fate in soils, in: Pesticides in the soil environment: Processes, Impacts, and Modeling, Cheng HH (ed.), pp.315-400.

Warmenhoven JP *et al.*, 1989, The contribution of the input from the atmosphere to the contamination of the North Sea and the Dutch Waddensea. Model calculations on basis of European emission estimates, TNO, Delft, The Netherlands.

Wulf A & Wichmann C, 1989, Uber Art und Umfang der Anwendung chemischer Pflanzenschutzmittel im Forst, Erhebungsdaten aus den Forstwirtschaftsjahren 1976, 1985 und 1986. Biologischen Bundesanstalt für Land- Und Forstwirtschaft, Berlin-Dahlem.

Characteristics of the Rhine basin

APPENDIX 1

DIMENSIONS

Area of catchment	197000 km^2
Source of river	2344 m altitude
Length of river	1320 km
Discharge	2000 m^3/sec

PRECIPITATION

Alpine and Prealpine region: summer wet, up to 3000 mm, mostly 1200-1800 mm, dry in winter.
Above 1800 m more than 50% of precipitation as snow.
Mountains and Upper Rhine valley: mountains wet in summer, 800-1200 mm.
Upper Rhine Valley, 400-800 mm ?????
Lower Rhine typical maritime climate, 600-800 mm.

POPULATION

Population and industry are concentrated along the "Rheinschiene" from Basel to Rotterdam, with many large cities: Basel, Strasbourg, Karlsruhe, Ludwigshafen, mannheim, Frankfurt am Main, Mainz, Koblenz, Bonn, Köln, Düsseldorf, Krefeld, Duisburg, Ruhrgebiet, Wesel.

LAND USE

Above Bodensee: agriculture and forestry are dominant.
Upper Rhine Valley: intensive agriculture, wine, fruits, agriculture, forestry.
Middle Rhine: agriculture, wine, forestry in the mountains.
Lower Rhine: intensive agriculture
There is intensive industrial activity fron Basel to the lower Rhine and also intensive gravel mining in the flood beds of the Upper and Lower Rhine regions.

PHYSICAL FEATURES

Discharge at selected points (based on data for 1931-1960)

	Kaub	Rees
lowest ever recorded	482	590
mean annual minimum	700	990
mean	1560	2210
mean annual maximum	4040	6660
highest ever recorded	6150	9500

Substratum

High Rhine	rocks, limestone
Upper Rhine	gravel
Middle Rhine	rocks, gravel
Lower Rhine	gravel, mud in breakwater fields

Temperature °C.

(1971-1980) selected points from Deutsches Gewässerliches Jahrbuch, 1983.

	km	min.	mean	max.
Waldshut	102.8	1.2	10.6	23.2
Worms	443.4	2.7	13.7	26.2
Köln	668.0	0.0	12.5	25.2
Rees	837.4	1.8	12.8	26.2

Geographic data of the Rhine neighboring countries

APPENDIX 2

	GER	NL	FR	LUX	SW	AUS	TOTAL
area (*1000 km^2)	249	41	552	3	41	84	970.0
in Rhine basin	109	21	23	3	36.5	4.2	196.7
% in Rhine basin	43.8	51.2	4.2	100.0	89.0	5.0	20.3
% of Rhine basin	55.4	10.7	11.7	1.5	18.6	2.1	100.0
population (10^6)	61	14.5	54	0.37	6.5	7.6	144.0
in Rhine basin	34	7.25	3.7	0.37	5.8	0.4	51.5
% in Rhine basin	55.7	50.0	6.9	100.0	89.0	5.0	35.8
% of Rhine basin	66.0	14.1	7.2	0.7	11.2	0.7	100.0
agricultural area (x1000 km^2)	135	26	284	1.25	10.9	37.0	494.2
in Rhine basin	52	13	12	1.25	9.7	1.9	89.8
% in Rhine basin	38.5	50.0	4.2	100.0	89.0	5.0	18.2
% of Rhine basin	57.9	14.5	13.4	1.4	10.8	2.1	100.0
forest area (x1000 km^2)	74	0	115	1.0	10.5	27.0	227.5
in Rhine basin	39	0	7.4	1.0	9.3	1.4	58.1
% in Rhine basin	52.7	ERR	6.4	100.0	89.0	5.0	25.5
% of Rhine basin	67.2	0.0	12.7	1.7	16.1	2.3	100.0

Precipitation in the Rhine basin

APPENDIX 3

(Statistisches Bundesamt, 1986; Brockhaus, 1983)

	year average (mm)*	average in June (mm)*
GERMANY		
Schleswig	825	59
Emden-Nesserland	778	62
Bremen (Flughafen)	715	59
Hamburg-Fuhlsbüttel	714	64
Aachen	805	77
Köln-Wahn (Flughafen)	701	83
Essen-Bredeney	933	83
Münster (Westf.)	742	62
Hannover-Langenhagen	661	64
Lüchow	562	62
Lübeck	698	62
Berlin-Dahlem	581	62
Ludenscheid	1293	99
Kassel	629	64
Trier (Petrisberg)	719	74
Saarbrücken-St. Johann	781	70
Bad Kreuznach	520	57
Frankfurt am Main (Flughafen)	604	65
Karlsruhe	761	84
Stuttgart (Schnarrenberg)	703	94
Freiburg im Breisgau	849	105
Freudenstadt	1520	125
Würzburg	646	72
Nürnberg (Flughafen)	623	71
Weiden/Oberpfalz	672	76
Metten (kr. Deggendorf)	899	99
Ulm/Donau	754	101
München-Nymphenburg	910	121
Konstanz	806	101
Oberstdorf	1776	206
THE NETHERLANDS	796	
FRANCE, Nancy	712	
LUXEMBOURG	760	64
AUSTRIA, Innsbruck	868	110

	year average (mm)*	average in June (mm)
*SWITZERLAND		
Basel	783	93
Bern	986	123
Genf	852	89
Lugano	1742	198
Zürich	1136	136
Davos	1018	122
Lausanne	1051	113
Luzern	1159	150
Neuchâtel	994	98
Santis	2487	197

* = average precipitation in the period 1931-1960.

Sewage sludge production and destination in West Germany APPENDIX 4

In Germany in 1983 90% of the population was connected with a municipal sewage system. However, in villages with less than 1000 inhabitants just 60% was connected. Of the water ending up in the sewage system 95% was treated in sewage treatment plants. Overall, the waste water of 86% of the population was treated in 1983 in Germany.

year	% inhabitants connected to a sewer
1957	60
1963	70
1969	79
1975	86
1979	88.6
1983	90

(Umweltbundesamt, 1984)

Municipal sewage sludge production and destination in West-Germany

year	production of sludge in millions of tons dry matter	DESTINATION		
		dumps	incinerated	agriculture
1957	0.6	?	?	?
1975	1.8	43-49%	8%	30-36%
1980	2.2	——51%——		46%
1985	2.6	?	?	?

Umweltbundesamt, 1984

In Germany in 1983 a total amount of $7.8*10^9$ m^3 waste water has been treated, originating from households (41%), industries (16%) and the remaining 43% consisting of rain, groundwaters and other sources???.
6% of the waste water received a mechanical treatment only, 86% was offered a biological treatment as well, whereas 8% was also underwent an additional chemical precipitation of phosphate.

80% of the waste water of mining companies and manufacturers has been treated in industrial sewage treatment plants, whereas 20% of the waste water ended up in surface water without any treatment (or without treatment in municipal sewage treatment plant??)
In the industrial sewage treatment plants 43% of the offered water recieved a mechanical treatment, 8% a biological and 18% biological and further treatments and 31% of the waste water received a chemical/physical treatment. (Umweltbundesamt, 1986)

APPENDIX 5

Physical and chemical properties of hexachlorocyclohexane-isomers

Molecular weight 291 g/mol

Solubility in water at 25 °C (mg.l^{-1}):

α-HCH	β-HCH	γ-HCH	Reference (cited by Callahan *et al.*, 1979)
1.21-2.01	0.13-0.20	8.64-15.7	Kurihuri *et al.*, 1973
2.00	0.240	31.4	Weil *et al.*, 1974
1.63	0.7	21.3	Brooks, 1974
		7.5	Jury *et al* 1983, cited by Taylor & Spencer, 1990

Partitioncoefficient octanol-water (log K_{ow}):
α-HCH 3.81
β-HCH 3.80
δ-HCH 4.14
(Kurihara *et al.*, 1973 cited by Callahan *et al.*, 1979)

Hydrolysis disappearance time 50% (DT50) > 4 years, which can be interpreted as no significant hydrolysis (Eichelberger and Lichtenstein, 1971, cited by Callahan *et al.*, 1979).

Biodegradation of HCH-isomers decreases in the following order: $\gamma > \alpha > \beta > \delta$, with observed DT50 between days and years. Experiments showed resp. 5-10-30-50% remaining after 56 days (Callahan *et al.*, 1979).
"Apart from one reference which claims that gamma-HCH is highly persistent in water, most of the literature indicates limited persistence in either the terrestrial or aquatic environments with DT50 of 2 years" (Elskens, 1979).

Because of the slow degradation, sorption can be one of the major pathways of HCH.
Distribution according to Freundlich-isotherms:

1.9% C	1/n=0.91	K: 10-30 (α, β, δ)
5.2% C	1/n=0.71	K: 30-120

(Tsukano, 1973, cited by Callahan, 1979)

K_{oc}

Grey-Brown podzolic soil, Ap-horizon,	%OC= 2.2	K_{oc}=525, 1600
Podzolic soil, Ahe-horizon,	%OC=10.4	K_{oc}=2500, 4000

(Van den Berg, Lagas & Heusinkveld, 1990)

Schooff and Matthijssen have reviewed K_{oc}-values determined by 7 research groups on 25 soil types. The average K_{oc} was around 1300 (500-2250), equal to a K_{om} of 700.

Volatility of γ-HCH at 25°C

Henry's law coefficient:	1.3x10^{-4} (dimensionless)
Saturation vapor density	1.0 μg/l
Saturation vapor pressure	8.6

Bioaccumulationfactor (Elskens, 1979)
60-90 for crustaceans
20-100 for bacteria
33 for zooplankton
2-400 for molluscs
100-800 for fish

Acceptable Daily Intake (ADI): 0.01 mg/kg body weight (Sloof and Matthijssen, 1988)

APPENDIX 6

Commercial names of lindane formulations (Gewasbeschermingsgids, 1989) in the Netherlands

Commercial name	appearance l = liquid p = powder spp = spraypowder lks = granulates	concentration	function i = insecticide ls = life-stock
AAlindan emulsion oil 21%	l	210 g/l	i
AAlindan-inkrusta	p	75%	i
AAmeltex-korrels	lks	1,2%	i
AAritna	p	20%	i
AAScabol	l	70 g/l	ls
Aescab	l	70 g/l	ls
Agra-Schabi	l	70 g/l	ls
Amos Scabis	l	70 g/l	ls
Anti- Scabiosum	l	70 g/l	ls
Asepta lindaan flowable	l	1000 g/l	i
Asepta lindaan spuitpoeder 14%	p	14%	i
Asepta lindaan vloeibaar 21% gamma	l	140 g/l	i
Bodip	l	70 g/l	ls
Brabant Anti-Scabiosum	l	70 g/l	ls
Brabant lindaan 21% vloiebaar	l	210 g/l	i
Brabant lindagerm 20%	p	20%	i
Comchem lindaan flow	l	750 g/l	i
Comchem lindaan vloeibaar 21%	l	210 g/l	i
Deuka veewasmiddel	l	70 g/l	ls
Duphar lindaan mengolie-21	l	210 g/l	i
Duphar lindaan M.O.	l	210 g/l	i
Gamma-col	l	800 g/l	i
Gammexane rookontwikkelaar no.25	f	16%	i
Gammexide	l	70 g/l	ls
Jebolinpar stuif (lindaan/parathionetyl)	p	0.7/2%	i
Jeboscab	l	70 g/l	ls
Lidazon (diazinon/lindaan)	l	50/175 g/l	i
Lindafor flo	l	750 g/l	i
Lindol 21%	l	210 g/l	i
Lirogam rooktablet	f	10%	i
Lirogam stuifpoeder 0.7%	p	0.7%	i
Luxan lindaan 20%	spp	20%	i
Luxan lindaan 14% spuitpoeder	spp	14%	i
Luxan lindaan 21% vloeibaar	l	210 g/l	i
Luxan lindaan emeltenkorrels	lks	1,2%	i
Luxan Scabisix V.S.	l	70 g/l	ls
M.S. Super Veecleaner	l	70 g/l	ls
Neo-Scabexaan	l	70 g/l	ls
Scabexol	l	70 g/l	ls
Scabia	l	70 g/l	ls
Scabicidin	l	70 g/l	ls
Scabicurin	l	70 g/l	ls
Scabigon	l	70 g/l	ls
Scabinol	l	70 g/l	ls
Scablin	l	70 g/l	ls
Schapenwasmiddel wolfederatie	l	70 g/l	ls
Sectosol	l	70 g/l	ls
Smedip	l	70 g/l	ls

APPENDIX 7

Pesticides containing lindane used in allotment gardens in West Germany
(Neitzel, 1987)

Against ants:	amount of active ingredient
Ameisen-Streu- und Gießmittel "Schacht"	1.3%
Blumetta-Ameisenmittel	1.3%
Ameisenmittel "Schering"	1.5%
Ameisen Frei	2.5%
Ameisenvernichter	2.5%
Ameisenmittel Hortex	2.5%
ASB-Ameisenvernichter	2.5%
Terrason Ameisentod	4%
Egasa-Ameisentod	4%
Insecticide	
Terrasan-Pflanzenspray	
(dichloorvos+lindane+dinocap)	0.5%+0.75%+0.25%
Lindan: C-B-Ho-Neu-staub	0.8%
Pflanzenspray Hortex (Lindane+Parafinoil)	0.5%

APPENDIX 8

Application of lindane-containing pesticides in allotment gardens (Neitzel, 1987)

Results of an interview under 353 allotment garden holders:

	Pflanzenspray Hortex	**Lindan C-B-Ho-Neu staub**	**Terrasan Pflanzen-spray**
1 applied product (kg)	0.2	0.04	0.15
2 applied active ingredient (kg)	0.001	$3.2\text{x}10^{-4}$	$2.25\text{x}10^{-3}$
3 treated surface area (m^2)	7	20	5
4 product/treated surface area (kg/m^2)	0.029	0.002	0.03
5 a.i./treated surface area (kg/m^2)	$1.4\ \text{x}10^{-4}$	$1.6\ \text{x}10^{-5}$	$4.5\ \text{x}10^{-4}$
6 a.i./crop area (kg/m^2)	$2.48\text{x}10^{-8}$	$7.94\text{x}10^{-9}$	$5.58\text{x}10^{-8}$
7 a.i./allotment garden area (kg/ha)	$7.43\text{x}10^{-5}$	$2.38\text{x}10^{-5}$	$1.89\text{x}10^{-4}$

Chance of application is 6/5 = 0.00018
Fraction of crop in the allotment gardens is 7/6 = 0.29

Average application of active ingredient is
$7.43\text{X}10^{-5} + 2.38\text{x}10^{-5} + 50\%^{*}\text{x}1.89\text{x}10^{-4} = 1.93\text{x}10^{-4}$ a.i./ha
[*] The active ingredients in Terrasan Pflanzenspray consists for 50% of lindane, 12.5% of dinocap and 37.5% of dichloorvos.

Overview of emissions into the the Rhine basin area. APPENDIX 9

Direct emissions of HCH to the soil (tons)

	GER	NL	FR	LUX	SW	AUS	TOTAL (tons %)
cereals	134	33.4	44	4.5	9	6.7	231.7 **73.7**
beet	9	2.3	5	1.4	3	2	22.7 **7.2**
maize	17	5.8	9	0	3	0	34.8 **11.1**
tulips	0.0070	0.0018	0.0016	0.0002	0.0013	0.0002	0.012 **0**
greenhouse roses	0.0003	0.0001	0.0001	0.0000	0.0001	0.0000	0.001 **0**
livestock	0.4	0.3	0.07	0.02	0.13	0.01	0.930 **0.3**
forest	5.8	0	1.2	0.15	3.1	0.2	10.5 **3.3**
municipal pest control	0.199	0.043	0.022	0.002	0.034	0.002	0.302 **0.1**
allotment gardens	0.09	0.019	0.01	0.0007	0.015	0.001	0.136 **0**
sludge reuse	0.11307	0.00556	0.00652	0.0007	0.0103	0.0007	0.137 **0**
dumps	0.03567	0.00275	0.00264	0.0003	0.0041	0.0003	0.046 **0**
sum	166.6	41.9	59.3	6.1	18.3	8.9	301.2 **95.9**
% of total	**55.3**	**13.9**	**19.7**	**2.0**	**6.1**	**3.0**	
Indirect emissions to the soil							
rain	4	0.8	0.8	0.1	2.2	0.2	8.1 **2.6**
dry deposition	2.7	0.5	0.6	0.1	0.9	0.1	4.9 **1.6**
sum	6.7	1.3	1.4	0.2	3.1	0.3	13 **100**