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Catch-up operation on old pesticides:  
an integration.

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## PREFACE.

The present report is a compilation of the activities carried out by the Toxicology Advisory Centre of the National Institute of Public Health and Environmental Protection (RIVM-ACT) as part of the project "Catch-up operation on old pesticides" in the period January 1988 to December 1989 inclusive, and was commissioned by the Ministry of Housing, Physical Planning and the Environment, Directorate-General for Environmental Management/Substances and Risk Management Directorate (VROM/DGM/SR). The project has resulted in a summary and RIVM conclusion for 152 pesticides and subsequently in an environmental synopsis. The ACT has presented the summaries and RIVM conclusions in advisory reports to the SR, thus achieving the primary objective of the project. A secondary objective was the incorporation of the summaries into the automated toxicological database of the ACT (TOXBANK) in order to have an up-to-date summary of the data available at any given moment. This report was written to inform also a broader public about the activities. At the same time it offers the reader the opportunity to form a picture of the environmental properties of the pesticides evaluated. It will be clear that the project and the report have been accomplished by intensive collaboration between a large number of persons.

On the part of the RIVM-ACT, which was commissioned to carry out the project, and the authors of this report, a word of thanks is extended to:

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## SUMMARY.

The "Catch-up operation on old pesticides" project has resulted in a summary and RIVM conclusion of the environmental aspects of 152 pesticides which were already marketed in the Netherlands before 1975. The RIVM conclusion was subsequently rewritten to form an environmental synopsis. The present report describes the procedure followed and the results obtained in the evaluation of the environmental effects of these chemicals.

Pesticides have been evaluated on the basis of the test results submitted with regard to their behaviour in soil and water, their effects on organisms present in the environment, such as birds, aquatic organisms (algae, crustaceans and fish), bees and earthworms, and their bioaccumulation potential. Behaviour in soil concerns the rate and route of conversion of a pesticide and its sorption to soil particles. The risks of leaching to the saturated soil layers and of accumulation in the plough layer one year after application of the chemical have been estimated using the Support Group M model developed for this purpose. Behaviour in water includes the rates of hydrolysis and photolysis, and especially the rate and route of conversion of a pesticide in water/sediment systems.

Several proposals have been made for classification systems of environmental properties of pesticides in general. A classification system for persistence in particular is badly needed for the intercomparison of the pesticides. It appeared that various data necessary for the evaluation are still lacking for many pesticides.

The report also makes proposals for developing several aspects of the evaluation, such as behaviour in air, risks to terrestrial organisms and risks of biomagnification.

## 1. INTRODUCTION.

The Pesticides Act of 1962 was amended in 1975 in order to increase the possibilities of evaluating pesticides with regard to risks to the environment. Before that date, the evaluation only concerned risks to public health and the risk of leaching. A large number of pesticides were already on the market before 1975 and these chemicals had been granted licences valid for periods ranging from 5 to 10 years. As a result of this amendment, the companies were asked additional environmental questions about the so-called old pesticides as a condition for renewing the licence. The reason is that the authorities responsible for the registration of pesticides became increasingly aware of the consequences which continued input to the environment of chemical substances, including pesticides, can entail. Because of these changed insights into the environmental risks from pesticides, industry has carried out many studies since 1975. In addition to tests considered necessary for the registration of pesticides before 1975, such as the route and rate of conversion in soil and the risk of leaching from soil to groundwater, it also became mandatory from 1980 onwards to provide data on the behaviour of pesticides in surface water, adsorption onto suspended solids and toxicity to aquatic organisms, such as algae, crustaceans and fish. The flow of environmental information on the various pesticides became so large that the scientific evaluation of their environmental risks could not keep pace with it. To clear up the backlog, the Toxicology Advisory Centre (ACT) of the National Institute of Public Health and Environmental Protection (RIVM) started the project "Catch-up operation on old pesticides", commissioned by the Directorate-General of Environmental Management, Substances and Risk Management Directorate (DGM/SR). The objective of the project can be formulated as follows:

- to summarize and evaluate the environmental data on selected pesticides, supplied by the companies applying for registration.
- to evaluate these data as unambiguously and uniformly as possible, enabling intercomparison of the evaluations.
- to incorporate the summaries into the automated database of RIVM-ACT.

The ACT also took this opportunity to adjust the evaluation of the environmental aspects of these pesticides to the current insights.



Of the more than 350 active ingredients which are currently used in the various formulations for pesticides, the supplementary environmental studies have meanwhile been mostly completed. Within the Committee for the Registration of Pesticides (CTB), about 100 compounds have been evaluated concerning their environmental effects during most of the past 3 years. This two-year project had to evaluate at an accelerated pace some 150 pesticides with regard to their risks to the environment. These compounds were selected in close consultation with the DGM/SR, the Plant Protection Service (PD) and the RIVM, in which the following criteria have played a part:

- already on the Dutch market before 1975;
- proven problem substance because of known environmental properties;
- expiry of renewal term in 1987, 1988 or 1989;
- substantial production or market volume in the Netherlands;
- environmental summary absent or incomplete.

The selection of "old" pesticides made in this way finally comprised 162 active ingredients. The list does not contain chemicals which are already banned, but all black substances, that is, substances not allowed to be used in water-collection areas, have been placed on it. The list of pesticides finally included in the project is given in appendix 1. The pesticides which have also been evaluated by the Support Group M (environment) of the CTB are marked with an \*. Of the pesticides still to be processed by the Support Group M, some figures may still be subject to a few alterations. Finally, a few more changes were made during the project, so that 152 pesticides were eventually summarized, of which 148 have been incorporated in this report. Reports and publications sent by the companies concerned to the RIVM or DGM through the Office for Pesticides (BB) were the only source of information used. Consequently, much of the existing information about the behaviour and effects of a pesticide in the environment was sometimes not included in the evaluation. However, the evaluation of new pesticides is also based solely on information provided by the companies, so that the procedure followed in this report was in accordance with this. Additional information was included in the evaluation if there was good reason for doing so, for example, when the evaluating bodies had received conflicting information. Any controversial or supplementary data to which the internal and external experts concerned had access was also included in the evaluation.

The evaluation method, as developed by working groups of the Support Group M of the CTB for three aspects, was used in the evaluation of the test results provided. It concerns:

- behaviour in soil;
- behaviour in water; and
- risk to aquatic organisms.

A few other aspects of the evaluation, such as behaviour in air, risk to terrestrial organisms and risk of biomagnification, will be worked out in more detail at a later stage.

The structure of the report is as follows:

Chapter 2 gives a general description of how an evaluation is made with the relevant government bodies. Chapter 3 elucidates the procedure used in the "Catch-up operation" project, while chapter 4 discusses the results of the project. Finally, chapter 5 presents a number of conclusions which could be drawn after completion of the project.

## 2. PROCEDURE AND EVALUATION.

A summary was made of the data supplied by the company or companies concerned according to the usual protocol performed at the Toxicology Advisory Centre (ACT), which implies that the evaluated data are suitable for inclusion in the automated database of the ACT: the TOXBANK. The summary and evaluation were made in close collaboration with experts from other RIVM laboratories. For environmental aspects, these are the Laboratory for Ecotoxicology, Environmental Chemistry and Drinking-water Research (EMD), the Laboratory for Soil and Groundwater Research (LBG) and the Laboratory for Organic-analytical Chemistry (LOC). These discipline-oriented experts were responsible for the contribution of specific subject matter in the various fields. They were regularly consulted by the literature researchers during the interpretation of the data supplied. In the RIVM conclusion which concludes the summary, a value judgement was assigned as far as possible to the various environmental properties of a pesticide. Summary and conclusion were discussed integrally in the Toxicology II Advisory Group, of which staff members of the above-mentioned laboratories are also members. Gaps in the package of studies for a pesticide supplied by the companies concerned were noted, and a request sent to those companies either to perform the missing tests or to supply relevant data upon them.

Next, the RIVM advisory report was discussed by the Support Group M of the CTB regarding the scientific weighing up of the environmental aspects. The following bodies have representatives in the Support Group M: Staring Centre (SC) - formerly Institute for Pesticides Research (IOB) -, Plant Protection Service (PD) and Centre for Agro Biological Research (CABO until 1/1/90), the RIVM and the Department of Inland Waterways/National Institute for Waste Water Research (DBW/RIZA), the last-mentioned especially by virtue of its responsibility for the compartment surface water. The RIVM was also represented as the organization producing the draft evaluation. After approval by the Support Group M, the RIVM conclusion was re-written to form an environmental synopsis, an evaluated summary of the environment-relevant properties, and directed via the Office for Pesticides into the CTB channels. First, the Subgroup LM (agriculture and environment) gave an opinion for the purpose of weighing up the policy implications, and then the Working Group L (agrochemicals) prepared the policy decision. The final

advice was ratified by the CTB, after which the registration order was drawn up by the Minister of Agriculture, Nature Management and Fisheries (LNV). This procedure is schematically presented in figure 2.1. It may be mentioned here that the RIVM-ACT also follows this procedure for new pesticides. To enable the evaluation of the large number of pesticides in the catch-up project in a consistent and rational way, the risk evaluation procedure used had to be geared to the problem as well as possible. The RIVM and the Support Group M are currently working on the development of an evaluation system for pesticides. This system will assign value judgments to the environmental properties of pesticides in relation to environmental criteria, and to the processes which play an important role for the pesticide under consideration.

Table 2.1. Evaluation aspects according to behaviour and effect.

Evaluation aspect	behaviour	effect
Physicochemical properties	*	
Degradability in soil	*	
Mobility	*	
Accumulation and leaching	*	
Biodegradation in water/sediment systems	*	
Hydrolysis	*	
Photolysis	*	
Toxicity to birds		*
Risk to birds		*
Toxicity to aquatic organisms		*
Emission	*	
Risk to aquatic organisms		*
Bioaccumulation	*	
Toxicity to bees		*
Toxicity to earthworms		*
Soil respiration and nitrification		*

The processes and effects on organisms included in the evaluation are presented in table 2.1. A distinction has been made between behaviour and effect of a pesticide. Classification criteria are now available for most of the processes or effects mentioned, while criteria are being developed for others, such as persistence. As regards emission into surface water, emission percentages have been estimated, which are related to the crop to which the chemical is applied.

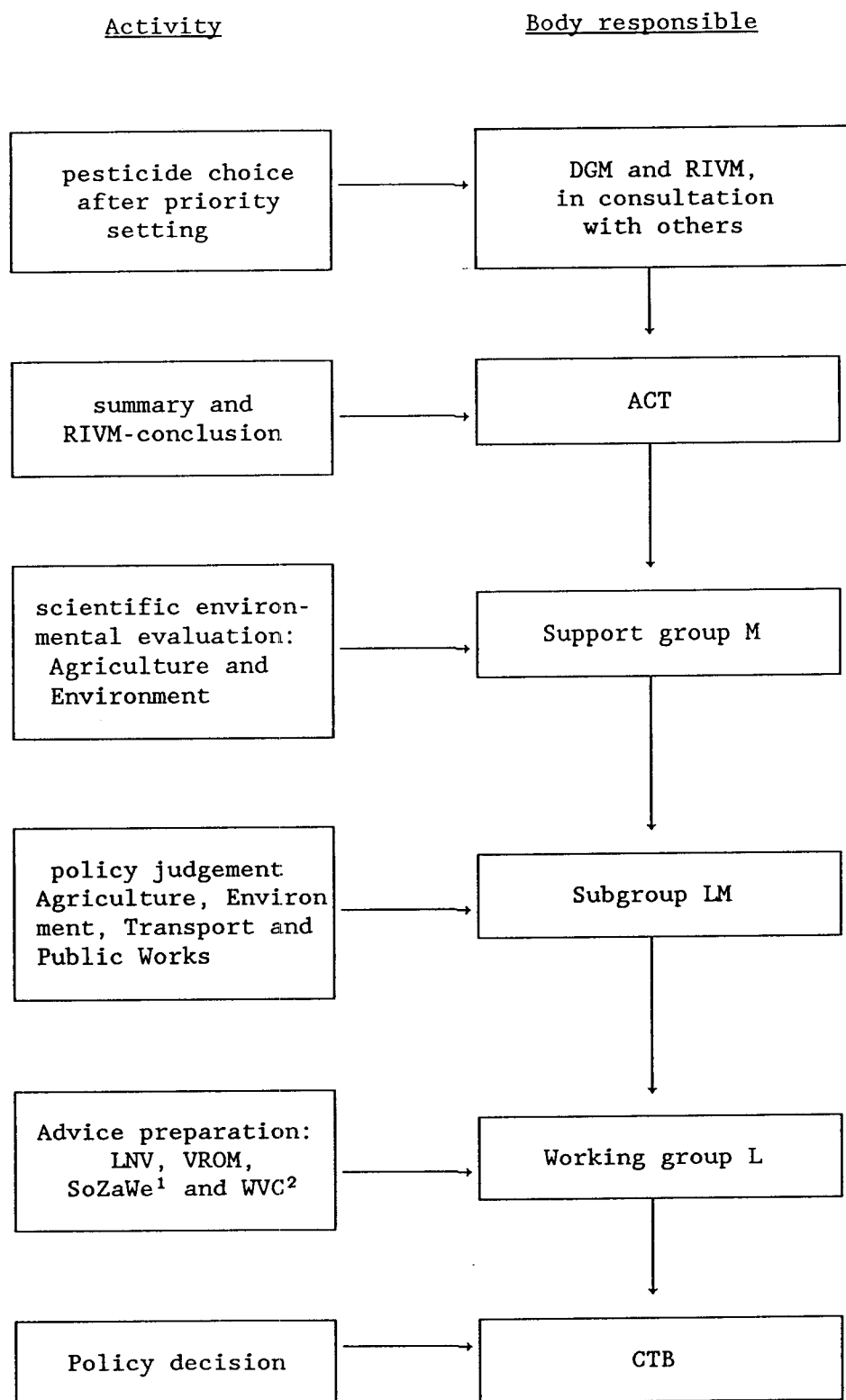


Figure 2.1.: Procedure and information flows in the evaluation of pesticides: <sup>1</sup> = Ministry of Social Affairs and Employment; <sup>2</sup> = Ministry of Welfare, Public Health and Culture.

The principal criteria in the current evaluation procedure are accumulation in, and leaching from, the soil, the estimation of emission into surface water and the resulting risk to aquatic organisms, and bioaccumulation. A brief characterization of the criteria is given below, while they are discussed in more detail in the following chapters.

An estimate of leaching and accumulation is made on the basis of the rate of conversion of a pesticide and its mobility in soil. An important factor here is the EC imperative standard for drinking water.

The concentration in surface water is estimated assuming a 25 cm-deep ditch into which a percentage of the dosage is emitted. The resulting concentration in the water is compared with the toxic levels for different types of aquatic organisms, such as algae, crustaceans and fish. Risk to the organism concerned is not ruled out when these two concentrations are of the same order of magnitude. This does not yet take into account safety factors for extrapolating the results of laboratory tests at single-species level to the ecosystem in the field, and bioavailability. These extensions will be included at a later stage of the evaluation process.

Whenever possible, the bioaccumulating properties are related to the octanol/water partition coefficient, the  $K_{ow}$ . This estimation is only permitted for compounds with a  $\log K_{ow} < 6$  and not too high a molecular weight ( $M < 500$ ). If the water solubility exceeds 2000 mg/l, bioaccumulation will be negligible and calculation is then considered not useful. On the basis of a comparison of the bioconcentration factor (BCF) of a compound and the octanol/water partition coefficient, a double logarithmic relationship has empirically been established, which appears to hold reasonably well in practice [18].

The evaluation system does not yet contain the risks of pesticides to terrestrial organisms and insects (bees), nor an estimate of the exposure and any consequences of emissions to the compartment air. The risks of biomagnification in birds have also still to be detailed. Attention will be paid to this matter in the future. Within the framework of Support Group M, three working groups are further developing the risk evaluation procedure for pesticides, and the project has made use of this work. In addition, the results from the Implementation of the Environmental Criteria for Pesticides, for which a DGM/LNV working group has been set up, have been utilized; DBW/RIZA and RIVM-ACT also participated in this.

### 3. THE PRODUCTION OF SUMMARIES.

This chapter describes how the summaries have been made. Details are given of the information processed, the selection criteria used and the interpretation of the studies. The first section considers general rules and the subsequent sections deal with the various aspects of soil, water, toxicity and emission into surface water.

#### 3.1. Starting points.

##### 3.1.1. General.

The advisory report on the data of a pesticide broadly consists of the following 4 parts:

1. General.
2. Human toxicology.
3. Ecotoxicology.
4. Conclusions.

Within the framework of the Catch-up operation on "old" pesticides, no attention was paid to the above-mentioned part 2.

- re 1. The general part describes the nature of the chemical (nomenclature, structural formula and physical/chemical data). General information about purity, application area, dosage, formulations, occurrence in the environment, metabolites and conversion pathway are also included.
- re 3. The ecotoxicology part describes the environmental studies supplied by the companies. Relevant data on experimental design and the results considered to be important are taken from these studies. In addition, observations made by the literature researcher about the study described can be entered under "remarks". They usually concern deficiencies (lack of information, unreliable results) or results calculated by the literature researcher himself.
- re 4. The data on the behaviour in soil, water and sometimes also air are evaluated in the RIVM conclusion. The toxicity to aquatic organisms, birds, bees and earthworms are also evaluated, and the risk to birds

and bees is assessed. To that end, a value judgment is assigned to the various properties of a pesticide according to the system given in appendix 6. In addition, a number of (model) calculations are performed.

### 3.1.2. Sources.

Besides the studies supplied by the companies, summaries previously made by the RIVM, the DGM or the PD, and supplementary notes from the CTB or DGM were also processed. Special attention was paid to missing data. These summaries and notes were included when the information was sufficiently detailed. In addition, literature supplied by members of the Support Group M and by experts within the RIVM was included. In general, it concerned controversial or missing data. Also included were data on measured concentrations of pesticides in groundwater, these usually being results from monitoring programmes of the RIVM [24, 25, 50]. The PD provided information about application area, dosage, frequency and time of application of the pesticides concerned. Handbooks were consulted for the physicochemical properties of the pesticides.

In addition to studies with the active ingredient, studies with formulations and metabolites of the active ingredient were processed.

### 3.1.3. Categories.

Since a large amount of data had to be summarized and the studies in many cases did not meet the current requirements [11], the literature was first examined for its usefulness, whereafter each study was placed in a category. Studies were assigned to one of 3 categories on the basis of quality criteria in the field of experimental conditions, reporting and relevance to the Dutch situation (appendix 2). The most valuable studies (category 1) were summarized as well as the results of studies which were less reliable or inadequately reported (category 2). However, the latter were only described in the RIVM conclusion when there was no information available from category 1 studies on the aspect concerned. Furthermore, unreliable and



irrelevant studies were distinguished (category 3) when no information from category 1 or 2 studies was available. Studies on metabolism in plants were not processed, because they are covered by the human evaluation of a pesticide in connection with residue tolerance.

#### 3.1.4. Test criteria.

When summarizing studies which were performed according to a recognized protocol [4 to 6, 14 to 16, 29 to 43 inclusive, and 48], the experimental design was not described but the reader was referred to this protocol.

In the course of the project, agreed methods of summarizing were arrived at. These agreements concerned, for example, the way in which data were processed, or the selection of data from the summary which had to be included in the RIVM conclusion. Since this has been a continuous process, the various pesticides have not all been summarized according to the same agreements. This report presents the most recent agreements.

In addition, guidelines have been drawn up by the Support Group M on the usefulness of various studies for an estimation of the extent of leaching and accumulation, based on the Support Group M model [26].

#### 3.2. Soil studies.

##### 3.2.1. General.

Different types of studies were supplied regarding the behaviour of pesticides in soil. A distinction was made between studies investigating conversion and studies determining mobility in soil. These studies were included in the relevant section of the summary when they had been satisfactorily carried out and described. In addition, studies were supplied in which runoff via slopes was investigated. However, these studies are considered to be irrelevant to the situation in the Netherlands, where pesticide runoff is insignificant.

In the interpretation of the data on conversion rate and mobility, a model calculation was performed as part of the RIVM conclusion, to make a

prediction about the leaching and accumulation of a pesticide in soil possible [26].

### 3.2.2. Conversion.

Conversion rate and pathway.

One of the most important factors in the registration of pesticides is insight into the rate and route of conversion of the active ingredient and the formation of any metabolites [11].

Conversion is the process in which the original structure of the active ingredient is affected such that the molecular formula changes. This change may be very small and, moreover, involve an increase as well as a decrease in the molecular mass. Consequently, the size of the metabolite is in some cases virtually the same as or even greater than that of the parent compound, so that it is inaccurate to speak of degradation. For this reason, the term "conversion" is preferred in this report to the less correct "degradation".

When the decrease in concentration of the active ingredient cannot solely be attributed to conversion, then dissipation is involved. Processes such as volatilization, leaching, adsorption, dilution, but also conversion can play a part in dissipation.

The rate of conversion of a pesticide is usually expressed in the half-life. The DT50 as used in this report therefore refers to conversion only. When determining the DT50, disappearance of the active ingredient other than by conversion must be precluded. In most cases, DT50 values could be taken directly from the studies. Some were calculated from the results of a study or recalculated in case of doubt. Beside DT50 values for the active ingredient and any metabolites formed, results were included regarding formation percentages of metabolites, CO<sub>2</sub> and soil-bound residue, and the kinetics of the conversion reaction. The relevant test criteria are described in appendix 3.1.

Note that this also applies to aquatic studies.

## Persistence and intrinsic persistence

The concept of persistence is often used in connection with the residence time of a pesticide in a particular compartment. The longer the residence time, the more persistent a substance is, and it is too persistent when the residence time exceeds a certain period. Therefore, the degree of persistence is usually expressed in the DT50 [28, 47].

A DT50 for conversion has been determined in this report. However, it is also possible to determine a DT50 for dissipation. Both methods have their supporters in practice, and consequently the meaning assigned to the term "persistence" is not always the same.

To avoid confusion, a new term has been introduced in this report: intrinsic persistence. Intrinsic persistence refers to the residence time of a substance in a compartment which depends solely on conversion; other dissipation processes are excluded. This contrasts with persistence where the residence time is also determined by dissipation processes other than conversion only.

## Classification.

It follows from the above that the DT50 is a measure of the intrinsic persistence of a pesticide; on the basis of this value, the intrinsic persistence can be assessed. A generally accepted classification scheme for persistence in soil is not yet available. The differences of insight can possibly be explained by lack of political consensus rather than by gaps in the scientific underpinning. Therefore, an assessment of persistence was not given in the RIVM conclusion. When interpreting the results of tests, attention was paid only to the value of the DT50 in relation to adsorption and the risks of leaching and accumulation as these could be calculated with the model.

As regards the DT50 values used for the model calculation, a number of selection criteria were applied. These criteria concerned, among other things, the type of study, temperature, dosage, and moisture content and freshness of the soil (appendix 3). Furthermore, the model calculation was in principle performed with reliable (category 1) values. When these were

not available, category 2 values were used, and this was recorded with the results.

### 3.2.3. Mobility.

Various experiments can be carried out to gain an insight into the mobility of a pesticide in soil, such as shaking tests, column studies and soil thin-layer chromatography. The reader is referred to appendix 3 for a description of the conditions relevant to the evaluation.

In shaking tests, the distribution of a pesticide over the solid and liquid phases is established, after which the adsorption coefficient ( $K_{s/l}$ ) is determined with the help of an adsorption isotherm.

In column studies and soil thin-layer chromatography, a retardation factor ( $R_f$ ) can be determined from the distance moved by a pesticide in relation to the water front. A  $K_{s/l}$  can be derived from the  $R_f$  using the relationship:

$$K_{s/l} = \frac{\epsilon (1 - R_f)}{\rho * R_f} .$$

Assuming a standard value for the bulk density of the soil ( $\rho = 1.4 \text{ kg/dm}^3$ ) and for the moisture volume fraction ( $\epsilon = 0.4$ ), then it follows that:

$$K_{s/l} = \frac{0.286}{R_f} - 0.286.$$

The  $K_{om}$  equals the quotient of the  $K_{s/l}$  and the organic matter fraction of the soil, and was used as input parameter for the model calculation.  $K_{om}$  values were only included in the model calculation if a number of conditions had been fulfilled. These conditions usually concerned the accuracy of the measurement results (appendix 3.2.). Here, too, the model calculation was in principle performed with  $K_{om}$  values obtained from category 1 studies. An exception was made when reliable values were not available.

For the classification of the mobility of pesticides in soil, the values for  $K_s/1$  and  $R_f$  obtained from adsorption studies, column studies and soil thin-layer chromatography were grouped according to the classification based on the internationally accepted system of Helling [22]. The mobility class involved (from immobile to highly mobile) was recorded in the RIVM conclusion.

#### 3.2.4. Calculation of leaching and accumulation.

As another item of the conclusion, a calculation was performed with the Support Group M model to make a prediction possible about the extent of leaching and accumulation of a pesticide as a function of the DT50 and  $K_{om}$ . The model has been developed by the working group "Behaviour in soil" (Support Group M) and is based on the following data:

- Soil type: relatively vulnerable sandy soil. The organic matter content was 4.7% in the Ap horizon (0-30 cm) and 0.8% and 0.2% in the lower B3 and C11 horizons (30-50 cm and 50-59 cm, respectively); the C12 horizon (110-120) cm contained 0.1%;
- Soil treatment: none (untilled soil). After applying a pesticide, the soil is not ploughed or otherwise tilled so that displacement of the substance through mixing of soil layers is excluded;
- Culture: maize (important for evaporation, evapotranspiration);
- Dosage: a single spring or autumn application, 1 kg a.i./ha;
- Precipitation: data from a 74% wet year (gross precipitation in 73% of the years is lower [26]).

The results obtained are:

- concentration of the substance in the shallow groundwater ( $\text{mg}/\text{m}^3$ );
- leaching from the upper one metre of the soil (as a percentage of the dosage);
- residue in the plough layer after 1 year (as a percentage of the dosage; the absolute concentration in  $\mu\text{g}/\text{kg}$  in the plough layer (the upper 20 cm of the soil) was calculated assuming a soil density of  $1310 \text{ kg}/\text{m}^3$ . The conversion factor of 3.8 thus obtained was rounded off to 4.

Of the DT50 and  $K_{om}$  values selected, the average and standard deviation were calculated, after which the corresponding results were read from graphs obtained by means of computer calculations (appendix 3.5).

For pesticides which may be present in soil water in ionized form (indicated by the  $pK_a$ ), the  $K_{om}$  may depend on the pH of the soil. In such cases the model calculation was performed for both the low (pH 4-5) and the high (pH 7-8) pH range.

The model is not suitable for volatile pesticides, that is, for compounds with a Henry coefficient greater than  $10^{-5}$ . When the value ranged between  $10^{-4}$  and  $10^{-5}$ , the results from the model calculation were included with the addition of a "remark".

When over 10% of one metabolite was formed from the parent compound, leaching and accumulation of this metabolite were also assessed. The results obtained with the model were then multiplied by two correction factors:

- The molecular mass of the metabolite divided by that of the parent compound, and
- The formation percentage of the metabolite (maximum value found) as a fraction of the dosage of the parent compound.

### 3.3. Aquatic studies.

Pesticides can be converted in water by physical/chemical processes (for example, hydrolysis and photolysis) and by the action of microorganisms (biodegradation). Adsorption of pesticides onto sediment may also occur. The so-called laboratory water/sediment study is prescribed for the assessment of the behaviour of pesticides in water and sediment, in which hydrolysis, photolysis and biodegradation all play a role [11].

Hydrolysis and photolysis studies were supplied as well as water/sediment studies. The most important result from these studies is the DT50 value for the active ingredient. In addition, information about formation percentages of metabolites and  $CO_2$  production were also included.

In the case of biodegradation in water/sediment systems, a distinction was made between a DT50 value for the pesticide in the water phase (DT50 water) and a DT50 value for it in the whole system (water and sediment; DT50

system). From the point of view of environmental behaviour, the greatest value is attached to the DT50 system.

Furthermore, a distinction was made between DT50 values based on CO<sub>2</sub> production (DT50(C)) and DT50 values for conversion of the active ingredient. The DT50(C) value provides an indication of the rate at which a compound is completely mineralized. The DT50 values for conversion give a generally good indication of the rate at which the active ingredient is converted. In aquatic studies, however, the DT50 is often not strictly based on conversion, and volatilization, for example, may also be a contributory factor in the disappearance of the pesticide. The distinction between a DT50 based on conversion and a DT50 based on dissipation was in most cases clearly reported.

The reader is referred to appendix 4 for a description of the test conditions relevant to the evaluation.

### 3.4. Toxicity studies.

#### 3.4.1. General.

Toxicity studies with birds, aquatic organisms, earthworms, bees and soil microorganisms are considered to be important for determining the possible adverse effects of pesticides on organisms present in the environment. The provision of these studies depends on the use and time of application of the pesticide. A brief description of the different types of studies is given in appendix 5. The data which have been incorporated into the summaries are given below.

#### 3.4.2. Aquatic organisms.

Studies with aquatic organisms were divided into short-term (< 120 hours) and long-term (> 120 hours) tests. The application form requires tests with algae, crustaceans and fish. Tests with other types of freshwater organisms were described in the summaries and RIVM conclusion, but are not discussed in this report owing to the relatively low number available. When only the

original data were reported in a short-term (acute) study with crustaceans or fish, the L(E)50 was calculated according to the "trimmed Spearman-Kärber method" [19]. The pesticides were classified according to the scheme in appendix 6 on the basis of the L(E)C50 or NOEC values.

Data on bioaccumulation were obtained from various studies: bioaccumulation, field- and model-ecosystem studies. The bioconcentration factor (BCF) was determined in these studies. In the absence of an experimentally determined BCF, where a Kow was available the BCF was calculated as follows:

$$\log \text{BCF} = 0.79 * \log \text{Kow} - 0.40 \quad [18]$$

This formula was only used for hydrophobic organic compounds if the following conditions had been fulfilled:

- $\log \text{Kow} < 6$ ;
- Molecular weight  $< 500$ .

Pesticides with a high water solubility accumulate to a limited extent only. Calculation of the BCF is not considered useful in these cases, so that a third condition was introduced:

- Solubility  $< 2000/\text{l}$ .

Next, the substances were classified according to the scheme in appendix 6 on the basis of an experimentally determined, or a calculated, BCF.

A risk estimate was made for aquatic organisms in the RIVM conclusion. The risk was assessed by relating the toxicity to the exposure level. The exposure level has provisionally been equated with the theoretical concentration in the surface water of a standard ditch (depth: 25 cm) immediately after application of the pesticide. The concentration was estimated by performing a drift calculation, which is based on the following assumptions:

- The pesticide is applied only once;
- The pesticide is rapidly distributed homogeneously over the water compartment; complete mixing occurs;
- There is no change in concentration with time; dissipation due to, for example, adsorption, hydrolysis, volatilization or dilution is disregarded;
- A fixed percentage of the dosage is emitted per application area (appendix 5.6).



The concentration in water (mg/l) can then be easily calculated from the amount of pesticide emitted (kg/ha):

$$\text{concentration} = 0.4 * \text{dosage} * \text{emission fraction}.$$

This concentration was called the predicted environmental concentration (PEC), which was subsequently related to the acute and chronic toxicity data for algae, crustaceans and fish. On the basis of the ratio between the L(E)C50 or NOEC and the PEC, a statement was made about the risk of adverse effects on aquatic organisms. In general, only acute toxicity data were available for crustaceans and fish. When long-term toxicity studies were also available, an assessment was made of the risk of effects if the pesticide was converted slowly in water.

#### 3.4.3. Birds.

As regards toxicity to birds, (sub)acute and (semi)chronic studies were included. Only (sub)acute studies were usually available. They can be subdivided into acute studies in which the LD50 is determined after oral administration, and diet studies to determine the LC50.

#### 3.4.4. Bees.

A large number of files lacked the toxicity data for bees. These gaps were filled by consulting several reviews in which reliable data had been collected [2, 23, 46]. The pesticides were classified according to the scheme in appendix 6.

In combination with data on the time of application and the dosage, the hazard of a chemical to bees was evaluated on the basis of the system of Oomen [44]. However, this risk evaluation differs from that for aquatic organisms. This report (4.3.4.) proposes an adaptation of the above-mentioned risk evaluation for bees, so that there is greater agreement between the two systems.

#### 3.4.5. Earthworms.

Although toxicity studies with earthworms are now required in principle for each pesticide, information about this was usually not yet available. In these cases the company was asked for supplementary information. In view of the time which elapses between request and delivery, it was not possible to process these data as part of this project.

#### 3.4.6. Other organisms.

Various studies investigating the influence of pesticides on microbial and enzymatic processes in the soil were incorporated into the summaries and RIVM conclusion. They were mostly studies in which (de)nitrification, soil respiration or enzyme activity had been determined in treated soils. The results from these studies are for the most part not exact values and cannot therefore be presented in tabular form. For this reason, they are not discussed in this report. Occasionally, studies were supplied on toxicity to organisms other than the ones mentioned above. The results were included in the summary and RIVM conclusion but are not discussed in this report because it concerned only a very small number of tests.

#### 4. RESULTS.

This chapter describes and processes the results which have been summarized in appendices 7.1 to 7.8 inclusive. They are discussed per aspect, and concern the results of 148 pesticides. In all, 152 pesticides have been evaluated, but the results of four substances have not been included in this report because they consisted of collections of a number of compounds (benzalkonium chloride, didecyldimethylammonium chloride, mineral oil) or, in one case, a bacterial preparation, making comparison with the other pesticides difficult.

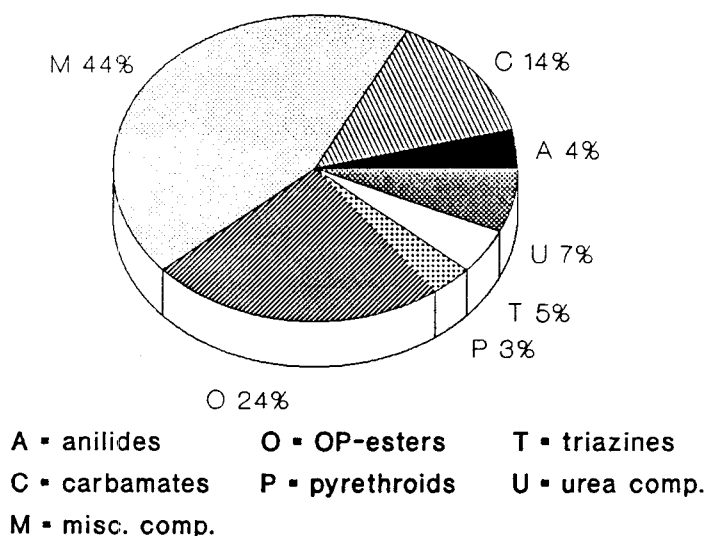


Figure 4.1. Subdivision of the pesticides evaluated in this report per pesticide group according to the classification of the Crop Protection Guide [12]. A = 6 anilides; C = 20 carbamates<sup>1</sup>; M = 65 miscellaneous compounds<sup>2</sup>; O = 35 OP-esters; P = 5 (synthetic) pyrethroids; T = 7 triazines, and U = 10 urea compounds.

<sup>1</sup> Carbamates including (di-)thiocarbamates.

<sup>2</sup> Miscellaneous compounds including 20 specified groups with fewer than 5 representatives.

Frequency distributions were constructed as far as possible per aspect from the available data. Pesticides for which data were lacking have been disregarded. This method of presentation produces a summary of the percentage of pesticides with a particular environmental property for each aspect. The frequency distributions are mostly based on the classification schemes given in appendix 6. An alternative or new scheme was employed in a

few cases. These schemes were developed with a view to increasing the expansion of the already existing risk evaluation.

In addition, the ten pesticides posing the greatest environmental risk were identified for each aspect. Attention was also paid to a possible relationship between the type of pesticide and the observed environmental effects. For this purpose, 6 pesticide groups of which a summary was available for at least 5 representatives were selected (figure 4.1).

#### 4.1. Soil studies.

##### 4.1.1. Conversion.

Data on conversion in the soil environment are presented in appendices 7.1 and 7.6. For 2,4-D, cypermethrin and dicofol, data have been included for 2 different forms (2,4-D for  $\text{pH} < 5$  and  $> 5$ , cis- and trans-cypermethrin, and o,p- and p,p-dicofol, respectively).

In addition, data on 1,2-dichloropropane, a contaminant of 1,3-dichloropropene, have been included, so that the number of compounds involved in soil studies totalled 152. No data on conversion in soil were available for 12 substances, and for 29 substances the data were less reliable.

In general, the conversion of pesticides proceeds as shown in figure 4.2. In most cases, conversion is (wholly or partly) brought about by microorganisms. This has actually been demonstrated for 49 pesticides. In addition, a pesticide can also be converted abiotically, for example, by hydrolysis or photolysis. Simazine and 1,3-dichloropropene are examples of pesticides which are converted by both hydrolysis and microbial metabolism. The conversion of pesticides in soil can be mathematically described. The conversion of most of the pesticides followed a first-order reaction. After 80-90% of the applied pesticide had been converted, the remaining portion was in many cases converted more slowly than might be expected on the basis of these first-order kinetics.

The conversion of pesticides in soil nearly always produces a soil-bound residue, the composition of which is unknown. It is known that the soil-bound residue is present mainly in the humin fraction [7]. For 50

pesticides, the content of soil-bound residue was over 30% of the amount added, and for 19 pesticides it was more than 60%. It should be noted that this content was determined at very different times following application of the chemical. If this content has been measured shortly after application, it can still increase or decrease with time.

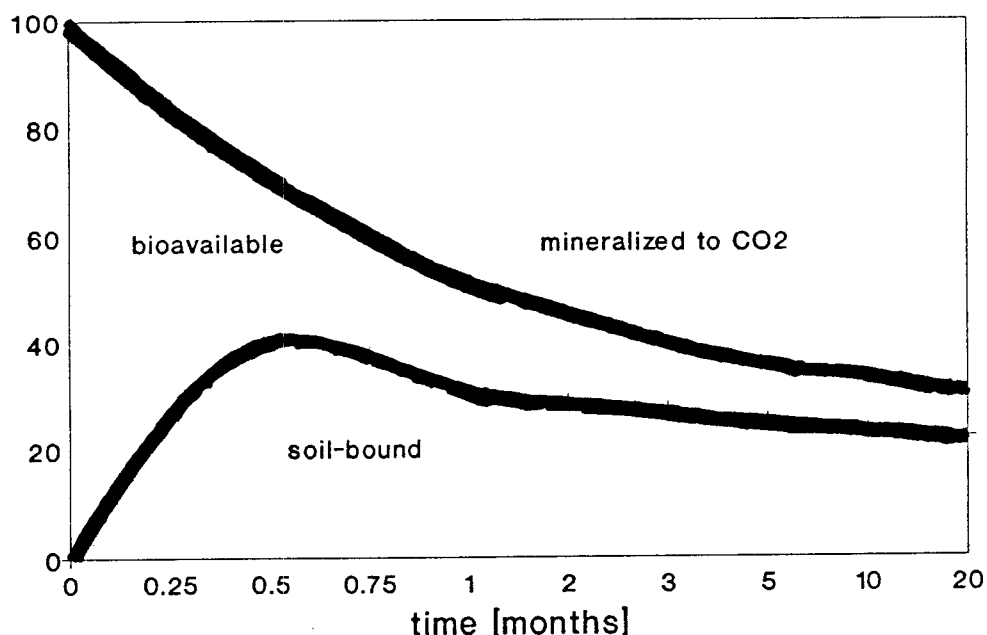


Figure 4.2. The fate of pesticides in soil [7].

At present the significance of the soil-bound residue is not clear. Firstly, it is usually not possible to establish the chemical identity of soil-bound residues. This is because the concentration of soil-bound residue is in most cases determined by extraction with strong acids or strong bases, or by combustion of the soil sample, which causes the chemical structure of the soil-bound residue to change [7]. Secondly, comparison of percentages of soil-bound residues is often difficult owing to the lack of a standard measurement procedure. Different extractants are used which extract to varying degrees. Thirdly, it is still not clear what proportion of soil-bound residues can become biologically available and thereby cause adverse effects. However, it is known that microorganisms, earthworms and plants can take up soil-bound residues. The registration policy should pay more attention in the future to the problem of soil-bound residue.

A DT50 was available for most of the pesticides. For 12 compounds, however, this value could not be derived from the available data. The 10 pesticides with the highest average DT50 at 20 °C are presented in table 4.1.

Table 4.1. The 10 most persistent pesticides arranged according to decreasing DT50 for conversion in soil at 20 °C.

pesticide	DT50 (days)	
	average	standard deviation
1. dicloran	414-913 (*)	
2. pirimicarb	208	114
3. trifluralin	186-255	
4. dikegulac-sodium	>195 (*)	
5. pendimethalin	171	42
6. dodemorph	170	19
7. etrimfos	146	80
8. chlortoluron	143 (*)	
9. methabenzthiazuron	135	25
10. lenacil	134	

(\*) = less reliable data.

The DT50 is an important piece of information because it can be used as a measure of the intrinsic persistence of pesticides [27]. As has already been described in section 3.2, this report uses the concept of intrinsic persistence, since the rate of conversion of a pesticide is taken as the criterion. This contrasts with a broader definition of persistence in which processes such as volatilization and leaching also play a role. At present the registration procedure of pesticides does not yet employ a classification scheme in the evaluation of intrinsic persistence, because of the ongoing discussion concerning persistence. The discussion centres round the question of whether, and if so to what extent, environment-foreign substances are permissible in soil. Another important question is how great the influence of the soil on the persistence of a pesticide might be. It is not clear at present what the possible harmful effects can be of chemicals which accumulate in soil because of their poor degradability or strong adsorption. For example, this matter was raised during legal proceedings started by the producers of the pesticide paraquat. Paraquat

has a DT50 of about 20 years. Also, it is adsorbed so strongly that leaching from the top layer of the soil is negligible [1].

Several proposals for a classification scheme are now available. The Technical Committee on Soil Protection (TCB) has presented the scheme of table 4.2 in the memorandum "Pesticides advice".

Table 4.2. Classification scheme for persistence in soil as proposed by the TCB [47].

klasse	DT50 (dagen)
1. highly persistent	> 100
2. moderately persistent	30 - 100
3. moderately degradable	15 - 30
4. readily degradable	5 - 15
5. highly degradable	< 5

There are two reasons why this scheme is not suitable for classifying the intrinsic persistence of pesticides in soil. The main reason is the imbalance of the classification: a division into 3 classes is made for DT50 values below 30 days, whereas only 2 classes are distinguished for DT50 values above 30 days. Secondly, the scheme uses DT values based on both biodegradation and volatilization.

The memorandum "Environmental criteria for substances to protect soil and water" of the Ministry of VROM gives a limit of 2 months above which substances should be regarded as too persistent [28]. Assuming a DT50 of 60 days, about 1.5% of the dosage is still present after one year. As a safe limit for the occurrence of adverse effects on flora and fauna within a reasonable period, a DT50 of ½-1 month has been suggested. This figure is based on the multifunctionality of the soil, that is, changes in soil properties caused by the application of pesticides must be reversible or restorable within a reasonable period of time [28].

It is proposed to use the classification scheme as presented in table 4.3 in classifying the intrinsic persistence of pesticides on the basis of the DT50. The dividing line between persistent and moderately persistent is set at 60 days, in conformity with the Environmental Criteria memorandum.

Table 4.3. RIVM proposal for a classification scheme for intrinsic persistence.

class	DT50 (days)
1. highly persistent	> 120
2. persistent	60 - 120
3. moderately persistent	30 - 60
4. slightly persistent	15 - 30
5. not persistent	< 15

A frequency diagram has been constructed in figure 4.3, in which the average and the maximum DT50 at 20 °C are classified according to the scheme in table 4.3.

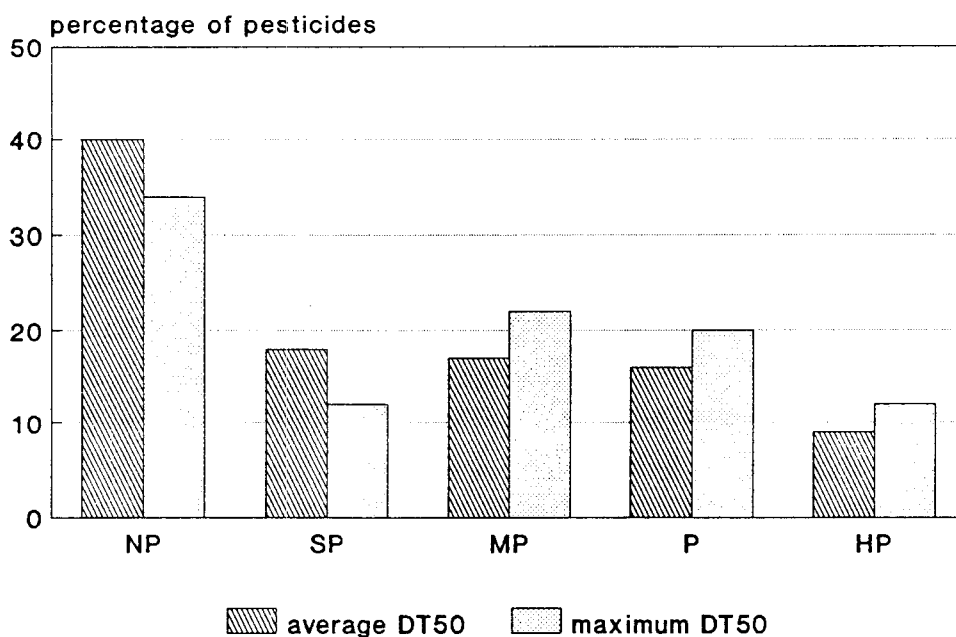


Figure 4.3. Distribution in percentages over the persistence classes according to the RIVM classification scheme, for the average and maximum DT50 at 20 °C. NP = not persistent ; SP = slightly persistent; MP = moderately persistent; P = persistent; HP = highly persistent.

The percentage of pesticides in each class is shown, the number of pesticides for which data were available being taken as 100%. This has been done to make the diagrams comparable, because an average DT50 and a maximum DT50 were not available for 11 and 52 of the 152 compounds, respectively.



It can be observed from figure 4.3 that, based on the average DT50, 24% of the pesticides for which an average DT50 was available can be regarded as persistent to highly persistent. This corresponds to 33 pesticides. Based on the maximum DT50, 31 pesticides (31%) for which a maximum DT50 was available can be regarded as persistent to highly persistent.

To obtain an idea of the intrinsic persistence of the various pesticide groups, the distribution of the number of pesticides over the different persistence classes has been subdivided according to pesticide group. Seven pesticide groups have been distinguished (figure 4.2), based on the average DT50 at 20 °C.

The table shows that the OP-esters and anilides are in general readily degradable in soil. Most of these compounds are classified as slightly and not persistent, although there are also a few falling into the persistent and highly persistent classes. The pyrethroids fall mostly into the slightly persistent and moderately persistent classes. On the other hand, the triazines and urea compounds are in general poorly degradable. They are mostly classified as moderately to highly persistent. Finally, the carbamates are distributed over all classes with the greatest concentration in the not persistent and moderately persistent classes.

Table 4.4. Persistence classification subdivided according to pesticide group. Division based on the RIVM classification scheme (table 4.3).

group	total	average DT50 in days					- <sup>1</sup>
		<15	15-30	30-60	60-120	>120	
anilides	6	2	3	0	1	0	0
carbamates	20	9	1	5	2	1	2
OP-esters	35	18	7	4	4	1	1
pyrethroids	6	1	2	2	1	0	0
triazines	7	0	1	2	2	1	1
urea compounds	10	1	2	2	2	3	0
misc. compounds	68	24	10	11	7	8	8

<sup>1</sup> = No DT50-value available.

When using the DT50 as a measure of intrinsic persistence, the following should be noted. The DT50 is a measure of the conversion of the pesticide

(including conversion to bound residue). Intermediates (metabolites) are often formed which, in turn, can be converted. Ultimately this can lead to inorganic end-products ( $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_2$ , etc.). In many studies the formation of  $\text{CO}_2$  is measured to demonstrate that parts of the pesticide can be converted into inorganic end-products. From the rate of  $\text{CO}_2$  formation and the formation percentage, a rough indication of the intrinsic persistence of (a part of) the molecule can be deduced. In by far most cases, parts of a pesticide are incorporated into the biomass in soil or immobilized in the organic matter in the form of bound residue (as an indication: the average turn-over time of biomass is 6 months, that of organic matter about 100 days). Therefore, 100% mineralization is never expected within the duration of an experiment. A half-life for mineralization cannot in principle be derived because there are several fractions, and a first-order approach is then not possible.

The fact that the rate of mineralization is partly related to certain sites in the molecule is also important. Mineralization studies are performed with compounds in which a particular carbon atom has been radioactively labelled. Readily degradable parts of a molecule will be converted into  $\text{CO}_2$  more rapidly than less readily degradable parts. The latter are usually ring structures whereas side chains of a molecule are often readily degradable. For example, in an experiment with triazole-labelled propiconazole, 3% was converted into  $\text{CO}_2$  within one year, while this was 42-46% in 168 days in another experiment with dioxolane- and phenyl-labelled propiconazole.

An example of a less readily degradable part of a molecule is the triazine ring structure in triazines such as atrazine and simazine. Atrazine has a DT50, based on the active ingredient, of 50 days. However, only 12-25% has been converted into  $\text{CO}_2$  after 180 days. A persistent metabolite is formed, namely hydroxyatrazine, which has a DT50 of 164 days. In addition, another metabolite, desethylatrazine, is formed with a DT50 of 45 days. The triazine ring is still intact in both metabolites. To determine the half-life for mineralization of the triazine ring, a study should be carried out with atrazine having a labelled carbon atom in the triazine ring.

It is clear from the above that persistent metabolites may be formed. At present a formation percentage of at least 10% is used as a limit in the

registration procedure (chapter 3). This means that above this limit, data on conversion and mobility of metabolites must be supplied according to a standard procedure. However, it is also possible that a complex of almost identical metabolites is formed in which, for example, the ring structure is still intact. The formation percentages of these metabolites could then be added together.

Data on conversion and mobility were available for 15 metabolites. Using the classification from table 4.3 and the average DT50 at 20 °C, 9 metabolites can be regarded as persistent to highly persistent.

#### 4.1.2. Mobility.

Data on pesticide mobility are given in appendices 7.1 and 7.6; there were no mobility data for 21 pesticides. As with conversion, the mobility data processed concerned 152 pesticides (see section 4.1.1).

Mobility depends, among other factors, on the content of organic matter in soil and solubility. Mobility may also be dependent on the pH of soil, in which case the pKa of a pesticide is an important piece of information. For example, the average  $K_{om}$  for 2,4-D at pH > 5 and pH < 5 is 230 and 25 dm<sup>3</sup>/kg, respectively. Separate model calculations have therefore been performed for this compound.

Table 4.5. The 10 most mobile and 10 most immobile pesticides arranged on the basis of the average  $K_s/l$  (dm<sup>3</sup>/kg).

MOBILE		IMMOBILE	
pesticide	$K_s/l$	pesticide	$K_s/l$
1-5. methamidophos	0.00	1. trifluralin	262 (*)
foseethyl-aluminium	0.00	2. aclonifen	210
dikegulac-sodium	0.00	3. fenvalerate	162
acephate	0.00	4. chlorothalonil	161
demeton-S-methyl sulphone	0.00 (*)	5. dodemorph	61
6. dalapon	0.01	6. chloroxuron	45
7. ziram	0.03	7. fenpropathrin	28
8. dicamba	0.06	8. dicloran	28
9. MITC	0.08	9. tridemorph	25 (*)
10. mefluidide	0.09 (*)	10. pirimicarb	20

(\*) = less reliable value.

The 10 most mobile and 10 most immobile pesticides are listed in table 4.5. They have been arranged on the basis of the  $K_s/l$  and the  $R_f$  (column or TLC), where the  $R_f$  values have been converted to  $K_s/l$  values according to the formula given in section 3.2.3.

As has been mentioned in chapter 3, the registration of pesticides procedure groups pesticides into 5 classes, varying from immobile to highly mobile on the basis of the classification system of Helling [22]. Twenty-four pesticides were classified on the basis of less reliable data. In many cases, a pesticide fell into more than one class depending on the observed range in  $K_s/l$  or  $R_f$  (column or TLC) values. This range could as a rule be attributed to experiments performed with different soil types. These soil types usually had different soil properties, such as pH and organic matter content.

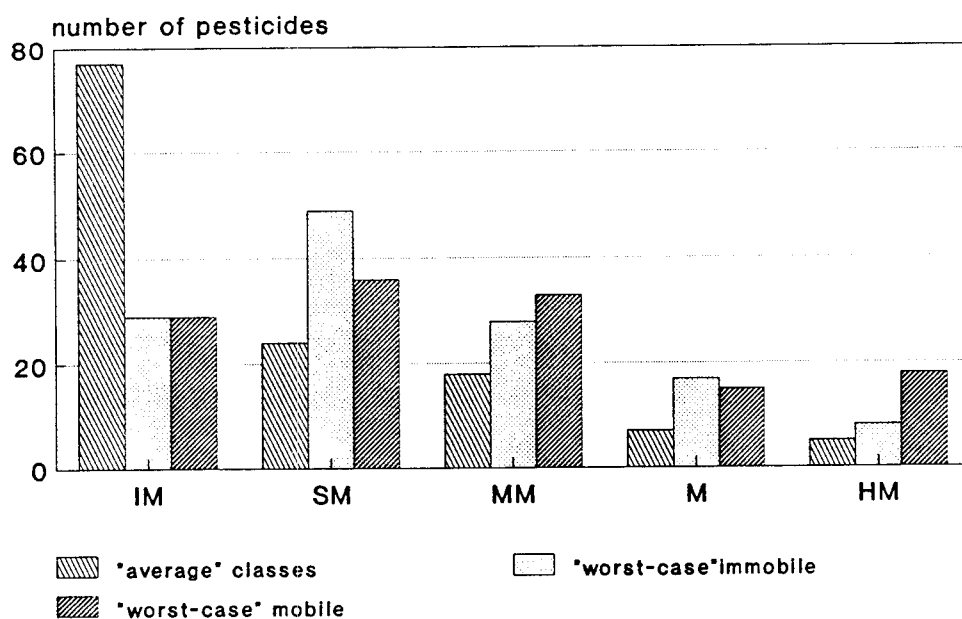


Figure 4.4. Distribution of numbers of pesticides over the mobility classes on the basis of the classification scheme of Helling [22], based on three different groupings of a pesticide by mobility class: "average" class, "worst-case mobile" and "worst-case immobile". IM = immobile; SM = slightly mobile; MM = moderately mobile; M = mobile; HM = highly mobile.

The following frequency distributions have been constructed in figure 4.4:

- one based on the "average" classes. If a pesticide fell into 2 successive classes, the most mobile class was chosen;

- one in which a "worst-case immobile" diagram has been made: the most immobile class was chosen for a pesticide falling into a composite class;
- one in which a "worst-case mobile" diagram has been made: the most mobile class was chosen for a pesticide falling into a composite class.

"Worst-case immobile" is based on maximum accumulation and "worst-case mobile" on maximum leaching.

It can be inferred from the division on the basis of "average" classes that a large proportion of the pesticides falls into the slightly mobile and immobile classes, namely, 59% of the compounds for which data were available. Based on "worst-case immobile" or "worst-case mobile", the picture looks quite different. For example, for "worst-case immobile" and "worst-case mobile", 58% and 21% respectively of the compounds for which data were available are immobile.

The distribution of the various pesticide groups over the mobility classes is presented in table 4.6. It is based on the "average" classes; if a compound fell into 2 successive classes, the most mobile class was chosen.

Table 4.6. Mobility classification based on the "average" classes, subdivided according to pesticide group.

group	total	IM <sup>1</sup>	SM	MM	M	HM	- <sup>2</sup>
anilides	6	0	2	3	0	1	0
carbamates	20	4	6	4	2	2	2
OP-esters	35	7	12	6	4	2	4
pyrethroids	6	3	2	1	0	0	0
triazines	7	0	4	3	0	0	0
urea comp.	10	2	6	2	0	0	0
misc. comp.	68	13	18	8	12	2	15

<sup>1</sup>) Symbols of mobility classes, see figure 4.4.

<sup>2</sup>) - = no data.

Table 4.6 shows that the pyrethroids and urea compounds are immobile to moderately mobile in soil, with the greatest concentration in the immobile class for the pyrethroids and in the slightly mobile class for the urea compounds. The mobile and highly mobile classes comprise only representatives of the carbamates, OP-esters and miscellaneous compounds groups. The carbamates and OP-esters are actually distributed over all classes, with the greatest concentration in slightly mobile.

# Mobility classification on the basis of $K_{om}$ .

As has already been mentioned in this section, the mobility of a pesticide depends in most cases on the content of organic matter in soil. In the classification of mobility on the basis of  $K_s/l$ , values obtained from soils with different percentages of organic matter are intercompared. However, the  $K_s/l$  can vary greatly between soil types. If it is known that the mobility of a pesticide is strongly determined by the organic matter content, classification on the basis of  $K_{om}$  would be preferred, because the  $K_{om}$  is independent of the content of organic matter in soil. However, it is known of a number of pesticides that they do not bind to organic matter and that mobility is also not affected by this. Calculation of a  $K_{om}$  is not useful for these chemicals.

The division shown in table 4.7 is proposed for classification on the basis of  $K_{om}$ . The class limits for  $K_{om}$  have been calculated by converting the limits of the classification system of Helling [22] to  $K_{om}$  assuming an organic matter content of 2.5%. This is consistent with the content of organic matter in the standard soil on which Helling based his classification [22].

Table 4.7. Classification scheme for mobility on the basis of  $K_{om}$ .

class	$K_{om}$ (dm <sup>3</sup> /kg)
immobile	> 100
slightly mobile	20 - 100
moderately mobile	5 - 20
mobile	1 - 5
highly mobile	< 1

Figure 4.5 shows the frequency distribution over the various mobility classes, based on the  $K_{om}$  values. For comparison, the distribution on the basis of the  $K_s/l$  is also shown. The frequency distributions are based on the "average" classes (see figure 4.4).

Mobility classification on the basis of  $K_{om}$  was possible for 123 pesticides, while 131 pesticides could be classified on the basis of  $K_s/l$ .

To make comparison of the 2 classifications possible, the distribution over

the classes has been given in percentages of the total number of pesticides that could be classified.

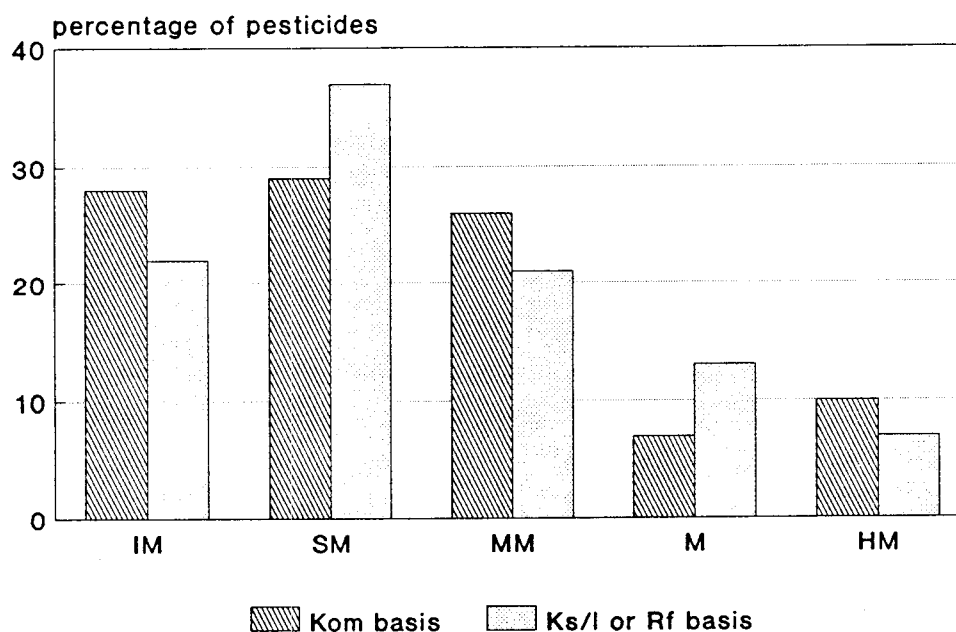


Figure 4.5. Distribution in percentages over the mobility classes assuming the "average" class, on the basis of Ks/l and Kom. See figure 4.4 for the symbols of the mobility classes.

#### 4.1.3. Model calculations.

The Support Group M model gives a relative classification of leaching and accumulation of pesticides with a quantitative indication of the extent of leaching and accumulation. The results of the model calculations are based on a standard dosage of 1 kg a.i./ha and a single application. A summary of the results for the active ingredients is given in appendix 7.2. Appendix 7.7. presents the results of the model calculations for a number of metabolites. No calculations were performed for 39 of the 152 pesticides, mostly because of the absence of reliable Kom and/or DT50 values. The calculations for 27 pesticides are based on less reliable values.

Leaching.

Figure 4.6 shows the frequency distribution of the evaluated pesticides over the various leaching ranges with spring application. Both average and maximum leaching are shown.

The EC drinking-water directive [13] stipulates that drinking water should contain no more than 0.1 mg/m<sup>3</sup> of an individual pesticide and no more than 0.5 mg/m<sup>3</sup> of the pesticides together. Since all fresh groundwater in the Netherlands can be regarded as potential drinking water, the Environmental Criteria memorandum has declared the directive also applicable to groundwater [28].

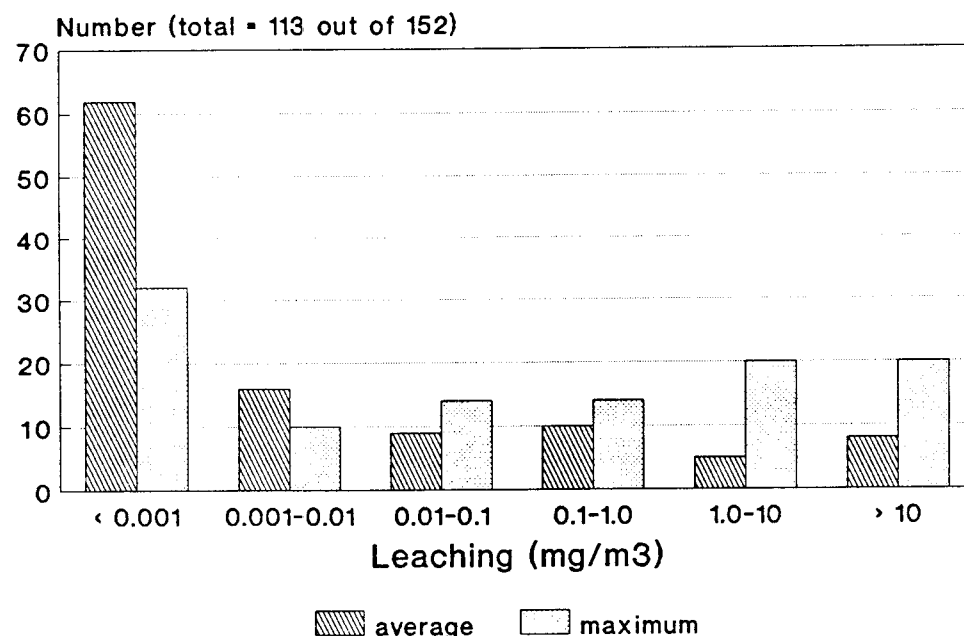


Figure 4.6. Distribution of numbers of pesticides over 6 leaching classes on the basis of average and maximum leaching with spring application, as calculated with the Support Group M model.

Average leaching was less than 0.001 mg/m<sup>3</sup> for 58% of the pesticides for which a model calculation had been performed. The EC drinking-water standard of 0.1 mg/m<sup>3</sup> was reached or exceeded by 20% of the chemicals. The latter group includes representatives of all the pesticide groups distinguished, with the exception of the pyrethroids (table 4.8).



Table 4.8. Division into leaching classes subdivided according to pesticide group on the basis of average leaching (mg/m<sup>3</sup>) following spring application, as calculated with the Support Group M model.

group	total	<0.001	0.001-0.01	0.01-0.1	0.1-1	1.0-10	=>10	-
anilides	6	3	0	0	2	0	0	1
carbamates	20	8	0	2	1	0	1	8
OP-esters	35	20	6	0	2	0	0	7
pyrethroids	6	5	1	0	0	0	0	0
triazines	7	3	0	1	1	1	0	1
urea comp.	10	4	3	0	1	0	0	2
misc. comp.	68	22	6	6	3	4	7	20

Based on maximum leaching, 49% of the pesticides for which the model calculation had been performed reached or exceeded the standard, with 36% of the pesticides leaching more than 10 times more strongly than the standard permits.

Forty-two of the evaluated pesticides are also applied in the autumn. Therefore, leaching of these chemicals has also been calculated following autumn application. Figure 4.7 shows the frequency distribution over the leaching ranges (analogous to figure 4.6 for spring application).

Leaching was invariably higher than with spring application, which was to be expected. The pesticide is applied during a period in which the net precipitation is higher and the temperature lower. Both factors increase the risk of leaching: higher net precipitation also causes greater water transport, and a lower temperature leads to slower conversion of the pesticide.

Based on average leaching following autumn application, 48% of the pesticides for which the model calculation had been performed reached or exceeded the drinking-water standard; this was 71% on the basis of maximum leaching.

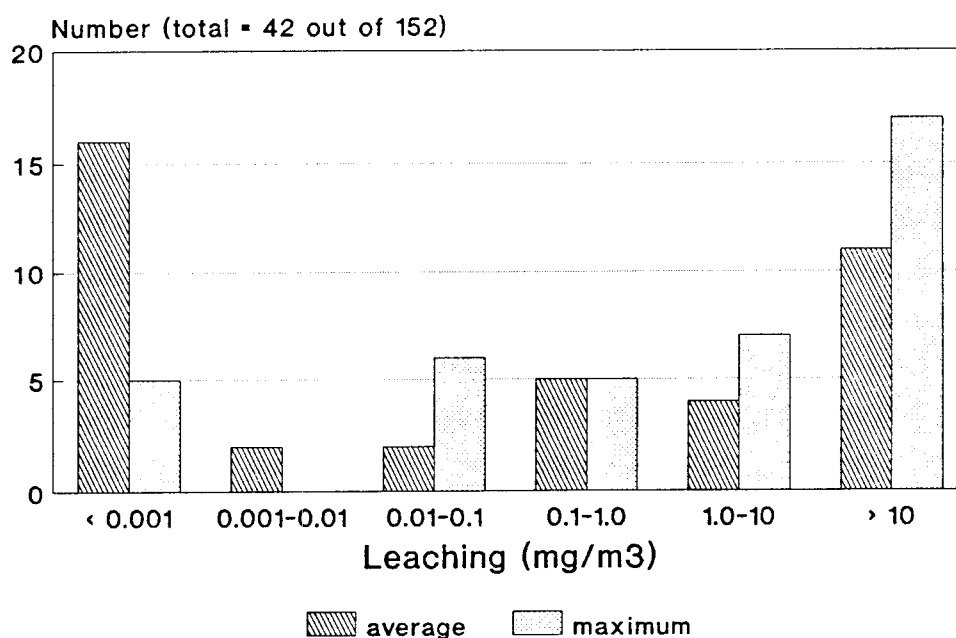


Figure 4.7. Distribution of numbers of pesticides over 6 leaching classes on the basis of average and maximum leaching following autumn application, as calculated with the Support Group M model.

Table 4.9 shows that on comparison of autumn leaching of the various pesticide groups, the same picture emerges as with spring application. The EC standard for drinking water was exceeded by representatives of all pesticide groups distinguished, with the exception of the pyrethroids.

Table 4.9. Division into leaching classes subdivided according to pesticide group on the basis of average leaching (mg/m<sup>3</sup>) following autumn application, as calculated with the Support Group M model.

group	total	<0.001	0.001-0.01	0.01-0.1	0.1-1	1.0-10	≥10	-
anilides	6	2	0	0	0	0	0	4
carbamates	20	2	1	0	1	0	2	14
OP-esters	35	2	0	1	1	0	1	30
pyrethroids	6	0	0	0	0	0	0	6
triazines	7	1	0	0	0	1	0	5
urea comp.	10	2	1	0	0	1	0	6
misc. comp.	68	9	0	1	3	2	8	45

The model has been applied not only to the active ingredient but also to the afore-mentioned metabolites (see appendix 7.7). Based on average leaching, 80% of the metabolites exceeded the drinking-water standard by more than 10 times; this was 100% on the basis of maximum leaching (table 4.10).

Table 4.10. Division of metabolites into leaching classes on the basis of average and maximum leaching (mg/m<sup>3</sup>) following spring application, as calculated with the Support Group M model.

Leaching	total	<0.001	0.001-0.01	0.01-0.1	0.1-1	1.0-10	≥10
average	15	1	1	1	0	8	4
maximum	15	0	0	0	2	5	8

The Support Group M model has not yet been validated, and tested to a limited extent only against field measurements. By comparing field measurements with calculated concentrations, an indication can be obtained of the predictive value of the model in practice. It should be noted however that the model is based on a standard dosage of 1 kg a.i./ha and a single application.

As part of a study conducted by the RIVM underneath potato, maize and bulb fields and uncultivated plots, with vulnerable and less vulnerable soils, the concentrations of 19 pesticides have been measured in the groundwater at a depth of about 1-2 m [24, 25, 50]. Table 4.11 compares the median concentrations measured in groundwater samples with the calculated average concentrations.

The ratio of the field median and the calculated average concentrations could be determined for 14 pesticides; for 5 compounds, only a "smaller than" value could be given for the ratio. When a tenfold difference between the field value and the model value is considered to be the maximum acceptable, then for 7 pesticides the model was in good agreement with the field. The difference is more than a factor of 10 for 6 pesticides, while for 5 pesticides with a ratio of a "smaller than" value, it can only be concluded that the field observations do not contradict the values calculated with the model.

A special problem in terms of environmental protection exists when the model predicts concentrations which are lower than those observed in the field. The field concentrations of aldicarb, diuron and ethoprophos were more than 10 times higher than the model had predicted. It should be noted however that for aldicarb and diuron, the high field median is based on very few observations above the detection limit. The model calculated a much higher concentration for MITC than was observed in the field. This is probably due to volatilization possibly being greater than was corrected for in the model.

calculation, and to conversion of the compound in deeper layers (because of the relatively large contribution of chemical transformation, the correction for depth-dependent conversion used in the model cannot be applied.

Table 4.11. Median concentrations in groundwater (mg/m<sup>3</sup>) [24, 25, 50].

	field <sup>1</sup>	model <sup>2</sup>	ratio <sup>3</sup>	n/N <sup>4</sup>	soil <sup>5</sup>
aldicarb	0.45	0.001	450	1/5	+
aldicarb-sulfone <sup>6</sup>	11.3	9	1.2		
atrazine	0.13	0.06	2.2	43/65	+ en -
desethylatrazine <sup>6</sup>	0.14	1.5	0.09	25/30	
bentazone	0.05	14	0.003	13/47	+ en -
dalapon	<0.1	0.01	<10	0/2	+
dichlobenil	0.045	0.01	4.5	2/2	-
1,2-dichloorpropane <sup>7</sup>	2.5	>6->26	<0.4-<0.1	8/15	+
(1,2-dichloorpropane <sup>7</sup> )	(7.8)	(>6->26)	(<1.3-<0.3)	(13/13)	(+)
1,3-dichloorpropene <sup>8</sup>	2.5	13-50	0.2-0.05	8/47	+
dinoseb	0.45	0.6	0.75	22/66	+ en -
diuron	0.13	0.001	130	2/4	+
ethoprophos	0.05	0.001	50	8/22	+
linuron	<0.05	0.005	<10	0/8	+
MCPA	<1	0.005	<200	0/8	+ en -
mecoprop	2	0.3	6.7	1/8	+
metolachlor	0.1	0.3	0.3	7/31	+ en -
MITC <sup>13</sup>	0.2	600-3000	0.00	9/18	+ en -
simazine	0.44	0.1	4.4	1/1	+
2,6-dichlorobenzamide 143	>50		<2.9	2/2	-

<sup>1</sup> - Median concentrations of pesticides measured in groundwater (depth about 1-2 m) in the field study conducted by the RIVM. The median of the field observations is based on the measurements above the limit of detection of the pesticide concerned.

<sup>2</sup> - Average leaching concentrations (depth 1-2 m) calculated with the Support Group M model (standard dosage, 1 kg a.i./ha; a single application).

<sup>3</sup> - Ratio between measured (<sup>1</sup>) and calculated(<sup>2</sup>) values.

<sup>4</sup> - n: number of measurements above the detection limit.  
N: total number of analyses.

<sup>5</sup> - Soil vulnerability:

+: vulnerable soil ("vlakvaag" soil, "gooreerd" soil, raised profile).

-: less vulnerable soil ("veldpodzol", "eerd" soil).

The type of soil in which leaching was observed is shown unless n=0, in which case the type of soil where measurements were made is given.

<sup>6</sup> - Metabolite.

<sup>7</sup> - Contaminant of 1,3-dichloropropene (the model calculation assumes a contaminant level of 0.1%). The concentration found in the field at a depth of between 2 and 6 m is given in brackets.

<sup>8</sup> - The values calculated with the model have been corrected for volatilization and dosage.

Residues in the plough layer.

Table 4.12 presents the frequency distribution of the chemicals from the various pesticide groups over the classes of accumulation in the plough layer, 1 year after application, as calculated with the Support Group M model.

Accumulation is on average  $< 0.04 \mu\text{g/kg}$  for 39% of the pesticides. The highest accumulation class includes representatives of especially the urea compounds and carbamates.

Table 4.12. Distribution of the pesticides over different classes of accumulation in the plough layer, 1 year after application ( $\mu\text{g/kg}$ ), as calculated with the Support Group M model.

group	total	$<0.04$	$0.04-0.4$	$0.4-4$	$4-20$	$20-40$	$40-100$	$\geq 100$	-
anilides	6	1	1	2	0	0	1	0	1
carbamates	20	5	0	1	1	2	1	2	8
OP-esters	35	14	2	4	1	3	4	0	7
pyrethroids	6	1	0	0	2	1	2	0	0
triazines	7	0	1	0	1	2	2	0	1
urea comp.	10	1	1	0	1	1	1	3	2
misc. comp.	68	23	2	4	7	2	7	4	19

Difficult cases.

- Creosote oil. This distillation product of coal tar contains more than 100 identified products, especially polycyclic aromatic hydrocarbons (PAHs). Each of these components has its own degradation rate and adsorptive properties, so that a model calculation on creosote oil as a total mixture was not possible. Leaching of polar metabolites cannot be excluded.

- Dichloropropene and MITC. These soil fumigants are highly volatile, so that application of the model is in fact not suitable. Moreover, these two pesticides are applied in extremely high doses. Nevertheless, the model has been used but with corrections for volatilization and dosage. Volatilization percentages of 20 and 25% have been assumed for 1,2-dichloropropene and MITC, respectively.

Comments on the Support Group M model.

The principal assumptions of the model have been presented in chapter 3. The dosage of 1 kg/ha employed in the model is a fair estimate for half of the pesticides: the maximum dosage is  $\leq 2$  kg/ha. Nineteen pesticides (13%) have an extremely high maximum dosage level (10-840 kg/ha), and it is especially for this group that the model calculation can underestimate leaching and accumulation. The high dosage levels of 1,2-dichloropropene and MITC have already been corrected for in the model calculation.

The model assumes one single application. However, 70% of the pesticides are applied more than once, so that the model calculation can also underestimate their leaching and accumulation.

The model assumes a vulnerable sandy soil. This is a soil type with a relatively high risk of leaching, so that it is a "safe" choice as far as leaching is concerned. However, there are differences in leaching and accumulation between soil types. Application of the model to a clay soil yielded lower values for both leaching and accumulation in the plough layer [8, 9].

It can be concluded that the model is suitable for intercomparison of the pesticides, but that its estimate of the concentrations in practice is only indicative, the more so since validation with field observations has thus far been limited.

#### 4.2. Aquatic studies.

##### 4.2.1. General.

A summary of the DT50 values determined in water/sediment systems, hydrolysis and photolysis studies is given in appendix 7.3. For a large number of pesticides there were no data on conversion in water. Data on biodegradation were available for 78 of the 148 pesticides, namely, a DT50 system or DT50 water. Both types of data were available in 19 cases. Of the 56 pesticides for which a DT50 system was available, only 36 had a reliable DT50 value based on the decrease in the active ingredient. The data of 12 pesticides were less reliable, and the DT50 of 9 pesticides was based on

CO<sub>2</sub> production (mineralization). Data on the rate of hydrolysis were available for 108 pesticides, the information being less reliable for 21 of them. Data on photolysis were available for 60 pesticides. There were no data at all on biodegradation, hydrolysis or photolysis for 27 pesticides.

#### 4.2.2. Water/sediment systems.

The large variation in test conditions makes comparison and interpretation of the results difficult. Table 4.13 summarizes the scatter in a number of parameters of studies in which a reliable DT50 had been determined, based on the decrease in the active ingredient. The variation in test conditions of all reliable water/sediment studies is in fact even greater than is indicated here. For example, some experiments had been carried out (according to old guidelines) in a system of nutrient solution, inoculated with filtrate from ditch sediments, the final proportion of sediment being less than 1%. These studies have not been included in table 4.13.

Table 4.13. Variation in test conditions and DT50 values of reliable water/sediment studies (36 pesticides).

pH	% sediment	% org. matter	temperatuur	DT50-system
5.8 - 9.2	1 - >50	0.5 - 47	16-25 °C	<1 - 230 d.

A high percentage of sediment can retard the conversion rate because of binding of active ingredient to organic matter. On the other hand, a high percentage of sediment/organic matter increases the microbial activity of the system. Also, a thick layer of sediment can drive the system (partially) anaerobic.

Studies conducted by the Institute for Pesticides Research (IOB) showed that the acclimatization time of the system and the organic solvent used, rather than the percentage of sediment, have a large influence on the conversion rate. When a sediment had acclimatized for 2 months before the pesticide was added, degradation was quite different from that observed after a shorter period. The probable reason is that all kinds of organisms which play a role in degradation need time to recover from the disturbance.

In a number of cases a DT50 value of "smaller than" or "greater than" was determined. The change in concentration of the active ingredient with time could not be derived here because only one measurement was made. The above shows that interpretation and comparison of the results is possible to a limited extent only.

A classification system for the persistence of pesticides in water does not exist. It is therefore obvious to use only provisionally the classification scheme which is proposed for intrinsic persistence in soil (see section 4.1.1). If the persistence limit of 60 days for DT50 values in soil is also adopted for water/sediment studies, then 16 pesticides (see table 4.15) fall above and 35 below this limit (corresponding to 21% and 45% of the pesticides for which data were available, respectively), based on the average DT50 system. It is not clear for 35 pesticides, because only a DT50 for the water phase or for mineralization was known, or because a value of "greater than" or "smaller than" had been determined.

The distribution of the number of pesticides over the two classes "DT50 < 60 days" and "DT50 > 60 days" has been subdivided according to pesticide group in table 4.14. The table shows that nearly all the triazines and urea compounds for which data were available fall into the persistent class. The carbamates and OP-esters are generally classified as less persistent. A definitive statement cannot be made on this matter for the anilides and pyrethroids because of insufficient data.

Table 4.14. Classification of pesticides for intrinsic persistence in water/sediment systems, subdivided according to pesticide group.

group	total	DT50 < 60 d.	DT50 > 60 d.	no (or not exact) data
anilides	6	1	0	5
carbamates	20	4	1	15
OP-esters	35	9	0	26
pyrethroids	5	2	0	3
triazines	7	0	4	3
urea comp.	10	1	5	4
misc. comp.	65	18	6	41



It is not really possible to arrange the 10 most persistent pesticides according to increasing DT50 value, as has been done for degradation in soil. Since a DT50 system was available for less than half the pesticides, such a list would be very incomplete. Also, in many cases the DT50's were not exact figures and consequently cannot be arranged in increasing order (see table 4.15).

However, a half-life for the active ingredient sheds no light upon the disappearance of the total residue from the system. This matter has already been discussed under conversion in soil (section 4.1.1). A pesticide can be converted into metabolites which, in turn, may be poorly degradable. Therefore, the fate of metabolites should also be traced, but in many cases this was not done.

A half-life for mineralization was determined for 9 pesticides, which ranged between 8 and 100 days with one peak of 259 days (propachlor).

Mineralization was negligible for 19 pesticides, since less than 5% CO<sub>2</sub> was formed after 60 days. The pesticides with a DT50 > 60 days and pesticides which scarcely mineralize at all are compared in table 4.15. The limit of less than 5% CO<sub>2</sub> after 60 days has been arbitrarily chosen. It should also be noted here that the measured percentage of CO<sub>2</sub> depends on the position of the radioactive label. As has already been stated under conversion in soil (section 4.1.1), ring structures are often less readily degradable, while side chains are more rapidly degraded. The list of 19 pesticides is certainly not complete, owing to the absence of data on CO<sub>2</sub> formation in many cases.

Twelve of these pesticides had moreover DT50 values exceeding the persistence limit of 60 days, while the DT50 of 3 compounds (dichlofluanid, dimethachlor and pyrazophos) fell below this limit, being <7, 46 and 11 days, respectively. Dichlofluanid was very rapidly converted into chiefly dimethylaminosulfanilide, with the ring structure remaining intact; this metabolite is highly persistent (DT50 > 113 days).

Whenever considerable proportions of metabolites are formed, data on their degradation and toxicity should be supplied. However, such information was lacking in most cases.

For 12 of the 43 pesticides where the sediment had been analyzed, the amount of sediment-bound residue ultimately formed was more than 30%. It is not clear what the consequences, if any, may be of a high percentage of

sediment-bound residue. First, the nature of the bound residue is usually not known. Secondly, the adsorption of pesticides to the sediment does not remove them completely from the aquatic system, because they may be taken up again by certain organisms [28]. Also, this bound residue might migrate again to the water phase in course of time.

Table 4.15. Active ingredients with a DT50 for disappearance from a water/sediment system of more than 60 days, and pesticides of which less than 5% was converted into CO<sub>2</sub> after 60 days.

group	pesticide with DT50 > 60 days	DT50 in days	pesticide of which less than 5% was converted into CO <sub>2</sub> after 60 days.
anilides :			dimethachlor metazachlor
carbamates:	carbetamide <sup>1</sup>	> 61	
OP-esters :			pyrazophos
triazines :	atrazine	> 77	atrazine
	cyanazine	> 84	cyanazine
	prometryne <sup>1</sup>	63	prometryne
	simazine	> 70	simazine
urea comp.:			chlorbromuron
	chlortoluron <sup>1</sup>	> 79	chlortoluron
	chloroxuron <sup>2</sup>	> 63	chloroxuron <sup>2</sup>
	linuron <sup>1</sup>	132	
	methabenzthiazuron	182	methabenzthiazuron
	metoxuron	145	
misc. comp:	bromopropylate	63	bromopropylate
	chloridazon	> 56	chloridazon
			dichlofluanid
	ethofumesate	125	ethofumesate
	iprodione	126	
			lenacil
	pendimethalin	> 84	pendimethalin
			propiconazole
	triadimenol	> 91	triadimenol

<sup>1</sup> based on the decrease of the active ingredient in the water phase (DT50-water > 60d).

<sup>2</sup> based on less reliable data.

Difficult cases.

Field studies with the pyrethroids cypermethrin and fenvalerate have shown that these substances do not disperse homogeneously in surface water. Initially a kind of thin film is formed in the top layer, followed by slight migration into the layers below. Very high concentrations were measured in the upper layer (about 1 cm) of the surface water immediately after spraying, which gradually decreased with time. In the layer below (up to about 0.5 m) the concentrations first rose and then fell. This type of information is not known for the other pyrethroids evaluated but it can be expected that they behave in a similar manner. More insight into this specific behaviour is of great importance for the assessment of the risk to aquatic organisms.

#### 4.2.3. Hydrolysis and photolysis.

Although data on hydrolysis are not mandatory, they were available in more instances than results from water/sediment studies. The reason for this is that in the past it was mandatory to supply hydrolysis studies in the Netherlands, and this still obtains in other countries. Appendix 7.3 shows that many pesticides have DT50 values for hydrolysis which vary over a wide range depending on the pH. For carbaryl, for example, the DT50 measured at pH 5 was more than 180 days, was 27 days at pH 7 and less than 1 day at pH 9 (all at a temperature of 25 °C). Another example of a pesticide where the hydrolysis rate is heavily dependent on the pH is sethoxydim: the DT50 values at pH 3, 6 and 9 were 1.6, 45 and 438 days, respectively (at 25 °C). The pH had little influence on the rate of hydrolysis of a pesticide such as terbufos: the DT50 values ranged between 4.5 and 8.5 days at pH 5 to 9. By comparing hydrolysis and photolysis rates of a substance, an idea can be obtained of the contribution of light to the conversion rate. For most of the pesticides for which both types of data were available, photolysis proceeded more rapidly than hydrolysis. However, satisfactory comparison is not possible because photolysis studies were often conducted without temperature and pH control. With artificial lighting, the heat of the lamps can raise the temperature in the medium. Also, more volatilization can

occur as a result of a higher temperature, or incubation outdoors. Very marked differences were observed with chloroxuron, chlorpropham and propham, the DT50 for photolysis being a factor of 1000 lower than the DT50 for hydrolysis. These are pesticides possessing a benzene ring, which are known to be very sensitive to UV light with  $\lambda \approx 250$  nm. However, the studies used natural sunlight or artificial light with a wavelength of  $\lambda > 250$  nm. Under natural conditions, the conversion of these substances will be very strongly determined by lighting.

#### 4.2.4. Comparison of biodegradation and hydrolysis rates.

The conversion of pesticides in water/sediment systems might be expected to proceed more rapidly than in hydrolysis studies, because a combination of processes may occur in water-sediment systems (e.g. biodegradation, hydrolysis, photolysis) whereas only one process is involved in the hydrolysis studies. However, conversion in water-sediment systems can be retarded by adsorption of the active ingredient to the sediment. The evaluation of the behaviour of pesticides in water often assumes that if a compound is rapidly hydrolyzed, conversion in a water/sediment system will also proceed rapidly. Whether or not the above-mentioned expectations are in agreement with the actual results was checked for a number of pesticides.

To compare DT50 values for hydrolysis with DT50 system values for biodegradation, 15 pesticides were selected for which both types of data were available and moreover determined at approximately the same pH and temperature. Twelve of them had a DT50 system which was considerably lower than the DT50 for hydrolysis; the two DT50 values were of the same order of magnitude for 2 pesticides, and 1 pesticide had a half-life for hydrolysis which was 6 times lower than the DT50 system. In the last-mentioned case, however, the DT50 water was a factor of 20 lower than the DT50 system and a factor of 3 lower than the DT50 for hydrolysis. One explanation for this could be that a considerable proportion of the active ingredient was adsorbed to the sediment, resulting in a much higher dissipation time for the system as a whole.

#### 4.3. Toxicity studies.

##### 4.3.1. Toxicity to aquatic organisms.

###### General.

In the first part of this section (4.3.1) an inventory is made of the available data on toxicity, exposure concentration and risk for each group of organisms. Next, a relationship is established between toxicity and risk. The last part (4.3.2) presents a selection of reliable and intercomparable BCF values.

As regards aquatic toxicology, algae, crustaceans and fish represent the different groups from the food chain for which toxicity data are required [11]. Although toxicity data supplied for species from other groups of organisms have been recorded in the RIVM conclusion, they are too few in number to be discussed in this report.

In assessing the toxicity to aquatic organisms, the risk of effects on algae, crustaceans and fish have been presented separately in the RIVM conclusion. This contrasts with, for example, the risk evaluation advocated by the EPA, in which a "safe" concentration for the ecosystem as a whole is determined by extrapolation.

###### Toxicity data.

The files supplied contained mostly toxicity data as determined in short-term (96-h) tests. The acute toxicity value used in this report for crustaceans and fish is the 96-h L(E)C50. For algae this is the 96-h NOEC; it is true that the duration of the test is short but in view of the short life cycle of this kind of organism it is in fact a chronic toxicity value. Data from long-term tests were available in a few cases only, and for this reason they are not discussed in this report.

All the toxicity data from the RIVM conclusion have been collected in appendix 7.4. Less reliable data and data obtained from tests with a pesticide formulation have been marked as such. These toxicity data have in principle not been used in compiling the tables in the text. An exception

was made when they were the only data available, in which case formulation data were first corrected for the active ingredient content.

A toxicity classification was made for each of the three groups of organisms on the basis of the available toxicity data (appendix 6). When several data were available (involving those cases where various species were tested and cases where a number of tests were carried out with a single species), the classification was based both on the highest and on the lowest concentrations. Consequently, a range of toxicity classes was assigned to these pesticides (appendix 7.4.). The lowest toxicity value was always used in the further processing of the data in the text and tables below. The reason for this choice is that the assessment of the risk to the ecosystem should relate to the most sensitive organism.

Table 4.16. Distribution of the aquatic toxicity of pesticides over the four toxicity classes.

CLASS	ALGAE		CRUSTACEANS		FISH	
	n	%	n	%	n	%
VS	33	32	13	11	25	17
ST	27	26	30	24	24	17
MT	22	22	28	22	46	33
HT	20	20	54	43	46	33
total	102	100	125	100	141	100
-	46		23		7	

Key to symbols: VS = very slightly toxic; ST = slightly toxic; MT = moderately toxic; HT = highly toxic; - = no data

Appendix 7.4 showed the following gaps: there were no data on the toxicity of 46, 23 and 7 pesticides to algae, crustaceans and fish, respectively. In the case of the algae, most pesticides fell into the lowest toxicity class, and the number of compounds per class decreased in the succeeding classes. The reverse distribution was observed for crustaceans and fish (table 4.16).

The distribution from table 4.16 has been subdivided in table 4.17 according to pesticide group corresponding with the division shown in figure 4.1.

Table 4.17. Subdivision of the aquatic toxicity of pesticides according to pesticide group.

pesticide	total	ALGAE					CRUSTACEANS					FISH				
		HT <sup>1</sup>	MT	ST	VS	- <sup>2</sup>	HT	MT	ST	VS	-	HT	MT	ST	VS	-
A anilides	6	2	3	0	0	1	0	1	4	1	0	1	3	1	1	0
C carbamates	20	1	7	5	1	6	10	3	4	0	3	5	7	5	1	2
D misc. comp.	65	8	5	14	13	25	10	17	10	10	18	16	18	8	18	5
O OP-esters	35	0	3	8	16	8	28	2	2	1	2	18	9	4	4	0
P pyrethroids	5	0	0	0	2	3	5	0	0	0	0	5	0	0	0	0
T triazines	7	3	2	0	0	2	0	2	5	0	0	0	5	1	0	1
U urea comp.	10	6	2	0	1	1	1	3	5	1	0	1	3	5	1	0

<sup>1</sup> = Symbols of toxicity classes as in table 4.16. <sup>2</sup> = No toxicity data available

As expected, it can be stated that some of the pesticides tested showed specificity to a particular type of organism. For example, algae were found to be particularly susceptible to herbicides which inhibit cell division (anilides) or photosynthesis-inhibiting herbicides (triazines and urea compounds): 18/23 were moderately or highly toxic. Fish and especially crustaceans were less susceptible to these compounds: 13/23 and 7/23, respectively, were moderately or highly toxic. On the other hand, the reverse relationship was found for insecticides: virtually all OP-esters were moderately or highly toxic to crustaceans and fish, namely 30/35 and 27/35 respectively, against 3/35 to algae. The pyrethroids were all highly toxic to crustaceans and fish and very slightly toxic to algae. Carbamates and (di-)thiocarbamates are used as herbicides or fungicides but are also known to be toxic to fish. The differences between algae, crustaceans and fish as to their susceptibility to these compounds were much smaller: 8/20, 13/20 and 12/20 compounds, respectively, were moderately to highly toxic. The ten most toxic pesticides have been arranged in order of decreasing toxicity in table 4.18. The range between the highest and lowest toxicity values is given in appendix 7.4. As with the preceding tables, the lowest toxicity value was used in the compilation of this table.

Comparison of the LC50's of pyrethroids for crustaceans and fish shows that the difference in susceptibility between these two groups of organisms is also considerable, fish generally being less susceptible. The same relationship was found for OP-esters (data have not been included in this table).

Table 4.18. The 10 most toxic pesticides for aquatic organisms arranged on the basis of the lowest toxicity value in  $\mu\text{g/l}$ .

ALGAE				CRUSTACEANS			FISH		
no	group	pesticide	NOEC	group	pesticide	LC50	group	pesticide	LC50
1.	D	chlorothalonil	$\leq 0.1$	P	cypermethrin	0.009	P	cypermethrin	0.01
2.	U	monolinuron	1 <sup>1</sup>	P	fenvalerate	0.03	P	deltamethrin	0.58
3.	T	atrazine	1.5	D	thiram	0.06	P	fenvalerate	0.64
4.	D	dodine	3	O	mevinphos	0.16 <sup>1</sup>	O	terbufos	0.8
5.	D	aclonifen	3.2	O	pyrazophos	0.18	O	sulfotep	1.6 <sup>1</sup>
6.	D	pendimethalin	6	O	dichlorvos	0.19	P	fenpropathrin	1.8
7.	U	chloroxuron	$< 6.3$	O	chlorfenvinvos	0.2	O	methidathion	2.2
8.	A	dimetachlor	8	D	dithianon	0.29	O	chlorpyrifos	3
9.	U	chloortoluron	$\leq 10$	P	fenpropathrin	0.53	D	dinoterb	3.4
10.	D	lenacil	10	P	deltamethrin	0.8 <sup>1</sup>	O	pyrazophos	16
	U	linuron	10 <sup>1</sup>						
	A	propachlor	10						
	T	cyanazine	10						

<sup>1</sup> = less reliable value. There were no data on the toxicity of 46, 23 and 7 pesticides to algae, crustaceans and fish, respectively.

In view of the method of application of granules and soil fumigants, it was not considered necessary to supply toxicity data for these pesticides; additional information was required for the other compounds. Because of the structural analogy between a number of highly toxic pesticides and pesticides for which data were lacking, table 4.18 may have to be adjusted after the missing data have been supplied.

It should be noted when table 4.18 is extended to 30 pesticides, the toxicity data of the tenth and the twentieth compound would differ by a factor of 3 to 5 only. The difference between the toxicity data of the tenth and thirtieth compound would be a factor of 8 to 32.

#### Drift calculation.

The risk of a pesticide to aquatic organisms is assessed by relating its toxicity to the exposure level. The exposure level has been provisionally equated with the theoretical concentration in the surface water of a 25 cm-deep standard ditch immediately after application of the pesticide. The concentration in the surface water was estimated by performing the drift calculation (see 3.4.2).



The drift calculation was performed for 131 of the 148 pesticides (appendix 7.3). The RIVM conclusion gives the exposure concentration for each type of use, while this report confines itself to giving the range only (no more than one concentration was available for 23 pesticides). Many pesticides have a wide variety of uses, which can lead to a large range of concentrations when very different dosage levels are involved. The ratio between the highest and the lowest exposure concentration was  $\leq 10$  for 56 of the 131 pesticides (43%) and  $> 10$  for 52 of them (39%) (table 4.19).

Table 4.19. Ratio between the highest and the lowest exposure concentration

- <sup>1</sup>		1-10		10-25		25-100		100-1000		>1000		Total	
n	%	n	%	n	%	n	%	n	%	n	%	n	%
23	18	56	43	14	11	15	11	19	14	4	3	131	100

<sup>1</sup> = only one value available.

The exposure concentrations ranged between 0.000015 and 5 mg/l. The majority of the lowest concentrations were between 0.001 and 0.01 mg/l and of the highest concentrations between 0.01 and 0.1 mg/l (table 4.20).

Table 4.20. Distribution of the number of pesticides per exposure concentration.

highest concentration		lowest concentration				1 <sup>1</sup>	Total
< 0.0001		0.0001-0.001	0.001-0.01	0.01-0.1			
< 0.001		1	2	0	0	0	3 (2 %)
0.001 - 0.01		1	8	17	0	9	35 (27 %)
0.01 - 0.1		4	16	40	8	14	82 (63 %)
> 0.1		1	4	4	2	0	11 (8 %)
Totaal		7	30	61	10	23	131 (100 %)

<sup>1</sup> = only one value available.

The magnitude of the exposure concentration is determined to a considerable extent by the emission percentage. These percentages were determined on the basis of field measurements and are considered to be similar to the Dutch average or slightly higher. However, with the exception of the emission percentage after aerial spraying, the percentages do not apply to a worst-case situation [20, 21]. Furthermore, the effect of any periodic

applications was not taken into account, so that the exposure concentration is underestimated in a number of cases.

In addition, the supposition that the exposure concentration does not change in the period between application and attainment of the incipient LC50 causes an overestimation. In actual fact it is possible that the PEC falls before a maximum effect has been produced.

A model calculation will be performed in the future to determine the concentration in the receiving surface water. This model takes into account the cumulative effect of repeated applications. It will also become possible to make a long-term estimate by taking into account relevant dissipation processes such as degradation, adsorption, volatilization and dilution. The interpretation of toxicity data from long-term tests is then possible.

#### Risk to aquatic organisms

The risk to each of the three groups of organisms was determined separately in the RIVM conclusion, based on the highest and lowest exposure concentrations and the lowest toxicity value, so that a range was obtained (appendix 7.3).

Table 4.21. Risk assessment of pesticides subdivided according to pesticide group.

		ALGAE					CRUSTACEANS					FISH					
group	total	N <sup>1</sup>	P	L	-	N	S	P	L	VL	-	N	S	P	L	VL	-
A	anilides	6	2	2	1	1	6	0	0	0	0	5	0	1	0	0	0
C	carbamates	20	4	6	0	10	4	3	2	3	2	7	7	2	0	0	4
D	misc. comp.	65	28	7	5	25	31	9	5	1	0	35	11	5	2	0	12
O	OP-esters	35	19	5	1	10	4	2	1	11	13	12	6	9	5	1	2
P	pyrethroids	5	2	0	0	3	0	0	1	1	3	0	0	1	2	2	0
T	triazines	7	0	4	1	2	6	1	0	0	0	6	0	0	0	0	1
U	urea-comp.	10	1	2	6	1	7	3	0	0	0	7	2	1	0	0	0

<sup>1</sup> = Symbols of risk classes: N = negligible; S = small; P = present; L = large; VL = very large, and - = no data available.

In representing tables 4.21 and 4.22, a worst-case approach has been chosen based on the highest exposure concentration. Using this approach, it was

found for algae and crustaceans that relatively many pesticides fell into the highest risk category: 14/148 and 18/148, respectively, as against 3/148 for fish (table 4.21).

Furthermore, table 4.21 shows that the herbicides previously mentioned as being relatively toxic to algae also pose a relatively large risk to these organisms: for 16/23 pesticides the risk of effects on algae is present or large, as against 0/23 pesticides with a large or very large risk of effects on crustaceans and fish. OP-esters and pyrethroids, mentioned as being relatively less toxic to algae but toxic to crustaceans and fish, presented little risk to algae whereas they are the compounds posing the greatest risk to crustaceans and fish.

#### Relationship between toxicity and the risk of effects

A trend emerged in the preceding section suggesting that more toxic chemicals also entail an increased risk. The supposition that such a relationship between toxicity and risk exists seems justified in the first instance.

Table 4.22. Risk evaluation of pesticides subdivided according to the four aquatic toxicity classes.

Class <sup>1</sup>	ALGAE					CRUSTACEANS							FISH						
	N <sup>2</sup>	P	L	-	Total	N	S	P	L	VL	-	Total	N	S	P	L	VL	-	Total
VS	29	2	0	2	33	13	0	0	0	0	0	13	25	0	0	0	0	0	25
ST	22	4	0	1	27	28	0	0	0	0	2	30	20	0	2	0	0	2	24
MT	4	12	3	3	22	17	8	1	0	0	2	28	25	15	0	0	0	6	46
HT	1	8	11	0	20	0	10	8	16	18	2	54	2	11	17	9	3	4	46
TOTAL	56	26	14	6	102	58	18	9	16	18	6	125	72	26	19	9	3	12	141

Pesticides for which no toxicity data were available have not been included. <sup>1</sup>= symbols of toxicity classes: see table 4.16; <sup>2</sup> = symbols of risk classes: see table 4.21.

The relationship between toxicity and risk is presented in table 4.22. This table shows that the previously assumed relationship can indeed be demonstrated. The risk of effects from nearly all the very slightly toxic pesticides (about 90-100%) was considered to be negligible. This proportion

fell to about 80-90% with the slightly toxic compounds. A higher proportion of the moderately toxic pesticides presented a greater risk: - about 60% to algae, risk: present; - about 30% to crustaceans and fish, risk: small. All the highly toxic pesticides posed a risk, increasing to large and very large in relatively many cases (about 55, 65 and 30% to algae, crustaceans and fish respectively).

It can be concluded from the above that the risk to aquatic organisms from the use of pesticides can be minimized by not using the most toxic chemicals.

#### 4.3.2. Bioconcentration factor.

##### General.

Data on bioaccumulation are required when the nature of a pesticide, its persistence and the frequency and method of application give cause for this (requirement) [11]. Bioaccumulation is the process in which the concentration of a substance in an organism increases in relation to its concentration in the surrounding water. It involves by definition the direct uptake from the water. The extent of accumulation in aquatic organisms depends primarily on the physicochemical properties of the substance and its persistence in water.

The bioaccumulation potential of a substance is expressed in the bioconcentration factor, BCF, which can be determined experimentally. For most organic compounds, however, an indication of the bioaccumulation potential can also be obtained from the octanol/water partition coefficient ( $K_{ow}$ ) or from the water solubility (3.4.2).

##### Biomagnification.

Pesticides which are readily transferred through food chains may lead to biomagnification [11], which means the body burden of residues increases with increasing trophic levels. The risk of biomagnification is not confined to aquatic organisms.

Extremely lipophilic pesticides such as DDT, in particular, present a biomagnification risk. These compounds are ingested with the food but scarcely excreted at all, so that the residues can accumulate in the tissues of the consumer during its entire life. The relevance of this parameter was demonstrated in the recent past by the finding that treatment of crops with these pesticides eventually led to effects on populations of birds of prey.

The first impetus towards a risk evaluation for biomagnification in piscivorous birds is given in section 4.3.3.

## Results.

All the BCF values from the RIVM conclusion have been collected in appendix 7.4. If required, the BCF was calculated from the author's rough data as the ratio of the concentration of pesticide in the organism to that in the water, under steady state conditions. When no steady state value was available and could also not be calculated, the study was regarded as less reliable. For pesticides for which an experimentally determined BCF value was lacking, it was calculated on the basis of the log Kow, where possible. A BCF was available for 83 pesticides, comprising a calculated value for 39, a measured value for 27 and both values for 17 compounds. The pesticides were distributed over the classes as follows: slightly accumulating: 44 (53.0%), moderately accumulating: 27 (32.5%) and highly accumulating: 12 (14.5%). This division is based on the highest BCF from appendix 7.4. Only reliable BCF's have been included in principle; nevertheless, the values cannot be intercompared because, in compiling appendix 7.4, no distinction was made according to species, number of determinations and tissue on which the determination was performed. In many cases the BCF was calculated on the basis of the accumulation of radioactivity instead of active ingredient. Moreover, the values were derived from both standard tests with two compartments (organism and water) and (micro)ecosystem and field studies.

There were no bioaccumulation data for the relatively large number of 65 pesticides. Additional data were requested for a proportion of these

compounds. This information was not considered necessary for readily water-soluble pesticides (solubility > 2000 mg/l) since it is assumed that they fall into the lowest accumulation class [18].

A selection has been made in table 4.23 of the 10 most accumulating pesticides in fish analogous to that for the other parameters. Only adequate and intercomparable values for fish were used for this purpose. The following selection criteria were applied in principle for the BCF:

- calculated on the basis of concentrations of the pure substance;
- determined in a continuous flow system;
- determined after establishment of the steady state; and
- determined on the basis of wet weight of the whole organism.

During the selection process, practically none of the experiments was found to meet all the criteria, and for this reason deviations from the criteria were tolerated if it may be assumed that they result in only small variations in the BCF.

Table 4.23. The 10 most accumulating pesticides in fish arranged on the basis of measured and calculated BCF values.

measured BCF				calculated BCF			
no	group	pesticide	BCF	group	pesticide	log Kow	BCF
1.	D	dicofol	10.000	O	bromophos-ethyl	6.5	54.000
2.	D	trifluralin	3.261	P	cypermethrin	6.32	39.200
3.	P	fenvalerate	3.000	D	bromopropylate	5.4	7.350
4.	T	simazine	2.464	P	deltamethrin	5.4	7.350
5.	P	fenpropathrin	2.200	P	fenpropathrin	5.1	4.103
6.	D	pendimethalin	1.446	P	fenvalerate	5.0	3.350
7.	C	tri-allate	778	O	chlorpyrifos	4.8	2.560
8.	D	pyridate	464	C	tri-allate	4.7	1.912
9.	O	etrimfos	336	D	aclonifen	4.2	784
10.	O	fenitrothion	221	D	tolyfluanid	4.0	575

As is apparent from the "remarks", the selected studies also call for comment. The BCF of half the pesticides evaluated did not meet the criteria mentioned. Adjustment of the list cannot therefore be excluded when better values become available. This supposition is supported by the column with calculated BCF values: according to this arrangement, the tenth compound (fenitrothion) would be ranked twenty-second.

One very striking fact in table 4.23 is the extreme lipophilicity of the pyrethroids. Two of these compounds were classified as highly bioaccumulating on the basis of a measured BCF in fish. A reliable measured BCF was not available for the other pyrethroids. Determination of the BCF proved to be difficult because the compounds accumulate in the upper water layers owing to their poor miscibility and are moreover rapidly adsorbed. The available data make it possible to select pesticides with a bioaccumulation potential. However, for a reliable interpretation of bioaccumulation data, additional knowledge about the behaviour of a pesticide in the environment is required.

#### 4.3.3. Toxicity to birds.

If the method and time of application of a pesticide entails a distinct risk of exposure for birds, data on its toxicity to birds are required. With short or occasional exposure, an acute oral study (LD50 study with one pesticide application, followed preferably by an observation period of 14 days) will usually suffice. If there is a possibility that birds will repeatedly ingest a pesticide within a 2 to 3-week period, a subacute study (LC50 study with administration of the compound via the diet for 5 days, followed by an observation period of at least 3 days) is also necessary. In addition, a semi-chronic study may be required, for example, when there are indications of long-term exposure and bioaccumulation, or reproductive and teratogenic effects.

A summary of the LD50 and LC50 values for birds is given in appendix 7.5. LD50 studies were available for 72 of the 148 pesticides evaluated. Twenty-five of the 72 studies were inadequately carried out or reported. Data on a formulation were the only data available for 10 pesticides, and an exact LD50 value could not be given for 18 pesticides because mortality was less than 50% at the highest concentration tested.

LC50 studies were available for 59 of the 148 pesticides. Thirteen of the 59 studies were less reliable because they were inadequately carried out or reported. Data on a formulation were the only data available for 13

pesticides and an exact LC50 value could not be given for 27 pesticides because mortality was less than 50% at the highest concentration tested.

At present, only a classification for the toxicity of a pesticide to birds on the basis of LD50 values can be given (appendix 6). The results of this classification have been summarized in table 4.24, applying the following rules:

- if a pesticide fell into three classes, it was placed in the middle class, and in the most toxic class when it fell into only two classes;
- if an exact LD50 value was not available ("greater than" figure), and the pesticide was not classified as "slightly toxic", it was placed in a lower toxicity class.

Table 4.24. Toxicity classification of a number of pesticides (active ingredient or formulation) for birds.

		ST <sup>1</sup>	MT	T	HT
active ingredient	reliable studies :	22	6	4	6
	less reliable studies:	9	7	7	1
formulation	reliable studies :	8	1	-	-
	less reliable studies:	-	-	1	-

<sup>1</sup> Key to symbols: ST = slightly toxic; MT = moderately toxic; T = toxic; HT = highly toxic.

Table 4.25. Toxicity classification for birds subdivided according to pesticide group.

group	total	ST <sup>1</sup>	MT	T	HT	- <sup>2</sup>
anilides	6	2	1	0	0	3
carbamates	20	1	1	2	0	16
OP-esters	35	4	9	7	4	11
pyrethroids	5	4	0	0	0	1
triazines	7	1	1	0	0	5
urea comp.	10	1	0	0	0	9
misc. comp.	65	18	1	2	3	41

<sup>1</sup> = Key to symbols: see table 4.24. <sup>2</sup> - = no data available.



It can be concluded on the basis of this classification that 7 pesticides can be regarded as highly toxic and 39 as very slightly toxic. The distribution over the classes is subdivided according to pesticide group in table 4.25, excluding data on formulations.

Table 4.25 shows that the class "highly toxic" comprises only representatives of the OP-esters and miscellaneous compounds. However, the heaviest concentration of the OP-esters lies in the class "moderately toxic" and that of the miscellaneous compounds in "slightly toxic". The anilides and pyrethroids are generally classified as slightly toxic. The carbamates for which data were available fell into the classes "slightly toxic" and "toxic".

Although an LD50 value was available for only about 50% of the pesticides evaluated, the 10 most toxic of them are presented in table 4.26.

Table 4.26. The 10 most toxic pesticides for birds arranged according to increasing LD50 value.

stof	LD50 (mg/kg body weight)
mevinphos	0.75 - 7.5
thiofanox	1.2 - 3.4
phosphamidon	2 - 9
parathion	2.1
chloorfenvinfos	3 - 240 *
aldicarb	3.4
diazinon	3.5 - 14.7 *
oxamyl	4.6
ethoprophos	5.62
chlorpyrifos	8 - 76

\* = inadequately executed or reported study.

An estimate of the risk of acute death or of effects on birds cannot yet be given. In both America and the Netherlands, a risk evaluation model is currently being developed. The Ecological Effects Branch of the U.S. Environmental Protection Agency (EPA) is working on a system which will give a risk estimate for birds depending on the form in which the pesticide is applied (granules or a liquid). The risk estimate is based on the LD50 value in the case of a granular formulation and on the LC50 value for a liquid formulation, where the maximum expected concentration is calculated

for each component of the diet of a particular species of bird. In the Netherlands, the Working Group on Implementation of the Environmental Criteria Memorandum is currently designing a system for assessing the effects of pesticides on terrestrial organisms. This design will be further developed by the Working Group on Terrestrial Organisms still to be set up, under the Support Group M. Also, a literature search has begun at the Toxicology Advisory Centre of the RIVM in order to make an evaluation of the available literature on biomagnification.

Although the development of a risk estimation model falls outside the scope of this report, the first impetus can already be given to a risk evaluation for a particular group of birds, namely the piscivorous birds such as the cormorant, using the available data. The parameters required for this model are the estimated concentration in surface water, the bioconcentration factor (BCF) and the LC50 value in mg/kg feed. Multiplication of the BCF by the estimated maximum concentration of a pesticide in surface water yields the concentration of the pesticide per kg of fish. If this "PEC" is divided by the LC50 value in mg/kg feed, the risk to birds can be estimated analogous to the risk evaluation (on the basis of toxicity) for aquatic organisms (i.e., very large, present, small and negligible; appendix 6). Provisionally this model assumes that the measured BCF pertains to the whole fish (the BCF has sometimes been determined on a part of a fish, for example, the liver or the edible parts). In addition, it assumes that the LC50 value obtained from an experiment with certain species of birds (mostly chicken, mallard, quail or pheasant) is also valid for piscivorous bird species.

Table 4.27 presents the "PEC/LC50 values" and the expected risk of death or of effects on piscivorous birds of the pesticides for which data on the BCF (measured and/or calculated), the estimated maximum concentration in surface water and the LC50 were available.

It follows from the incomplete set of data that with "standard applications", most pesticides will have negligible effects on piscivorous birds. The risk of effects must be considered small for two pesticides (fenpropathrin and parathion). With "aerial spraying", the risk of effects on piscivorous birds is considered to be small for two pesticides (chlorothalonil and malathion) and negligible for five.

When interpreting the data, it should be remembered that most BCF studies are rather unreliable. In addition, the conversion rate in water should also be taken into account. When a pesticide is rapidly degraded in water, this will in the majority of cases entail a reduced risk to piscivorous birds. The DT50 of fenpropathrin in water is < 1 day. The DT50 values based on hydrolysis of phosalone, phosmet, terbufos and triforine are less than 7 days, and no conversion times at all are available for malathion.

Table 4.27. Risk evaluation of a number of pesticides for birds.

pesticides	remarks on tests		maximum concentration in surface water (mg/l)				risk evaluation			
	BCF test <sup>1</sup>	LC50 test	* BCF / LC50 (mg/kg feed).							
			stand. appl. meas.	stand. appl. calc.	aerial spr. meas.	aerial spr. calc.	stand. appl. meas.	stand. appl. calc.	aerial spr. meas.	aerial spr. calc.
chlorothalonil	bad	unr.	<0.001	-	0.025	-	N	-	S	-
dimethoate	fair	unr.	<0.001	-	<0.001	-	N	-	N	-
DNOC	na	rel.	-	0.003	-	-	-	N	-	-
etrimfos	bad	unr.	0.003	-	-	-	N	-	-	-
fenpropathrin	mod.	rel.	0.012	0.023	-	-	S	S	-	-
fenvalerate	mod.	rel.	0.002	0.002	0.005	0.004	N	N	N	N
phosalone	bad	rel.	0.005	-	0.034	-	N	-	N	-
phosmet	bad	rel.	<0.001	0.005	-	-	N	N	-	-
lenacil	na	rel.	-	<0.001	-	-	-	N	-	-
malathion	na	unr.	-	<0.001	-	0.017	-	N	-	S
parathion	mod.	unr.	0.035	0.042	-	-	S	S	-	-
parathion-methyl	mod.	rel.	0.014	-	-	-	S	-	-	-
pendimethalin	med.	rel.	0.003	-	-	-	N	-	-	-
pirimicarb	bad	rel.	<0.001	-	0.001	-	N	-	N	-
propyzamide	mod.	rel.	<0.001	-	-	-	N	-	-	-
terbufos	bad	unr.	<0.001	-	-	-	N	-	-	-
triclopyr	mod.	rel.	<0.001	-	-	-	N	-	-	-
triforine	na	rel.	-	0.001	-	0.001	-	N	-	N

<sup>1</sup> The usefulness of the measured BCF for the risk evaluation was examined. This assessment need not parallel the categorization "reliable", "less reliable" and "unreliable"; stand. appl. = standard application; aerial spr. = aerial spraying; meas. = BCF determined in study; calc. = BCF calculated from log Kow; rel. = reliable study; unr. = unreliable study (inadequately executed or reported); mod. = moderate; na = not applicable; N = negligible; S = small.

#### 4.3.4. Toxicity to bees.

##### Toxicity data.

The hazard of a pesticide to bees also is determined not only by its toxicity but also by the dosage and other factors such as the method of application and specific properties of the compound, and the crop. Data on the toxicity to bees are required when the pesticide is used on flowering crops and weeds visited by bees. These data must include:

- both the oral and the contact LD50 for the stage most at risk (usually the adult worker), determined in laboratory experiments;
- cage- and/or field-test data are also required if the values of the LD50 in relation to the highest recommended field dosage give cause for this;
- depending on specific application techniques (e.g. tree injection) and properties of the pesticide (e.g. selective effectiveness on larval stages), data on the hazard to bees other than those mentioned above may also be considered necessary.

A summary of the oral and contact LD50 values for bees is given in appendix 7.5.

Oral LD50 studies were available for 70 of the 148 pesticides. Ten of the 70 studies were inadequately carried out or reported. For 10 compounds, the only data known were on a formulation, and for 43 compounds an exact LD50 value could not be given because mortality was less than 50% at the highest concentration tested.

Contact LD50 studies were available for 66 of the 148 pesticides. Seven of the 66 studies were inadequately carried out or reported. For 3 compounds, the only data known were on a formulation, and for 42 compounds an exact LD50 value could not be given because mortality was less than 50% at the highest concentration tested.

Both the oral and the contact LD50 values can be placed in a toxicity class with the classification scheme as presented in appendix 6. This classification scheme differs from the system given in Pesticides part 2 (Guide for trade and industry, and health care) [3] in that in this guide,

the class "highly toxic" is further divided into toxic (0.1-1 µg/bee) and highly toxic (<0.1 µg/bee). The results of the classification used here are summarized in table 4.28, with the following explanatory notes:

- if a pesticide fell into three classes, it was placed in the middle class, and in the most toxic class when it fell into only two classes;
- if an exact DT50 ("greater than" value) was not available for a pesticide and it was not classified as "very slightly toxic", it was placed in a lower toxicity class.

Table 4.28. Toxicity classification of a number of pesticides (active ingredient or formulation) for bees.

LD50 oral		VS <sup>1</sup>	ST	MT	HT
active ingredient	reliable studies :	32	2	3	16
	less reliable studies :	3	-	1	3
formulation	reliable studies :	4	1	-	2
	less reliable studies :	2	-	1	-
LD50 contact		VS	ST	MT	HT
active ingredient	reliable studies :	36	3	4	14
	less reliable studies :	2	1	-	3
formulation	reliable studies :	2	-	-	-
	less reliable studies :	-	-	1	-

<sup>1</sup> Key to symbols: VS = very slightly toxic; ST = slightly toxic; MT = moderately toxic; HT = highly toxic.

Table 4.29. Toxicity classification for bees subdivided according to pesticide group.

stofgroep	totaal	LD50-oral					-	LD50-contact					-
		VS <sup>1</sup>	ST	MT	HT			VS	ST	MT	HT		
anilides	6	3	0	0	1	2		2	1	0	0	3	
carbamates	20	7	1	1	2	9		9	2	2	1	6	
OP-esters	35	1	0	2	9	23		1	0	2	10	22	
pyrethroids	5	0	0	0	3	2		0	0	0	3	2	
triazines	7	4	0	0	0	3		4	0	0	0	3	
urea comp.	10	5	0	0	0	5		4	0	0	0	6	
misc. comp.	65	15	1	1	4	44		18	1	0	3	43	

<sup>1</sup> Key for symbols: see table 4.28; - = geen gegeven.

On the basis of this classification it can be concluded that, using the oral LD50, 21 pesticides can be regarded as highly toxic and 41 as very slightly toxic. Based on the contact LD50, 17 pesticides can be regarded as highly toxic and 40 as very slightly toxic.

The distribution over the toxicity classes is subdivided according to pesticide group in table 4.29. Data on formulations have not been included. Table 4.29 shows that the OP-esters and pyrethroids for which data were available are mostly classified as highly toxic to bees. On the other hand, the triazines and urea compounds are all considered to be very slightly toxic.

Although both an oral and a contact LD50 were available for only about 50% of the pesticides evaluated, the 10 most toxic of them are presented in table 4.30 for these two quantities. A total of 15 different pesticides are included in the table.

Table 4.30. The 10 most toxic pesticides for bees arranged according to increasing oral and contact LD50 values.

no.	pesticide	oral LD50 $\mu\text{g}/\text{bee}$	pesticide	contact LD50 $\mu\text{g}/\text{bee}$
1.	cypermethrin	0.035	fenpropathrin	0.05
2.	parathion	0.04	thiofanox	0.058
3.	omethoate	0.048	omethoat	0.083
4.	thiofanox	0.062	etrimfos	0.1*
5.	methomyl	0.08	dimethoate	0.12
6.	dimethoate	0.08	methidathion	0.13
7.	aldicarb	0.09	aldicarb	0.15
8.	oxamyl	0.094	pyrethrines	0.15*
9.	acephate	0.11	formothion	0.18
10.	propoxur	0.12	oxamyl	0.31

\* = less reliable value.

Risk to bees.

In 1986, Oomen [44] described a method for assessing the risk of the use of pesticides to bees. This method is based on a risk factor which is obtained by dividing the highest dose per hectare (in grams of active ingredient per ha) by the toxicity to bees (lowest contact or oral LD50 in micrograms per

bee). When the risk factor is more than 2500, the use of the pesticide is dangerous to bees, and when this factor is less than 50 it is not dangerous. When the risk factor ranges between 50 and 2500, a cage and/or field test is necessary to determine the actual risk to bees. If no effect is observed in the cage test, the chemical is not dangerous; otherwise a field test must be conducted. The pesticide is not dangerous when the effects in the field test are smaller than or similar to those from a reference pesticide, and it is dangerous when the effects are greater. In case of special effects, a specific test may be necessary. In addition, the method takes into account whether bees will be exposed with the pesticide applications submitted for registration, and whether the evaluation system is suitable, given the properties and the use of the pesticide.

The model of Oomen assumes that there is no large difference between the oral and the contact LD50 (this supposition has also been verified, pers. comm. P.A. Oomen). Using the set of data presented in this report, it was possible to establish the degree of agreement between these two LD50's for 16 pesticides. The average quotient of the contact LD50 and the oral LD50 is 3.1 (range 0.6 to 9.3), showing that the degree of agreement is reasonably good.

This approach is practicable when it concerns a request for registration of a new pesticide or a new use of an existing pesticide, since it is then possible to prescribe further tests.

If only data on the oral and contact LD50 are available, a risk assessment can be made with the method described below.

If it is assumed that a bee (worker) is exposed to a pesticide from one direction only (from above, below or the side), then the exposed surface is about  $0.5 \text{ cm}^2$ . This value has been obtained by measuring the surface area with the help of a photograph. However, this approach is not entirely correct because a bee has many appendages such as wings, antennae and legs, and its whole body is covered with hair. Furthermore, the fact that a pesticide is usually spread over the field in the form of minute droplets must be taken into account. Using this surface area, the expected exposure concentration (PEC) can be calculated: if the dosage of a pesticide is  $D \text{ kg/ha}$ , then the PEC is  $5D \text{ ug/bee}$ . If this PEC is divided by the contact LD50, the risk to bees can be estimated analogous to the risk evaluation

(on the basis of acute toxicity) for aquatic organisms (i.e., very large, large, present, small and negligible; appendix 6).

Table 4.31 presents risk classifications for the pesticides for which reliable data on both the contact LD50 and the dosage were available. A distinction has been made between exact and not exact LD50 values (the latter have been expressed in a "larger than" figure). The calculation is based on the lowest possible LD50 value. The table also includes the classification according to Oomen [44], in which all pesticides with a risk factor ranging between 50 and 2500 are described as possibly dangerous.

The risk factors calculated with the above-mentioned model and those based on the model of Oomen differ by a factor a 200 (dosage in g/ha and no exposed surface). The classification limits of the two models can be compared by using this factor: the limit lies at greater than 12.5 for the classification "dangerous", and at smaller than 0.25 for the classification "not dangerous".

Table 4.31. Risk classification for bees on the basis of the contact LD50.

-----				
contact	exact LD50 values		not exact LD50 values ("greater than")	
-----				
effect	minimum dosage	maximum dosage	minimum dosage	maximum dosage
-----				
very large	5	10	-	-
large	10	8	2	11
present	4	3	20	19
small	2	-	9	5
negligible	-	-	5	1
-----				
Oomen method	maximum dosage		maximum dosage	
-----				
dangerous	9		-	
possibly dangerous	12		26	
not dangerous	-		10	
-----				

Table 4.32 presents risk classifications for those pesticides for which reliable data on both the oral LD50 and the dosage were available (method as in table 4.31; PEC = 5D µg/bee).



On the basis of these classifications (exact LD50 values), it can be concluded that, assuming the contact LD50 values, the risk to bees at the maximum dosage level must be considered to be very large from 10 pesticides, large from 8 and present from 3. The Oomen method classifies 9 pesticides as dangerous and 12 as "possibly" dangerous. Based on the oral LD50 values, the risk to bees at the maximum dosage level must be considered to be very large from 15 pesticides, large from 8 and present 1. The Oomen method classifies 14 pesticides as dangerous and 6 as "possibly" dangerous.

Table 4.32. Risk classification for bees on the basis of the oral LD50.

oral risk	exact LD50 values		not exact LD50 values ("greater than")	
	minimum dosage	maximum dosage	minimum dosage	maximum dosage
very large	9	15	-	-
large	6	4	-	6
present	5	1	15	20
small	-	-	13	6
negligible	-	-	4	-
<hr/>				
Oomen method	maximum dosage		maximum dosage	
dangerous	14		-	
possibly dangerous	6		21	
not dangerous	-		11	

#### 4.3.5. Toxicity to earthworms.

Data on acute toxicity to earthworms are required for all active ingredients, unless proof is given that the pesticide does not reach the soil. Acute toxicity is preferably determined with Eisenia fetida as the test organism. The duration of the test must be 14 days with observations after 7 and 14 days. Data on subacute toxicity are required in certain cases, namely when:

- there is a possibility of long-term exposure (frequency of application, persistence);

- the results of the acute toxicity tests give cause for this;
- there are indications of effects on reproduction.

Subacute toxicity tests (mortality, behaviour and reproduction) should preferably be carried out with Eisenia fetida or Lumbricus rubellus as the test organism. The duration of the test must be at least 14 days and preferably no longer than 28 days.

Of the 148 pesticides, data on their effects on earthworms were available for only 20, 8 of which were an LC50 value. The LC50 values and the toxicity classification of these 8 pesticides are given in table 4.33.

Table 4.33. LC50 values and toxicity classification of a few pesticides for earthworms.

pesticides	group	LC50 mg/kg	toxicity classification
carbaryl	C	22-263	moderately to slightly toxic
dicofol (o,p)	M	> 708	(very) slightly toxic
dimethoate	O	18	moderately toxic
fonofos	O	> 218 (F)	(very) slightly toxic
heptenophos	O	206	slightly toxic
maneb	C	44 (*)	moderately toxic
metaldehyde	M	>3500 (*)	very slightly toxic
triadimenol	M	772	slightly toxic

F = 55 % formulation; \* = inadequately executed study

The absence of toxicity data for earthworms is not surprising because it is only very recently, and not even officially, that these data have been required. The Working Group on Implementation of the Environmental Criteria Memorandum is designing a system for assessing the effects of pesticides on terrestrial organisms. A system is envisaged for earthworms which takes into account the expected concentration in the top 2.5 cm of the soil (assuming a soil density of 1.4 kg/dm<sup>3</sup>), the DT50 value and the frequency of application.

#### 4.4. Integration.

The results of the project "Catch-up operation on old pesticides" are presented in appendix 7 of this report. They form an almost complete representation of the data from 148 environmental synopses.

For easy reference, an inventory of the distribution of the pesticides over the various risk classes was made in the preceding sections for each aspect. Two approaches were used, both with a view to making an intercomparison of environmental properties possible:

- Arrangement according to decreasing magnitude of the parameter, and presentation of the first 10 pesticides with a view to identifying the most outstanding chemicals;
- Subdivision according to pesticide group with a view to relating environmental properties to chemical identity.

The following section examines whether the available information is adequate both qualitatively and quantitatively for selecting those pesticides of greatest risk to the environment. The rough data were processed to that end.

##### 4.4.1. Available data

The reliability of a comparison of environmental properties is partly determined by the amount of available data. A summary of this data is given in figure 4.8. For none of the evaluation aspects were all data available. Most noticeable in this context is the large number of missing data on toxicity to earthworms and algae and the DT50 water. Toxicity data for earthworms are so scarce because the test requirement for this pesticide property is of such recent date.

When data were not available, it did not always mean that they were absent because it is not considered essential in all cases to supply data. This is especially true of toxicity to bees and birds, for which data are only required if method and time of application entail a distinct risk of exposure [11].

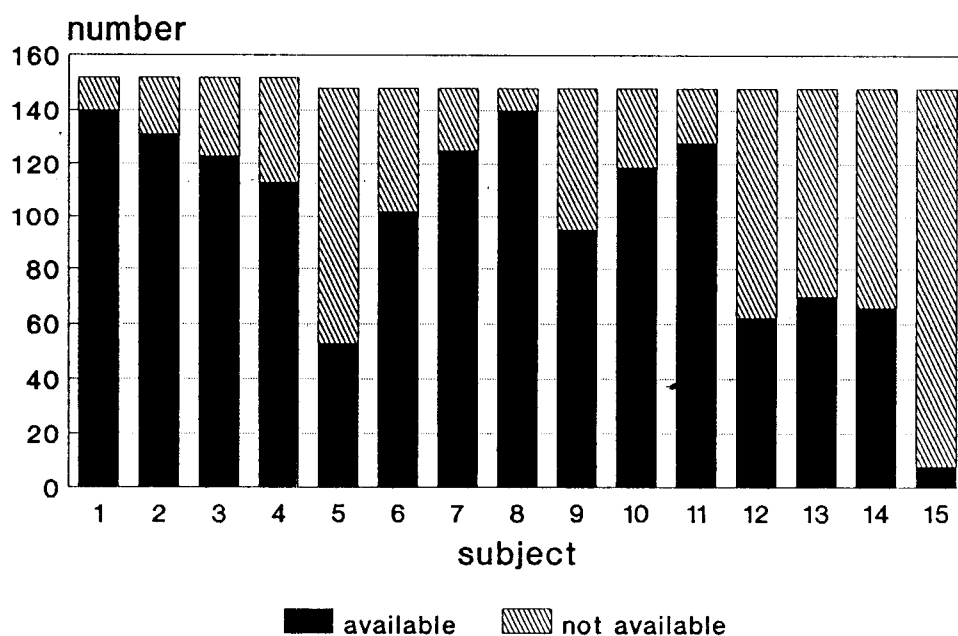


Figure 4.8. Summary of available data. 1 = DT50; 2 = Ks/l; 3 = Kom; 4 = model calculation; 5 = DT50 water; 6-8 = toxicity to algae, crustaceans and fish; 8-11 = risk to algae, crustaceans and fish; 12-15 = toxicity to birds, bees (oral and contact) and earthworms.

#### 4.4.2. Arrangement according to decreasing magnitude of parameter.

A total of 8 surveys was given in the preceding sections, containing the 10 highest values for DT50 soil and DT50 water, and the 10 lowest values for Ks/l and toxicity to algae, crustaceans, fish, birds and bees. Comparison of the various summaries showed 71 pesticides which occurred at least once. Twenty-eight of them were included more than once, mostly concerning a combination of toxicity data for crustaceans, fish, birds and bees. In a few cases (including a strikingly large number of triazines and urea compounds), a combination of the toxicity to algae and the DT50 water was involved.

There are no pesticides which comprise a spectrum of "negative qualities"; nearly half the pesticides have one or other "negative quality". Consequently, the most environmentally hazardous pesticide cannot be identified because a weight must then be assigned to the various aspects.

This falls outside the scope of this report. It is possible, however, to class some pesticides along with the most environmentally hazardous chemicals on the basis of only one parameter. For example, dicloran has an extremely high DT50 soil, and the toxicity of the pyrethroids, and especially of cypermethrin, stands out in this context as does the BCF of dicofol.

#### 4.4.3. Subdivision according to pesticide group.

When subdividing according to pesticide group, certain groups were found to produce very specific effects. To enable comparison of the aspects to be made, the observations have been quantified by calculating per aspect the average class for each pesticide group, using the following method:

- The consecutive classes were numbered;
- Each representative was given a number of points, equivalent to the class number;
- Next, the points were added together per pesticide group, after which the average class was calculated as the quotient of this sum and the number of pesticides involved. It should be noted that the average class is actually a fictitious class: the calculated value usually lay between the existing classes as plotted on the Y-axis of the diagrams 4.9 - 4.22;
- Finally, an average class was calculated on the basis of all available data. This value is indicated with a horizontal line in the diagrams.

One consequence of this method of calculation is that in some cases the average class is based on a small number of data. For pesticide groups with few representatives, in particular, this can readily lead to large effects in the calculation of the average class. The size of the respective pesticide groups is given in figure 4.1; where necessary, large deviations from the maximum number of available data are mentioned in the text below (the number of data not available is given in the respective tables of this chapter). When the class average is strongly influenced by an exceptional number of data, this was also mentioned. It should be noted that the class average of a small pesticide group will deviate more from the overall class average than that of a large pesticide group because a small group will make a relatively smaller contribution to the overall class average.

The results of the calculations are presented in the figures 4.9 - 4.22. In the discussion of the diagrams, the terms "higher" and "lower" have been introduced, and indicate that a parameter lies half a class higher and lower than the average for all data, respectively. The adverb "much" is used when the deviation is more than one class.

#### Soil.

The number of available data on conversion and mobility do not give cause for comment. In all groups, fewer data were available for the model calculation than for conversion or mobility. The persistence of triazines and urea compounds was much higher, which in the case of the moderately mobile triazines led to much higher leaching and accumulation. According to the model calculation, accumulation of the less mobile urea compounds was much higher while leaching was lower.

Of the OP-esters with lower persistence and average mobility, leaching and accumulation were lower.

The persistence of the other groups fluctuated around the average. The higher mobility of anilides was due to one exceptionally mobile compound and had no effect on the leaching and accumulation, while the lower mobility of the pyrethroids resulted in much lower leaching and much higher accumulation.

#### Water.

There were few data available on conversion in water.

As in soil, the triazines and urea compounds were found to belong to the most persistent pesticides. A striking phenomenon was also the usually positive correlation between persistence and toxicity to algae. The DT50 water and the toxicity to algae of triazines and urea compounds were both much higher. The anilides did not show this correlation: toxicity was also higher but persistence was much lower (note that only one DT50 water was available).

#### Toxicity and risk to aquatic organisms.

The toxicity data for aquatic organisms give no cause for comment.

The pesticide-specific susceptibility of algae on the one hand, and crustaceans and fish on the other, can be readily inferred from the diagrams. The toxicity of anilides, triazines and urea compounds is much higher for algae and (much) lower for crustaceans and fish, while the converse is true for the OP-esters and pyrethroids.

The average toxicity of all evaluated pesticides was found to be somewhat lower for fish than for crustaceans; furthermore, much less marked differences between pesticide groups were found for fish than for crustaceans.

A striking phenomenon was also the positive correlation between toxicity and risk to aquatic organisms: (much) higher toxicity leads to (much) higher risk, and conversely.

#### Toxicity to birds and bees.

Relatively many data were not available for birds and bees so that the relevant diagrams must be regarded as less reliable. As has been pointed out under 4.4.2, there are similarities between the pesticide-specific susceptibilities of birds, bees, crustaceans and fish. A (much) higher toxicity of OP-esters, pyrethroids (lower for birds) and carbamates (lower for bees) was found, while the toxicity of the other pesticide groups was (much) lower.

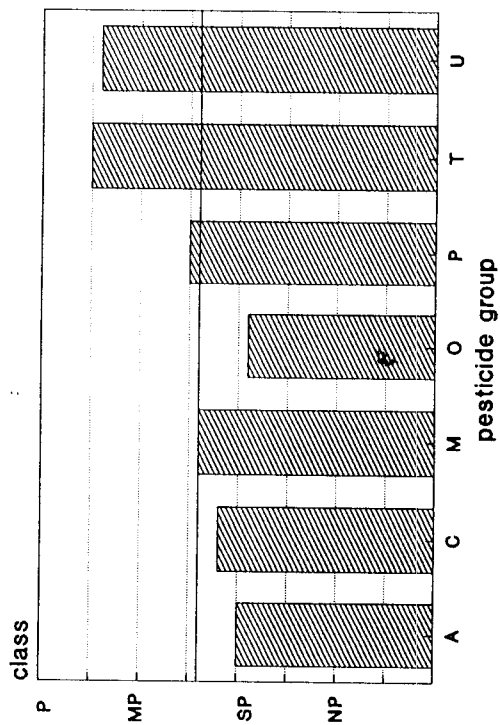


Figure 4.9. Persistence in soil; average class per pesticide group. NP = not persistent; SP = slightly persistent; MP = moderately persistent; P = persistent.

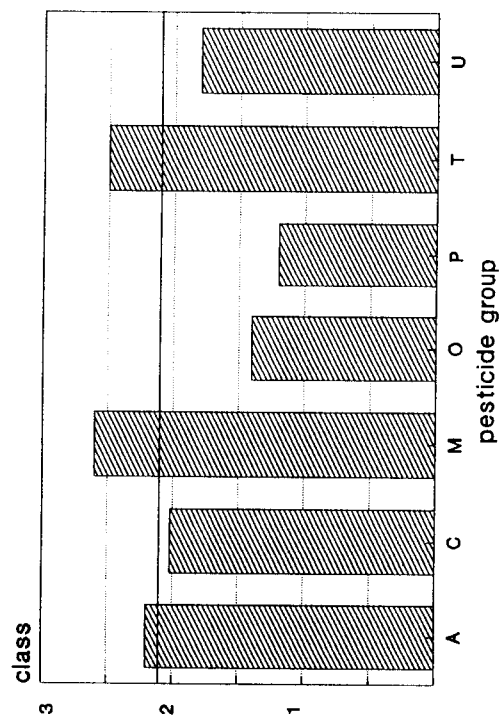


Figure 4.11. Leaching from the top metre of the soil; average class per pesticide group. 1 =  $<0.001 \text{ mg/m}^3$ ; 2 =  $0.001-0.01 \text{ mg/m}^3$ ; 3 =  $0.01-0.1 \text{ mg/m}^3$ .

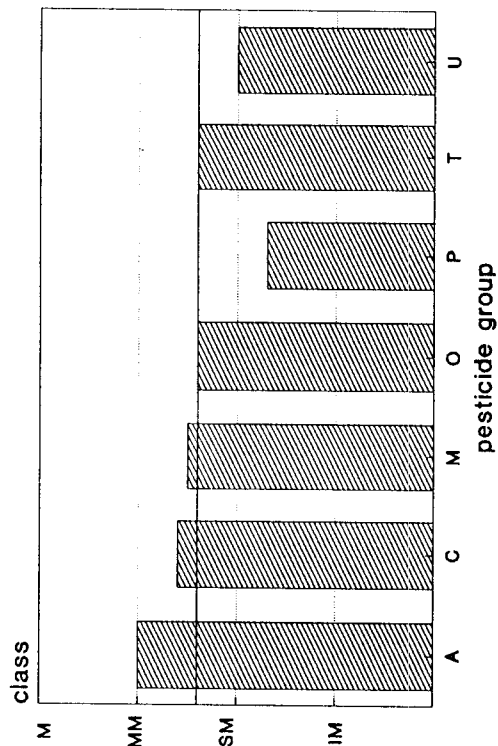


Figure 4.10. Mobility in soil; average class per pesticide group. IM = immobile; SM = slightly mobile; MM = moderately mobile; M = mobile.

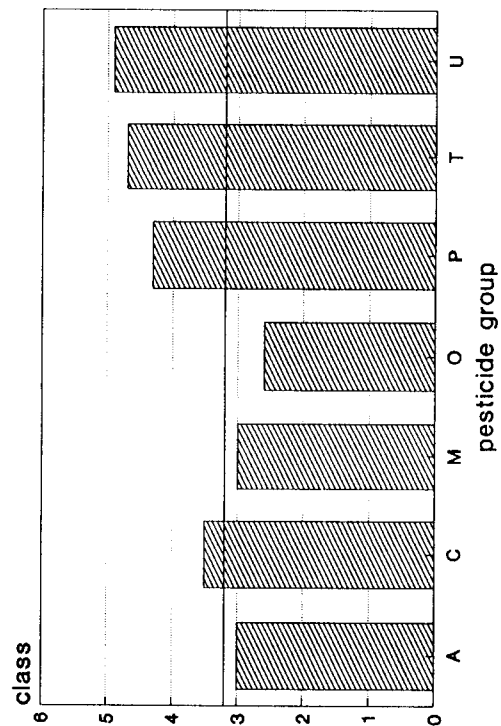


Figure 4.12. Accumulation in the plough layer 1 year after application; average class per pesticide group. 1 =  $<0.04 \text{ } \mu\text{g/kg}$ ; 2 =  $0.04-0.4 \text{ } \mu\text{g/kg}$ ; 3 =  $0.4-4 \text{ } \mu\text{g/kg}$ ; 4 =  $4-20 \text{ } \mu\text{g/kg}$ ; 5 =  $20-40 \text{ } \mu\text{g/kg}$ ; 6 =  $40-100 \text{ } \mu\text{g/kg}$ .



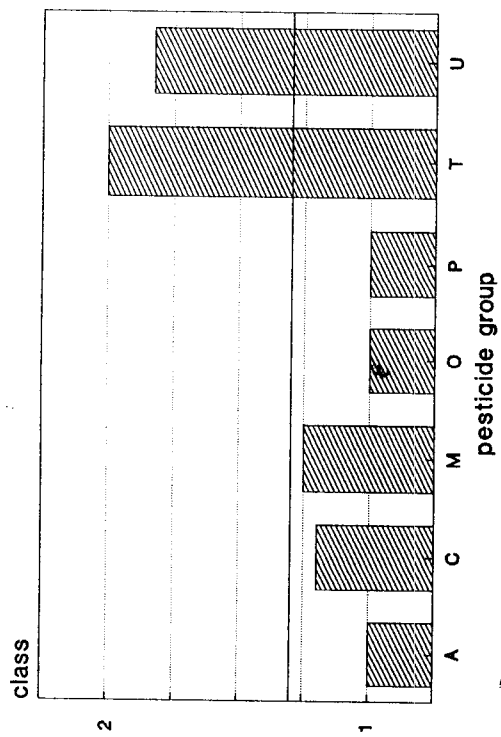


Figure 4.13. Persistence in water/sediment systems; average class per pesticide group. 1 = DT50 0-60 days; 2 = DT50 >60 days.

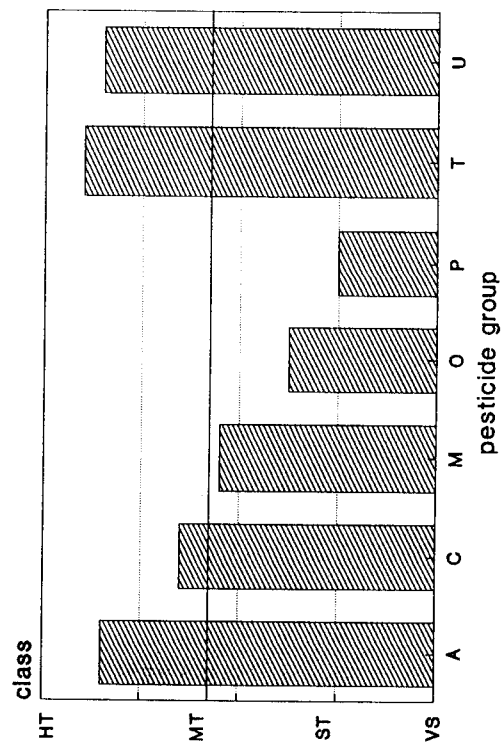


Figure 4.15. Toxicity to algae; average class per pesticide group. VS = very slightly toxic; ST = slightly toxic; MT = moderately toxic; HT = highly toxic.

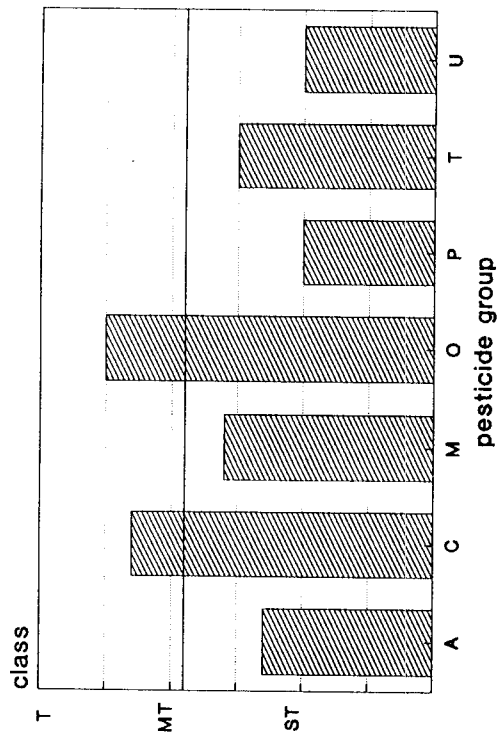


Figure 4.14. Toxicity to birds; average class per pesticide group. ST = slightly toxic; MT = moderately toxic; T = toxic.

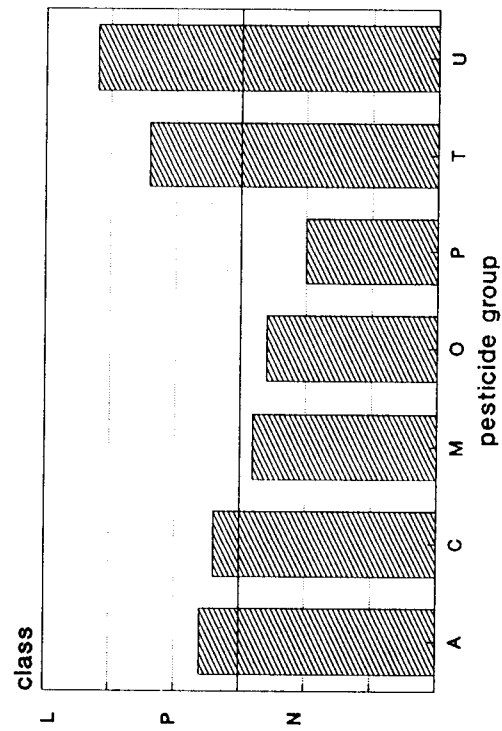


Figure 4.16. Risks to algae; average class per pesticide group. N = negligible; S = small; P = present; L = large; VL = very large.

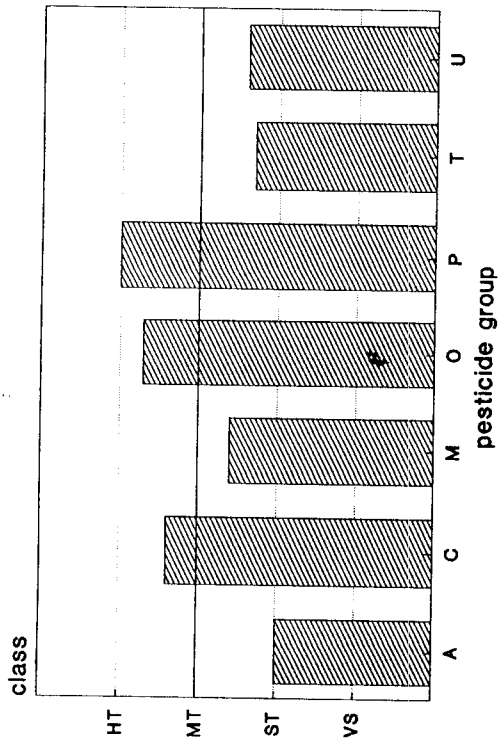


Figure 4.17. Toxicity to crustaceans; average class per pesticide group. See figure 4.15 for symbols of the classes class.

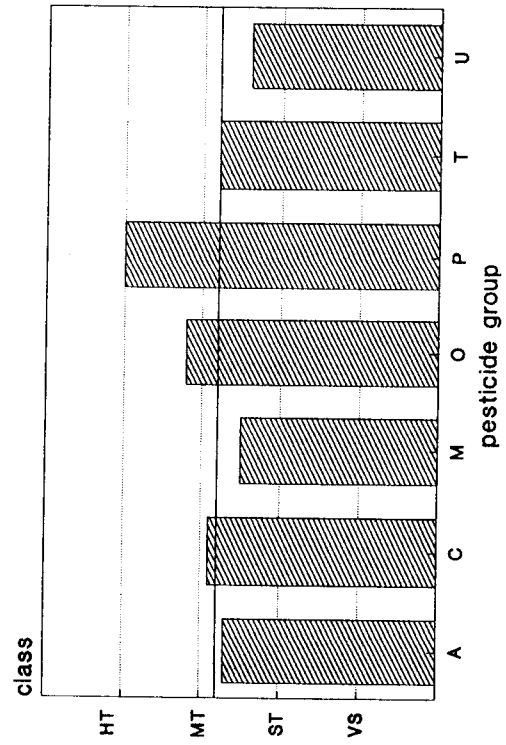


Figure 4.19. Toxicity to fish; average class per pesticide group. See figure 4.15 for symbols of the classes.

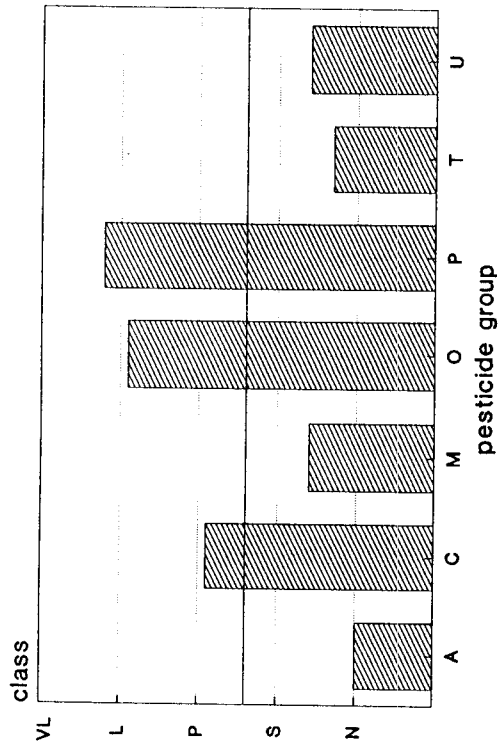


Figure 4.18. Risk to crustaceans; average class per pesticide group. See figure 4.16 for symbols of the classes.

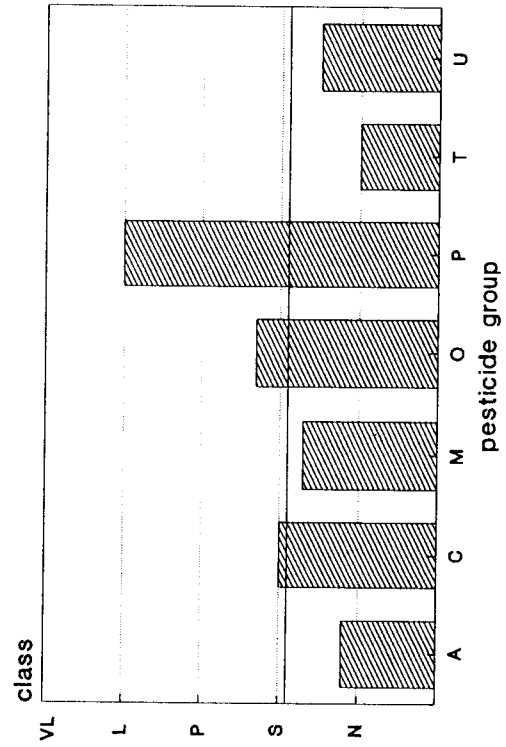


Figure 4.20. Risk to fish; average class per pesticide group. See figure 4.16 for symbols of the classes.

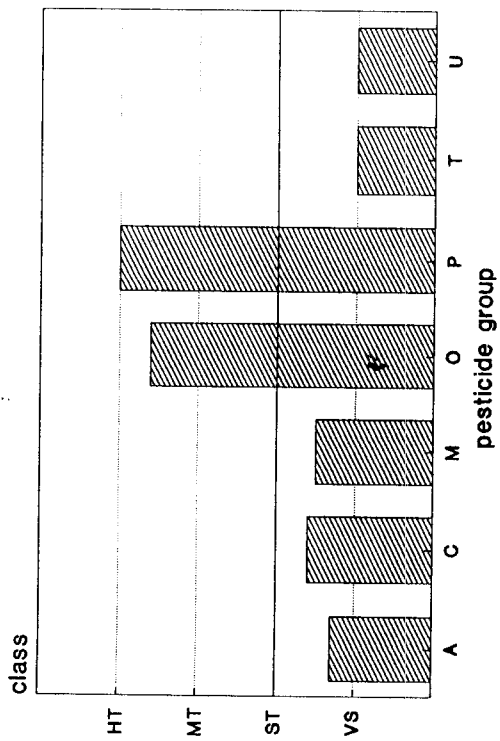


Figure 4.21. Toxicity to bees on the basis of LD50 contact; average class per pesticide group. See figure 4.15 for symbols of the classes.

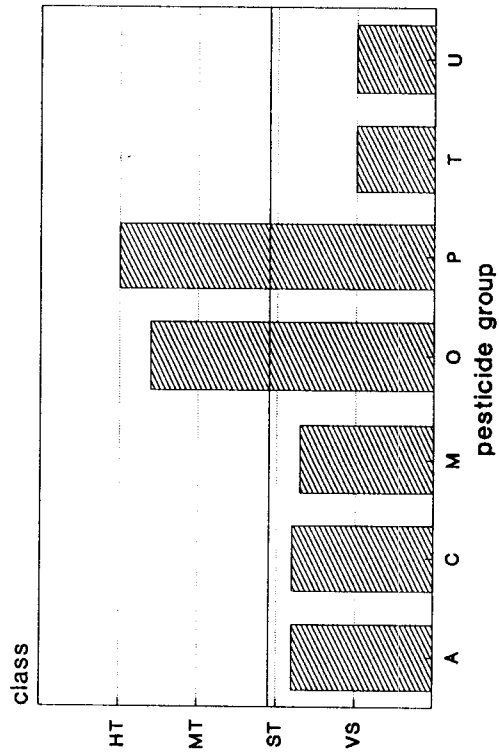


Figure 4.22. Toxicity to bees on the basis of LD50 oral; average class per pesticide group. See figure 4.15 for symbols of the classes.

## 5. CONCLUSIONS AND RECOMMENDATIONS.

The environmental aspects of the 148 pesticides which were summarized as part of the project "Catch-up operation on old pesticides" have been discussed in this report. This chapter presents the main conclusions concerning the environmental properties with respect to behaviour in soil and water, and toxicity. Also, conclusions are drawn and recommendations made about the completeness and usefulness of the information supplied by the companies. The chapter ends with a number of conclusions and recommendations regarding the evaluation system for pesticides.

### 5.1. Behaviour in soil.

1. Data on behaviour in soil were available for most pesticides. Only 12 compounds lacked a DT50 for conversion. Data on mobility were absent for 21 compounds. Finally, the standard calculation using the Support Group M model could not be performed for 39 pesticides.

2. The percentage of soil-bound residue formed was substantial in the majority of the conversion studies (30-60% of the dosage applied). Its chemical identity is not known. It is known that microorganisms, earthworms and plants can take up soil-bound residues. However, almost nothing is known as yet about the toxicity of soil-bound residues and thereby the risk they present. In view of the percentages formed, it is important for the evaluation of pesticides that further research is conducted into the nature and effects of these residues.

3. At present, there is no clear policy on persistence of pesticides in soil. One reason for this is the lack of a classification. There is an acute need for a classification scheme with which the pesticides can be grouped in such a way that it is evident which compounds cannot be registered, considering that the multifunctionality of the soil must be preserved. This report has proposed the following classification of intrinsic persistence:

Proposal for classification of  
intrinsic persistence.

DT50 (days)	classification
< 15	not persistent
15 - 30	slightly persistent
30 - 60	moderately persistent
60 - 120	persistent
> 120	highly persistent

Using this classification, 24% of the pesticides can be classified as persistent to highly persistent on the basis of the average DT50, and 31% of them on the basis of the maximum DT50. These percentages are based on the number of pesticides for which data were available.

4. At present, the assessment of the degradation of pesticides in soil is based mainly on the DT50 of the parent compound. The formation of any persistent metabolites is not taken into account. For the assessment of the persistence of pesticides in soil, more information about their conversion into inorganic end-products is desirable.

5. The mobility classification based on  $K_s/l$  and  $R_f$  assessed 60% of the pesticides for which data were available as slightly mobile to immobile, and 19% as mobile to highly mobile.

This report has also made a proposal for classification of pesticide mobility on the basis of  $K_{om}$ , because this value is independent of the content of organic matter in soil:

Proposal for classification of  
mobility on the basis of the  $K_{om}$

$K_{om}$ (dm <sup>3</sup> /kg)	classification
> 100	immobile
20 - 100	slightly mobile
5 - 20	moderately mobile
1 - 5	mobile
> 1	highly mobile

6. Using the Support Group M model (assuming a standard dosage of 1 kg/ha and one application), average leaching from the top metre of the soil was found to be less than 0.001 mg/m<sup>3</sup> for 58% of the pesticides for which the model calculation had been performed. The model calculated that, based on average leaching, 20% of the compounds reached or exceeded the EC drinking-water standard of 0.1 mg/m<sup>3</sup>. Based on maximum leaching, 49% of the pesticides reached or exceeded this standard, with 36% of the compounds leaching 10 times more strongly than the standard permits.

7. Although the Support Group M model could be used for most of the active ingredients, in many instances there were insufficient data for assessing the leaching behaviour of metabolites. It was found that considerable leaching can be expected of all the metabolites for which a calculation with the Support Group M model could be performed. This indicates that the mobility of metabolites should be a major area of attention in the assessment.

8. The chief value of the Support Group M model is that pesticides can be intercompared, because they are all evaluated in the same standardized way. However, when using the model estimates for leaching and accumulation in practice, some caution must be exercised, because the model has several limitations. The model is very sensitive when the DT50 and Kom values are low. In this situation the results should be examined with special caution. The Support Group M model has been tested against field observations to a limited extent only. It should be investigated whether there are possibilities for more thorough validation by additional testing, or further development and adaptation of the model.

9. The Support Group M model can also be recommended for soil types other than the vulnerable sandy soil when the pesticide is actually applied to other soil types. This has meanwhile been partly accomplished for clay.

10. At present, a standard calculation using the Support Group M model cannot be performed for volatile pesticides, but it can be recommended to extend the model to include these compounds.

## 5.2. Behaviour in water.

1. The data supplied on the behaviour of pesticides in water were insufficient for evaluating them systematically. Water/sediment studies were available for only 78 pesticides. The DT50 values determined in these studies could often not be intercompared either because they were based on different data or because the test conditions varied widely.

An extensive standardized water/sediment test, as described in the explanatory notes to the application form, should be made mandatory.

In addition, more fundamental research should be conducted into the influence of the various test parameters (sediment thickness, percent of organic matter, pH, composition of the microbial population, acclimatization time) on the conversion rate and pathway.

2. A classification scheme for persistence of pesticides in natural water is not available. In this report a persistence limit of 60 days was used analogous to the assessment of persistence in soil. Of the pesticides for which data on biodegradation were available, 21% was classified as persistent.

This procedure could be underpinned by demonstrating a correlation between the DT50 values of aerobic soil studies and the DT50 (system) values from water/sediment studies. Whether such a correlation exists would have to be investigated more closely. This project could not find such a correlation because of insufficient reliable data (notably water/sediment studies).

3. In the assessment of the persistence of a pesticide, only the active ingredient is generally considered, whereas it can also be converted into persistent metabolites. In assessing the behaviour of pesticides in water, more attention should be paid to their conversion products in the future. When the proportion of metabolites formed is >10%, their toxicity to aquatic organisms should also be determined.

4. In the assessment of the behaviour of pesticides in water, more attention should be paid to the distribution of a pesticide in the water phase. For example, field studies with pyrethroids showed that these

compounds concentrate in the upper layer, possibly resulting in an increased risk of effects on organisms living in or on the surface layer. The rate of adsorption to the sediment and any resuspension of the sediment are also important.

5. For 28% of the pesticides where the sediment had been analyzed, the amount of sediment-bound residue ultimately formed was more than 30%. It is not clear to what extent pesticides are removed from the aquatic environment by binding to the sediment. Fundamental research should be conducted into the question of how much of this bound residue is biologically available or can become available again (see also point 2 of section 5.1).

6. Hydrolysis and photolysis studies are often of very limited use for assessing the environmental behaviour of pesticides. Nevertheless, supplying hydrolysis studies remains useful in order to gain an insight into the pH-dependence of the conversion rate. This can also be important for understanding hydrolysis of pesticides in soil water where the pH can vary widely.

7. Comparison of the available results from water/sediment studies and hydrolysis studies showed that the DT50 for biodegradation was generally (much) lower than the DT50 for hydrolysis. However, the converse was observed for one pesticide, probably as a result of strong sorption to the sediment.

Since only 15 compounds could be compared, it is difficult to draw a general conclusion, but it seems incorrect to suppose that the half-life in water/sediment systems will invariably be lower than the half-life for hydrolysis.

8. The data on the behaviour of pesticides in water are practically all derived from laboratory experiments. Whether these data can be extrapolated to the field situation has not yet been sufficiently studied. It can therefore be recommended to test data from laboratory experiments against measurements in the field.



### 5.3. Toxicity to organisms in the environment.

1. The toxicity data for fish were available for all but 8 pesticides. The number of missing data for crustaceans and algae was higher, namely, 24 and 46 respectively. The companies have been requested to supply these missing data, with the exception of those for the soil fumigants and granular formulations, which are worked into the soil, and the seed-treatment agents (10 pesticides in all).

In the case of the algae, relatively many pesticides fell into the least toxic class. The numbers decreased with increasing toxicity. The reverse pattern was observed for crustaceans and fish.

2. A pesticide-specific susceptibility was observed: algae appeared to be especially susceptible to the herbicides (anilides, triazines and urea compounds); the pyrethroids and OP-esters were the most toxic compounds for crustaceans and fish.

3. A drift calculation could be performed for 131 pesticides. A highest (worst-case) and a lowest exposure concentration were calculated on the basis of the dosage and emission with the various applications. The ratio between the highest and lowest concentration ranged from <25 to >1000. The highest concentration used in calculations for the risk evaluation ranged between 0.01 and 0.1 mg/l for 55% of the pesticides.

4. 14, 29 and 10% of the pesticides for which data were available were expected to pose a large to very large risk to algae, crustaceans and fish, respectively. The pesticides presenting these large risks to crustaceans and fish were especially the OP-esters and pyrethroids, and those to algae were especially the urea compounds.

5. A clear relationship was found between toxicity and the risk of effects: practically all pesticides with a large risk were highly toxic, while conversely, only very few of the highly toxic pesticides presented a negligible risk.

6. It can be recommended to make a more detailed comparison of application areas and risk evaluation, and base any measures partly on this. It can then also be examined whether specific emission-control measures can be achieved with a risk-posing use.

7. An adequate evaluation of the extent of bioaccumulation is difficult. First, data were lacking in many cases; a BCF value was available for only 83 of the 148 pesticides. Moreover, the values could not be intercompared owing to differences in experimental design.

However, the bioaccumulation potential of pesticides can also be estimated on the basis of the octanol-water partition coefficient, water solubility and structural analogy.

This report advocates a more uniform method of testing, where a BCF is determined for the whole organism, based on the concentration of the active ingredient, at equilibrium. Specifications for such a test have been laid down in the OECD Guideline no. 305.

8. Based on the highest value, 33% of the pesticides for which a BCF was available were classified as moderately accumulating and 15% as highly accumulating. The pyrethroids for which a BCF had been measured or calculated were all classified as highly accumulating.

9. Toxicity data for birds were available for only about half of the pesticides evaluated; 72 LD50 studies and 59 LC50 studies were involved. Based on LD50 values, 26% of the pesticides for which data were available were classified as toxic to highly toxic to birds. They included especially OP-esters, and a few carbamates and miscellaneous compounds.

Since an evaluation system for exposure of birds to pesticides is lacking, it is recommended to develop such a system in the foreseeable future.

10. Toxicity data for bees, too, were available for only about half of the pesticides. Both oral and contact exposure were involved. Of the available data, relatively many results fell into the very slightly toxic class.

The classification system used for hazard to bees differs from that for aquatic organisms. It is therefore recommended to use the adapted scheme in order to achieve more uniformity in the evaluation methods.

11. It has only recently become mandatory to supply toxicity data for earthworms. Consequently, very little information is available and drawing conclusions from this is not justified. It is recommended to develop a system for assessing the risk to terrestrial organisms analogous to that for aquatic organisms. Regarding earthworms, a system is envisaged based on the expected concentration of a pesticide in the top 2.5 cm of the soil. The expected concentration in the upper 20 cm is currently being calculated using the Support Group M model. The model calculation should be attuned to the risk evaluation for terrestrial organisms (into harmony).

#### 5.4. Integration.

1. Comparison of the various surveys of the ten most persistent pesticides, the ten most immobile and mobile, and the ten most toxic, showed that 71 pesticides occurred at least once. It was not possible to distinguish any pesticides which scored negative on nearly all aspects.

2. When the various environmental properties were compared per pesticide group, the triazines and urea compounds were found to be the most persistent compounds in both soil and water. These pesticide groups also contained the most toxic compounds for algae.

3. The OP-esters were classified as highly toxic to crustaceans, fish, birds and bees alike. The pyrethroids were also considered to be highly toxic to these organisms with the exception of the birds.

#### 5.5. General aspects with regard to the evaluation

1. To optimize the evaluation of the environmental risks of pesticides, several improvements are advisable to optimize. A number of suggestions for improvements have already been made above for each aspect. Inspection of the total package of available information and evaluation methods revealed that three limitations currently still stand in the way of a complete risk evaluation, namely, the incompleteness of the files, several gaps in the

present application form, and the lack of workable risk evaluation methods in a number of fields.

2. The survey in appendix 7 shows that data have often not been supplied by the manufacturer. This is not necessarily a shortcoming, because it is possible that certain data do not have to be supplied for the pesticide concerned, these being considered not relevant in view of its properties and use.

However, data which should have been supplied under the requirements of the application form were quite often also lacking. This was especially true of studies on conversion in a water/sediment system, toxicity data for algae, earthworms, bees and birds, and data on the bioaccumulating properties of a pesticide. When judged necessary, the companies will be asked to supply the missing data.

3. The package of environmental data requested by the application form has been considerably enlarged in the past 10 years. However, several aspects are not yet included in the application form whereas information about this is desirable.

The data required on the behaviour of pesticides in the atmosphere are still very limited. In general, the available information only gives an impression of the volatility of a pesticide. Data on how the pesticide is transported through the air and where it is deposited are not required and generally also not supplied.

The number of species of organisms included in the risk evaluation is limited. It is advisable to increase this number for the assessment of the adverse effects of a pesticide in the environment. It concerns first of all toxicity tests for plants, amphibians and reptiles. It is also desirable to increase the number of species of insects and soil vertebrates included in the risk evaluation (currently only the bee and the earthworm).

The possible increase of the number of test organisms calls for two comments. Firstly, it can be stated that a limited number of test organisms keeps the registration procedure (and criteria) simple. Secondly, from the point of view of reducing animal experiments, it is desirable to minimize the number of tests involving animal organisms.

These two observations must be taken into account when the safest possible environmental evaluation of a pesticide is being made.

4. A great deal of attention is currently being paid to the development of risk evaluation models, which can assess the risk of effects on organisms present in the environment on the basis of data on exposure and toxicity. In the evaluation of the pesticides mentioned in this report, use has been made of risk evaluation models for bees and aquatic organisms. Work is being done on refining these models. There are no such models as yet for the other groups of organisms. A risk evaluation model for terrestrial organisms, including birds, is under development. An important aspect here is biomagnification. A proposal for a risk evaluation model for biomagnification in piscivorous birds has been elaborated in this report. For calculating the exposure of, for example, earthworms to a pesticide, the Support Group M model can be used, which estimates accumulation in the plough layer.

5. The further elaboration of the evaluation system for pesticides should take into account analogous developments elsewhere, for example, the Evaluation System for New Substances, the Uniform Evaluation System, and developments at international organizations (EEC, OECD) or sister institutions (the American EPA, the German UBA).

6. To date, only a proportion of the pesticides available on the market in the Netherlands have been evaluated with regard to their environmental effects. Clause 2 pesticides have not yet been considered. It is therefore recommended also to carry out an up-to-date environmental evaluation of the remaining clause 1 and clause 2 pesticides.

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## APPENDICES

Appendix 1: List of pesticides

\* 2,4-D  
\* acephate  
\* aclonifen  
\* aldicarb  
\* alloxym-sodium  
ns ammonium thiocyanate  
ns anthraquinone  
\* asulam  
\* atrazine  
azinphos-methyl  
nr Bacillus thuringiensis  
\* bentazone  
nr benzalkonium chloride<sup>1</sup>  
ns borates  
bromophos-ethyl  
bromofenoxim  
bromopropylate  
calcium cyanide  
\* carbaryl  
carbetamide  
ns carbofuran  
chlorbromuron  
ns chlorophacinone  
chlorfenvinfos  
ns chlorflurenol  
chlormequat  
chlorpropham  
chlorpyrifos  
chlorothalonil  
\* chlorthiamide  
chlortoluron  
\* chloridazon  
chloroxuron  
copper oxychloride  
creosote  
cyanazine  
cymoxanil  
cypermethrin  
\* dalapon  
daminozide  
\* dazomet  
deltamethrin  
demeton-S-methyl-sulphone  
desmetryne  
diazinon  
\* dicamba  
\* dichlobenyl  
dichlofluanid  
\* dichloropropene  
\* dichlorprop + dichlorprop-P  
dichlorvos  
dicloran

dicofol  
nr didecyldimethylammonium chloride<sup>2</sup>  
ns diethylene glycol  
difenoxuron  
diflubenzuron  
\* dikegulac-sodium  
dimethachlor  
dimethoate  
dinoseb  
dinoseb acetate  
\* dinoterb  
dithianon  
diuron  
\* DNOC  
\* dodemorph  
dodine  
EPTC  
ethephon  
ethofumesate  
\* ethoprophos  
etridiazole  
\* etrimfos  
fenaminosulf  
fenitrothion  
fenmedipham  
fenpropathrin  
fenpropimorph  
fenvalerate  
ns flurenol  
fonofos  
formothion  
fosetyl-aluminium  
gibberellin (A3, A4 + A7)  
guazatine  
heptenophos  
\* hexazinone  
\* iprodione  
lenacil  
\* linuron  
malathion  
\* mancozeb  
\* maneb  
\* MCPA  
\* mecoprop + mecoprop-P  
mefluidide  
mercaptodimethur  
metaldehyde  
\* metam-sodium  
\* metazachlor  
methabenzthiazuron  
methamidophos  
\* methidathion  
\* methomyl  
methyldodecylbenzyltrimethylammonium chloride

methyldodecylxylylbis(trimethyl)ammonium chloride  
\* methylisothiocyanate  
\* metiram  
\* metolachlor  
metoxuron  
mevinphos  
nr mineral oil  
\* monolinuron  
nitrothalisopropyl  
omethoate  
\* oxamyl  
oxydemeton-methyl  
\* parathion  
\* parathion-methyl  
pendimethalin  
\* phosalone  
phosphamidon  
phosmet  
piperonyl butoxide  
ns piproctanyl bromide  
pirimicarb  
pirimiphos-methyl  
propham  
prometryne  
\* propachlor  
propamocarb hydrochloride  
propazine  
propiconazole  
\* propoxur  
propyzamide  
pyrazophos  
pyrethrins  
\* pyridate  
sethoxydim  
simazine  
sodium dimethyl dithiocarbamate  
ns strychnine  
ns sulphur  
sulfotep  
terbufos  
terbutryn  
\* thiofanox  
thiometon  
\* thiram  
tolyfluanid  
triadimenol  
triallate  
triazophos  
trichlorfon  
\* triclopyr  
tridemorph  
trifluralin  
triforine  
ns trioxymethylene

- \* vamidothion
- vinclozolin
- zineb
- \* ziram

<sup>1</sup> this collective term comprises a number of quaternary ammonium compounds including alkyldimethylbenzylammonium chloride, alkyldimethylethylbenzylammonium chloride and lauryldimethylbenzylammonium chloride.

<sup>2</sup> this compound has been included in the advisory report on dialkyldimethylammonium chloride and bromide.

\* = 53 pesticides evaluated by Support Group M on 1-2-1990.

ns = not summarized.

nr = summarized but not incorporated into this report.



Appendix 2: Categorization.

- Category 1: Concerns adequately executed and reported studies which are, moreover, relevant to the risk evaluation with regard to the use of pesticides in the Netherlands.  
Application forms, physicochemical data and the Crop Protection Guide [12] also fall into this category.
- Category 2: Studies of which the data are relevant to the risk evaluation with regard to the use of pesticides in the Netherlands; however, they are less reliable because of inadequate experimental design or execution, or incomplete reporting. As an exception, the BBA-37 studies also fall into this category.
- Category 3: Concerns studies which are not relevant to the Dutch situation or studies which are relevant but not reliable (test conditions were not specified, irrelevant parameters or conditions, etc.). The review articles, studies performed in salt water and runoff studies fall into this category.

### Appendix 3: Soil studies.

#### 3.1. Conversion.

Although the application form requires only laboratory studies conducted under aerobic conditions, field studies and studies carried out under anaerobic or sterile conditions were also supplied. These studies have been incorporated if they had been adequately executed.

In summarizing the studies, attention was paid to the following aspects:

- incubation conditions: aerobic, anaerobic, sterile; temperature; light/dark; moisture content of the soil (see appendix 3.4 for this);
- soil type: classification according to the American texture classification system; pH and percent of organic matter;
- dosage and form in which the pesticide was applied;
- position of the label;
- extraction method; analysis method; recovery > 70 %;
- for field studies: temperature and precipitation, sampling depth.

The most important results are data on the degradation rate (DT50) and degradation kinetics of the active ingredient, and formation of metabolites including also CO<sub>2</sub> and soil-bound residue. In many cases a DT50 was determined which is not strictly based on degradation of the active ingredient but, for example, on dissipation (the disappearance of the pesticide from the soil), or on mineralization by measuring CO<sub>2</sub> production (radioactively labelled).

The most commonly used protocol for conversion studies in soil is the German BBA 36 guideline [5].

#### 3.2. Model calculation.

For the majority of the evaluated pesticides, the following rules have been applied in selecting DT50 values for the model calculation [10]:

1. Determined at a temperature ranging between 15 and 25 °C; the DT50 is corrected for temperature using the formula: **DT50 (20 °C) = DT50 (T) \* exp [0.08 (T-20)]**;
2. Determined at a moisture content of approximately field capacity, i.e., corresponding to a suction tension of 2-2.5 (see section 3.4 for pF curves of a number of soils);
3. Not derived from field experiments, or studies conducted under anaerobic or sterile conditions;
4. Not determined in muck soil (organic soils);
5. The dosage used in the experiment should be of the same order of magnitude as the field dosage. A study is rejected when the dose level differs more than a factor of 5 from the highest or lowest field dosage;
6. Not derived from bioassays;
7. Determined on fresh original soil taken from the field or from a well-drained temporary storage-place in the open air;
8. A sufficient proportion of the pesticide must have been converted; either 50% conversion must have been reached in the study, or conversion must have been followed for 6 months.

For the majority of the evaluated pesticides, the following rules have been applied in selecting Kom values for the model calculation:

1. Kom values determined in muck soils are not included;

2.  $K_{om}$  values determined for formulations of the active ingredient may differ from those of the technical product. In case of clear differences they are not included;
3. Not derived from bioassays;
4. With regard to shaking experiments,  $K_{om}$  values are only included when **the constant  $1/n$  lies within the 0.7 to 1.1 range**. If the concentration in soil has not been measured but calculated and the  **$K_s/l \neq$  the soil/water ratio ( $kg/dm^3$ ) is  $< 0.1$** , then the fall in concentration is so small that the calculated  $K_{om}$  becomes too inaccurate. The proportion of the pesticide converted during the shaking experiment must not exceed 3%. For pesticides with  $DT < 14$  days, the rule is: **the shaking time in hours  $\leq$  the  $DT_{50}$  in days**;
5. With regard to soil thin-layer experiments, pesticides must have  **$R_f$  (TLC)  $\geq 0.3$** . Lower  $R_f$  values are so inaccurate that conversion to  $K_{om}$  becomes unreliable. As regards conversion of the active ingredient during these experiments, the same rule applies as for shaking experiments;
6. With regard to column experiments, the distance moved by the active ingredient must be measurable.  $R_f$  values from studies with aged residue are not converted to  $K_{om}$  unless no other data are available.

### 3.3. Mobility

The following mobility studies have been processed:

- Sorption experiments: Determination of the  $K_s/l$  by means of a shaking experiment. Important factors are the soil/water ratio, the initial concentration in solution, the incubation time and temperature. On the basis of the values of a number of equilibrium concentrations in solution and the associated concentrations in soil, the  $K_s/l$  can be calculated using the Freundlich equation. The constant  $1/n$  from the equation indicates the degree to which adsorption depends on the concentration. There is a linear relationship when  $1/n = 1$ . A shaking experiment must be carried out with at least 4 different concentrations to permit determination of a reliable  $K_s/l$ .
- Column studies: Important factors are soil type, column length, water layer, duration of sprinkling, fresh or aged residue. The  $R_f(\text{column})$  is equivalent to the distance moved by the active ingredient divided by the distance moved by the water front. The movement of the active ingredient is equated with the movement of the peak or, if it is absent, the point below which and above which 50% of the pesticide is found. For unambiguous interpretation of the results, it is usually necessary that the column has been analyzed layer by layer, and that the fate of the active ingredient is known. When no clear pattern was observable or when the study had been carried out with aged residue, no  $R_f(\text{column})$  was calculated.
- Thin-layer chromatography: Here, too, the distance moved by the active ingredient must be measurable. A  $R_f(\text{TLC})$  is determined in the same manner as a  $R_f(\text{column})$ : the peak of the substance is found in the centre of the spot on the TLC plate. If this  $R_f(\text{TLC})$  differs more than a factor of 2 from the value determined for the front of the spot, both values are included.

### 3.4. pF curves

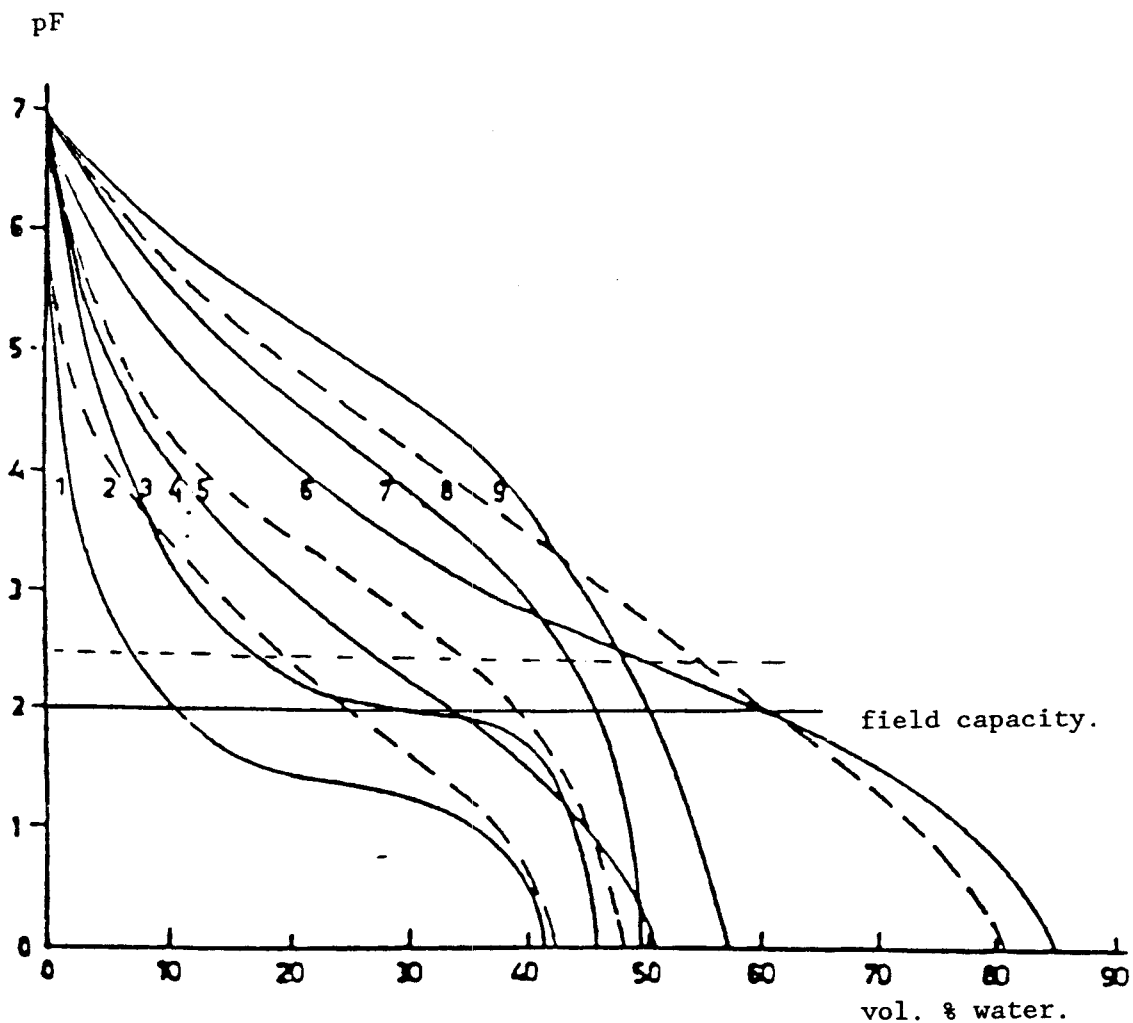


Figure 1. pF curves of a number of Dutch soils.

<u>curve</u>	<u>Dutch soil</u>	<u>name according to the American texture classification system</u>
1	duinzand	sand
2	lemig zand	loamy sand
3	lichte zavel	sandy loam
4	zavel	sandy clay loam
		loam
5	löss	silt
		silty loam
6/8	veen	muck
7	klei	sandy clay
		silty clay
		clay loam
		silty clay loam
8	laagveen	peat
9	zware klei	clay

Several concepts are used for indicating the moisture content of soil:

- maximum water-holding capacity: the moisture content under saturation conditions (hydrostatic pressure, 0 cm);
- field capacity:  $pF = 2-2.5$ ;
- moisture content: moisture mass divided by dry soil mass.

Conversion studies are often conducted at a moisture content of 40% of the maximum water-holding capacity, or 75% of the field capacity. By means of the  $pF$  curves it is possible to check whether the moisture content corresponds to a  $pF$  value of 2-3. An example: a clay soil (curve 9) with a moisture content of 75% of the field capacity. The moisture content at field capacity can be read off at  $pF = 2-2.5$ . The corresponding moisture content is 48-51%. Seventy-five per cent of this is 36-38%, the associated  $pF$  value being 4.0-4.2: the soil is too dry.

The  $pF$  values at 40% of the maximum water-holding capacity (MHC) and 75% of the field capacity are presented in the following table, for the soils of curves 1 to 9.

Curve no.	40% MHC	pF at 75%	
		FC1	FC2
1	1.6	2.3	2.8
2	2.4	2.1	2.9
3	2.7	2.5	2.9
4	3.0	2.5	3.0
5	3.5	2.8	3.0
6	3.1	2.6	3.0
7	4.9	3.5	3.7
8	4.1	3.1	3.5
9	5.1	4.0	4.2

The moisture level in conversion experiments conducted at 40% MHC was too high in the case of curve 1 soil, correct in the case of the curves 2, 3 and 4 soils, and too low in the case of the curves 5 to 9 soils. Conversion experiments conducted at 75% field capacity were performed at the correct moisture level in the case of the curves 1 to 6 soils, and at too low a moisture level in the case of the curves 7, 8 and 9.

### 3.5. Support Group M-model graphs for spring application.

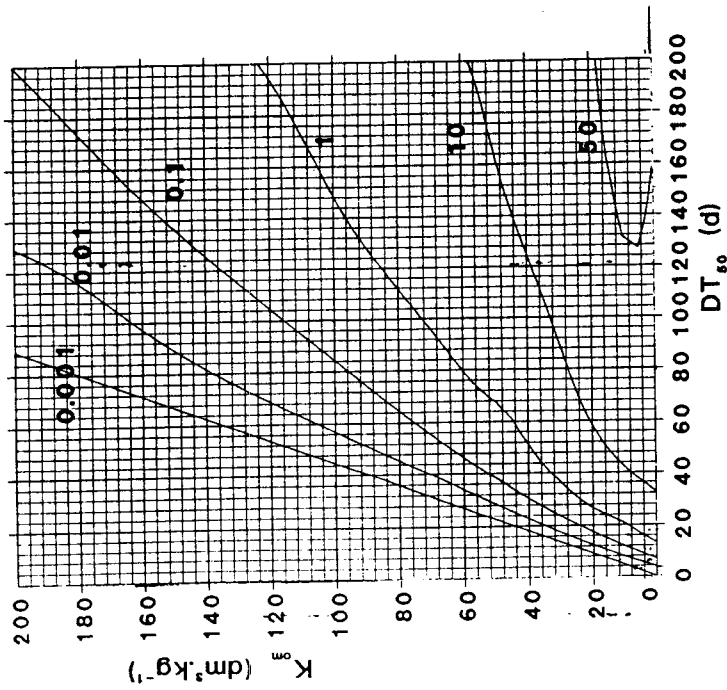


Figure 1. Maximum pesticide concentrations in groundwater at a depth between 1 and 2 m as a function of  $K$  and  $DT_{s0}$ . The lines are contour lines and the figures indicate the concentrations in  $\text{mg}/\text{m}^3$ .

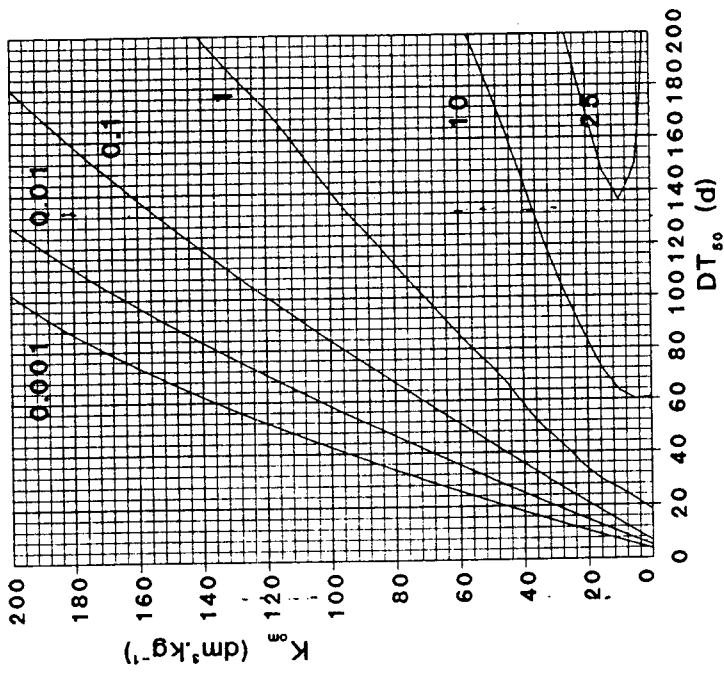


Figure 2. Leaching of pesticides from the top metre of the soil. The lines are contour lines, and the figures indicate leaching as a percentage of the dosage.

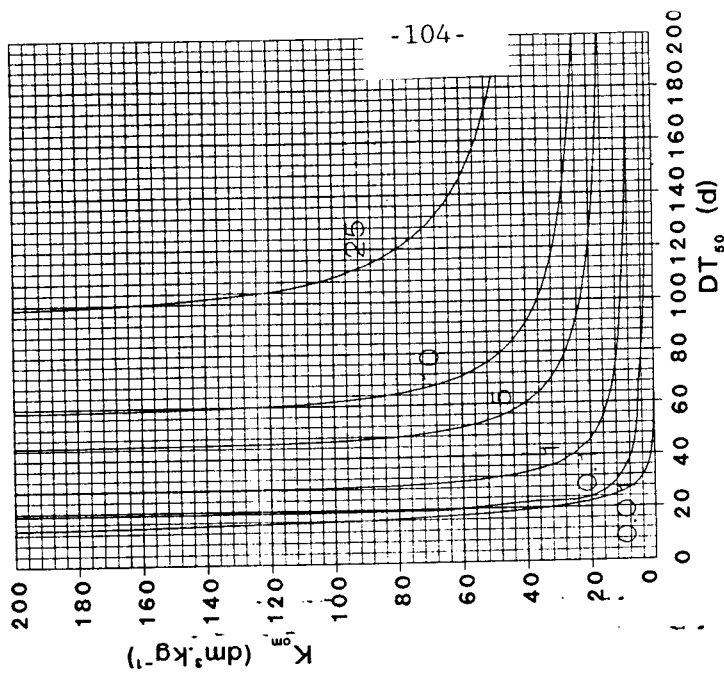


Figure 3. Amount of pesticide in the plough layer 1 year after application. The lines are contour lines, and the figures indicate the percentage of the dosage.

#### Appendix 4: Aquatic studies.

##### 4.1. Hydrolysis.

References 11, 15 and 34 were used in summarizing and evaluating hydrolysis studies.

Since hydrolysis studies had often been performed at high temperatures, it was important to specify the extrapolation method used (Arrhenius equation). In general, the relevant temperature range was taken to be 15-25 °C. This temperature range also applied to the photolysis and biodegradation studies.

In summarizing the studies, attention was paid to the following aspects:

- Incubation conditions: pH, temperature, sterilization method, and duration of the experiment;
- Type of buffer, origin of the water used (river, distilled);
- Dosage and form in which the pesticide was added;
- Position of the label.

It is important to check the temperature during the experiment: a deviation of 1 °C corresponds roughly to a deviation of 10% in the hydrolysis rate [15]. It is likewise important to check for possible biodegradation and photolysis.

The main results included for each study are: DT50 value(s), changes in concentration of the metabolites and CO<sub>2</sub> produced.

##### 4.2. Photolysis.

References 11 and 16 were used in summarizing and evaluating photolysis studies.

In summarizing the studies, attention was paid to the aspects mentioned under 4.1, whenever applicable, as well as to the following points:

- Characteristics of the light source;
- Use of a photosensitizer.

When artificial light is used in an experiment, it is important to compare the wavelength of the source with sunlight ( $\lambda > 290$  nm). When they differ, unnaturally rapid degradation in the experiment cannot be excluded. This is the case, for example, when UV light ( $\lambda < 330$  nm) is used in a test with a pesticide possessing a benzene ring ( $\lambda_{\text{max}}$ : 254 nm). It is important to check for possible biodegradation and hydrolysis. To minimize hydrolysis, a photolysis study must be carried out at a pH corresponding with maximal hydrolytic stability [16].

The main results included for each study are: DT50 value(s), changes in concentration of the metabolites and CO<sub>2</sub> produced.

##### 4.3. Biodegradation.

Reference 11 was used in summarizing and evaluating biodegradation studies. An internationally recognized protocol was not available since the test is currently required only in the Netherlands.

In summarizing the studies, attention was paid to the aspects mentioned under 4.1 and 4.2, whenever applicable, as well as the thickness and composition of the sediment. The thickness of the sediment is important because aerobic degradation only occurs in the upper 2 centimetres [11]. It

is also essential to check for any toxic effects on the microbial population. If these effects occur, conversion is retarded and the study is less useful. The method of application (add preferably dissolved in water to the water column) must also be taken into account in the interpretation. With volatile pesticides, aeration can lead to extra volatilization. To obtain a clear idea of both the rate and route of conversion, a well-executed mass balance study is essential. This implies that by far the greater part of the added radioactivity must be recovered (general rule, > 70%).

The main results included for each study are: DT50 value(s) (making a distinction between DT50 value in the water and DT50 value in the system, or water and sediment), changes in concentration of the metabolites (making a distinction between the water column and the sediment) and CO<sub>2</sub> produced, the non-extractable amount of active ingredient or activity in the sediment, and reaction kinetics.



## Appendix 5: Toxicity studies.

### 5.1. Toxicity to aquatic organisms.

In evaluating studies with aquatic organisms, attention was paid to the following aspects:

- the physicochemical properties of the pesticide: solubility, volatility, log Kow, etc.;
- the medium: pH, oxygen concentration, temperature, hardness, origin;
- test type: static, semi-static or continuous flow system;
- nominal or measured concentrations.

The OECD guidelines were used as the principal reference [35, 36, 37 and 38].

Usually only the short-term studies with algae, crustaceans and fish were available. In these studies the organisms are exposed to different concentrations of the pesticide for a given period, after which an L(E)C50 or an NOEC can be calculated.

Studies with algae result in an EC50 and an NOEC. A distinction was made between effects on the biomass and on the growth rate. Special attention was paid in the evaluation to the light source used and whether the algae population was in the exponential growth stage at the start of the test.

Studies with crustaceans result in an EC50, the criterion usually being immobilization. Studies with fish result in an LC50, the criterion being mortality. The studies with these two types of organisms reported whether the incipient L(E)C50 had been reached. This is the L(E)C50 at which the value no longer decreases with time. If the incipient L(E)C50 has not yet been reached, then the pesticide has a higher acute toxicity than can be predicted on the basis of the available L(E)C50.

### 5.2. Bioaccumulation.

The bioconcentration factor (BCF) is the most relevant parameter for making a judgement about the bioaccumulation potential of a pesticide. The BCF equals the ratio of the concentration of the pesticide in the organism to that in water, and can be determined experimentally in a simple system consisting of 2 compartments (for example, fish and water). The determination is preferably made in a continuous flow test (CF) in which the correct concentration is continually added to the water, so that a stable concentration is assured. It is very important that a steady state situation is reached, in which uptake and excretion are in equilibrium. Establishment of the steady state is verified by performing sufficient analyses during the uptake and plateau phases.

In making the summaries, the BCF in the steady state situation has as far as possible been given. The BCF can be calculated for the whole organism or for certain parts thereof (edible and inedible parts). This value can also be calculated on the basis of wet, dry or fat weight, or fat content. In the evaluation of the accumulation data, the greatest importance was attached to the BCF calculated for the whole organism on a wet weight basis [18, 43].

It was found in practice that partition is usually the dominant process in determining bioconcentration. For most hydrophobic organic compounds, the Kow, an intrinsic property, controls the magnitude of the BCF [18]. According to a literature search, a large number of empirical relationships

are known between the partition coefficient and the BCF for fish, which are mostly based on the following equation:

$$\log BCF = a \log Kow + b.$$

It was concluded from this investigation that the values 0.79 and -0.40 for a and b, respectively, gave the most reliable relationship. This relationship is based on experiments with 122 pesticides and log Kow values ranging from 1 to 7 [18, 49].

### 5.3. Toxicity to birds.

Both (sub)acute and chronic studies were supplied. For most pesticides only acute and subacute studies (diet studies) were available.

In an acute study, the pesticide under investigation, usually dissolved in a vehicle, is administered orally. The birds are then observed for several days, and the mortality is recorded, resulting in an LD50 in mg/kg body weight.

In a diet study, birds are given the pesticide in their feed. They usually receive the treated feed for 5 days, and are observed for another 3 days, resulting in an LC50 in mg/kg feed.

In evaluating the acute and diet studies, special attention was paid to vomiting and refusal of feed, respectively, because both symptoms result in a lower actual exposure concentration. Furthermore, the number of concentrations tested was in many experiments insufficient for calculating a statistically reliable LD(C)50, and too few birds per concentration had often been used (the OECD stipulates 10 birds per concentration for the diet study).

### 5.4. Toxicity to bees.

Several types of studies are available for determining the toxicity of a pesticide to bees [2, 23, 44 and 46]. The pesticide can be administered by various routes:

- oral: the pesticide is given in the feed, usually a glucose solution. This simulates the field, when the pesticide is sprayed.

- contact or topical: a drop of the pesticide, in most cases dissolved in acetone, is applied to the back or abdomen of the bee. This also simulates the field, when the pesticide is sprayed.

- deposit: a filter paper is treated with a solution of the pesticide under investigation, and a number of bees are then placed on the paper. This simulates the field situation a considerable time after spraying, when a residue of the pesticide is present on the plant.

In all cases the mortality is recorded after 24-48 hours. Only the first two types of studies were used in the risk assessment. Also, field experiments were frequently supplied in which the "flight density" had been measured with and without spraying.

### 5.5. Earthworms.

The test with an artificial soil is the most common one [29, 41]. The filter paper-contact test is less relevant in view of the mode of exposure. Both tests yield an LC50. In the first test, earthworms are introduced into a defined artificial soil. This soil has been treated with the pesticide under investigation. The test usually lasts 14 days. In the other test, earthworms are placed on filter paper which has been treated with a solution of the pesticide under investigation.

### 5.6. Emission percentages.

Percent of emission into surface water  
with different applications [20, 21]

application	emission
aerial spraying	100%
fruit-growing	10%
Brussels sprouts and the like	5%
potatoes, cereals	2%
uncultivated and/or paved land	1%
greenhouses	0.1%

Appendix 6: Classification of environmental properties.

**Solubility (S) at 20-25 °C.**

Class	S (mg/l)
very slightly soluble	< 0.1
slightly soluble	0.1 - 10
moderately soluble	10 - 1000
readily soluble	≥ 1000

**Vapour pressure (P) at 20-25 °C.**

Class	P (Pa)
very slightly volatile	< 0.0001
slightly volatile	0.0001 - 0.01
moderately volatile	0.01 - 1
volatile	1 - 100
highly volatile	≥ 100

**Mobility in soil.**

Class	Rf	Ks/l (dm <sup>3</sup> /kg)
immobile	0 - 0.09	> 2.6
slightly mobile	0.10 - 0.34	0.53 - 2.6
moderately mobile	0.35 - 0.64	0.15 - 0.53
mobile	0.65 - 0.89	0.03 - 0.15
highly mobile	0.90 - 1.00	< 0.03

**Bioaccumulation.**

Class	BCF
slightly accumulating	< 100
moderately accumulating	100 - 1000
highly accumulating	> 1000

**Toxicity to aquatic organisms:** algae (96-h EC50), Daphnia (48-h LC50) and fish (96-h LC50).

Class	E(L)C50 (mg/l)
highly toxic	< 1
moderately toxic	1 - 10
slightly toxic	10 - 100
very slightly toxic	> 100

**Toxicity to aquatic organisms:** chronic tests.

Class	NOEC (mg/l)
highly toxic	< 0.01
moderately toxic	0.01 - 0.1
slightly toxic	0.1 - 1
very slightly toxic	>1

**Toxicity to birds:** acute oral LD50 (mg/kg body weight).

Class	LD50
highly toxic	< 5
toxic	5 - 50
moderately toxic	50 - 500
slightly toxic	>500

**Toxicity to earthworms:**

Class	Test in soil LC50 (mg/kg dry soil).
highly toxic	< 1
toxic	1 - 10
moderately toxic	10 - 100
slightly toxic	100 - 1000
very slightly toxic	>1000

**Toxicity to bees.**

Class	LD50 contact and oral (ug/bee)
highly toxic	< 1
moderately toxic	1 - 10
slightly toxic	10 - 100
very slightly toxic	>100

**Risk estimation- aquatic organisms:** short-term toxicity tests (particularly fish and crustaceans), using the PEC/L(E)C50 ratio.

The risk of acute death or effects is: PEC/L(E)C50

-----		
very large		>10
large	1	- 10
present	0.1	- 1
small	0.01	- 0.1
negligible	< 0.01	

**Risk estimation - aquatic organisms:** long-term toxicity tests with fish and crustaceans, using the PEC/NOEC ratio.

The risk of effects (most sensitive parameter) is: PEC/NOEC

-----		
large		>1
small	0.1	- 1
negligible	< 0.1	

**Risk estimation - algae:** short-term toxicity tests, using the PEC/NOEC ratio.

The risk of growth inhibition is: PEC/NOEC

-----		
large		>1
present	0.1	- 1
negligible	< 0.1	

#### Appendix 7: Presentation of results.

This appendix presents the data on soil, water, toxicity, Support Group M model and drift calculation for 148 pesticides and 1,3-dichloropropane (a contaminant of dichloropropene) which have been evaluated as part of the "catch-up operation". In addition, the data are also presented for 15 metabolites which required (and permitted) application of the Support Group M model.

Of the four other substances evaluated (benzalkonium chloride, didecyldimethylammonium chloride, mineral oil and *Bacillus thuringiensis*), the data were found to be unsuitable for presentation in tabular form, and are therefore not included in this report.

For dichloropropene and MITC, the Support group M model has taken into account their dosage and volatilization.

For dimethoate, dodine, propyzamide and tridemorph, the Support Group M model was used in spite of the fact that the Henry coefficient does not fulfil the conditions for the model ( $> 10^{-5}$ ).

For information about chlorthiamid, the reader is always referred to dichlobenil because the former is rapidly converted into the latter.

Legend<sup>1</sup>.

symbol	pesticide group
A	anilides
C	carbamates <sup>2</sup>
M	miscellaneous compounds <sup>3</sup>
O	OP-esters
P	(synthetic) pyrethroids
T	triazines
U	urea compounds

symbol	remarks
*	less reliable datum (inadequately reported or executed study)
@	the frequency is probably higher than the maximum given in the table mentioned
?	number of uses unknown
!	no steady state (BCF = 1446 and 51 after 14 and 42 days, respectively)
#	dinoseb acetate is very rapidly converted into dinoseb
C	DT50 on the basis of CO <sub>2</sub> produced
vo	volatile pesticide
A	artificial (sun)light
N	(natural) sunlight
d	special application to dry ditch sediments
na	not applicable
F	data on formulation (figure indicates % active ingredient)
f	based on formulation data
av	average
SD	standard deviation

quantity	unit
DT50	d(ays)
Kom	dm <sup>3</sup> /kg
dosage	kg/ha
concentration in surface water	mg/l
NOEC and L(E)C50	mg/l
LD50 (birds)	mg/kg body weight
LC50 (birds)	mg/kg feed
LD50 (bees)	ug/bee
concentration in shallow groundwater	ug/l

<sup>1</sup> = deviations from the symbols and units used are mentioned in the tables; <sup>2</sup> = including (di-)thiocarbamate; <sup>3</sup> = including pesticide groups with fewer than 5 representatives



Appendix 7.1. Data on 148 pesticides relating to behaviour in soil and dosage and frequency of application.

No	Pesticide	group	DT50 av.	SD	Kom av.	SD	dosage kg a.i./ha	frequency	mobility classification
1	acephate	O	2	1	33	0	0.4 - 0.8	1-6	MM
2	acnifen	D	71	28	3484	921	1.7 - 3	1	IM
3	aldicarb	D	2	1	5	3	0.6 - 9	1-4	MM-M
4	alloxidim-sodium	D	20	18	4	4	0.6 - 1.5	1-2	M
5	asulam	C	24	15	64	38	0.8 - 3	1-2	SM-MM
6	atrazine	T	50	12	70	42	0.8 - 15	1	IM-MM
7	azinphos-methyl	O	52	0	862	968	0.3 - 1.5	1-3	IM
8	bentazone	D	48	29	1	2	0.24 - 1.44	1-3	MM-HM
9	bromofenoxim	D	67	94	123	--	0.75 - 2.25	1	IM
10	bromophos-ethyl	O	8*	2*	--	--	0.24 - 0.75	1-4	--
11	bromopropylate	D	47-70	--	--	--	0.65 - 0.975	1-2	IM
12	calcium cyanide	D	--	--	--	--	0.02-4.2 g/m <sup>3</sup>	1-3, a	--
13	carbaryl	C	=<14	--	73	59	0.36 - 1.5	1-2	SM
14	carbetamide	C	10	5	58	20	1.5 - 2.1	1-2	SM
15	chlorbromuron	U	>60*	--	635	621	0.75 - 1.5	1	IM
16	chlorfenvinfos	O	68	28	539	--	0.1 - 6	1-2	IM-SM*
17	chloridazon	D	15-46	--	64	27	1.1 - 3.2	1	SM-MM
18	chlomequat	D	1	--	--	--	0.04 - 1.62	1-2	--
19	chlorothalonil	D	24*	19*	8337	6636	0.38 - 3.7	1-15	IM
20	chloroxuron	U	36	--	883	520	0.5 - 3.5	1-2	IM
21	chlorpropham	C	5*	--	22	--	0.4 - 2.4	1-2	SM-MM
22	chlorpyrifos	O	89	77	390	188	0.55 - 6	1	IM-SM
23	chlorthiamid	D	--	zie dichlobenil	--	--	0.02 - 26.3	1	--
24	chlortoluron	U	143*	--	103	36	0.5 - 2.5	1	SM-MM
25	copper oxychloride	D	--	--	--	--	1.5 - 3.5	1-12	--
26	creosote	D	--	--	--	--	58	1?	--
27	cyanazin	T	--	--	--	--	0.5 - 2	1	SM-MM
28	cymoxanil	D	0.01	1	8*	11*	0.075 - 0.14	12	IM-MM*
29	cypermethrin (cis)	P	75	30	200	114	0.025 - 0.125	1-6	IM-SM
30	cypermethrin (trans)	P	28	10	186	90	--	--	IM-SM
31	dalapon	D	4	3	0.5	--	3.5 - 20	1	M
32	daminozide	D	4*	--	4	--	0.45 - 3.84	1-3	MM-HM
33	dazomet	D	<.04-<1	--	--	--	49.5 - 750	1	--
34	deltamethrin	P	27	18	563	529	0.005 - 0.031	1-6, a	IM
35	demeton-S-methyl-sulphone	O	1	1	0*	--	--	--	M*
36	desmetryne	T	19	--	137	99	0.25 - 0.38	1	IM-SM
37	diazinon	O	23	17	160	30	0.04 - 5.5	1-6	IM-SM
38	dicamba	D	48	43	0	--	0.06 - 0.96	1	HM
39	dichlobenil	D	70*	46*	125	36	0.1 - 24	1	SM-MM
40	dichlofluanid	D	3	1	--	--	0.5 - 3.13	>10	--
41	dichloropropene	D	13	11	15*	--	166 - 620	1	--
42	dichlorprop/prop P	D	15	5	0	--	0.4 - 3	1	MM-HM
43	dichlorvos	O	0.04-<2	--	--	--	0.44 - 1.94	>10	--

Appendix 7.1. Data on 148 pesticides relating to behaviour in soil and dosage and frequency of application.

No	Pesticide	group	DT50 av. SD	Kom av. SD	dosage kg a.i./ha	frequency	mobility classification
44	dicloran	D	414-913	1133	0.8 - 20	1-5	IM
45	dicofof (op)	D	15	--	0.28 - 0.96	1-3	--
46	dicofof (pp)	D	>60*	730 832	--	--	IM
47	difenoxuron	U	18	472 262	2.5	1	IM-SM
48	diflubenuron	U	3	62	0.1 - 0.45	1-4	IM-MM
49	dikegulac-sodium	D	>195	0	0.09 - 15	1-2	HM
50	dimethachlor	A	21	17 3	1.5 - 2	1	SM-MM
51	dimethoate	O	14 5	8 3	0.1 - 5	1-3	SM-M
52	dinoseb	D	50 20	23 18	3.5	2-3	IM-MM
53	dinoseb-acetate	D	#1 #1	--	1 - 2.16	1?	IM-MM
54	dinoterb	D	10 1	72 20	0.68 - 1.8	1-2	IM-MM
55	dithianon	D	5* 0*	103	0.28 - 1.13	1-8, a	IM
56	diuron	U	64*	144 127	0.4 - 16	1	IM-M
57	DNOC	D	9 6	38 24	1.3 - 6.44	1-2	IM-SM
58	dodemorph	D	170 19	5414 2906	1.5 - 3	6-10	IM
59	dodine	D	19 --	1340	0.6 - 0.9	1-4	IM-SM
60	EPTC	C	47* 7*	71 7	3.6 - 7.5	1	SM-MM
61	ethephon	D	1 0	87 143	0.2 - 3.2	1-2	IM-M
62	ethofumesate	D	44 9	87 22	1.25 - 5	1-2	IM-SM
63	ethoprophos	O	32 24	60 24	4 - 20	1	SM-MM
64	etridiazole	D	18* 12*	140	1.75 - 88	1-3	SM
65	etrimfos	O	146 80	--	0.5 - 0.8	1-2	<MM*
66	fenaminosulf	D	17*	>4*	7 - 175	1	SM*
67	fenitrothion	O	28 14	112 53	0.5	6	IM
68	fenpropathrin	P	46 30	525 528	0.5 - 1.25	3-5	IM
69	fenpropimorph	D	67* 78*	2075 617	11/ha	>1	SM
70	fenvalerate	P	32 12	1352 311	0.015-	0.06	1-3, a
71	fonofos	O	81 45	>163	3.3	1	IM
72	formothion	O	<1 --	--	0.24 - 0.75	1-2	SM-M
73	fosethyl-aluminium	O	.07 .04	0	2.4 - 80	1-5	HM
74	gibberelin	D	--	--	0.5 - 1.45 g	1	--
75	guazatine	D	35 --	--	0.085-	0.14	1
76	heptenophos	O	2 2	6.5*	0.14 - 0.69	1-2	IM-SM*
77	hexazinone	D	59-64	16	2.4 - 5.4	1	M
78	iprodione	D	41 --	281 134	0.25 - 2	1-8	IM-MM
79	lenacil	D	134 --	24 16	0.4 - 2.0	1-2	SM-M
80	linuron	U	131 105	233 68	0.2 - 1.5	1-2	IM-MM
81	malathion	O	--	105* 70*	0.325-	2	1-3
82	mancozeb	C	5 2	--	0.007-	6	1-6, a
83	maneb	C	56*	282	1.2 - 4.8	1-6, a	IM-MM
84	MCPA	D	15 9	29 7	0.25 - 3.2	1-2	MM-MM
85	mecoprop/prop P	D	11 5	0	0.2 - 3.4	1-2	MM-MM
86	mefluidide	A	1-24*	--	0.6	1-3	M-MM*

Appendix 7.1. Data on 148 pesticides relating to behaviour in soil and dosage and frequency of application.

No	Pesticide	group	DT50 av.	SD	Kom av.	SD	dosage kg a.i./ha	frequency	mobility	classification
87	mercaptodimethur	C	41	11	332	--	0.12 - 1	1-2	IM	IM
88	metaldehyde	D	10*	2*	10	6	0.45	1-2	MM*	MM*
89	metam-sodium	C	.009	.009	228	--	95 -840	1	IM	IM
90	metazachlor	A	19	9	81	21	0.75 - 1.5	1-2	MM	MM
91	methabenzthiazuron	U	135	25	310	169	0.5 - 3.5	1-2	IM-MM	IM-MM
92	methamidophos	O	3	2	0	2	0.34 - 0.8	1-4	HM	HM
93	methidathion	O	4.5	--	96	54	0.4 - 0.45	1-4	IM-SM	IM-SM
94	methomyl	D	6	5	12	1	0.25 - 0.62	5-10	SM-MM	SM-MM
95	methyldecylbenzyltrimethyl- ammonium chloride	D	--	--	--	--	--	--	--	--
96	methyldodecylxyleen-bis(tri- methyl ammonium chloride)	D	--	--	--	--	--	--	--	--
97	methylisothiocyanate (MITC)	C	6	3	3	1	79.2 -282	1	M-HM	M-HM
98	metiram	C	.04-10*	--	--	--	1.05 - 3.5	3-8	IM*	IM*
99	metolachlor	A	101	42	103	41	2 - 2.5	1-2	IM-SM	IM-SM
100	metoxuron	U	16*	21*	88	179	1.6 - 2.4	1	IM-SM	IM-SM
101	mevinphos	O	3*	3*	12*	--	0.075- 0.36	1-6,a	MM-HM*	MM-HM*
102	monolinuron	U	33-66	--	193	84	0.24 - 1.5	1-2	IM-MM	IM-MM
103	nitrothal-isopropyl	D	4*	5*	919*	118*	0.25	c.10	IM-SM	IM-SM
104	onethoate	O	1	0.2	15	8	0.28 - 1.27	1-3	SM->=MM	SM->=MM
105	oxamyl	D	18*	8*	2	2	0.25 - 10	1-4,a	MM-HM	MM-HM
106	oxydemeton-methyl	O	3	4	44	37	0.25 - 0.37	1-3	IM-MM	IM-MM
107	parathion	O	49	43	1764	1068	0.15 - 5	1-4	IM-SM	IM-SM
108	parathion-methyl	O	19	6	141	109	0.08 - 5	1-4	IM	IM
109	pendimethalin	D	171	42	265	396	1.0 - 2.0	1	IM-SM	IM-SM
110	phemedipham	C	55	25	400	215	0.2 - 6.7	1-2	IM-SM	IM-SM
111	phosalone	O	7	2	1345	451	0.45 - 1.25	1-6	IM-SM	IM-SM
112	phosmet	O	5	3	143	91	0.75	2	IM	IM
113	phosphamidon	O	4	3	4	1	0.25 - 0.56	1-3	MM-HM	MM-HM
114	phosonylbutoxide	D	12-14*	--	--	--	--	--	IM*	IM*
115	pirimicarb	C	208	114	436	447	0.1 - 1.3	1-2	IM	IM
116	pirimiphos-methyl	O	19	--	72	58	0.5 - 1.5	1-5	IM-SM	IM-SM
117	prometryne	T	41	4	152	126	0.4 - 0.7	1?	IM-M	IM-M
118	propachlor	A	5	2	40	16	1.75 - 4.55	1	SM-MM	SM-MM
119	propamocarb	D	12	12	163	168	0.72 -108	1-3	IM-SM*	IM-SM*
120	propazine	T	132	40	58	29	0.25 - 0.3	1?	IM-MM	IM-MM
121	propham	C	7*	--	11*	--	1.25 - 6	1-3	MM*	MM*
122	propiconazole	D	96	--	533	340	0.125	1-2	IM-SM	IM-SM
123	propoxur	C	79	53	15	14	0.3 - 1	1-3,a	M-HM	M-HM
124	propyzamide	A	25	--	149*	160*	1 - 1.5	1	IM-SM*	IM-SM*
125	pyrazophos	O	48	8	178*	120*	0.15 - 1.47	2-5,a	IM*	IM*
126	pyrethrins	P	5*	9*	12*	9*	1.5	1?	IM-M*	IM-M*
127	pyridate	D	5	--	--	--	0.5 - 1	1-2	IM-SM*	IM-SM*

Appendix 7.1. Data on 148 pesticides relating to behaviour in soil and dosage and frequency of application.

No	Pesticide	group	DT50 av.	SD	Kom av.	SD	dosage kg a.i./ha	frequency	mobility classification
128	sethoxydim	D	1	0.4	14	20	0.2 - 0.8	1-2	MM
129	simazine	T	60	27	59	48	0.1 - 5	1	IM-M
130	sodium-dimethyldithiocarbamat	C	--	--	--	--	0.01 - 0.02	1	--
131	sulfotep	O	12-36*	--	--	--	1.09 - 1.37	3	--
132	terbufos	O	15	17	3636	8616	0.5	1	IM
133	terbutryn	T	66	53	387	225	0.7 - 2	1?	IM-SM
134	thiofanox	D	4	2	10	6	0.6 - 6	1-2	MM
135	thiometon	O	2	2	469	257	0.25 - 0.375	1-3	IM-SM
136	thiram	C	13* 13*	--	>2*	--	0.8 - 10	1-7, a	MM-M*
137	tolyfluanid	D	2	1	>4->19*	--	0.3 - 1.88	1-13	--
138	triadimenol	D	114	--	134	37	0.13 - 0.2	>10	SM
139	triallate	C	102	2	1089	386	0.6 - 1.6	1	IM-SM
140	triazophos	O	65	53	165	89	0.2 - 0.9	1-7	IM-SM
141	trichlorfon	O	19	13	17*	6*	0.48 - 1.8	3-4	MM-M*
142	triclopyr	D	34	30	32	14	0.015 - 0.375	1	MM-HM
143	tridemorph	D	33* 12*	--	>1785*	--	0.563	1	IM*
144	trifluralin	D	186-255	--	--	--	0.8 - 1.2	1	IM*
145	triforine	D	19	11	83*	34*	0.1 - 15	1-3, a	IM*
146	vamidothion	O	2	--	--	--	0.4 - 0.75	1-2	--
147	vinclozolin	D	30	21	157*	68*	0.25 - 10	1-6	IM-MM*
148	zineb	C	--	--	--	--	0.88 - 7.5	1-10, a	IM-SM
149	ziram	C	35-45*	--	4-12*	--	0.75 - 3.2	1-4	HM*
150	1,2-dichloropropane	D	800	--	11*	--	0.17 - 0.62	1	--
151	2,4-D (pH <5)	D	8	6	230	123	0.5 - 3	1-2	SM-HM*
152	2,4-D (pH >5)	D	--	--	26	24	--	--	--

No Pesticide	group concentration in shallow groundwater			Support Group M model			Support Group M model			Support Group M model			Support Group M model				
	average	range	leaching from the top metre (%)	average	range	residue in plough layer after 1 year	average	range	concentration in shallow groundwater	average	range	leaching from the top metre (%)	average	range	residue in plough layer after 1 year		
1 acephate	0	<0.001	<0.001	<0.001	<0.001	<0.01	5	-25	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	15	6	-27
2 acionifen	D	<0.001	<0.001	<0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
3 aldicarb	D	0.001	<0.001-0.008	<0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
4 alloxidim-sodium	D	4	<0.001-10	1	<0.001-6	<0.01	<0.01-0.1	<0.01-0.1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
5 asulam	C	<0.001	<0.001-1.2	<0.001	<0.001-1	0.2	<0.01-3	<0.01-3	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
6 atrazine	T	0.06	<0.001-6	0.05	<0.001-4	5	1	-11	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
7 azinphos-methyl	O	<0.001	<0.001	<0.001	<0.001	7	<0.01-0.1	<0.01-0.1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8 bentazone	D	14	2 -24	8	1 -13	0.02	<0.01-0.1	<0.01-0.1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
9 bromofenoxim	D	0.008	<0.001-0.7	0.008	<0.001-0.8	13	<0.01-25	<0.01-25	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
10 bromophos-ethyl	O	--	--	--	--	--	--	--	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
11 bromopropylate	D	--	--	--	--	--	--	--	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
12 calcium cyanide	D	--	--	--	--	--	--	--	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
13 carbaryl	C	<0.001	<0.001-0.001	<0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
14 carbetamide	U	--	--	<0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15 chlorbromuron	C	<0.001	<0.001	<0.001	<0.001	12	1 -23	<0.01-4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
16 chlorfenvinfos	O	<0.001	<0.001	<0.001	<0.001	2	<0.01-4	<0.01-4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
17 chloridazon	D	0.01	<0.001-1	0.01	<0.001-0.8	<0.001	<0.01-5	<0.01-5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
18 chlormequat	D	--	<0.001*	<0.001*	<0.001*	0.5*	<0.01-5	<0.01-5	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	0.5*	<0.01-6*	<0.01-6*
19 chlorothalonil	D	<0.001	<0.001	<0.001	<0.001	3	<0.01*	<0.01*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
20 chloroxuron	U	<0.001	<0.001	<0.001	<0.001	<0.01*	<0.01*	<0.01*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
21 chlorpropham	C	<0.001*	--	<0.001*	<0.001*	<0.01*	<0.01*	<0.01*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
22 chlorpyrifos	O	<0.001	<0.001-0.05	<0.001	<0.001-0.05	23	<0.01-25	<0.01-25	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
23 chlorthiamid	D	--	--	see dichlobenil	see dichlobenil	--	--	--	--	--	--	--	--	--	--	--	--
24 chlortoluron	U	0.9*	0.3 -5*	1*	0.4 -6*	>25*	25	->25*	1	0.4	-6	1	0.5	-6	>30	28	->30
25 copper oxychloride	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
26 creosote	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
27 cyanazin	T	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
28 cyomoxanil	D	<0.001*	<0.001*	<0.001*	<0.001*	<0.01*	<0.01*	<0.01*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*
29 cypermethrin (cis)	P	<0.001	<0.001-0.7	<0.001	<0.001-0.7	15	4 -25	<0.01-4	--	--	--	--	--	--	--	--	--
30 cypermethrin (trans)	P	<0.001	<0.001	<0.001	<0.001	1	<0.01-4	<0.01-4	--	--	--	--	--	--	--	--	--
31 dalapon	D	0.01	<0.001-0.1	0.01	<0.001-0.1	<0.01	<0.01	<0.01	0.1	0.01	->10	0.1	0.01	->10	<0.01	<0.01	<0.01
32 daminozide	D	0.005*	--	<0.001*	--	<0.01*	--	--	--	--	--	--	--	--	--	--	--
33 dazomet	D	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
34 deltamethrin	P	<0.001	<0.001-1	<0.001	<0.001-0.4	1	<0.01-5	<0.01-5	--	--	--	--	--	--	--	--	--
35 demeton-S-methyl-sulphone	O	0.002*	<0.001-0.005*	<0.001*	<0.001*	<0.01*	<0.01*	<0.01*	--	--	--	--	--	--	--	--	--
36 desmetryne	T	<0.001	<0.001-0.002	<0.001	<0.001-0.002	0.08	0.01-0.08	0.01-0.08	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
37 diazinon	O	<0.001	<0.001	<0.001	<0.001	0.9	<0.01-4	<0.01-4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
38 dicamba	D	20	0.02 -30	5	0.01 -15	0.01	<0.01-0.02	<0.01-0.02	>100	>100	>100	>10	5	->10	0.2	<0.01-4	<0.01-4
39 dichlobenil	D	0.01*	<0.001-1*	0.01*	<0.001-1*	14*	0.1 -25*	0.1 -25*	--	--	--	--	--	--	--	--	--
40 dichlofuanid	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

[illegible]

No Pesticide	group	concentration in shallow groundwater	Support Group M model	Support Group M model	residue in plough layer after 1 year	concentration in shallow groundwater	autumn application	Support Group M model
		average	range	top metre (%)	average	range	leaching from the top metre (%)	residue after 1 year layer average range
81 malathion	O	--	--	--	--	--	--	--
82 mancozeb	C	--	--	--	--	--	--	--
83 maneb	C	--	--	--	--	--	--	--
84 MCPA	D	0.005	<0.001-0.8	0.003	<0.01	<0.01-0.2	0.05	<0.01-0.2
85 mecoprop/prop P	D	0.3	0.02 -2	0.2	<0.01	<0.01	>10	<0.01
86 mefluthide	A	--	--	--	--	--	--	--
87 mercaptodimethur	C	<0.001	<0.001	<0.001	5	1 -8	--	--
88 metaldehyde	D	0.05*	0.001-0.5*	0.01*	<0.01*	<0.01*	1*	<0.01*
89 metam-sodium	C	<0.001	<0.001	<0.001	<0.01	<0.01	<0.001	<0.01
90 metazachlor	A	<0.001	<0.001-0.0015	<0.001	0.1	<0.01-1.0	<0.001	<0.01-1
91 methabenzthiazuron	U	0.001	<0.001-0.3	<0.001	40	25 -55	<0.001	30 -60
92 methamidophos	O	<0.001	<0.001	<0.001	<0.01	<0.01	--	--
93 methidathion	O	<0.001	<0.001	<0.001	<0.01	<0.01	--	--
94 methomyl	D	0.001	<0.001-0.07	<0.001	<0.01	<0.01	<0.001-1	<0.01
95 methyldecylbenzyl(tri-methyl ammonium chloride)	D	--	--	--	--	--	--	--
96 methyldecylxyleen-bis(tri methyl) ammonium chloride	D	--	--	--	--	--	--	--
97 methylisothiocyanate (MITC)	C	--	not calculated (lowest boundaries)	--	--	--	0.6 -10	<0.01
98 metiram	C	--	--	--	--	--	--	--
99 metolachlor	A	0.3	<0.001-7	0.3	24	7 -->25	--	--
100 metoxuron	U	--	--	--	--	--	--	--
101 mevinphos	O	<0.001*	<0.001-0.01*	<0.001*	<0.01*	<0.01*	--	--
102 monolinuron	U	<0.001	<0.001-0.04	<0.001	7	1 -18	<0.001-0.07	6 1 -20
103 nitrothal-isopropyl	D	<0.001*	<0.001*	<0.001*	<0.01*	<0.01*	--	--
104 omethoate	O	<0.001	<0.001-0.001	<0.001	<0.01	<0.01	--	--
105 oxamyl	D	2*	0.2 -6*	0.9*	<0.01*	<0.01*	>10*	<0.01*
106 oxydemeton-methyl	O	<0.001	<0.001-0.01	<0.001	<0.01	<0.01	--	--
107 parathion	O	<0.001	<0.001	<0.001	8	<0.01-20	--	--
108 parathion-methyl	O	<0.001	<0.001-0.07	<0.001	0.1	<0.01-0.3	--	--
109 pendimethalin	D	0.01	0.001->50	0.01	>25	<0.01->25	--	--
110 phenedipham	C	<0.001	<0.001	<0.001	10	3 -18	--	--
111 phosalone	O	<0.001	<0.001	<0.001	<0.01	<0.01	--	--
112 phosmet	O	<0.001	<0.001	<0.001	<0.01	<0.01	--	--
113 phosphamidon	O	0.008	0.001-0.04	<0.001	<0.01	<0.01-0.01	--	--
114 piperonylbutoxide	D	--	--	--	--	--	--	--
115 pirimicarb	C	<0.001	<0.001->100	<0.001	28	<0.01->30	--	--
116 pirimiphos-methyl	T	<0.001	<0.001-0.6	<0.001	0.1	0.01-0.1	--	--
117 prometryne	A	<0.001	<0.001-3	<0.001	4	1 -5	--	--
118 propachlor	A	<0.001	<0.001	<0.001	<0.01	<0.01	--	--

Appendix 7.2. Data on 148 pesticides relating to Support Group M-model calculation.

No Pesticide	group concentration in shallow groundwater			Support Group M model			residue in plough layer after 1 year			concentration in shallow groundwater			Support Group M model			residue in plough layer after 1 year		
	average	range	top metre (%)	average	range	leaching from the top metre (%)	average	range	leaching from the top metre (%)	average	range	leaching from the top metre (%)	average	range	leaching from the top metre (%)	average	range	leaching from the top metre (%)
119 propamocarb	D	<0.001	<0.001-5	<0.001	<0.001-2	<0.001	<0.01	<0.01-0.6	<0.001	<0.001	<0.001-0.12	<0.001	<0.001	<0.001-0.05	<0.01	<0.01	<0.01	<0.01
120 propeazine	T	6	0.5 -25	7	0.5 -19	7	20	7 ->25	20	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*
121 protham	C	0.01*	--	0.01*	--	0.01*	<0.01*	--	<0.01*	--	--	--	--	--	--	--	--	--
122 propiconazole	D	<0.001	<0.001-0.03	<0.001	<0.001-0.04	<0.001	24	14 ->30	24	<0.001	<0.001-0.04	<0.001	<0.001	<0.001-0.04	<0.001	<0.001	<0.001	<0.001
123 propoxur	C	20	0.2 ->50	12	0.08 -24	12	2	<0.01-10	2	<0.001*	<0.001-10*	<0.001*	<0.001*	<0.001-10*	<0.001*	<0.001*	<0.001*	<0.001*
124 propyzamide	A	<0.001*	<0.001-10*	<0.001*	<0.001-4*	<0.001*	0.5*	<0.01-4*	0.5*	<0.001*	<0.001-4*	<0.001*	<0.001*	<0.001-4*	<0.001*	<0.001*	<0.001*	<0.001*
125 pyrazophos	O	<0.001	<0.001-0.04	<0.001	<0.001-0.3	<0.001	6	3 -9	6	<0.001	<0.001-0.3	<0.001	<0.001	<0.001-0.3	<0.001	<0.001	<0.001	<0.001
126 pyrethrins	P	0.002*	<0.001-0.1*	<0.001*	<0.001-0.1*	<0.001*	<0.01*	<0.01*	<0.01*	<0.001*	<0.001-0.1*	<0.001*	<0.001*	<0.001-0.1*	<0.001*	<0.001*	<0.001*	<0.001*
127 pyridate	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
128 sethoxydim	D	<0.001	<0.001	<0.001	<0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001-0.12	<0.001	<0.001	<0.001-0.05	<0.01	<0.01	<0.01	<0.01
129 simazine	T	0.1	<0.001-20	0.1	<0.001-16	0.1	8	0.1 -19	8	<0.01	<0.01-19	<0.01	<0.01	<0.01-19	<0.01	<0.01	<0.01	<0.01
130 sodium-dimethyldithiocarbamat	C	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
131 sulfotep	O	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
132 terbufos	O	<0.001	<0.001-10	<0.001	<0.001-3	<0.001	0.01	<0.01-1	0.01	<0.01	<0.01-0.09	<0.001	<0.001	<0.001-0.09	<0.01	<0.01	<0.01	<0.01
133 terbutryn	T	<0.001	<0.001-0.05	<0.001	<0.001-0.06	<0.001	13	0.01-30	13	<0.01	<0.01-30	<0.001	<0.001	<0.001-0.09	<0.01	<0.01	<0.01	<0.01
134 thiofanox	D	<0.001	<0.001-0.3	<0.001	<0.001-0.003	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001-0.01	<0.001	<0.001	<0.001-0.01	<0.001	<0.001	<0.001	<0.001
135 thioneton	O	<0.001	<0.001	<0.001	<0.001-0.001	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001-0.001	<0.001	<0.001	<0.001-0.001	<0.001	<0.001	<0.001	<0.001
136 thiram	C	<0.5*	0.001-5*	<0.5*	<0.001-2*	<0.5*	<0.01	<0.01	<0.01	<0.001	<0.001-2*	<0.001	<0.001	<0.001-2*	<0.001	<0.001	<0.001	<0.001
137 tolylfluanid	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
138 triadimenol	C	0.09	0.02 -0.7	0.1	0.03 -0.7	0.1	>25	>25	>25	>25	>25	>25	>25	>25	>25	>25	>25	>25
139 triallate	C	<0.001	<0.001	<0.001	<0.001	<0.001	25	25	25	<0.001	<0.001-0.001	<0.001	<0.001	<0.001-0.001	<0.001	<0.001	<0.001	<0.001
140 triazophos	O	<0.001	<0.001-2	<0.001	<0.001-2	<0.001	11	<0.01-30	11	<0.001	<0.001-2	<0.001	<0.001	<0.001-2	<0.001	<0.001	<0.001	<0.001
141 trichlorfon	O	0.5	<0.001-5	0.1	<0.001-2	0.1	0.02	<0.01-0.3	0.02	<0.001*	<0.001-0.3	<0.001*	<0.001*	<0.001-0.3	<0.001*	<0.001*	<0.001*	<0.001*
142 triclopyr	D	0.7	<0.001-12	0.3	<0.001-8	0.3	0.9	<0.01-6	0.9	<0.001*	<0.001-8	<0.001*	<0.001*	<0.001-8	<0.001*	<0.001*	<0.001*	<0.001*
143 tridemorph	D	<0.001*	--	<0.001*	--	<0.001*	2*	<0.01-15*	2*	<0.001*	<0.001-15*	<0.001*	<0.001*	<0.001-15*	<0.001*	<0.001*	<0.001*	<0.001*
144 trifluralin	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
145 triforine	D	<0.001*	<0.001-0.002*	<0.001*	<0.001-0.003*	<0.001*	0.1*	<0.01-1.5*	0.1*	<0.001*	<0.001-0.003*	<0.001*	<0.001*	<0.001-0.003*	<0.001*	<0.001*	<0.001*	<0.001*
146 vamidothion	O	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
147 vinclozolin	D	<0.001*	<0.001-0.01*	<0.001*	<0.001-0.01*	<0.001*	1*	<0.01-7*	1*	<0.001*	<0.001-0.05*	<0.001*	<0.001*	<0.001-0.02*	<0.001*	<0.001*	<0.001*	<0.001*
148 zineb	C	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
149 ziram	C	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
150 1,2-dichloropropane	D	>6->26*	--	>25*	--	>25*	2.8*	--	2.8*	<0.01	<0.01-0.02	<0.01	<0.01	<0.01-0.02	<0.01	<0.01	<0.01	<0.01
151 2,4-D (pH <5)	D	<0.001	<0.001	<0.001	<0.001	<0.001	<0.01	<0.01-0.02	<0.01	<0.001	<0.001-50	<0.001	<0.001	<0.001-12	<0.01	<0.01	<0.01	<0.01
152 2,4-D (pH >5)	D	<0.001	<0.001-1	<0.001	<0.001-0.5	<0.001	<0.01	<0.01	<0.01	<0.001	<0.001-50	<0.001	<0.001	<0.001-12	<0.01	<0.01	<0.01	<0.01



Appendix 7.3. Data on 148 pesticides relating to behaviour in water, estimated concentrations in surface water, and risk to aquatic organisms.

No	Pesticide	group	DT50 system	DT50 water	% CO2 dsy	DT50 hydrolysis	DT50 fotolysis	estimated conc. surface water	aerial spraying	algae-- normal air	drift calculation normal air	fish-- normal air
1	acephate	O	49-56 C	--	52-57 56	66-16	2 K	0.0004 -0.016	0.16 -0.24	N	N	N
2	acetonifon	D	--	--	--	--	--	0.007 -0.012	--	L	N	N-S
3	aldicarb	D	6*	--	--	77->300	8 N	granules	--	--	--	--
4	aloxym-sodium	D	--	--	--	0.1->30*	0.04-0.4 N*	0.005 -0.012	--	N	N	N
5	asulam	C	--	--	--	--	--	0.012	--	--	N	N
6	atrazine	T	>77	--	0.4-6 77-84	86	--	0.0064 -0.06	--	S-L	N-S	N
7	azinphos-methyl	O	--	--	--	2-41	0.4 K	0.002 -0.013	--	N	L-VL	S-L
8	bentazone	D	--	--	--	--	--	0.002 -0.012	--	N	N	N
9	bromofenoxim	D	<7	--	20-52 77	--	--	0.008 -0.018	--	N	N	P
10	bromophos-ethyl	O	--	--	--	18-36*	--	0.0015 -0.019	0.23	N-L	P-L	S
11	bromopropylate	D	49-77	<1-<7	<1.3 77	>200-4	--	0.026 -0.039	--	S	P	L
12	calcium cyanide	D	--	--	--	--	--	0.002-0.42 ug/l	--	--	--	--
13	carbaryl	C	--	--	--	0.01->137	--	0.004 -0.06	0.32	--	L*	S*
14	carbetamide	C	--	53->69	--	21->30	9 K	0.042	--	P	f:N*	f:N*
15	chlorobromuron	O	<77	25-79	4 77	--	--	0.006 -0.012	--	P	N	N
16	chlorfeninfos	O	--	7*	2* 42	>28*	--	0.008 -0.024	--	N	L-VL	S-P
17	chloridazon	D	>56	>56	1 56	72-144	30 N	0.009 -0.026	--	N	N-P	N
18	chlormequat	D	14-56 C	<21	51-70 56	>730	--	0.00016-0.065	--	--	N	N
19	chlorothalonil	D	--	--	--	38*	--	0.0015 -0.024	0.7	L	S	VL
20	chloroxuron	U	>63*	--	0.4* 63	1208-4583	<0.04 K	0.0004 -0.07	--	L	S	P
21	chlorpropham	C	--	--	--	>10000*	5* K	0.003 -0.019	--	N	N	N
22	chlorpyrifos	O	--	--	--	23-210	--	0.0022-0.048	--	--	S-P	P-VL
23	chlorthiamid	D	--	--	see dichlobenil	--	--	--	--	see dichlobenil	--	--
24	chlortoluron	U	--	>77-80	4-7 77	--	--	0.02	--	L	N	N
25	copper oxychloride	D	--	--	--	--	--	0.001 -0.13	--	--	--	N-S
26	creosote	D	--	--	--	--	--	--	--	--	P*	L*
27	cyanazin	T	>84	--	0 84	9-297	--	0.001 -0.008	--	S	N	N
28	cymoxanil	D	60-100 C	--	46-62 91	<1->33	<1-2 K	0.0012	0.03 -0.058	N*	N	N
29	cypermethrin (cis)	P	<14	--	10-60 441	<7	>32 N	0.0002 -0.005	0.0012	--	S-VL	VL
30	cypermethrin (trans)	P	--	--	see cypermethrin (cis)	--	--	--	--	see cypermethrin (cis)	--	--
31	dalapon	D	--	--	--	--	--	0.072 -4.68	--	--	N	N
32	daminozide	D	=<7	--	63-64 84	>91*	--	0.00018-0.154	--	N-P	N	N
33	dazomet	D	--	--	--	--	--	granules	--	na	na	na
34	deltamethrin	P	--	2-4*	--	>30	--	0.00008-0.0004	0.002	--	P*	L
35	demeton-S-methyl-sulphone	O	--	--	--	--	--	--	--	--	--	--
36	desmetryne	T	--	22-45	1	--	--	0.003 -0.007	--	--	N	--
37	diazinon	O	--	7-15	59 49	2-185	>14 N*	0.00008-0.043	0.18	N	N-VL	VL
38	dicamba	D	--	60	--	>28	>8 K	0.0005 -0.005	--	N*	N*	N*
39	dichlobenil	D	--	6	--	>150	4.5-8 N	0.0004 -0.0096	1.4-2.7 sl	N	N,sl	N,sl
40	dichlofluanid	D	<7	--	3-5 120	<1*	--	0.0003 -0.06	--	N-P	N-S	N-P
41	dichloropropene	D	<2* vl	--	2-3 7	11	--	na	--	na	na	na
42	dichlorprop/prop P	D	<8-15 C	--	50	<8-15	--	0.003 -0.024	--	N*	N*	N*

Appendix 7.3. Data on 148 pesticides relating to behaviour in water, estimated concentrations in surface water, and risk to aquatic organisms.

No	Pesticide	group	DT50 system	DT50 water	% C02 dsy	DT50 hydrolysis	DT50 photolysis	estimated conc. surface water	aerial spraying	algae- normal air	drift calculation crustaceans- normal air	fish- normal air
43	dichlorvos	O	<1	--	76	16	<1-32*	0.00018-0.024	--	N	VL	S
44	dieldrin	D	--	--	--	--	--	0.0001-0.16	--	--	--	N-S
45	dicofof (op)	D	--	--	--	--	--	0.0001-0.0148	--	N-P	N	f:N-S
46	dicofof (pp)	D	6-52	--	7-41	84	<0.04-47*	see dicofof (op)	--	--	--	--
47	difenoxuron	U	--	--	--	--	>950	0.02	--	S	N	N
48	diflufenzuron	U	24	--	--	--	>150-42	0.0008-0.008	0.04	N	N	N
49	dikegulac-sodium	U	--	--	--	--	2.4->365	0.00004-0.3	--	--	--	N*
50	dimethachlor	A	<84	15-77	2	84	>200	0.006-0.008	--	P	N	N
51	dimethoate	O	12*	--	--	--	156-4	0.0004-0.008	0.04-0.08	N	N	N
52	dinoseb	D	--	--	--	--	>30	0.028	--	N	S	L
53	dinoseb-acetate	D	--	--	--	--	0.1-5	0.004-0.018	--	N	P	P
54	dinoterb	D	--	=94	9	94	--	0.004-0.014	--	N	S	P
55	dithianon	D	--	<1*	--	--	12.3-<1	0.0017-0.0028	--	N	L	N-S
56	diuron	U	--	--	--	--	--	0.002-0.064	--	--	S	S
57	DNOC	D	--	--	--	--	--	0.01-0.056	--	N	N	N
58	dodemorph	D	--	12	--	--	--	0.0006-0.06	--	N	N-S	N
59	dodine	D	--	1-2	--	--	--	0.024-0.036	--	L	S	S
60	EPTC	C	--	--	--	--	>300*	na	--	na	na	na
61	ethephon	D	--	--	--	--	<1->6*	0.0002-0.076	--	--	na	na
62	ethofumesate	D	125	13	2	84	>28	0.005-0.020	--	--	--	N*
63	ethoprophos	O	<en>82	--	--	--	39-273	granules	--	--	--	--
64	etridiazole	D	<1-4	--	17-29	84	81-83	0.0014-0.352	--	N	N	N
65	etrimfos	O	10-14*	--	0	28	17-12	0.004-0.0064	--	N	L	N-S
66	fenamiosulf	D	--	--	--	--	1-2	0.0028-0.07	--	N	N	N
67	fenitrothion	O	--	10-16	65-70	28	84-25	0.0002-0.02	0.2	S	VL	N S
68	fenprophathrin	P	<28	<1	--	--	3-1130	0.02-0.05	--	N	VL	P-VL
69	fenpropimorph	D	22*	--	10*	56	--	0.006	--	N	N	N
70	fenvalerate	P	--	--	--	--	--	0.00012-0.0024	0.006	N	L-VL	S-L
71	fonofos	O	--	--	--	--	67-161	0.0132	--	N	L	P
72	formothion	O	--	--	--	--	101-2*	0.002-0.02	0.096	N	--	N N
73	fosethyl-aluminium	O	--	--	67	96	0.4-0.01	0.019-0.64	--	P	N	N
74	gibberelin	D	--	--	--	--	>33-<8	0.00004-0.06	--	--	N	N
75	guazatine	D	--	--	--	--	--	seed-treatment agent	--	--	--	--
76	heptenophos	O	1-3	--	3	7	3-23	0.001-0.12	--	N	VL	N
77	hexazinone	D	--	--	--	--	>56	0.04	--	--	--	N
78	iprodione	D	126	6	--	--	<1->35	0.00015-0.08	0.2-0.3	N	N	N-S P
79	lenacil	D	<91	--	6	91	>30	0.0016-0.016	--	P-L	N	N
80	linuron	U	--	24-239	10-53	92	>30-1460	0.001-0.006	--	S-L*	N-S	N-S
81	malathion	C	--	--	--	--	--	0.00013-0.016	0.13-0.8	--	S-VL	N-P L-VL
82	mancozeb	O	--	--	--	--	0.8-1.4	0.001-0.072	0.6-1.3	--	--	S P
83	maneb	C	--	--	--	--	<0.04-11	0.001-0.084	0.6-1.3	S	VL	S P
84	MCPA	D	<8-35 C	--	90	95	>28	0.008-0.4	--	N*	N*	N*

Appendix 7.3. Data on 148 pesticides relating to behaviour in water, estimated concentrations in surface water, and risk to aquatic organisms.

No	Pesticide	group	DT50 system	DT50 water	% CO2 dsy	DT50 hydrolysis	DT50 fotolysis	estimated conc. surface water	aerial spraying	algae-- normal air	drift calculation -crustaceans- normal air	fish-- normal air
85	meoprop/prop P	D	12-44 C	--	50	12-44	--	0.002 -0.027	--	N*	N*	-
86	mefluidide	A	--	--	--	--	--	0.0048	--	-	N	-
87	mercaptodimethur	C	<3*	<3*	--	>28	<5->37 K*	0.004 -0.008	--	-	N*	-
88	metalddehyde	D	--	--	--	--	--	0.018	--	-	N*	-
89	metam-sodium	C	--	--	--	--	<0.5 K	granules	nvt	na	na	na
90	metazachlor	A	33	--	<2	56	--	0.003 -0.006	--	N	N	-
91	methabenzthiazuron	U	182	90->182	3-5	182	--	0.011 -0.028	--	P-L	N	-
92	methamidophos	O	--	16	--	--	--	0.0002 -0.0064	--	-	N-P	-
93	methidathion	O	<70	6-7	16-37	70	--	0.018	--	N	L	-
94	methomyl	D	--	--	--	--	--	0.0003 -0.0005	--	-	N	-
95	methylidodecylbenzyltrimethyl- ammonium chloride	D	--	--	--	--	--	--	--	-	-	-
96	methylidodecylxylyleen-bis(tri methyl ammonium chloride)	D	--	--	--	--	--	--	--	-	-	-
97	methylisothiocyanate (MITC)	C	--	--	--	--	>8 K	granules	na	na	na	na
98	metiram	C	--	--	--	1-20	--	0.028 -0.064	0.84 -1.4	-	S	L
99	metolachlor	A	--	--	--	0.7-4.8	--	0.01	--	P	N	-
100	metoxuron	U	60-230	--	--	390->550	--	0.019	--	L	N	-
101	mevinphos	O	15-26	--	--	11-22	--	0.002 -0.009	--	N*	VL*	-
102	monolinuron	U	--	--	--	--	--	0.001 -0.006	--	L*	N	-
103	nitrothal-isopropyl	D	3*	--	5*	14	--	0.01	--	N	N	-
104	onethoate	O	4-5	4-5	22-25	40	--	0.0045 -0.051	--	N	L	-
105	oxamyl	D	--	--	--	>83-2	<1->7 K+N	0.004	--	N	N	-
106	oxydemeton-methyl	O	--	--	--	3-94	19 K	--	--	N	P-L	-
107	parathion	O	--	7 N	--	130-170	--	0.01 -0.02	--	-	VL	-
108	parathion-methyl	O	--	--	--	>21*	--	0.0038 -0.01	--	-	L	-
109	pendimethalin	D	>84	--	3-4	84	<7 N	0.004 -0.008	--	L	P	-
110	phenmedipham	C	<1 u	--	15-52	70-90	--	0.008 -0.019	--	-	N-S	-
111	phosalone	O	--	<7	7	84	0.01-0.013	0.0036 -0.036	0.18 -0.24	N-P	L-VL	-
112	phosmet	O	--	--	--	0-13	0.04-0.1 N	0.03	--	-	VL	-
113	phosphamidon	O	--	11-15	20-66	77	--	0.002 -0.03	--	N	P-L	-
114	piperonylbutoxide	D	--	--	--	60-12	--	--	--	-	-	-
115	pirimicarb	C	--	--	--	>23*	<1 N*	0.0001 -0.0212	0.048-0.212	N	P-L	N
116	pirimiphos-methyl	O	--	--	--	<3-6	<1 N	0.002 -0.047	--	-	L	-
117	prometryne	T	--	35-90	0.2	77	>30 N	0.0032 -0.0056	--	P	N	-
118	propachlor	A	259* C	2-7	18-19	84	>16 K	0.007 -0.036	--	P-L	N	-
119	propamocarb	D	--	--	--	>365	--	0.00043-0.404	0.9 -1.5	N	N	N
120	propazine	T	>49	--	--	83*	<1 K	0.0012	--	S	N	-
121	propham	C	--	--	--	>10000*	>8-32 N	0.008 -0.024	--	P	N	-
122	propiconazole	D	--	25-85	<0.5	70	12 N*	0.0006 -0.0012	0.05	N	N	S
123	propoxur	C	>10	1-3	1-3	<1-93	<1 K	0.00012-0.025	--	N	S-L	-
124	propyzamide	A	--	--	--	--	<2 K*	0.004 -0.006	--	-	N	-



Appendix 7.4. Data on 148 pesticides relating to toxicity to aquatic organisms, toxicity classification and bioconcentration factor (BCF).

No	Pesticide	group	algae NOEC	algae EC50	crustaceans LC50	fish LC50	algae crust fish toxicity classification	class measured	BCF calculated
1	acephate	O	>500	--	57-67	175->1000	VS	S	2-3
2	acetonifon	D	0.0032	0.029	F60 2.5	F60 1-3.3	HT	MT	784
3	aldicarb	D	--	--	--	0.1-8.3	--	MT-HT	7
4	aloxym-sodium	D	18	--	>4000*	2000-6500*	VS*	S*	4-5*
5	asulam	C	--	--	32	F60 >3000->5000	VS	S	0.3
6	atrazine	T	0.0015-0.015	--	5.7-6.9	6.3-26	MT-HT	ST-MT	45
7	azinphos-methyl	O	1.8	--	0.0011	0.012-0.02	VS	HT	--
8	bentazone	D	25.7	--	64	F26-50 510-3000	VS	VS	--
9	bromofenoxim	D	0.8	--	1.6	0.09-0.18	ST	HT	--
10	bromophos-ethyl	D	<0.1	--	0.0086	0.18	HT	HT	54000*
11	bromopropylate	D	<0.42	0.92	0.17	F25 4-34	HT	f:ST-MT	7350
12	calcium cyanide	D	--	--	--	--	--	--	--
13	carbaryl	C	--	--	0.006-0.008*	0.75-20	HT*	ST-HT	<1
14	carbetamide	C	0.14-<0.75	--	50*	F70 >100*	ST*	ST*	--
15	chlorbromuron	U	--	0.17*	5.8	5.0-9.0	HT*	MT	33-73
16	chlorfenvinfos	O	<1*	--	0.0002	0.039-4	ST*	MT-HT	398
17	chloridazon	D	0.73	1.9	0.18-50.1	34.0-145	ST	ST-HT	2-23*
18	chlormequat	D	--	--	16.9	>1000	--	VS	--
19	chlorothalonil	D	<0.0001	--	0.070	0.047	HT	HT	187*
20	chloroxuron	U	<0.0063	0.016	4.3	0.27->150	HT	VS-HT	193
21	chlorpropham	C	0.32	3.3	4.1	13.7	ST	ST	--
22	chlorpyrifos	D	--	--	0.11	0.003-0.013	HT	HT	2560
23	chlorthiamid	O	--	--	see dichobenil	--	--	--	--
24	chlortoluron	U	<0.01	--	67->70	20-270	HT	VS-ST	32
25	copper oxychloride	D	--	--	--	F23.4 7.6	--	MT	--
26	creosote	D	--	--	>3-<20*	0.7-<100*	--	ST-MT*	--
27	cyanazin	T	0.01	--	42-48*	5-16*	HT	ST*	3-311
28	cymoxanil	D	5.8*	--	>30	81	ST*	ST	--
29	cypermethrin (cis)	P	--	--	0.00009-0.0042	0.00001-0.0028	--	HT	500-1300
30	cypermethrin (trans)	P	--	--	see cypermethrin (cis)	--	--	--	--
31	dalapon	D	--	--	800*	F? 345-430	--	VS*	2-3
32	daminozide	D	1-80	--	98.5	423	ST	VS	--
33	dazomet	D	--	--	--	F98 1	--	MT	--
34	deltamethrin	P	--	--	0.0008*	0.00058-0.0012	--	HT*	144
35	demeton-S-methyl-sulphone	O	10	--	35.4	54.6-102	VS	VS-ST	7345
36	desmetryne	T	--	--	45	--	--	ST	--
37	diazinon	O	10	--	0.0009-1.5	0.13-22.7	VS	MT-HT	2-206
38	dicamba	D	>25-250*	--	111*	23-465*	VS*	VS-ST*	501
39	dichlobenil	D	--	1->10*	>13-16	4.2-32*	VS*	ST	0.4
40	dichlofluanid	D	0.1-1.0	--	>1.8	0.05-0.12	ST-MT	MT	15-63
41	dichloropropene	D	--	5*	6.2	9	MT*	MT	278
42	dichlorprop/prop P	D	180*	--	1300*	2300*	VS*	VS*	9

Appendix 7.4. Data on 148 pesticides relating to toxicity to aquatic organisms, toxicity classification and bioconcentration factor (BCF).

No	Pesticide	group	algae NOEC	algae EC50	crustaceans LC50	fish LC50	algae crust fish toxicity classification	BCF measured	BCF calculated
43	dichlorvos	O	18	--	0.00019	1.4-1.9	VS HT MT	-	-
44	dieldrin	D	--	--	--	1.6-37*	--	-	-
45	dicofof (op)	D	<0.05-<0.5*	--	4.5	F21 0.52-3.6	MT-HT* MT	-	-
46	dicofof (pp)	D	--	--	see dicofof (op)	--	--	-	-
47	difenoxuron	U	>0.01	--	79	10.7	HT ST	-	22
48	diflubenuron	U	F25 <1-25*	--	F25 13.5*	F25 135-390*	VS* VS*	-	327
49	dikegulac-sodium	D	--	--	--	>10000*	VS*	-	-
50	dimethachlor	A	0.008	0.13	14.2	4-15*	HT	-	-
51	dimethoate	O	32	--	2.9-4.7	10-699	VS MT	-	-
52	dinoseb	D	0.44->2.4	--	1.8	0.032-0.98	VS	-	-
53	dinoseb-acetate	D	0.1	--	0.07	0.03	VS-ST	-	-
54	dinoterb	D	1.0	--	0.47	0.0034-0.025	ST HT	-	-
55	dithianon	D	<1.0	--	0.00029	0.08-4.2	VS HT	-	-
56	diuron	U	--	--	1.4-2.0	5.6-6.6	ST HT	-	-
57	DNOC	D	3.2-10	--	5.7	F50 4-12*	VS ST-MT	-	70
58	dodemorph	D	5.4	--	3.34	22	VS MT	-	31
59	dodine	D	0.003	--	0.13	1-1.8	HT HT	-	-
60	EPTC	C	0.5	--	15.4	14-27	ST ST	-	-
61	ethephon	D	--	--	--	357-386	VS	-	-
62	ethofumesate	D	--	--	--	15*	--	-	-
63	ethoprophos	O	3.2	28.3	0.05	0.27-13.8	VS HT	-	20
64	etridiazole	D	0.32	1.82	4.9	1.2-3.3*	ST MT	-	44
65	etrimfos	O	0.4	--	0.0037	0.1-5.5	ST HT	-	108-336
66	fenamiosulf	D	10	--	14.4	67-96	VS ST	-	-
67	fenitrothion	O	0.1->100*	3.9*	0.0016-0.0022*	2.0-3.7*	VS-MT* HT*	-	-
68	fenprophathrin	P	>2.0	>2.0	0.00053	0.0018-0.096	VS HT	-	6-221
69	fenpropimorph	D	<0.25	2.21	F25 3.9	3.2-11.7	ST-HT	-	2100
70	fenvalerate	P	>10	>10	0.00003-0.00005	0.00064-0.0062	VS HT	-	34
71	fonofos	O	0.5	--	0.0023	0.028-0.05	ST HT	-	180-4600
72	formothion	O	5.5	--	--	38.3	VS	-	-
73	fosethyl-aluminium	O	1	--	188	161-428	VS	-	0
74	gibberelin	D	--	--	795*	9.1-14.6*	VS*	-	-
75	guazatine	D	--	--	--	F55 0.98 ug/l	--	-	-
76	heptenophos	O	25*	--	0.002	9.3	VS*	-	-
77	hexazinone	D	--	--	--	274-490	HT MT	-	18
78	iprodione	D	3.2	15.3	4.7	2.3-6.7	VS	-	5-7
79	lenacil	D	0.01	0.014	33	>100-134*	HT ST	-	112
80	linuron	U	0.01*	--	0.75	3.2-6.5	HT*	-	27
81	malathion	O	--	--	0.001-0.0035	0.062-12.9	HT	-	-
82	mancozeb	C	--	F36 1.1	F36 1.3	2.1-200*	--	-	76
83	maneb	C	--	3.2	0.0024-1.0	0.34-6.0	MT	-	-
84	MCPA	D	180*	--	1100*	2000*	VS*	-	<1

Appendix 7.4. Data on 148 pesticides relating to toxicity to aquatic organisms, toxicity classification and bioconcentration factor (BCF).

No	Pesticide	group	algae NOEC	algae EC50	crustaceans LC50	fish LC50	algae toxicity classification	crustaceans toxicity classification	fish toxicity classification	BCF measured	BCF calculated
85	metoprop/prop P	D	180*	--	420*	1100*	VS*	VS*	VS*	S	0.02-22
86	mefluidide	A	--	--	F? 11000	>1200-1600	--	VS	VS	S	<1-<3
87	mercaptodimethur	C	--	--	--	0.79-3.16*	--	MT-HT*	MT-HT*	--	--
88	metalddehyde	D	--	--	--	>100000*	--	VS*	VS*	--	--
89	metam-sodium	C	--	--	--	--	--	--	--	--	--
90	metazachlor	A	0.34	1.63	22.3	4.6-14.7	ST-MT	ST	ST	S	19
91	methabenzthiazuron	U	0.018	--	30.6	16-29	MT	ST	ST	--	--
92	methamidophos	O	--	--	0.026	46->100*	--	HT	VS-ST*	--	--
93	methidathion	O	<10	--	0.0072	0.0022-6.8	ST	HT	MT-HT	--	0
94	methomyl	D	--	--	--	0.87	--	--	HT	S	--
95	methyldodecylbenzyltrimethyl- ammonium chloride	D	--	--	--	6.4*	--	--	MT*	--	--
96	methyldodecylxyleen-bis(tri- methyl ammonium chloride	D	--	--	--	F10? 1.2-4.8*	--	--	MT*	--	--
97	methylisothiocyanate (MITC)	C	--	--	--	--	--	--	--	S	3
98	metiram	C	--	F39 1.8*	2.55*	1.1*	MT*	MT*	MT*	--	--
99	metolachlor	A	0.031	--	25.1	2-15	MT	ST	ST-MT	S-M*	8-110*
100	metoxuron	U	0.017	--	216	30.5*	MT	VS	ST*	--	--
101	mevinphos	O	50*	--	0.00016-0.31*	11.5*	VS*	HT*	ST*	S	1.1
102	monolinuron	U	--	0.001*	32-34	74	HT*	ST	ST	S	22
103	nitrothal-isopropyl	D	<0.25	--	2.8	0.56-0.8	ST	MT	HT	--	--
104	omethoate	D	100	--	0.022	8.7-139	VS	HT	VS-MT	S	<1
105	oxamyl	O	0.5-2.0	--	5.7	--	ST	MT	--	--	--
106	oxydemeton-methyl	O	F50 100	--	F50 0.0033	F25 15.5-27*	VS	HT	ST-MT*	--	--
107	parathion	O	--	--	0.0008-0.0128	0.48-1.6	--	HT	MT-HT	M*	50-500*
108	parathion-methyl	O	--	--	0.0048	9.4	--	HT	MT	S*	40*
109	pendimethalin	D	0.006	0.055	0.08	0.14-1.9	HT	HT	MT-HT	S-H	5-1446,1
110	phenmedipham	C	--	--	0.5-6.5	2.7->100	--	MT-HT	VS-MT	M	228
111	phosalone	O	0.1	--	0.0012	0.11-2.0	ST	HT	MT-HT	S-M	48-238
112	phosmet	O	--	--	0.0024-0.1	0.022-11	--	HT	ST-HT	S	2-11
113	phosphamidon	O	70	--	0.022	F? 3.2-600	VS	HT	VS-MT*	--	--
114	piperonylbutoxide	D	--	--	--	--	--	--	--	--	--
115	pirimicarb	C	50	140	0.019	32	VS	HT	ST	S*	2-25
116	pirimiphos-methyl	O	--	--	F2-50 .15-.27 ug	0.40	--	HT	HT	--	--
117	prometryne	T	--	0.02-0.07*	18.9	7	HT*	ST	MT	--	--
118	propachlor	A	0.01-0.015	0.021-0.083	7.8	0.17-3.6	HT	MT	MT-HT	S	4-79*
119	propamocarb	D	22	--	284	163-428	VS	VS	VS	--	--
120	propazine	T	0.07*	--	17.7*	17.0->100*	MT*	ST*	VS-ST*	M	525
121	propham	C	0.32	26	23	36-50*	ST	ST	ST	--	--
122	propiconazole	D	0.32	--	11.5	3.3-10.2	ST	ST	ST-MT	M	303
123	propoxur	C	1.0	--	0.011	3.7-49	ST	HT	ST-MT	--	--
124	propyzamide	A	F50 <2-5.5	--	>5.6	F75 72->200	MT	ST	VS-ST	S	6-20

No	Pesticide	group	algae NOEC	algae EC50	crustaceans LC50	fish LC50	algae crust fish	toxicity -- algae	class	BCF
									measured	calculated
125	pyrazophos	O	<6.5	65.5	0.00018-0.09	0.016-6.1	ST	HT	M	400
126	pyrethrins	P	--	--	F20 0.011-0.042	F25 .023-0.132*	--	HT*	--	--
127	pyridate	D	48	--	1	48->100	ST	VS	M-H	7238
128	sethoxydim	D	--	--	120	30-148	--	VS	S	0.2-2
129	simazine	T	0.1->=1	--	13->2500*	2.6->32	MT	VS-ST*	S-H	0-2464
130	sodium-dimethyldithiocarbamat	C	--	0.24-0.8	0.67	2.6	HT	HT	--	--
131	sulfotep	O	--	--	--	0.0016-0.17*	--	HT*	--	--
132	terbufos	O	1	--	0.0031	0.0008-0.005	ST	HT	S	3-14*
133	terbutryn	T	--	--	2.7-7.8	F80 3.5-4.5	MT	MT	S-M	9-80
134	thiofanox	D	--	--	--	0.13-0.33	--	--	--	--
135	thiometon	O	<5	12.8	8.2	8.0-13.2	ST	MT	--	--
136	thiram	C	--	1.0	0.00006-0.21	0.27	MT	HT	--	--
137	tolyfluenid	D	<0.1	1.5	F50 0.72	0.05-0.06	MT	HT	M	575
138	triadimenol	D	1.0	--	2.5	17.4-23.5	ST	MT	S-M	78-112
139	triallate	C	0.032*	--	0.43	1.2-1.3	MT*	HT	M	282-778
140	triazophos	O	0.1	--	0.003	F40 0.041-5.6	MT	HT	--	--
141	trichlorfon	O	>=3.2	--	0.00096	1.6-2.2	VS	MT	--	--
142	triclopyr	D	--	--	--	117-148	--	VS	S	0.02
143	tridemorph	D	0.015	--	1.3	3.4	MT	MT	--	--
144	trifluralin	D	F20 0.056	--	0.27	>1.4->1.6	MT	HT	H	878-6000
145	triforine	D	--	--	>28	>1000	--	ST	S	31
146	vamidothion	O	100	--	0.19	590	VS	HT	--	--
147	vinclozolin	D	F50 2	--	F50 4	27	VS	MT	S-M	78-112
148	zineb	C	--	1.8	0.97	7.2	MT	HT	S	6-34
149	ziram	C	--	1.2	0.14	0.27-2.28	MT	HT	S	5-90
150	1,2-dichloropropane	D	--	--	--	--	--	--	--	--
151	2,4-D (pH <5)	D	--	--	153-162	4-31	VS	ST-MT	S	66
152	2,4-D (pH >5)	D	--	--	--	--	--	--	--	--



Appendix 7.5. Data on 148 pesticides relating to toxicity to birds and bees.

No	Pesticide	group	birds LD50	birds LC50	bees LD50 contact	bees LD50 oral
1	acephate	O	140-350	--	0.54	0.11
2	acronifen	D	F60 15000	--	--	--
3	aldicarb	D	3.4	--	0.15	0.09
4	alloxidim-sodium	D	2960	--	>20	--
5	asulam	C	F40 >2600->4000	F60 >75000	>16	>20
6	atrazine	T	--	F80 5760-19650*	>16	>160
7	azinphos-methyl	O	--	--	--	--
8	bentazone	D	F26-50 720-14483	--	>100	>100
9	bromofenoxim	D	--	>2.5*	--	--
10	bromophos-ethyl	O	200*	--	--	--
11	bromopropylate	D	--	F25 >5620	>16	>10
12	calcium cyanide	D	--	--	--	--
13	carbaryl	C	197	>5000	1.3	0.14
14	carbetamide	C	--	--	>500	--
15	chlorbromuron	U	--	--	>16	>20
16	chlorfenvinfos	O	3-240*	--	>16	>40
17	chloridazon	D	--	--	--	F? >100*
18	chlormequat	D	>1000	>400*	--	--
19	chlorothalonil	D	>4640*	>5200*	>181*	--
20	chloroxuron	U	--	--	--	--
21	chlorpropham	C	--	--	--	--
22	chlorpyrifos	O	8-76	--	--	--
23	chlorthiamid	D	--	see dichlobenil	--	--
24	chlortoluron	U	--	--	--	--
25	copper oxychloride	D	--	--	F23.4 >100	F23.4 34
26	creosote	D	--	--	--	--
27	cyanazin	T	400-500*	--	>16->193	>20
28	cymoxanil	D	--	3360->12500	--	--
29	cypermethrin (cis)	P	>300*	--	--	0.035
30	cypermethrin (trans)	P	--	see cypermethrin (cis)	--	--
31	dalapon	D	--	--	>12.7	>63.5
32	daminozide	D	--	--	--	--
33	dazomet	D	--	--	--	--
34	deltamethrin	P	1000->4640	>4640->10000	--	F2.5 0.2-10
35	demeton-S-methyl-sulphone	O	--	--	--	--
36	desmetryne	T	--	--	--	--
37	diazinon	O	3.5-14.7*	--	0.37*	--
38	dicamba	D	673-2000*	>4640->10000	>100	>10
39	dichlobenil	D	>50	>5200	>16	>160
40	dichlofluanid	D	>5000*	--	--	>100*
41	dichloropropene	D	--	--	--	--
42	dichlorprop/prop P	D	--	--	>16	>20
43	dichlorvos	O	--	--	--	--

Appendix 7.5. Data on 148 pesticides relating to toxicity to birds and bees.

No	Pesticide	group	birds LD50	birds LC50	bees LD50 contact	bees LD50 oral
44	dicloran	D	F75 2438-8850	--	--	--
45	dicofof (op)	D	--	F21 320->=640	--	--
46	dicofof (pp)	D	-----	see dicofof (op)	-----	-----
47	difenoxuron	U	--	--	--	--
48	diiflubenzuron	U	>2000->5000	>4650	>30*	>30*
49	dikegulac-sodium	D	--	>50000	--	F1 >100*
50	dimethachlor	A	--	>10000	20*	0.8*
51	dimethoate	O	82-86*	332-1011*	0.12-0.16	0.08-0.15
52	dinoseb	D	7.1-42.9*	--	--	--
53	dinoseb-acetate	D	--	--	--	--
54	dinoterb	D	--	--	>100	--
55	dithianon	D	--	--	--	--
56	diuron	U	--	--	--	--
57	DNOC	D	--	637	31.7	20.4
58	dodemorph	D	--	--	--	--
59	dodine	D	--	F10 >5000	--	>200
60	EPTC	C	--	20000	>16	>160
61	ethephon	D	912*	--	--	--
62	ethofumesate	D	>1600	>10000	F20 >16	F20 >16
63	ethoprophos	O	5.62	--	--	--
64	etridiazole	D	560-1640*	F12 17800-21500	--	--
65	etrimfos	O	1334	740-4035*	0.1*	0.21*
66	fenaminosulf	D	--	--	--	--
67	fenitrothion	O	115-140	--	--	--
68	fenpropathrin	P	1089	9026->10000	0.05	--
69	fenprothimorph	D	1600->17776	--	--	F75 >100
70	fenvalerate	P	>4640	5502->10000	0.41	0.29
71	fonofos	O	--	F10 16.5	--	--
72	fomothion	O	630*	--	0.18	0.15
73	fosethyl-aluminium	O	4997	--	>400	>400
74	gibberelin	D	--	F38 >8000	>200	--
75	guazatine	D	F? 125-263	--	--	--
76	heptenophos	O	55*	--	--	--
77	hexazinone	D	--	>5000	--	--
78	iprodione	D	930-10400	>20000	>5 g/l	>5 g/l
79	lenacil	D	--	2300-5620	--	--
80	linuron	U	--	--	>16	>160
81	malathion	O	--	3497-4320*	0.71	--
82	mancozeb	C	--	--	>16	>20
83	maneb	C	--	>10000*	>12.1	>130
84	MCPA	D	--	--	>100	>10
85	mecoprop/prop P	D	--	--	>100	>20
86	nefluidide	A	>4640	>10000	--	--

Appendix 7.5. Data on 148 pesticides relating to toxicity to birds and bees.

No	Pesticide	group	birds LD50	birds LC50	bees LD50 contact	bees LD50 oral
87	mercaptodimethur	C	9.5-24*	--	--	--
88	metalddehyde	D	181-1030	3455	--	--
89	metam-sodium	C	--	--	--	--
90	metazachlor	A	>2510	>5620	--	>20
91	methabenzthiazuron	U	--	--	--	>100*
92	methamidophos	O	25-57*	--	0.86	0.22
93	methidathion	O	23.6-150*	--	0.13	0.21
94	methomyl	D	28*	--	--	0.08
95	methyl dodecyl benzyl trimethyl- ammonium chloride	D	--	--	--	--
96	methyl dodecyl xylene-bis(tri- methyl ammonium chloride)	D	--	--	--	--
97	methyldisothiocyanate (MITC)	C	--	--	--	--
98	metiram	C	--	--	>16	>40
99	metolachlor	A	--	>10000	--	--
100	metoxuron	U	--	--	--	--
101	mevinphos	O	0.75-7.5	--	--	--
102	monolinuron	U	--	--	>14	>30
103	nitrothal-isopropyl	D	F13-17 >4.2->6.3	--	--	F13-17 >100
104	omethoate	O	10*-83	--	0.083	0.048
105	oxamyl	D	4.6	F25 225-5000	0.31	0.094
106	oxydemeton-methyl	O	--	--	--	--
107	parathion	O	2.1	194*	--	0.04
108	parathion-methyl	O	7.5-82	29	0.165 ug/l	--
109	pendimethalin	D	--	4187-10388	--	--
110	phenmedipham	C	--	--	2.95	--
111	phosalone	O	>2150	1659-2033	5.8-8.9	4.5-10.2
112	phosmet	O	18-2009	500->5000	1.1	--
113	phosphamidon	O	2-9	--	--	--
114	piperonylbutoxide	D	--	--	--	--
115	pirimicarb	C	8-20	5508	17.8	2.2
116	pirimiphos-methyl	O	200-400*	--	--	--
117	prometryne	T	--	F80 20-32 g/kg	>16	>160
118	propachlor	A	91	>5620	>11.3	>14.1
119	propamocarb	D	>=3050	>=9040	--	--
120	propazine	T	--	F80 7850-32000	--	--
121	propham	C	--	--	--	--
122	propiconazole	D	2223->3000	>1000	--	2
123	propoxur	C	--	--	0.72	0.12
124	propyzamide	A	F75 8020->14000	4000	>16	>20
125	pyrazophos	O	118-480*	--	--	--
126	pyrethrins	P	F20 >2500->10000	--	0.15*	0.21*
127	pyridate	D	1269-<10000	>5000	>16	>10

Appendix 7.5. Data on 148 pesticides relating to toxicity to birds and bees.

No	Pesticide	group	birds LD50	birds LC50	bees LD50 contact	bees LD50 oral
128	sethoxydim	D	>5000	>5000	>10	--
129	simazine	T	--	--	>16	>160
130	sodium-dimethylthiocarbamat	C	--	--	--	--
131	sulfotep	O	--	--	--	--
132	terbufos	O	--	145-185*	--	4.1*
133	terbutryn	T	8000*	F80 >7025*	--	--
134	thiofanox	D	1.2-3.4	43-109	0.058	0.062
135	thiometon	O	--	--	F25 2.72*	F25 5.64*
136	thiram	C	--	--	>12.6	>7.9
137	tolylfluaniid	D	>100*	--	--	--
138	triadimenol	D	>1000->10000	>5000	--	F13 >100
139	triallate	C	2251	--	>16	>160
140	triazophos	O	F40 23-63*	--	--	F40 0.2-<1
141	trichlorfon	O	110*	720-1901*	--	--
142	triclopyr	D	1698	2935->5000	>60	--
143	tridemorph	D	--	F93 1800-10600*	>20	>16
144	trifluralin	D	F2.5 >5000	>2000->2500	--	>50-100
145	triforine	D	--	1849->4640	--	--
146	vamidothion	O	--	--	0.56	0.25
147	vinclozolin	D	--	--	--	--
148	zineb	C	--	--	>13.1	>16.4
149	ziram	C	--	--	46.7	--
150	1,2-dichloropropane	D	--	--	--	--
151	2,4-D (pH <5)	D	--	--	>16	>160
152	2,4-D (pH >5)	D	--	--	--	--

Appendix 7.6. Data on 15 metabolites relating to behaviour in soil.

Metabolite	DT50		Kom		mob. clas.	formation percentage	metabolite of:
	av	SD	av	SD			
aldicarb-sulfone	48	9	1	1	HM	50	aldicarb
aldicarb-sulfoxide	22	5	1	2	SM-HM	76	aldicarb
desethylatrazine	45	--	18	8	SM-MM	21	atrazine
sethoxydim-sulfoxide	41	8	0	--	HM	63	sethoxydim
6(2-ethylsulfoxypropyl)-4-oxy-2-propyl-4,5,6,7-tetrahydro-1,3-benzoxazole	72	--	0	--	MM-HM	21	sethoxydim
oxamic acid	150	--	0	--	-	17	metazachlor
thiophanox-sulfone	134	--	7	5	MM-M	44	thiophanox
thiophanox-sulfoxide	67	--	8	6	MM-M	78	thiophanox
2,6-dichlorobenzamide	>660*	--	0	--	-	50	dichlobenil and chlorthiamide
2-hydroxyatrazine	162	--	288	176	IM	33	atrazine
2-(1-aminobutylidene)-5,5-dimethyl-4-methoxycarbonyl-cyclohexane-1,3-dione	42	16	35	53	SM-M	10	aloxym-sodium
3,5,6-trichloropyridinol	96	31	133	18	SM	11	chlorpyrifos and triclopyr
4-hydroxy-2,5,6-trichloro-isophthalonitril	387*	267*	14	5	SM-MM	15	chlorothalonil
5-amino-4-chloro-3(2H)-pyridazon	95	28	15	7	SM-MM	50	chloridazon
6-chloro-4-hydroxy-3-phenyl-pyridazine	38*	3*	7	1	SM-M	70	pyridate

Appendix 7.7. Data on 15 metabolites relating to photolysis in water, toxicity to aquatic organisms and toxicity classification.

Metabolite	photolysis DT50	algae NOEC	algae LC50	fish LC50	birds LD50	LC50	classification algae	crust. fish	metabolite of:
aldicarb-sulfone	--	--	--	>64	34	5706->10000	--	--	aldicarb
aldicarb-sulfoxide	--	--	--	4	--	--	--	--	aldicarb
desethylatrazine	--	--	--	--	--	--	--	--	atrazine
sethoxydim-sulfoxide	--	--	--	--	--	--	--	--	sethoxydim
6(2-ethylsulfoxypropyl)-4-oxy-2-propyl-4,5,6,7-tetrahydro-1,3-benzoxazole	--	--	--	--	--	--	--	--	sethoxydim
oxamic acid	--	--	--	--	--	--	--	--	metazachlor
thifanox-sulfone	--	--	--	--	--	--	--	--	thiofanox
thiofanox-sulfoxide	--	--	--	--	--	--	--	--	thiofanox
2,6-dichlorobenzamide	--	18	292-856	235-346	--	--	ST	VS	dichlobenil en chlorthiamide
2-hydroxyatrazine	--	--	--	--	--	--	--	--	atrazine
2-(1-aminobutylidene)-5,5-dimethyl-4-methoxycarbonyl-cyclohexane-1,3-dione	--	--	--	--	--	--	--	--	alloxydim-sodium
3,5,6-trichloropyridinol	1 u K	--	--	--	--	--	--	--	chlorpyrifos en triclopyr
4-hydroxy-2,5,6-trichloro-isophthalonitril	<=1.5 K	--	26	16-45	158	--	--	ST	chlorothalonil
5-amino-4-chloro-3(2H)-pyridazon	--	--	--	--	--	--	--	--	chloridazon
6-chloro-4-hydroxy-3-phenyl-pyridazine	19u N	--	26	--	--	--	--	VS	pyridate

Metabolite	Support group M model						Support group M model					
	concentration in shallow groundwater			spring application			residue in plough layer after 1 year			autumn application		
	av	range		av	range		av	range		av	range	
aldicarb-sulfone	9	0.02-17	4	0.1-8	<0.01	<0.01-0.02	--	--	S	--	0.14	aldicarb
aldicarb-sulfoxide	4	0.9-6	1	0.5-2.1	<0.01	<0.01	--	--	S	--	0.14	aldicarb
desethylatrazine	1.5	0.8-2.0	1	0.4-1.1	0.2	0.1-0.4	--	--	--	--	--	atrazine
sethoxydim-sulfoxide	9	6-12	3	2-4	<0.01	--	>60	<0.01	--	--	--	sethoxydim
6(2-ethylsulfoxypropyl)-4-oxy-2-propyl-4,5,6,7-tetrahydro-1,3-benzoxazole	5	--	2	--	0.01	--	>20	<0.01	--	--	--	sethoxydim
oxamic acid	45	--	20	--	<0.01	--	--	--	--	--	--	metazachlor
thiofanox-sulfone	28	24-28	12	10-12	0.3	<0.01-1.3	--	--	--	--	--	thiofanox
thiofanox-sulfoxide	16	12-18	9	7-10	0.3	0.02-0.8	--	--	--	--	--	thiofanox
2,6-dichlorobenzamide	>50	--	>25	--	<0.01	--	--	--	--	--	--	dichlobenil and chlorthiamid
2-hydroxyatrazine	0.003	<0.0003-0.3	0.003	<0.0003-0.2	>7.5	>7.5	--	--	--	--	--	atrazine
2-(1-aminobutylidene)-5,5-dimethyl-4-methoxycarbonyl-cyclohexane-1,3-dione	0.08	<0.001-1.5	0.05	<0.001-0.8	0.08	<0.01-0.65	--	--	S	1-9*	--	aloxym-sodium
3,5,6-trichloropyridinol	<0.004	<0.001-0.15	<0.004	<0.001-1.5	1.8	<0.01->1.8	--	--	--	--	--	chlorpyrifos and triclop
4-hydroxy-2,5,6-trichloro-isophthalonitril	>7*	4->7*	4*	2-4*	0.5*	0.1-1*	--	--	S	4-80	--	chlorothalonil
5-amino-4-chloro-3(2H)-pyridazon	10	3.5-18	5	2.5-7.2	0.8	0.08-2	--	--	--	--	--	chlorthidazon
6-chloro-4-hydroxy-3-phenyl-pyridazine	8*	6-10*	4*	3-5*	0.05*	0.02-0.1*	--	--	--	--	--	pyridate

GLOSSARY:

Application area:

Crop to which a pesticide is applied.

Bioaccumulation:

Buildup of a substance in biological tissue, resulting in a higher concentration than in the surrounding environment.

BCF:

Bioconcentration factor: The ratio of the concentration of a substance in the (test) organism to that in the surrounding environment.

Biodegradation:

Conversion of a substance by the action of microorganisms

Conversion:

A process in which the parent compound disappears through change of the molecule. Degradation is a form of conversion in which the molecule becomes smaller. This report uses the terms conversion and degradation interchangeably, but does not always rigorously adhere to the strict meaning.

Degradation:

See conversion.

Dissipation:

Disappearance of the parent compound from a compartment (such as soil or water) in which various processes such as conversion, evaporation, leaching, etc. can play a role.

Drift calculation:

Estimate of the expected concentration of a pesticide in the surface water of a fictitious ditch, assuming a given dosage and emission.

DT50:

Time in which 50% of the parent compound has disappeared from soil or water by conversion.

EC50:

The concentration of a substance at which 50% of the (test) organisms exhibit the effect under consideration.

Emission:



Dispersion of a substance outside the actual application area, in this case the treated area. This undesirable movement may be due to drift (see also emission percentage).

Emission percentage:

The emission is calculated as a fraction of the dosage used. The emission percentage depends on the method of application and thereby also on the application area.

Formulation:

Form and composition in which a pesticide is marketed (such as a dust, granules, a liquid). The formulation contains ingredients which make it more manageable, or increase its application potential, effectiveness or safety.

Henry coefficient = water/air partition coefficient:

The ratio between the concentration of a substance in water and its partial pressure in the gas phase.

Hydrolysis:

A chemical reaction of a substance with water in which a part of the molecule of the reacting substance is replaced by a OH group.

Incipient LC50:

LC50 which has been shown not to aggravate the effects after chronic exposure.

Intrinsic persistence:

Measure of the residence time of a substance in a compartment, the disappearance rate being dependent on conversion only.

Ks/l:

soil/water partition coefficient: adsorption coefficient; indicates how strongly a substance is bound to soil particles.

Kom:

Adsorption coefficient divided by the fraction of organic matter in soil.

Kow:

octanol/water partition coefficient: The ratio of the solubility of a substance in n-octanol to that in water, at equilibrium.

LC50:

The concentration of a substance which is lethal to 50% of the (test) organisms.

LD50:

The dose which is lethal to 50% of the (test) organisms

Metabolite:

Substance formed from the parent compound by conversion.

Mineralization:

Degradation of a substance into inorganic end-products; it is usually estimated in terms of CO<sub>2</sub> production.

NOEC:

No-observed effect concentration: The highest of a series of concentrations used in a toxicity test at which no effect is observed.

PEC:

Predicted environmental concentration: The expected concentration in an environmental compartment, calculated using a model approach.

Percolate:

Water leached out from a soil column.

Persistence:

Measure of the residence time of a substance in a compartment, the disappearance rate being dependent on one or more dissipation processes.

Photolysis:

Chemical conversion of a substance in aqueous solution by the action of light.

Photosensitizer:

Substance which promotes the photochemical conversion of another substance.

Rf:

Retardation factor: The distance moved by a substance relative to the distance moved by the water front, measured, for example, in a soil column.