

RIVM report 500002003/2003

**Ecological effects of pesticide use in the
Netherlands**

Modeled and observed effects in the field ditch

D. de Zwart

This investigation has been performed by order and for the account of the Ministry of Spatial Planning, Housing and the Environment, within the framework of project M/500002, “Modeling ecological effects”.

RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Abstract

This study dealing with risks to the aquatic ecosystem imposed by the application of pesticides in the Netherlands made use of a novel method to calculate aquatic exposure to a large variety of pesticides (261 in total), which is worked out in detail here. Since the entire calculation is founded on GIS-based maps of agricultural land use (51 crops in open culture), it is possible to generate country-wide maps of the results. Through the application of Sensitivity Distributions for aquatic species (SSD), in combination with rules for mixture toxicity calculation, the modeled exposure is transformed to a risk estimate for the species assemblage in the aquatic ecosystem. The risk is expressed as the proportion of species likely to be suffering any effect from the exposure. In the summary of the risk maps, the majority of predicted effects is observed to be caused by the pesticide application practice in growing potato crops: 95% of the predicted risk is caused by only 7 of the 261 pesticide ingredients. The maximum local risk of pesticide use is estimated to affect about 50% of species. For the purpose of validation, local toxic risk estimates were compared to observed species composition in field ditches using simple statistical methods (regression analysis). However, the number of field observations was not sufficient enough to generate quantitative results. The unexplained variability in the biotic field data collected by a range of non-aligned monitoring networks does not allow highly significant conclusions. Nevertheless, there is a weak indication that the predicted risks are associated to biodiversity changes in field-exposed communities.

Contents

Samenvatting	7
Summary	9
1. Introduction	11
1.1 Problem definition.....	11
1.2 Towards quantification of risks.....	11
1.3 Aims.....	12
2. Available data	13
2.1 Data on active pesticide ingredients.....	13
2.2 Grid-based soil properties.....	13
2.3 Climatic data.....	14
2.4 Land use and Crops.....	14
2.5 Application regimen of pesticide ingredients per crop.....	16
2.6 Direct spray drift of pesticide ingredients to a field ditch.....	16
2.7 Direct transfer of pesticide ingredients to the soil.....	16
2.8 Pesticide ingredients in air and wet precipitation.....	16
2.9 Pesticide concentration in run-off and drainage water.....	16
2.10 Chemical and species monitoring data in ditches.....	17
3. Methods for calculating exposure	19
3.1 Exposure assumptions and data storage.....	19
3.2 Start of the exposure and risk calculation process for a single gridcell.....	19
3.2.1 Amount of precipitation transferred to ditch and soil.....	19
3.2.2 Concentration of pesticide ingredients in rain water.....	19
3.2.3 Aquatic exposure by direct spray drift.....	20
3.2.4 Aquatic exposure by dry deposition.....	20
3.2.5 Soil loading by application of pesticides, A.....	20
3.2.6 Soil loading by dry deposition of pesticide ingredients, B.....	20
3.2.7 Soil loading of pesticide ingredients by rain input, C.....	21
3.2.8 Total loading of soil.....	21
3.2.9 Concentration in run-off and drainage water.....	21
3.2.10 Amount of R&D water transferred to ditch.....	21

3.2.11 Iteration of the weekly concentration in ditch water	22
3.3 <i>Gridcell-based concentration results</i>	23
4. Methods for calculating toxic risk for aquatic species	25
4.1 <i>The method of toxic risk calculation</i>	25
4.1.1 Toxic risk per pesticide ingredient	26
4.1.2 Overall toxic risk	27
4.2 <i>Handling temporary data, and subsequent gridcell analyses</i>	27
5. Method for validation of toxic risk	29
6. Results and discussion	31
6.1 <i>Toxic risk of individual pesticide ingredients</i>	31
6.2 <i>Frequency distribution of total toxic risk (msPAF)</i>	34
6.3 <i>Mapping of total pesticide risk in field ditches</i>	35
6.4 <i>Effects of modeled risk: GLM-regression results</i>	36
6.5 <i>Effects of modeled risk: Comparison with field data</i>	40
References	43
Appendix 1: Pesticides and physico-chemical properties	45
Appendix 2 Mailing list	50

Samenvatting

Deze studie toont aan dat het mogelijk is om het ecotoxicologische risico te berekenen van het gebruik van bestrijdingsmiddelen in de Nederlandse landbouw, en dat deze berekende risicowaarden betekenisvol zijn in het licht van waarneembare effecten. Voor de risicoberekening is uitgegaan van het agrarisch bodemgebruik in het jaar 1998. De 51 verschillende teeltgewassen, die in de open lucht gekweekt worden, kennen alle een eigen standaard regiem van bestrijdingsmiddelengebruik. In totaal worden in de open teelt van landbouwgewassen 261 verschillende werkzame stoffen (ingrediënten van bestrijdingsmiddelen) toegepast. In een waterrijk land als Nederland is het waarschijnlijk dat een aanzienlijk deel van de gebruikte bestrijdingsmiddelen onbedoeld in het oppervlaktewater terecht komt. De blootstelling van het oppervlaktewater is berekend, waarbij de volgende processen in beschouwing werden genomen:

- Direct transport van spuitnevel naar kavelsloten;
- Droge depositie van gasvormige bestrijdingsmiddelen in sloten;
- Natte depositie van bestrijdingsmiddelen door uitregenen in sloten;
- Afstroom- en drainagewater dat van het veld de sloot in loopt;
- Adsorptie van bestrijdingsmiddelen aan bodemmateriaal;
- Afbraak van bestrijdingsmiddelen in sloot en bodem.

De berekende aquatische blootstelling aan bestrijdingsmiddelen wordt met behulp van de verdeling van de gevoeligheid over soorten waterorganismen en regels voor combinatietoxiciteit omgezet in een maat voor het ecotoxicologische risico. Dit risico wordt uitgedrukt als de fractie van de soorten die geacht worden te zijn blootgesteld aan een concentratie of mengselconcentratie die uitgaat boven het niveau waarop geen effecten meer optreden.

De diverse berekeningen zijn per gridcel van 500 x 500 meter uitgevoerd voor het hele droge areaal van Nederland. Het maximum risico dat voor enige gridcel in NL is berekend bedraagt 51%. Het risico komt, omvang en oppervlakte gewogen, voor 58% voor rekening van de aardappelteelt. Slechts 7 van de 261 stoffen dragen voor 95% bij aan het berekende risico. Van deze 95% nemen 2 verschillende fungiciden met 60% het leeuwendeel voor hun rekening. Een drietal insecticiden draagt voor 29% bij aan het risico, terwijl de resterende twee herbiciden voor 7% van het risico verantwoordelijk zijn.

Het risico, in termen van de potentieel aangetaste fractie van de soorten, is vergeleken met de door waterkwaliteitsbeheerders gemeten soortensamenstelling van macrofauna en waterplanten in sloten. Ondanks de beperkte beschikbaarheid van waarnemingen en een grote mate van onverklaarde variabiliteit in de dataset, is er een zwakke indicatie dat het berekende risico gerelateerd is aan een verarming van de macrofauna soortensamenstelling in het veld.

Voor de waterplanten is een dergelijke relatie niet aantoonbaar, hetgeen vermoedelijk wordt veroorzaakt door het geringe aandeel van de herbiciden aan het berekende risico.

Summary

This study demonstrates that it is possible to calculate the ecotoxic risk associated with the use of pesticides. This risk estimate is calculated from the agricultural landuse map of the Netherlands for the year 1998. The 51 different open air cultured crops all have a standard regimen of pesticide application. It total 261 active substances are used as pesticide ingredients. In a flat and wet country, like the Netherlands, it is highly likely that a considerable proportion of the applied pesticides is transferred to surface water. The exposure of surface water (adjacent field ditches) is calculated, taking the following processes into account:

- Direct spray drift;
- Dry deposition of airborne pesticides;
- Direct rain deposition of airborne pesticides in ditches;
- Run-off and drainage from the crop field to adjacent surface water;
- Adsorption to soil particulates and soil organic matter;
- Degradation in soil and surface water.

The calculated exposure of the field ditch is converted to the estimate of risk by applying species sensitivity distributions and theory on mixture toxicity. The risk is expressed in terms of the fraction of species that is expected to be exposed to concentrations or mixture concentrations exceeding the levels where effects are considered negligible.

All the calculations are performed per gridcell of 500-meter square for the entire dry area of the Netherlands. The maximum risk calculated for any gridcell mounts up to 51%. Risk and area-wise, 58% of the risk can be attributed to the culture of potato crops. If the exposed area is also taken into account, only 7 out of 261 pesticide ingredients contribute to 95% of the risk. The 95% contribution to the overall risk can be attributed to two different fungicides (60%), 3 insecticides (29%) and 2 herbicides (7%).

The calculated risk in terms of the potentially affected fraction of species is compared to measured data on the species composition in field ditches. Despite the few observations available, that are also of relatively poor quality, there is a weak indication that the predicted risk is reflected in a comparable reduction in the diversity of macrofauna species. For the macrophytes this phenomenon could not be detected, most probably due to the small contribution of herbicides to the overall risk.

1. Introduction

1.1 Problem definition

The Netherlands is a small country with a very intense agricultural practice. Table 1 shows the landuse pattern for the Netherlands in the year 1998. Of the total dry surface area of about 32500 km², about 22000 km² is dedicated towards open use for culturing crops and feeding cattle. In 1998, a total amount of 6.5 million kg of a variety of 261 different active pesticide ingredients was applied to grass and crop lands together. The Netherlands is also a very flat, low-lying country. About half the country is about level with the sea. Without dunes and water barriers, more than half of the Netherlands would be flooded. The highest point is only 300 m above sea level. Therefore, the agricultural land is drained by an extensive system of man-made ditches. The ditches are connected to canals, from where the excess water is pumped to rivers and eventually to the sea. In the lower regions of the country, the ditches form a network with an interdistance of between 25 and 100 meters. The many dykes, locks, pumping stations, flood barriers, canals and ditches keep the Netherlands habitable.

Table 1 Land use pattern in the Netherlands for 1998, (modified after CBS, <http://statline.cbs.nl/>, September 2003).

Type	Use	Area (km ²)	%	Sub totals
Salt water	Sea and estuaries	4174	10.1%	
Freshwater	Rivers, lakes and canals (> 6m wide)	3479	8.4%	
	Field ditches	1098	2.6%	Wet area: 8751 km ² -21.1%
Nature	Forest	3233	7.8%	
	Other natural areas and reserves	1379	3.3%	
Urban	Living	3327	8.0%	
	Industrial	1086	2.6%	Dry area: 32775 km ² -78.9%
	Traffic	1340	3.2%	
Agriculture	Crops, glasshouse culture	143	0.3%	
	Crops, open culture	9757	23.5%	Open agricultural area:
	Pasture	12510	30.1%	22267km ² -53.6%
Total area		41526		

Due to these geographical conditions, it is very likely that a considerable proportion of the pesticides applied to agricultural land is unintendedly transferred to the water in the field ditches. The question is, whether this unintended exposure bears risks for the aquatic community.

1.2 Towards quantification of risks

With the input of the type and area of 51 different crops grown in the open air (including grass land) for about 120,000 gridcells of 500 * 500 m, together with a standard weekly agricultural regimen in applying pesticides to those crops, a GIS-based (Geographical Information System) estimate of pesticide concentrations in those ditches is generated.

Exposure pathways and processes incorporated in the calculations of water concentrations include:

1. Aquatic exposure by direct spray drift;
2. Run-off and drainage from the soil (R&D);
3. Wet and dry deposition for airborne pesticides;
4. Sorption to soil particulates;
5. Leaching to deeper groundwater;
6. Degradation in soil and water.

By using sensitivity distributions for aquatic species, together with criteria for mixture toxicity evaluation (Posthuma et al., 2002), the calculated concentrations are transformed into an ecotoxic risk estimate for the aquatic community, that is also GIS-based. The risk is expressed as the multi-substance Potentially Affected Fraction of species (msPAF), that is defined as the proportion of species exposed to a mixture of pesticide concentrations exceeding their respective Predicted No Effect Concentration (PNEC).

Local and regional water management in the Netherlands is in the hands of regional Water Authorities. The Water Boards are responsible for flood control, water quantity, water quality and treatment of urban wastewater. All of the about 35 Water Boards do operate a monitoring network. Concentration of pollutants and classical water quality variables are regularly measured in combination with the occurrence of aquatic species. Though very elaborately quantified, the measured concentrations of pesticides (about 500,000 records over the past 10 years) do not reflect actual aquatic exposure. This has been concluded in a qualitative pilot study performed in 1999 (not reported). Lack of realism in measured pesticide concentrations may in part be due to the fact that the sampling schemes are not adjusted to the regimen of pesticide application. There may also be regional discrepancies between the types of pesticide measured and the types of pesticide used. Furthermore, lack of realism may be caused by analytical difficulties in quantifying low concentrations of pesticides in the medium “surface water”.

Calculating the aquatic exposure concentrations from the types of crops locally grown has the advantage that the modeled effects can locally be attributed to the types of crops, as well as to the types of pesticides. This enables us to conduct scenario studies that can guide policy decisions in spatial planning and in pesticide regulation.

1.3 Aims

In this report it is tried to:

1. Calculate concentrations from the use of pesticides and compound behavior;
2. Calculate the ecotoxic risk per compound and for the mixture as a whole;
3. Associate calculated risks with pesticides, crops and observed species occurrence in the field.

2. Available data

2.1 Data on active pesticide ingredients

In this study a total of 261 active pesticide ingredients is evaluated (Appendix 1). For all of those chemicals it was possible to generate estimates of the properties presented in Table 2 by consulting open literature and the internet, as well as by querying publicly available databases on chemical properties.

Table 2 Chemical properties of active pesticide ingredients gathered from a large variety of open data sources (too many to be specified here).

Property	Clarification
kW (1/wk)	The degradation rate constant in water per week. Needed for calculating the remaining concentration as a left-over from last weeks exposure
Kom (l/kg)	The partitioning coefficient between soil organic material and pore water. Needed to calculate the concentration of pesticide in run-off and drainage water as interpolation input for the meta-model PEARL
kS (1/wk)	The degradation rate constant in soil per week. Needed to calculate the concentration of pesticide in run-off and drainage water as interpolation input for the meta-model PEARL
VdW (cm/s) for 34 compounds	The downward dry deposition velocity to water in centimeter per second. Needed to calculate dry deposition of airborne pesticide per unit area of surface water
VdS (cm/s) for 34 compounds	The downward dry deposition velocity to soil in centimeter per second. Needed to calculate dry deposition of airborne pesticide per unit area of soil
LC ₅₀	Toxicity of the compound for a variety of aquatic species, sub-divided in major taxon. Needed for constructing species sensitivity distributions that form the basis for toxic risk estimation
Toxic mode of action TMOA	An indication of the molecular processes affected by the chemical. 99 different modes of action are recognized. Needed for taking decisions on applying a concentration- or a response addition strategy in calculating the combined risk of exposure to multiple chemicals

2.2 Grid-based soil properties

From the 500-m square gridcell-based soil map of the Netherlands (De Vries and Denneboom, 1992), a number of soil properties were extracted as presented in Table 3.

Table 3 Soil properties in the Netherlands.

Property	Clarification
f _{om}	The fraction of organic matter in the soil. Needed to calculate the concentration of pesticide in run-off and drainage water as interpolation input for the meta-model PEARL
f _{water}	The fraction of surface water per gridcell. Needed to calculate the additional effect of exposure to the pesticide content in drainage and run-off water
Soil permeability (m/d)	The leeching velocity of water in soil in meters per day. Needed to calculate the proportion of precipitation excess that will end up as run-off and drainage water

2.3 Climatic data

Over the years 2000-2001, TNO operated a monitoring program, quantifying the amount of deposition (mm) at 18 stations in the Netherlands per period of 4 weeks (TNO, 2002). The measured amounts of deposition were converted to nation-wide 10-km square gridcell-based maps of 4-week average deposition by applying kriging interpolation. The weekly amount of rain is calculated as $\frac{1}{4}$ of the 4-weekly amount.

Daily average temperature data over the period 1991-2000 (file: etmgeg_260_1991.gz) were obtained from KNMI (www.knmi.nl/product, September 2003). Weekly potential evapotranspiration (PET) was calculated from the 10-year series of daily average temperature values, using the relationship between T and PET from the 30-year monthly averages given in Table 4.

Table 4: Long-year monthly average of temperature and potential evapotranspiration.

Month	Temp (°C)	PET (mm/month)
1	2.8	8.3
2	2.9	15.7
3	5.6	32.9
4	8.1	56.4
5	12.5	85.1
6	15.0	90.2
7	17.2	95.1
8	17.1	83.1
9	14.2	50.3
10	10.4	27.8
11	6.3	11.5
12	4.0	6.5

2.4 Land use and Crops

Geographical land use data were obtained from a database on land use based on satellite images of the years 1999 and 2000 (LGN4; <http://www.lgn.nl/>, September 2003). The land use data were combined with the 1998 crop areas from the Agricultural Economics Research Institute (LEI-DLO, BedrijvenInformatieNet, <http://www.lei.dlo.nl/home.htm>, September 2003). These crop areas were available for 540 out of 548 municipalities in the Netherlands. The crop definitions for 1998 are based on a classification system of Statistics Netherlands (<http://statline.cbs.nl/>, September 2003).

Clustering the non-agricultural land use into the land use types urban area, nature area, and open water area reduced the number of land use classes in LGN4. These 3 land use types were combined with the 9 agricultural classes of LGN4 (pasture, corn, potatoes, sugar beet, cereals, greenhouses, fruit orchards, flower bulbs, and other agricultural crops). The land use data were aggregated to the scale level of gridcells of 500 m by 500 m, by calculating the distribution of the land use classes from the 400 pixels within each gridcell. The national acreage of the 8 open-air agricultural land use classes is shown in table 5.

Table 5: Land use classes; national acreage and open air crop distribution for the year 1998, based on LGN4.

Land use class	Surface area (km²)	Number of crops
Pasture	12510	3
Corn	2590	3
Potatoes	1790	5
Sugar beet	1140	2
Cereals	1870	7
Fruit orchards	280	6
Flower bulbs	230	8
Other agricultural crops	1850	51
Total	22260	85

In order to relate pesticide application data to open air land use, the 85 crop types were distributed among the agricultural land use classes. The largest number of crops was assigned to the land use class that contains other types of agricultural crops. The procedure for calculating the spatial distribution of crop areas among the gridcells uses the land use class area and the crop area expressed as a fraction of the total area of land use class.

$$CA_{GC,CR} = LUAR_{GC,LU} \cdot CRAR_{MU,CR} / LUARMU_{MU,LU}$$

where,

$CA_{GC,CR}$	the gridcell-based crop area (ha)
$LUAR_{GC,LU}$	the gridcell-based land use class area (ha)
$CRAR_{MU,CR}$	the municipality-based crop area (ha)
$LUARMU_{MU,LU}$	the land use area in all gridcells of a municipality (ha)

This procedure generated estimated open-air crop areas for 51 out of 85 crops on a total of 122259 gridcells of 500 x 500 m square. The 51 different crops are given in table 6.

Table 6: Crops quantified.

Crop name	Crop name	Crop name
Strawberry	Gladiolus	Leek
Apple, young	Grass seed	Rose
Apple, old	Hyacinth	Oyster plant
Asparagus	Iris	Conifer
Cabbage storable	Marrowfat pea	Headed cabbage
Permanent pasture	Corn	Fodder maize
Hedge plants	Park trees	Sprout cabbage
Brown beans	Lily	Dwarf bean
Chicory root	Daffodil	Sugar beet
Potato on clay	Other flowers	Temporary pasture
Potato, other	Pear, young	Tulip
Corn-cob-mix	Pear, old	Perennial garden plants
Flowers to be dried	Plant onion	Field bean
Green peas	Plant potato on clay	Other fruit tree
Starch potato	Plant potato, other	Small carrot
Summer barley	Winter wheat	Winter carrot
Cocktail onion	Seed onion	French endive

2.5 Application regimen of pesticide ingredients per crop

For 51 of the 85 open-air crops, the total national use in 1998 of 261 active pesticide ingredients was available per week (<http://statline.cbs.nl/>, September 2003). The data were kindly provided by a query from the Informatie Systeem Bestrijdingsmiddelen (ISBEST 4.0) conducted by Alterra. This information together with the estimated gridcell-based crop area generates the estimated weekly gridcell-based use of active ingredients.

2.6 Direct spray drift of pesticide ingredients to a field ditch

Per crop and per active ingredient, the direct spray drift to a standardized adjacent field ditch is given by ISBEST 4.0 (kindly received from Alterra). The drift given by ISBEST is expressed as the percentage of the applied dose (kg/gridcell) transferred to a hectare of surface water ([Drift (%Dose)]).

2.7 Direct transfer of pesticide ingredients to the soil

Based on the application data for the individual pesticide ingredients per week, per crop and per gridcell, together with chemical properties, ISBEST 4.0 generated data on the average fraction of the ingredients transferred to the soil ([SDvsUse]).

2.8 Pesticide ingredients in air and wet precipitation

Over the years 2000-2001, TNO operated a monitoring program, quantifying the amount of pesticide ingredients in air and deposition at 18 stations in the Netherlands (TNO, 2002). 34 pesticide ingredients were selected for this monitoring program by virtue of their ability to evaporate and get airborne. Both the air and deposition quantities of pesticides were converted to nation-wide 10-km square gridcell-based maps by applying kriging interpolation. The concentration in air was expressed in ng/m^3 , averaged over a 4-week period. The quantity of pesticide constituents in rainwater was given as a load expressed in grams per hectare per 4-week period. Divided by 4 this yielded the estimated weekly load (g/ha/wk), as used in the current analysis.

2.9 Pesticide concentration in run-off and drainage water

The model "PEARL" (Leistra et al., 2000) generated a table giving the pesticide concentrations in run-off and drainage water (pore water) after application of 1 kg per hectare as a function of two chemical properties of a range of imaginary pesticides:

1. Half-life in soil (DT50), ranging between 1 and 200 days;

2. Partitioning between soil organic matter and pore water ($K_{om} * f_{om}$), ranging between 0 and 200 (l/kg). The table is generated under the assumption that the soil contains 4.7 percent of organic matter.

2.10 Chemical and species monitoring data in ditches

For the year 1998, the Water Boards operated an ecological monitoring network that provided species census data for 257 field ditches in the Netherlands where macrofauna and macrophyte data were collected. The data were retrieved from the Limnodata Neerlandica database, kindly received from Royal Haskoning (Status: April 17th, 2003). The database comprised counts of 1007 macrofauna and 291 macrophyte taxa. Removing extremely scarce species, a total of 344 macrofauna and 113 macrophyte taxa were retained. If a station was evaluated two or more times during the year 1998, the maximum count per taxon was used. The taxa comprised individual species, as well as higher taxonomic levels. For ease of language, the term “species” will be used for all taxonomical entities.

The biological dataset was matched by a chemical dataset for 212 out of 257 stations. The dataset was comprised of data on the local concentrations of Chloride, Total phosphorus, Kjeldahl Nitrogen, Dissolved Oxygen and pH. If the stations were visited several times over the year 1998, the average was taken over the number of observations.

3. Methods for calculating exposure

3.1 Exposure assumptions and data storage

In order to simplify the exposure calculations, the following assumptions were made:

1. All calculations are performed for a standardized ditch. A standard ditch is assumed to have an overall width of 1 m and a depth of 0.30 m, with sides sloping 45 degrees. One meter of standard ditch thus has a water content of 210 liters.
 2. All fluxes of pesticide input to the ditches are weekly assumed to take place at a single moment in time.
 3. The surface water in the ditches is assumed to be completely stagnant, despite the input of rain and drainage water.
 4. All calculations, including the risk estimation, are performed one gridcell at a time, without taking influences of adjacent gridcells into account.
- Intermediate results are stored in a temporary database, being discarded after a round of single gridcell calculations.
 - Temporary and permanent database entities are represented by field codes between brackets [.....].

3.2 Start of the exposure and risk calculation process for a single gridcell

3.2.1 Amount of precipitation transferred to ditch and soil

Using the TNO precipitation data, the direct rain input per week is calculated according to:

$$[\text{Amount of rain transferred to ditches (l/l/wk)}] = [\text{Amount of Deposition (mm/wk)}] / 210$$

$$[\text{Amount of rain transferred to the soil (l/m}^2\text{/wk)}] = [\text{Amount of Deposition (mm/wk)}]$$

3.2.2 Concentration of pesticide ingredients in rain water

Using TNO data per week and per pesticide ingredient, the concentration of 34 pesticide ingredients in rainwater is calculated:

$$[\text{Concentration of pesticide ingredients in rain (}\mu\text{g/l)}] =$$

$$[\text{RainLoad (g/ha/wk)}] * 10^6 / [\text{Amount of Deposition (mm/wk)}] / 10^4$$

3.2.3 Aquatic exposure by direct spray drift

Using crop area per gridcell in relation to the national crop area and the national use of ingredients, together with the drift percentage, the aquatic drift exposure per active ingredient and per gridcell is calculated by the following formula. Since only half of the ditches are located downwind of the application field, the calculated drift input is divided by 2:

$$\begin{aligned} &[\text{Drift exposure in ditch } (\mu\text{g/l/wk})] = \\ &\text{Sum over all crops in gridcell}([\text{CropAreaGridcell (ha)}] / [\text{TotalCropAreaNL (ha)}] * \\ &[\text{UseCropNLperWeek (kg)}] * [\text{Drift (\%Dose)}]) * 10^9 \text{ (kg to } \mu\text{g)} / 2100000 \text{ (ha ditch to l} \\ &\text{water} / 2 \text{ (only downwind ditches)} \end{aligned}$$

3.2.4 Aquatic exposure by dry deposition

Using the (TNO-derived) 4-week maps of average concentration of 34 pesticides ingredients in air, together with the downward dry deposition velocity to water in centimeter per second, the dry deposition exposure to the standard ditch was calculated per gridcell and per ingredient:

$$\begin{aligned} &[\text{Dry deposition exposure in ditch } (\mu\text{g/l/wk})] = \\ &[\text{AirConcentration (ng/m}^3\text{)}] / 1000 * 7*24*60*60 * [\text{VdW (cm/s)}] / 100 / 210 \end{aligned}$$

3.2.5 Soil loading by application of pesticides, A

Using crop area per gridcell in relation to the national crop area and the national use of ingredients, together with the soil transfer fraction, the soil loading in kg of active ingredient per hectare was calculated by the following formula, where the soil surface area treated is corrected for the area of surface water per gridcell:

$$\begin{aligned} &[\text{Soil transfer by use (kg/ha/wk)}] = \\ &\text{Sum over all crops in gridcell}([\text{CropAreaGridcell (ha)}] / [\text{TotalCropAreaNL (ha)}] * \\ &[\text{UseCropNLperWeek (kg)}] * [\text{SDvsUse}] / (25 * (1 - [f_{\text{water}}]))) \end{aligned}$$

3.2.6 Soil loading by dry deposition of pesticide ingredients, B

Using the (TNO derived) 4-week maps of average concentration of 34 pesticides ingredients in air, together with the downward dry deposition velocity to soil in centimeter per second, the weekly dry deposition exposure on soil was calculated:

$$\begin{aligned} &[\text{Dry deposition on soil (kg/ha/wk)}] = \\ &[\text{AirConcentration (ng/m}^3\text{)}] / 10^{12} * 7*24*60*60 * [\text{VdW (cm/s)}] / 100 * 10^4 \end{aligned}$$

3.2.7 Soil loading of pesticide ingredients by rain input, C

Using TNO-data, the wet loading of pesticides to soil can be calculated:

$$[\text{Wet deposition on soil (kg/ha/wk)}] = [\text{RainLoad (g/ha/wk)}] / 10^3$$

3.2.8 Total loading of soil

Per pesticide ingredient and per gridcell, the total loading of the soil (kg/ha/wk) is the sum of the three soil loadings A, B and C.

$$[\text{TotalSoilLoad (kg/ha/wk)}] = A + B + C$$

3.2.9 Concentration in run-off and drainage water

The meta-model “PEARL”, the Kom partitioning coefficient of the pesticide and the soil organic fraction were used to calculate the concentration of pesticides in run-off and drainage water (R&D).

DT50(d) in soil can be calculated from the degradation rate constant, [kS (1/wk)]:

- $C_t = C_o * e^{-kS * t(\text{wk})}$
- $C_t / C_o = e^{-kS * t(\text{wk})}$
- $\ln(0.5) = -[kS (1/\text{wk})] * \text{DT50}(\text{wk})$
- $\text{DT50}(\text{wk}) = -\ln(0.5) / [kS (1/\text{wk})]$
- $\text{DT50 (d)} = \text{DT50}(\text{wk}) * 7 = 4.852 * [kS (1/\text{wk})]$

The actual partitioning in the field requires a correction for the local fraction of organic matter:

- $K^* = [K_{om}] * [f_{om, \text{gridcell}}] / 0.047$

To calculate the concentration of a particular pesticide in R&D-water [Concentration in R&D ($\mu\text{g/l}$)], the “PEARL”-table is interpolated with the actual pesticide specific values of DT50(d) and K^* . The result is subsequently multiplied by the total soil loading of the pesticide ingredient [TotalSoilLoad (kg/ha/wk)] for the gridcell.

3.2.10 Amount of R&D water transferred to ditch

According to Meinardi and Schotten (in prep.), the fraction of precipitation surplus (precipitation – potential evapotranspiration) that is transferred to surface water by R&D-water is related to soil permeability. The empirically derived relationship is given in Figure 1.

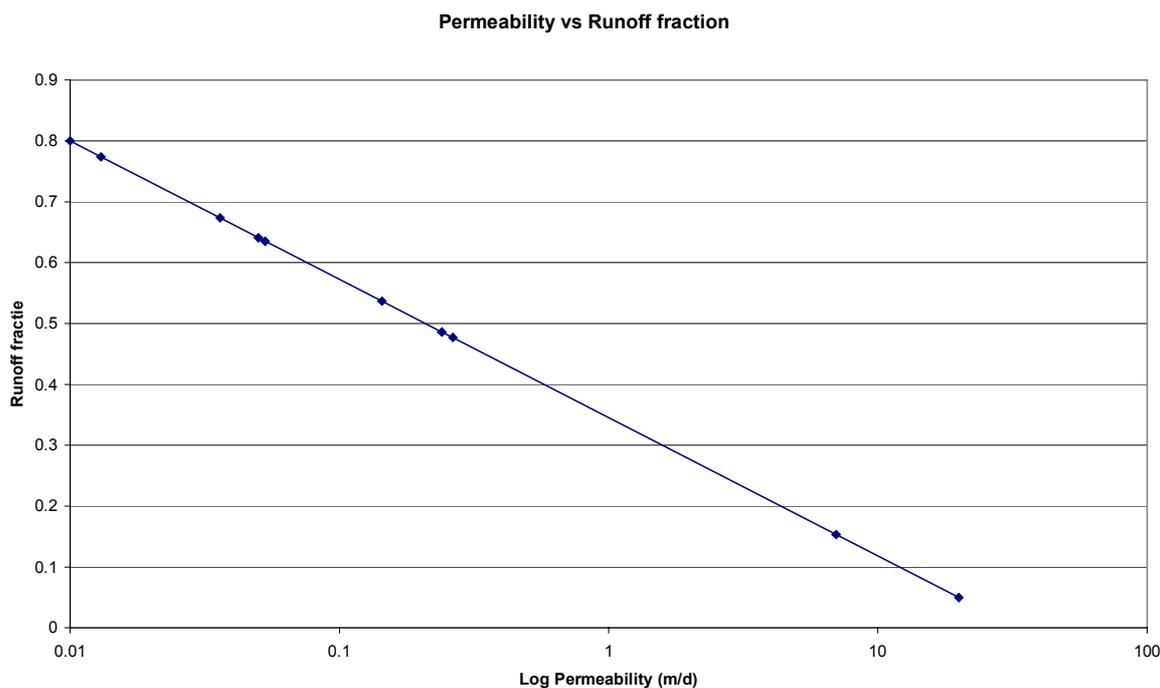


Figure 1 The relationship of log(permeability) in m/day versus run-off and drainage fraction.

TNO-derived precipitation is expressed in mm/wk, which is equal to $l/m^2/wk$. The volume of R&D-water received per liter of water in the ditches is calculated according to the following formula, where the ratio between the wet and the dry surface area is taken into account:

$$[\text{Amount of R\&D (l/l ditch/wk)}] = \frac{([\text{Amount of Deposition (mm/wk)}] - [\text{PET (mm/wk)}]) * [\text{R\&DFraction}] * (1 - [f_{\text{water}}]) / [f_{\text{water}}]}{210}$$

3.2.11 Iteration of the weekly concentration in ditch water

All the above calculations are performed for a single gridcell at a time, for all 261 pesticide ingredients and for all 52 weeks in the year. The results are stored in a temporary database that is discarded as soon as the toxic risk is calculated.

Per ingredient, the iteration starts with calculating the concentration that is left over from last week's final concentration after one week of degradation in the water of the ditch:

$$[\text{Present week's start concentration } (\mu\text{g/l})] = \text{Past weeks } [\text{Present week's final concentration } (\mu\text{g/l})] * e^{-[kW(1/wk)]}$$

Subsequently, the drifted and the dryly-deposited concentrations are added to the start concentration to form a [Sub-total concentration ($\mu\text{g/l}$)] after "dry addition".

The final concentration for the present week is calculated by adding the water contained pesticide input from rain and run-off and drainage, with a correction for volume change:

$$\begin{aligned} &[\text{Present week's final concentration } (\mu\text{g/l})] = \\ &([\text{Sub-total concentration } (\mu\text{g/l})] * 1 + \\ &+ [\text{Amount of rain transferred to ditches (l/l/wk)}] * [\text{Concentration in rain } (\mu\text{g/l})] + \\ &+ [\text{Amount of R\&D (l/l ditch/wk)}] * [\text{Concentration in R\&D } (\mu\text{g/l})]) / \\ &(1 + [\text{Amount of rain transferred to ditches (l/l/wk)}] + [\text{Amount of R\&D (l/l ditch/wk)}]) \end{aligned}$$

Furthermore, the weekly individual pesticide load is attributed to the origin of the exposure in terms of percentages of pesticide originating from past week exposure (old), drift exposure (drift), dry deposition (dry), wet deposition (wet) and R&D, respectively.

Per week and per pesticide, the [Present weeks final concentration ($\mu\text{g/l}$)], as well as the contributing loading percentages ([Old%], [Drift%], [Dry%], [Wet%] and [R&D%]) are stored in the temporary database.

In order to stabilize the concentration of pesticide ingredients remaining from past week, this iteration loop is continued for 5 times 52 weeks (5 years). The first week of the first year, the final concentration from past week is set to 0. The first week of the second year, the final concentration from past week is set to the final concentration of the last week of the first year, etc.

3.3 Gridcell-based concentration results

This final calculation in the exposure assessment yielded weekly concentrations of the 261 pesticide ingredients in field ditches, together with the percentages of load origin per gridcell. Without proceeding to the next gridcell, the calculated data were handed over to the routine for risk calculation. Only after finalizing the risk calculation routine, the concentration calculation routine is repeated for the next gridcell.

4. Methods for calculating toxic risk for aquatic species

4.1 The method of toxic risk calculation

Toxic risk is calculated by the Species Sensitivity Distribution (SSD) methodology (Posthuma et al., 2002). An SSD-curve (Figure 2) is a cumulative distribution function of laboratory derived toxicity data for a single toxicant. SSD-curves are used to derive Environmental Quality Criteria (EQC) and to quantify ecotoxicological risk. As an EQC, the Hazard Concentration for 5% of the species (HC_5) predicts an environmental concentration below which only an acceptably small proportion of species (5%) would be affected. As a risk estimate, the SSD is used to predict the proportion of species exposed to a concentration generating some kind of effect (the Potentially Affected Fraction: PAF). In the present study, the SSD-curves are assumed to follow a log-normal distribution.

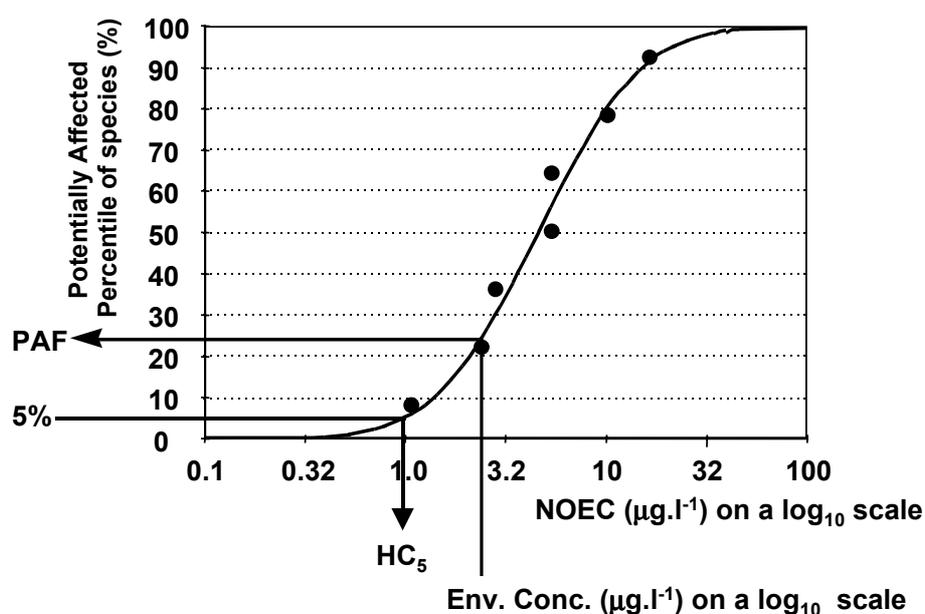


Figure 2 Exemplary cumulative probability distribution of species sensitivity fitted (curve) to observed chronic toxicity values (NOEC; dots). The arrows indicate the inference of a Potentially Affected Fraction of species (PAF-value) and the HC_5 .

The laboratory derived toxicity data for the pesticide ingredients were derived from the RIVM e-toxBase database. Both acute median effect concentrations (EC_{50}) and chronic No Observed Effect Concentrations (NOEC) were $^{10}\log$ transformed before calculating the average $\log(\text{toxicity})$ (AVG) over major taxonomical groups of organisms and the associated standard deviation (STDEV). In case sufficient chronic toxicity data were available, risk evaluation was based on NOEC. For many of the pesticide ingredients, chronic data were

extremely scarce. In those cases, the risk calculation is performed with chronic toxicity data extrapolated from acute observations. The acute SSD is left shifted by a factor of 10, or in other words: $AVG_{\text{chronic}} = AVG_{\text{acute}}/10$ and $STDEV_{\text{chronic}} = STDEV_{\text{acute}}$ (De Zwart, 2002). The SSDs can be reconstructed using AVG and STDEV. For the 261 pesticide ingredients a total of 1143 AVG and STDEV values were calculated to be used as input for the toxic risk calculation per major taxonomic group ($[AVG_{\text{Tax. Grp}}]$ and $[STDEV_{\text{Tax. Grp}}]$). A total of 18 different major taxonomical groups were recognized (Table 7) with up to 46 different species per group.

Table 7: Taxonomic groups represented in the toxicity data.

Taxonomic group	Taxonomic group
Insects (larval stage)	Amphibians
Worts and Ferns	Annelids
Reed and grasses	Mites and spiders
Molluscs	Bacteria
Nematoda	Arrowworms
Fish	Hydroids
Flatworms	Crustaceans
Protozoa	Cyanobacteria
Rotatoria	Algae

4.1.1 Toxic risk per pesticide ingredient

From the calculated weekly exposure concentrations, the toxic risk for individual pesticide ingredients and major taxonomical groups can be calculated by the MS Excel function $NORMDIST(x, \text{mean}, \text{standard_dev}, 1)$, that returns the normal cumulative distribution for the specified mean and standard deviation:

$$[PAF_{\text{Ingredient, Tax. Grp}}] = NORMDIST(10\log([\text{Present week's final concentration } (\mu\text{g/l})]), [AVG_{\text{Tax. Grp}}], [STDEV_{\text{Tax. Grp}}], 1)$$

The toxic risk per ingredient and per major taxon was subsequently averaged over the major taxonomic groups:

$$[PAF_{\text{Ingredient}}] = \text{Avg}([PAF_{\text{Ingredient, Tax. Grp}}])$$

The total permanent dataset to be generated by this calculation would be too large to be stored ($122000 * 261 * 52 \approx 1.7$ giga-records). Therefore, the PAF values per ingredient and per gridcell are averaged over the 52 weeks. If all 261 pesticides would be present in all gridcells, this would produce a dataset of 32 mega-records. However, this is not the case. Only the non-zero values of the yearly average PAF in these records are retained for future use. For the same pesticide ingredients, the yearly average origin of loading percentages ($[Old\%]$, $[Drift\%]$, $[Dry\%]$, $[Wet\%]$ and $[R\&D\%]$) were also stored in this permanent database.

4.1.2 Overall toxic risk

The combined toxic risk of all 261 pesticide ingredients is evaluated by sequentially applying the following calculations (Traas et al., 2002):

1. For ingredients with the same Toxic Mode of Action (TMoA), concentration additivity is assumed. The weekly calculated concentrations per ingredient are transformed to Hazard Units per taxonomic group ($HU_{\text{Ingredient, Tax. Grp}}$), by dividing them by $10^{[\text{AVG}_{\text{Tax. Grp}}]}$, followed by summation ($\Sigma HU_{\text{TMoA, Tax. Grp}}$). The weekly combined toxic risk per TMoA and per major taxonomic group ($\text{msPAF}_{\text{TMoA, Tax. Grp}}$) is then calculated by applying the MS Excel function:

$$\text{msPAF}_{\text{TMoA, Tax. Grp}} = \text{NORMDIST}(10^{\log(\Sigma HU_{\text{TMoA, Tax. Grp}})}, 0, \text{Avg}([\text{STDEV}_{\text{Tax. Grp}}]), 1)$$

2. For ingredients with different TMoA, response addition per major taxonomic group is calculated, where it is assumed that the species are uncorrelated in their sensitivity for the different toxicants (Traas et al., 2002):

$$\text{msPAF}_{\text{Tax. Grp}} = 1 - \Pi(1 - \text{msPAF}_{\text{TMoA, Tax. Grp}})$$

3. The final toxic risk (msPAF) is calculated as the average $\text{msPAF}_{\text{Tax. Grp}}$ over taxonomical groups, assuming equal weight of major taxonomical groups:

$$\text{msPAF} = \text{Avg}(\text{msPAF}_{\text{Tax. Grp}})$$

4. This final calculation would eventually contain about 6.5 mega-records ($122000 * 52$), which is too much to be stored permanently. Therefore, for all gridcells, the average [msPAF per 4 week period] is stored for future use (1.6 mega-records).

4.2 Handling temporary data, and subsequent gridcell analyses

After this step in the calculation, the temporary database is emptied, and the next gridcell is selected. The entire calculation of exposure and risk starts a new loop:

End of the exposure and risk calculation process for a single gridcell

Select next gridcell and GoTo Start (§3.2, page 19)

5. Method for validation of toxic risk

The risk scale (PAF) is dimensionless, but based on the sensitivity of species under lab conditions. In view of these facts, the association between risk and changes in biodiversity is not obvious. However, if the calculated overall toxic risk of pesticide exposure to aquatic species, that is expressed as the proportion of species expected to suffer effects from the exposure, is considerable and properly scaled, it is expected that this will be reflected in the species composition in the field.

Pesticide toxicity is not the only environmental condition governing species composition. A plethora of physico-chemical and habitat characteristics, as well as biological interactions all determine the type of community to be expected. The observed species composition in the field, in terms of the number and abundance of species, may directly be related to the predicted toxic risk of pesticide exposure. This will be easy to determine when the driving force of pesticide toxicity has a major influence over other driving forces. However, in view of the absence of extreme exposure levels, and the expected relevance of other driving forces, this approach was considered unlikely to yield sufficient explanatory power.

In order to be able to isolate the possibly slight effects of pesticide exposure from a dataset on measured biodiversity, as many as possible of the other driving forces have to be taken into account. Since the available dataset on biological and chemical observations in the field is only comprised of 212 sites, it is statistically impossible to include many of the variables possibly governing the wax and wane of species. The number of predictors (related to degrees of freedom) should be at least a factor of about 10 less than the number of observations. Especially, with habitat characteristics that are generally expressed in categories the degrees of freedom will quickly exceed this requirement. It was therefore decided to limit the analysis to a few chemical water characteristics, next to pesticide toxic risk. The chemical characteristics used (pH, Chloride (Cl), Total P (TP), Kjeldahl N (KN) and DO) were selected based on an earlier analysis of the importance of factors determining aquatic community composition (Ertsen and Wortelboer, 2002). The influence of individual environmental predictors can only be discerned if the variables are not highly correlated. The dataset of chemical observations in field ditches, joined with the corresponding yearly average of estimates on total toxic risk (msPAF) was therefore analyzed to reveal correlation structure. The association between the observed abundance of the macrofauna and macrophyte species and the 6 abiotic predictors was established by Generalized Linear Model regression (GLM, McCullagh and Nelder, 1989), yielding a GLM model for every species. Assuming a Poisson distribution, species-specific regressions took the form:

$$\begin{aligned} \text{Observed Abundance of species } i &= O_i^A \\ \ln(O_i^A) &= a_i + \\ &+ b_{1,i} \cdot \text{pH} + c_{2,i} \cdot \text{pH}^2 + \\ &+ d_{1,i} \cdot \text{Cl} + e_{2,i} \cdot \text{Cl}^2 + \\ &+ f_{1,i} \cdot \text{TP} + g_{2,i} \cdot \text{TP}^2 + \\ &+ h_{1,i} \cdot \text{KN} + i_{2,i} \cdot \text{KN}^2 + \\ &+ j_{1,i} \cdot \text{DO} + k_{2,i} \cdot \text{DO}^2 + \\ &+ l_{1,i} \cdot \text{msPAF} + m_{2,i} \cdot \text{msPAF}^2 \end{aligned}$$

The 6 predictors were added stepwise to the model with linear and quadratic terms. The quadratic terms were introduced to address non-linear response relationships, such as optima. The stepwise procedure used the Bayesian Information Criterion (BIC, Schwarz, 1978) to restrict the addition of terms to those that have a significant contribution to the overall model ($P < 0.05$), making the full model highly significant. Calculations were conducted using S-Plus 2000, Professional Release 3 (MathSoft, Inc., Cambridge, MA, USA). The models are used to isolate the driving force of predicted pesticide toxicity on species assemblage.

6. Results and discussion

6.1 Toxic risk of individual pesticide ingredients

Only 46 out of the 261 pesticide ingredients used produced a non-zero risk in one or more of the nation-wide gridcells. This implies that for 215 out of 261 pesticide ingredients the physico-chemical behavior of the compounds, in combination with the sensitivity of aquatic species, produced no significant risk for these species in field ditches. The national average of the toxic risk for individual pesticide ingredients over gridcells (zero values excluded) is shown in Table 8 (Avg PAF). The number of gridcells where the pesticide is calculated to be responsible for a non-zero risk is counted (#Gridcells). The pesticide ingredients are linked to the crops they are applied on, as well as to the proportion of the pesticide applied to a particular crop (Proportion of use). This table is further condensed by excluding 21 ingredients having an average risk below 5%, by grouping the 51 crops to 12 categories (see Table 9), and by excluding crop categories receiving less than 5% of a particular ingredient.

Table 8 makes it possible to score the crop categories on respective impact on pesticide toxic risk. Per crop category, the sum over pesticide ingredients is taken of the average PAF multiplied by the number of gridcells, multiplied by the proportion of use

(Crop score = $\sum_{\text{Ingredient}=1}^n ([\text{Avg PAF}_i] \times [\#\text{Gridcells}_i] \times [\text{PropUse}_{i,\text{crop}}])$). In Table 9, these sums are

expressed relative to each other. The number of pesticide ingredients per crop category is also indicated.

Table 8: Pesticide ingredients, arranged according to the average toxic risk they produce. Next to the number of gridcells where the ingredients produce non-zero risk, the associated crops and their proportion of pesticide use are also given.

Pesticide ingredient	Avg PAF	#Gridcells	Crops	Proportion of use
fentin-acetate	44%	36560	Potato	97%
maneb	34%	70558	Potato	57%
			Onions	18%
			Flowers	14%
metoxuron	24%	1	Potato	57%
			Vegetables	26%
			Flowers	13%
pirimifos-methyl	23%	3906	Flowers	98%
tolyfluanide	20%	209	Fruit trees	90%
isoproturon	19%	17657	Cereals	97%
linuron	18%	21	Potato	58%
			Vegetables	13%
			Fodder maize	10%
			Garden plants	6%
captan	18%	821	Fruit trees	84%
			Flowers	14%

Pesticide ingredient	Avg PAF	#Gridcells	Crops	Proportion of use
chloorthalonil	18%	9	Potato	75%
			Flowers	10%
			Onions	8%
monolinuron	17%	7553	Potato	94%
esfenvalerate	17%	814	Flowers	47%
			Potato	43%
			Potato	58%
lambda-cyhalothrin	15%	46153	Flowers	21%
			Cereals	9%
			Vegetables	8%
			Potato	55%
deltamethrin	15%	46959	Flowers	13%
			Onions	8%
			Potato	97%
diflubenzuron	12%	6314	Fruit trees	80%
thiram	11%		Strawberries	11%
			Potato	99%
			Potato	95%
metribuzin	9%	5	Fruit trees	40%
fentin-hydroxide	8%	668	Garden plants	26%
			Vegetables	14%
			Flowers	7%
			Potato	90%
diquat dibromide	8%	8	Fruit trees	81%
			Vegetables	19%
			Flowers	37%
fosalon	6%	4648	Potato	31%
			Grass	20%
			Flowers	37%
chloorpyrifos	6%	92874	Potato	31%
			Grass	20%
			Fruit trees	43%
			Garden plants	33%
fenbutatinoxide	5%	2335	Strawberries	19%
			Cereals	89%
			Grass	11%
metsulfuron-methyl	5%	1017	Vegetables	38%
			Grass	36%
			Flowers	12%
			Garden plants	5%
permethrin	5%	290	Onions	94%
			Potato	94%
			Onions	94%
propachloor	5%	387	Onions	94%

Table 9: Crops scored according to their impact on national risk.

Crop	#Pesticides	Score
Potato	27	58%
Flowers	37	14%
Cereals	20	9%
Onions	23	8%
Grass	17	4%
Vegetables	35	3%
Fruit trees	31	3%
Sugar beet	22	1%
Garden plants	34	0%
Strawberries	19	0%
Fodder maize	12	0%
Maize	12	0%

On a nation-wide scale, it can be concluded that only 7 pesticide ingredients account for 95% of risk for the aquatic community. This is calculated by multiplying the Avg PAF of an ingredient with the number of gridcells where this ingredient is producing non-zero risk (Table 8). The resulting product of the individual components is expressed relative to each other. Also the use of the pesticides is specified. The top-7 pesticide ingredients are:

1. maneb (36%, fungicide)
2. fentin-acetate (24%, fungicide)
3. lambda-cyhalothrin (11%, pyrethroid insecticide)
4. deltamethrin (10%, pyrethroid insecticide)
5. chloorpyrifos (8%, insecticide)
6. isoproturon (5%, herbicide)
7. monolinuron (2%, herbicide)

With 58% of responsibility for aquatic risk (Table 9), the culture of potatoes contributes most prominently to toxic risk.

For the 46 pesticide ingredients, Table 10 gives the average percentage of the origin of pesticide loading in ditches. For most ingredients, the amount left over from past week's exposure (Avg%Old) is the most prominent (58%). Drift exposure (Avg%Drift) is the second most important exposure pathway (33%), followed by the amount of pesticide in rain (Avg%Wet, 5%). Dry deposition (Avg%Dry), as well as run-off and drainage (Avg%R&D) are negligible as pathways of exposure.

Table 10: Pesticide ingredients and their origin of aquatic exposure.

Ingredient	Avg%Old	Avg%Drift	Avg%Dry	Avg%Wet	Avg%R&D
terbutryn	92	8	0	0	0
carbaryl	89	11	0	0	0
metribuzin	89	11	0	0	0
azinfos-methyl	89	11	0	0	0
isoproturon	88	12	0	0	0
diflubenzuron	84	16	0	0	0
carbendazim	81	19	0	0	0
dinoterb	79	21	0	0	0
fosalon	76	24	0	0	0
metsulfuron-methyl	75	25	0	0	0
terbutylazin	74	10	0	15	1
chloorfenvinfos	73	17	4	5	1
chloorpyrifos	72	12	6	10	0
atrazin	72	10	10	8	0
deltamethrin	71	29	0	0	0
triazofos	67	33	0	0	0
fentin-hydroxide	66	34	0	0	0
cyhexatin	66	34	0	0	0
propachloor	65	11	5	20	0
pirimifos-methyl	64	36	0	0	0
monolinuron	63	35	0	0	2
fentin-acetaat	62	38	0	0	0

Ingredient	Avg%Old	Avg%Drift	Avg%Dry	Avg%Wet	Avg%R&D
koperoxychloride	62	34	0	0	5
permethrin	61	39	0	0	0
DNOC	60	0	4	36	0
diazinon	59	23	0	19	0
lambda-cyhalothrin	57	43	0	0	0
simazin	55	41	0	0	4
linuron	53	47	0	0	0
fenbutatinoxide	51	49	0	0	0
mancozeb	50	50	0	0	0
maneb	49	39	0	0	13
dimethoat	48	36	12	2	1
lindaan	46	5	12	37	0
MCPA	44	18	0	33	5
metoxuron	42	58	0	0	0
esfenvaleraat	42	58	0	0	0
zineb	42	58	0	0	0
chloorthalonil	41	49	1	8	0
thiram	41	59	0	0	0
diquat dibromide	39	52	0	0	9
heptenofos	39	61	0	0	0
tolyfluanide	36	64	0	0	0
mevinfos	34	51	14	1	0
methiocarb	30	63	0	7	0
captan	1	84	1	13	0
Total Average	58	33	1	5	1

6.2 Frequency distribution of total toxic risk (msPAF)

The frequency distribution of toxic risk for the aquatic ecosystem, associated with the agricultural use of pesticides is given in Figure 3.

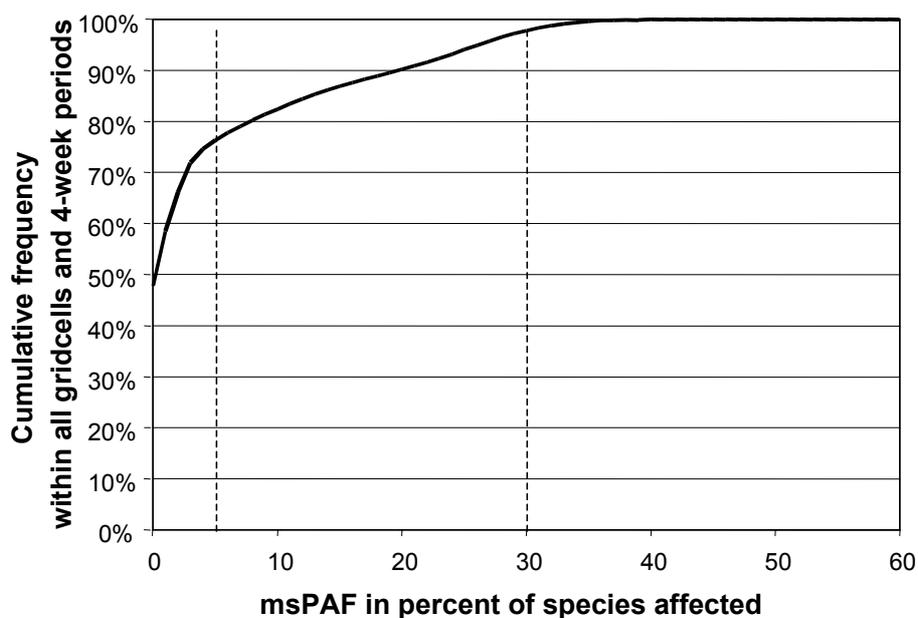


Figure 3 Frequency distribution of pesticide risk for all gridcells in the Netherlands and all 4-weeks periods in the year 1998.

Up to 75% of gridcells in place and time are expected to suffer minor impact with up to 5% of species affected. The maximum predicted impact of a mixture of a mixture of ingredients is estimated as 51%.

6.3 Mapping of total pesticide risk in field ditches

The 4-week average total toxic risk of pesticide use for the aquatic assemblage of species is depicted in the maps presented in Figure 4. From left to right, and from top to bottom, the maps represent the 13 periods of 4 weeks in 1998. White gridcells indicate a lack of data. The lightest pink color indicates an average toxic risk affecting less than 5% of the aquatic species potentially present in the field ditches. Increasingly, darker colors represent higher levels of expected effects.

The first three month of the year hardly any pesticides are used, and the toxic risk of the pesticide mixture stays below 5%. In April the pesticides start to be used. Overlaying the risk maps with the known distribution of crops, it can be identified that mainly the culture of flower bulbs, plant potatoes and fruit trees are responsible for this onset. The months of the year that suggest highest risk of pesticide use for aquatic species are June to August. The risks for the last three 4-week period are associated with the application of soil fumigation disinfectants, mainly in the flower bulb area.

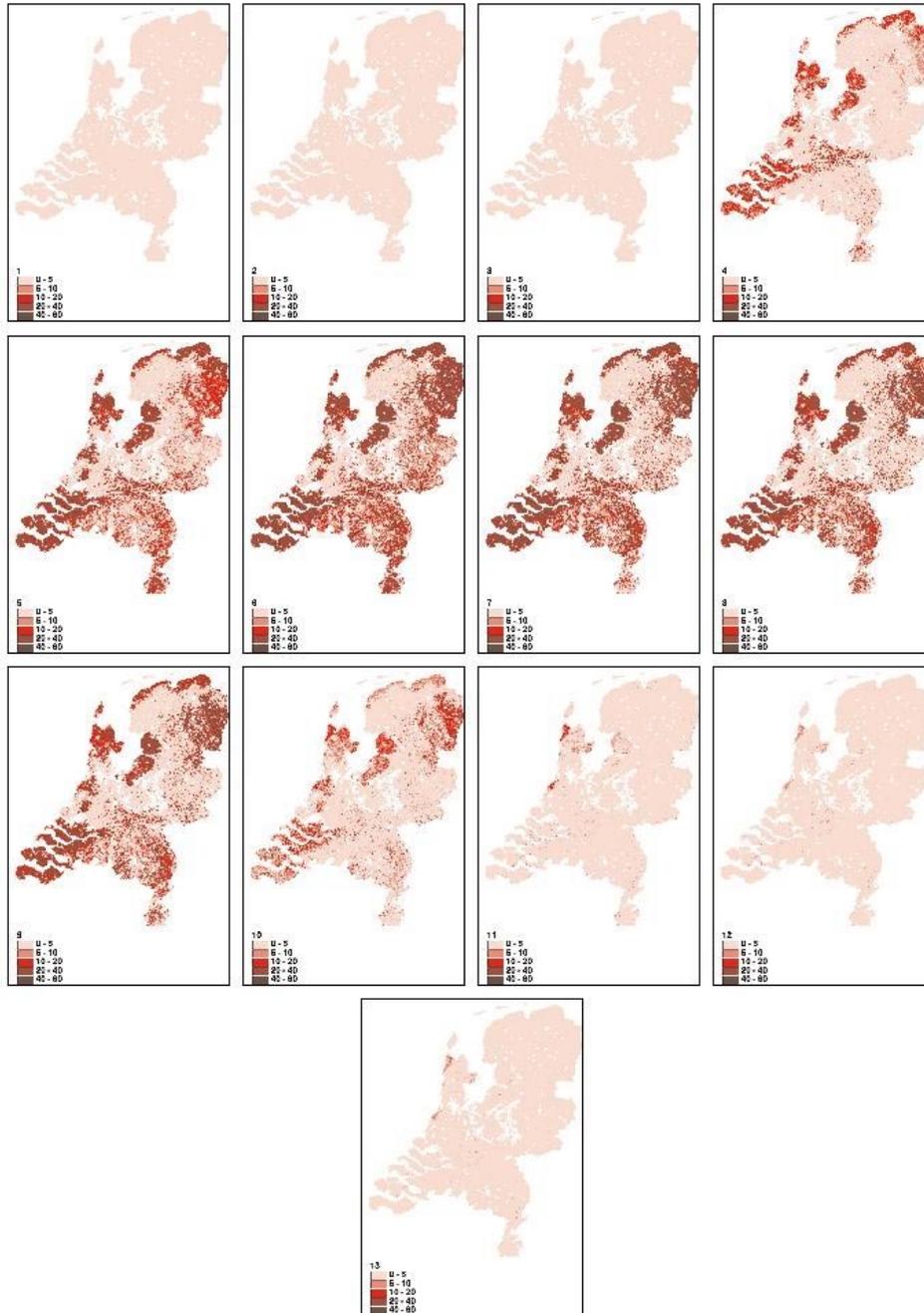


Figure 4 Predicted ecotoxic risk ($msPAF_{NOEC}$) of pesticide use in field ditches.

6.4 Effects of modeled risk: GLM-regression results

The abiotic set of field observations at 212 sites, that was used to explain the observed abundance of species, is having a correlation structure as presented in Table 11. The lower part of the table is giving the correlation coefficients (r), while the upper shaded part is related to the significance of the correlation. In the upper part, bold print is indicative for the

few significant relationships between the variables. Pesticide toxic risk (msPAF) only has a significant correlation with the chloride concentration ($P < 0.001$). As can be judged from examining Figure 5, this is due to only 4 outliers in the chloride data. It was decided not to correct for the chloride outliers in the abiotic dataset. The final objective of this study was only to relate the modeled risk of pesticide use to the species composition in the field. The analysis is specifically not meant to allow for a realistic prediction of community composition in field ditches. Therefore, the observed significance in the correlation of the other predictor variables was considered of less importance, as was the omission of habitat characteristics that generally have a very important influence on species composition.

Table 11: Correlation structure (lower left) and significance of correlation (upper right) for the abiotic set of field observations.

	CL	TP	KN	MSPAF	PH	DO
CL		0.564	0.284	0.000	0.000	1.000
TP	0.13		0.005	0.992	0.000	0.090
KN	0.16	0.25		0.874	0.363	0.007
MSPAF	0.40	-0.08	-0.11		1.000	0.069
PH	0.42	0.49	-0.15	0.04		0.000
DO	-0.06	0.19	-0.24	-0.19	0.57	

The scatterplot matrix in Figure 5 gives an idea about the value ranges of the variables in the abiotic dataset.

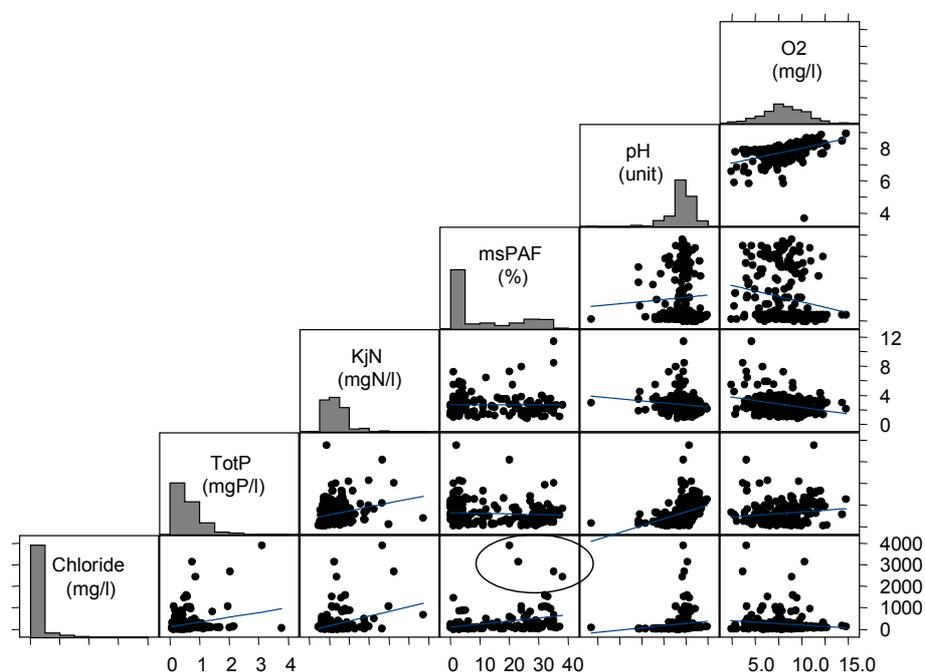


Figure 5 Scatterplot matrix displaying the ranges, distributions of values and linear relationships in the abiotic dataset. The ellipse in the CL-msPAF graph indicates 4 outliers with an extremely high value (> 2000 mg/l) in the CL data.

Of the 344 macrofauna and 113 macrophyte species entered in the GLM regression, 306 and 92 species, respectively, did produce a regression formula with significant explanatory capacity for one or more of the 6 predictor variables. Figure 6 shows the frequency distributions of the explained deviance of the regressions for macrofauna (average 35%) and macrophyte species (average 20%).

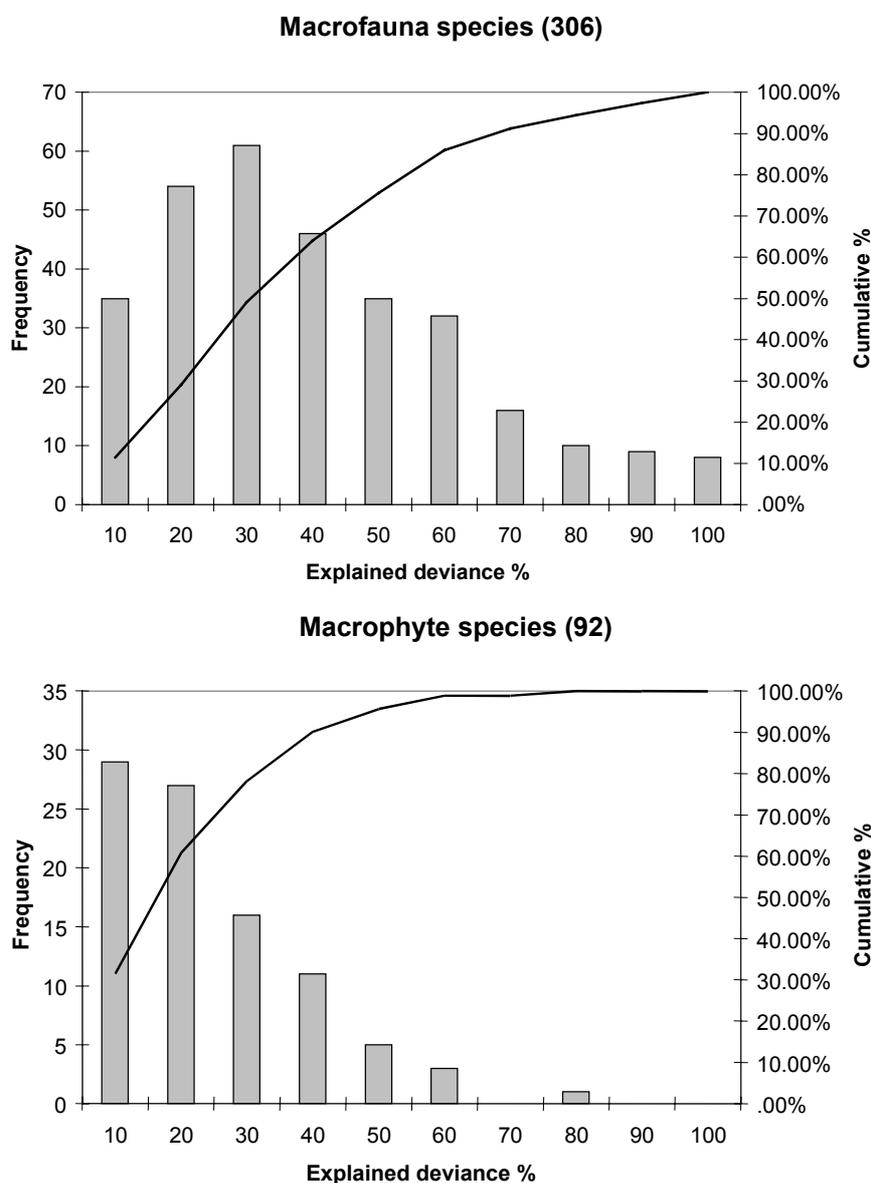


Figure 6 Frequency distributions of explained deviance in the GLM regression.

The regressions were also conducted without the addition of total toxic risk (msPAF) to the formulae. The average relative reduction in explained deviance by excluding msPAF was 16% and 10% (absolute: 6% and 2%), respectively for macrofauna and macrophytes.

When the values of the abiotic predictors for each of the 212 sites are substituted into the calibrated regression formulae, the part of the linear predictor related to msPAF

$(l_{1,i} \cdot \text{msPAF} + m_{2,i} \cdot \text{msPAF}^2)$ is giving an indication of the “driving force” of toxic risk in terms of the abundance of the species. The msPAF part of the linear predictor is called “contribution of msPAF”. Negative values of the contribution indicate a force lowering the species’ abundance; positive terms increase the abundance. In Figure 7 the msPAF contribution, irrespective of positive or negative contributions, is averaged over the respective groups of species, and plotted against the local toxic risk (msPAF) for the aquatic community.

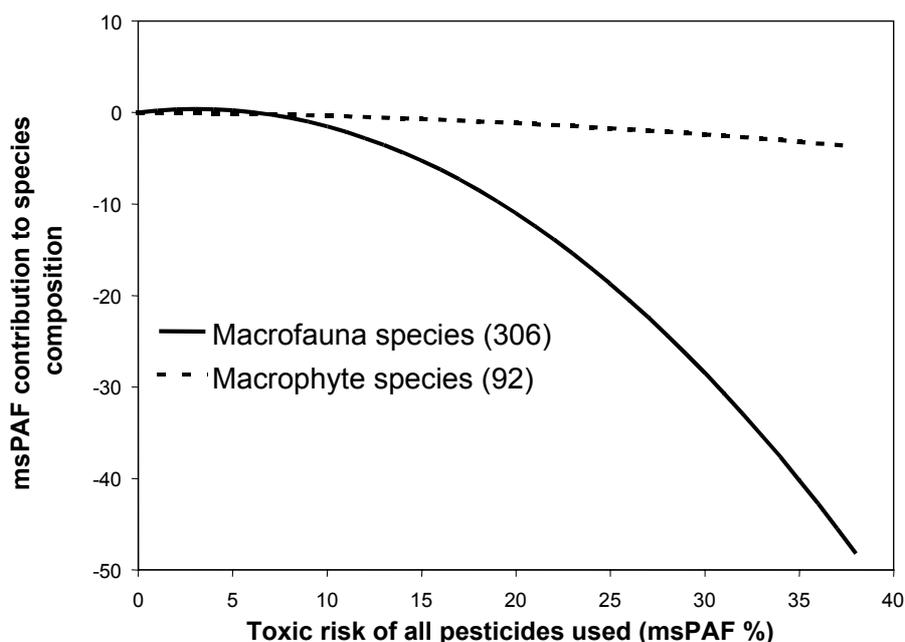


Figure 7 The relationship of mixture toxic risk and the modeled contribution of msPAF in terms of driving force to species abundance, separately for macrofauna and macrophytes.

Figure 7 illustrates that the macrophytes are relatively insensitive to the modeled pesticide toxic risk of pesticide mixtures. This is most probably due to the fact that only two herbicides, comprising 7% of risk, are amongst the top-7 pesticides (see page 33). The assembly of macrofauna species in the field is more strongly associated to mixture risk. Up to a toxic risk of about 10 percent, the toxicity is not reducing the abundance of species. When pesticide mixture risk is increasing, average modeled species abundance is gradually forced lower.

In terms of the predicted abundance of species (related to probability of occurrence), the negative trend of the msPAF-contribution with increasing toxic risk means that a sizeable abundance of species that may be predicted by the other predictors is gradually multiplied by an increasingly small number (minimum is: $e^{-50} \approx 10^{-22}$) at higher toxic risk. This implies that it becomes more and more likely that average species abundance, and thus probability of occurrence, is reduced at higher toxic risk of pesticide use.

6.5 Effects of modeled risk: Comparison with field data

A very weak relationship can be observed between predicted mixture risk values and the species composition in the field, both in terms of the number of species (Figure 8) and the overall abundance of individuals summed over species (Figure 9) in the macrofauna and macrophyte assemblages of species. To be able to observe these weak regression trends in the available biotic data, species with very high numbers at individual sites (>1400) and very scarcely occurring species (less than 10 individuals in the entire dataset) had to be removed from the analysis. The increased scatter introduced by those species totally obscured the weak signal present. After this treatment the dataset comprised 299 macrofauna and 106 macrophyte species. The high spread of the data can be caused by the fact that the data were gathered by about 35 different authorities, each operating their respective monitoring network with a non-standardized input of effort, skill and methodology. Although the slopes of the regression lines are clearly not significant ($R^2_{\text{macrofauna, \# species}}$ is 0.027 and $R^2_{\text{macrofauna, total abundance}}$ is 0.01), the percentual difference between the predicted number of macrofauna species at the calculated risks of 0% and 38% is 43%. For the number of macrofauna individuals, the percentual difference is 38%. Both reductions in species and individuals correspond remarkably well to the predicted risk of pesticide use for the aquatic community.

Figure 10 gives the ranking distribution of the correlation coefficients between the pesticide toxic risk values (msPAF) and the observed abundance of individual species, separately for macrofauna and macrophytes. Over the 212 monitored sites, 29 percent of the macrofauna species (n=299) have a positive correlation between their abundance and toxic risk. These species may be marked “opportunists” since they most probably display indirect effects by filling the gap left by the 71% of “sensitive” species that are reduced in abundance with increasing toxic risk. For the macrophytes (n=106) the percentages of opportunist and sensitive species are 20 and 80 %, respectively. Figure 10 clearly illustrates why diversity indices are not very sensitive indicators for ecological effects over a wide range of toxic exposure. Very often, diversity effects are obscured by a shift in species composition. Some species are reduced and others are increased in their abundance, leaving the change in biodiversity indices neutral, while biodiversity itself changes considerably. Without the attribution of a tolerance score to the individual species or without relating the species composition to a reference community, it is generally impossible to demonstrate toxic effects on diversity, unless an extremely high toxicity is detrimental to the majority of species. Table 12 gives the top-10 listing of both sensitive and opportunist species in macrofauna and macrophytes, respectively. At the moment, there is not sufficient knowledge available to compare the listing in table 12 to a known sensitivity of the individual species.

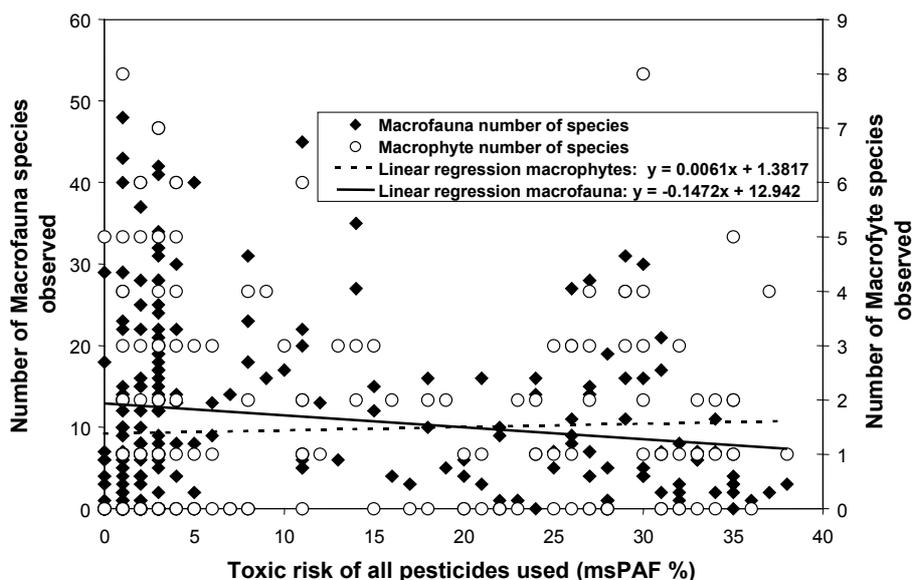


Figure 8 The relationship of the observed number of species and toxic risk for macrofauna and macrophyte species.

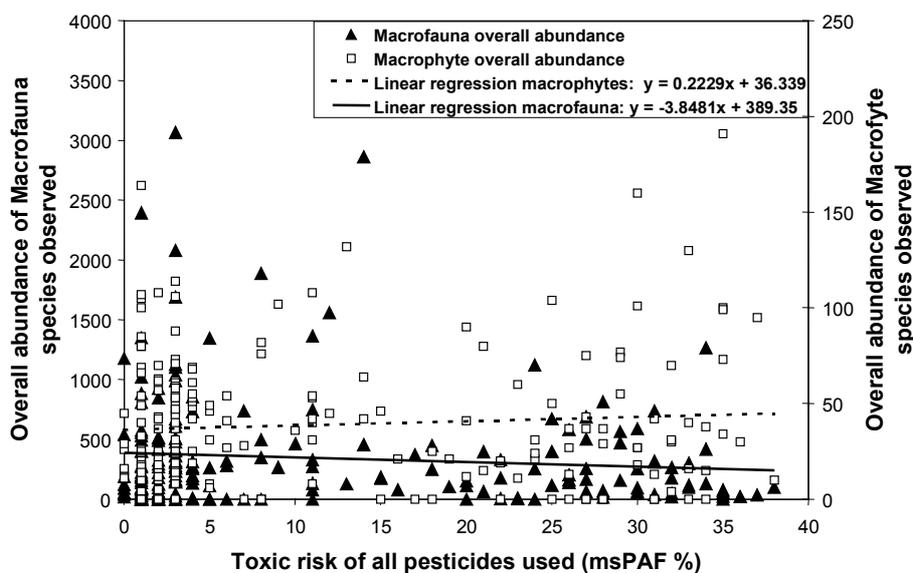


Figure 9 The relationship of the observed number individuals and toxic risk for macrofauna and macrophyte species.

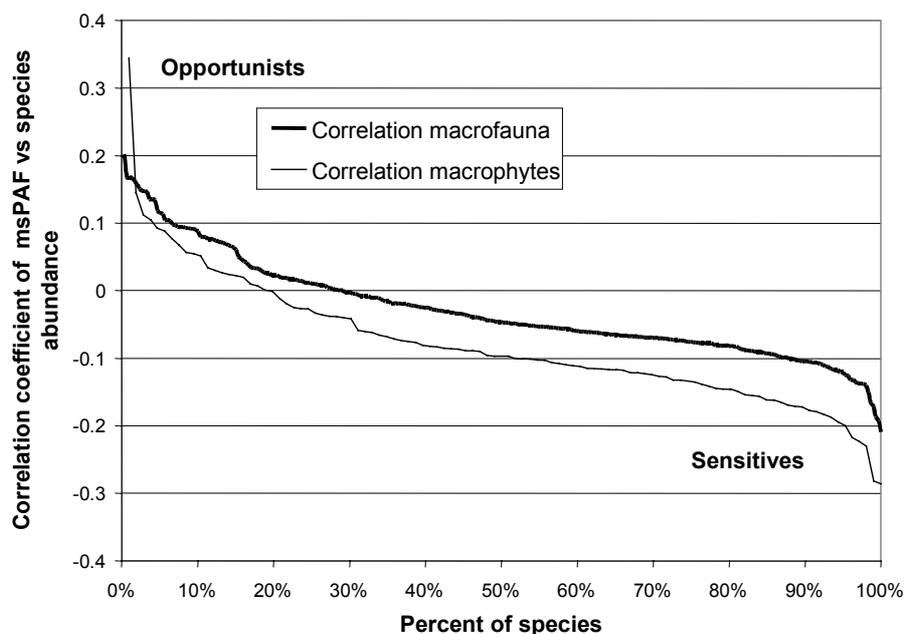


Figure 10 Distribution of the signed correlation coefficient (r^2) between pesticide toxic risk (msPAF) and the observed abundance of individual macrofauna ($n=299$) and macrophyte ($n=106$) species.

Table 12: The top-10 in sensitive and opportunist macrofauna and macrophyte species.

Macrofauna		Macrophytes	
Sensitives	Opportunists	Sensitives	Opportunists
Helochaeres	Anisus leucostomus	Butomus umbellatus	Phragmites australis
Limnesia maculata	Radix gr peregra	Solanum dulcamara	Spirodela polyrhiza
Radix ovata	Haliphus lineatocollis	Nuphar lutea	Callitriche
Erpobdella octoculata	Tetanocera sp	Peucedanum palustre	Lemnaceae
Piona imminuta	Chironomus gr plumosus	Nymphaea alba	Potamogeton pusillus
Polypedilum nubeculosum	Polypedilum gr nubeculosum	Galium palustre	Potamogeton pectinatus
Collembola	Valvata cristata	Mentha aquatica	Glechoma hederacea
Piona conglobata	Neomysis integer	Ranunculus sceleratus	Juncus effusus
Mideopsis orbicularis	Physa acuta	Rumex hydrolapathum	Ceratophyllum demersum
Arrenurus crassicaudatus	Cricotopus gr sylvestris	Lycopus europaeus	Wolffia arrhiza

The present validation study only gives an indication that the effects on aquatic ecosystems, predicted from the crop-based use of pesticides, may indeed be realistic. However, the available data on species abundance for the year 1998, obtained from the monitoring network of the Water Boards, proved to be too low in coverage (only 212 sites) to be quantitatively conclusive.

References

- De Vries, F and J Denneboom. 1992. De bodemkaart van Nederland digitaal. Wageningen, DLO-Staring Centrum.
- De Zwart, D. 2002. Observed regularities in SSDs for aquatic species. In: Posthuma, L, TP Traas and GW Suter. Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL, USA.
- Ertsen, ACD and FG Wortelboer. 2002. Ristori 2001; Responsmodellen voor aquatische systemen. Royal Haskoning report 38931/R0325/DE/DenB.
- Leistra M, AMA van der Linden, JJTI Boesten, A Tiktak and F van den Berg. 2000. PEARL: a model for pesticide behaviour and emissions in soil-plant systems. RIVM Rapport 711401009; Alterra report 28. 107 p in English.
- McCullagh, P and JA Nelder. 1989. Generalized Linear Models, 2nd edition. Chapman and Hall, London.
- Meinardi, CR and CGJ Schotten. Stroom van water en stikstof vanaf en door de bodem naar het open water. RIVM report in preparation.
- Posthuma, L., TP Traas and GW Suter. 2002. Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL, USA.
- Schwarz, G. 1978. Estimating the Dimension of a Model. The Annals of Statistics, 6, pp. 461-464.
- TNO. 2002. Atmosferische depositie van pesticiden, PAK en PCB's in Nederland. TNO report R 2002/606. 107 p in Dutch.
- Traas, TP, D van de Meent, L Posthuma, T Hamers, BJ Kater, D de Zwart and T Aldenberg. 2002. The potentially affected fraction as a measure of ecological risk. In: Posthuma, L, TP Traas and GW Suter. Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL, USA.

Appendix 1: Pesticides and physico-chemical properties

Active pesticide ingredients with estimates of physico-chemical properties (TMoA = toxic mode of action; kW = degradation rate constant in water; Kom = partitioning coefficient between water and soil organic matter; kS = degradation rate constant in soil; VdW = vertical displacement velocity to water; VdS = vertical displacement velocity to soil). The table is sorted according to toxic mode of action.

Toxicity data are omitted because the dataset comprises nearly 1150 records.

Active ingredient	TMoA	kW (1/wk)	Kom	kS (1/wk)	VdW (cm/s)	VdS (cm/s)
triazamaat	Unknown	1.00	138.95	0.50		
Na-p-tolueensulfonylchloramide	Unknown	1.00	7.20	0.50		
ethefon	Unknown	1.00	138949.55	0.43		
benazolin(-ethyl)	Unknown	1.00	56.60	0.50		
triforine	Unknown	1.00	5568.19	0.23		
buminafos	Unknown	1.00	138.95	0.50		
dazomet	Unknown	1.00	7.20	0.69		
polyvinylacetaat	Unknown	1.00	3.27	0.50		
trinexapac-ethyl	Unknown	1.00	3.40	0.50		
pyridaben	Unknown	1.00	233034.38	0.50		
d-karvon	Unknown	1.00	138.95	0.50		
azijnzuur	acid	1.00	0.72	0.50		
boraat	acid	1.00	0.14	0.50		
formaldehyde	aldehyde	2.31	1.97	0.50		
glutaaraldehyde	aldehyde	1.00	0.71	0.50		
metaldehyde	aldehyde	1.00	109.65	0.49		
cymoxanil	aliphatic nitrogen	1.00	3738.89	0.50		
dodine	aliphatic nitrogen	3.47	0.18	0.24		
guazatine	aliphatic nitrogen	1.00	138.95	0.50		
propyzamide	amide	0.09	93.63	0.08		
diflufenican	anilide	1.00	13453.65	0.02		
abamectine	antibiotic	1.00	1483.98	0.17		
kasugamycine	antibiotic	1.00	5.35	2.91		
streptomycine-sulfaat	antibiotic	1.00	7.20	0.50		
validamycine	antibiotic	1.00	0.00	0.50		
chloorfacinon	anticoagulant	1.00	43090.63	0.50		
fentin-acetaat	antifeedants	1.00	776.71	0.50		
fentin-hydroxide	antifeedants	1.00	5459.37	0.06		
chloorthalonil	aromatic	0.69	491.39	0.16	0.12	0.00
dichloran	aromatic	1.00	93.73	0.50		
kresol	aromatic	1.00	138.95	0.50		
nitrothal-isopropyl	aromatic	1.00	603.57	0.50		
clodinafop-propargyl	aryloxyphenoxypropionic	4.62	138.95	6.07		
fenoxaprop-P-ethyl	aryloxyphenoxypropionic	1.00	2578.86	0.54		
fluazifop-P-butyl	aryloxyphenoxypropionic	1.00	138.95	0.50		
haloxyfop-ethoxyethyl	aryloxyphenoxypropionic	1.00	4452.20	0.50		
haloxyfop-P-methyl	aryloxyphenoxypropionic	1.00	2688.47	0.09		
propaquizafop	aryloxyphenoxypropionic	1.00	7517.42	0.50		
quizalofop-ethyl	aryloxyphenoxypropionic	1.00	138.95	0.50		
quizalofop-P-ethyl	aryloxyphenoxypropionic	1.00	138.95	0.50		
1-naftylacetamide	auxins	1.00	28.15	0.50		
1-naftylazijnzuur	auxins	1.00	77.20	0.50		
3-indolylazijnzuur	auxins	1.00	15.43	0.50		
3-indolylboterzuur	auxins	1.00	86.73	0.50		
flutolanil	benzimidazole	1.00	8283.18	0.02		
carbendazim	benzimidazole	0.17	103.34	0.05		
thiabendazool	benzimidazole	1.00	598.61	0.01		
thiofanaat-methyl	benzimidazole	1.00	622.71	0.50		
ethofumesaat	benzofuranyl alkylsulfonate	1.00	147.43	0.16	0.43	0.15
benfuracarb	benzofuranyl methylcarbamate	0.69	4200.46	0.50		

Active ingredient	TMoA	kW (l/wk)	Kom	kS (l/wk)	VdW (cm/s)	VdS (cm/s)
dicamba	benzoic acid	0.14	0.45	0.25		
sulcotrion	benzoylcyclohexanedione	1.00	138.95	0.50		
broompropylaar	bridged diphenyl	1.00	35491.61	0.50		
dicofol	bridged diphenyl	0.17	1483.98	0.11		
asulam	carbamate	1.00	133.57	0.50		
benomyl	carbamate	0.69	647.78	0.04		
carbaryl	carbamate	0.09	105.40	0.49		
carbofuran	carbamate	0.35	14.08	0.06		
diethofencarb	carbamate	1.00	237.84	0.50		
methiocarb	carbamate	2.31	97.40	0.15		
pirimicarb	carbamate	0.03	42.52	0.09	0.40	0.25
propamocarb-hydrochloride	carbamate	1.00	138.95	0.50		
propoxur	carbamate	0.69	18.56	0.16		
carbeetamide	carbanilate	1.00	729.22	0.50		
chloorprofam	carbanilate	0.12	251.19	0.18	0.44	0.07
desmedifam	carbanilate	0.87	531.76	0.15		
fenmedifam	carbanilate	4.62	789.12	0.07		
profam	carbanilate	1.00	46.93	0.49		
buprofezin	chitin synthesis inhibitors	0.14	4200.46	0.07		
cyromazin	chitin synthesis inhibitors	1.00	93.63	0.04		
diflubenzuron	chitin synthesis inhibitors	0.35	1918.04	0.15		
teflubenzuron	chitin synthesis inhibitors	1.00	6956.10	0.50		
metazachloor	chloroacetanilide	1.00	101.29	0.50		
metolachloor	chloroacetanilide	0.17	128.40	0.05	0.42	0.14
propachloor	chloroacetanilide	0.17	118.65	0.81	0.45	0.03
atrazin	chlorotriazine	0.17	83.18	0.08	0.46	0.24
cyanazin	chlorotriazine	0.14	90.01	0.35		
simazin	chlorotriazine	0.09	63.10	0.08	0.47	0.13
terbutylazin	chlorotriazine	0.03	97.40	0.04		
azaconazole	conazole	1.00	138.95	0.01		
bromuconazool	conazole	0.05	537.24	0.50		
cyproconazool	conazole	1.00	547.77	0.01		
difenoconazool	conazole	1.00	24077.50	0.50		
epoxiconazool	conazole	0.03	138.95	0.02		
imazalil	conazole	1.00	1218.19	0.03		
myclobutanil	conazole	1.00	206.20	0.07		
penconazool	conazole	1.00	8610.90	0.50		
prochloraz	conazole	1.00	206.20	0.04		
propiconazool	conazole	1.00	256.20	0.04		
tebuconazool	conazole	0.01	1311.46	0.02		
triadimenol	conazole	0.01	372.76	0.03		
triflumizool	conazole	1.00	23.52	0.35		
koperhydroxide	copper	1.00	0.14	0.50		
koperoxychloride	copper	1.00	7.20	0.50		
brodifacum	coumarin	1.00	14808901.93	0.50		
bromadiolon	coumarin	1.00	822415.77	0.50		
difenacum	coumarin	1.00	2634112.30	0.50		
difethialon	coumarin	1.00	188057833.51	0.50		
cycloxydim	cyclohexene oxime	1.00	1859.59	4.85		
sethoxydim	cyclohexene oxime	1.00	51.79	0.97		
isoxaflutool	cyclopropylisoxazole	1.00	138.95	0.50		
captan	dicarboximide	19.41	93.63	1.62	0.45	0.01
folpet	dicarboximide	1.00	635.12	0.50		
iprodion	dicarboximide	1.00	277.24	0.35		
procymidon	dicarboximide	1.00	531.76	0.69	0.45	0.00
vinchlozolin	dicarboximide	1.00	9301.89	0.24	0.45	0.13
pendimethalin	dinitroaniline	1.00	1483.98	0.05		
dinoterb	dinitrophenol	1.00	1167.35	0.50		
DNOC	dinitrophenol	0.17	116.34	0.50	0.48	0.03
mancozeb	dithiocarbamate	1.00	138.95	0.07		
maneb	dithiocarbamate	1.00	3.33	0.07		
metiram	dithiocarbamate	1.00	76862.46	0.24		
thiram	dithiocarbamate	1.00	266.51	0.32		
zineb	dithiocarbamate	1.00	372.76	0.16		
ziram	dithiocarbamate	1.00	372.76	0.16		
amitraz	formamidine	6.93	372.76	3.43		
aluminium-fosfide	fosfide	1.00	7.20	0.50		

Active ingredient	TMoA	kW (l/wk)	Kom	kS (l/wk)	VdW (cm/s)	VdS (cm/s)
gibbereline	gibberellins	1.00	7.20	0.50		
gibberella zuur A3	gibberellins	1.00	1.59	0.50		
gibberellin A4 + A7	gibberellins	1.00	1.59	0.50		
dikegulac-natrium	growth inhibitors	1.00	138.95	0.50		
maleine hydrazide	growth inhibitors	1.00	2.43	0.16		
chloormequat	growth retardants	1.00	0.00	0.67		
daminozide	growth retardants	1.00	5.91	0.43		
cloquintoceet-mexyl	herbicide safeners	4.62	138.95	3.69		
fenchlorazool-ethyl	herbicide safeners	1.00	138.95	0.50		
n,n-diallyldichlooracetamide	herbicide safeners	1.00	35.53	0.50		
natriumhydroxide	hydroxide	1.00	0.14	0.50		
ferrosulfaat	inorganic	1.00	7.20	0.50		
codlemon	insect attractants	1.00	138.95	0.50		
fenoxycarb	juvenile hormone mimics	0.23	372.76	0.22		
desmetryn	methylthiotriazine	1.00	64.35	0.50		
prometryn	methylthiotriazine	1.00	277.24	0.08		
terbutryn	methylthiotriazine	0.03	673.86	0.12		
chlofentezin	mite growth regulators	1.00	2903.07	0.12		
hexythiazox	mite growth regulators	1.00	1772.44	0.16		
dimethomorph	morpholine	2.31	181.27	0.50		
dodemorf	morpholine	0.17	63518.05	0.03		
fenpropimorf	morpholine	1.00	2636.82	0.50		
bromoxynil	nitrile	0.87	330.77	0.88		
dichlobenil	nitrile	0.69	107.50	0.07	0.49	0.01
ioxynil	nitrile	1.39	776.71	0.38		
aclonifen	nitrophenyl ether	1.00	2536.46	0.08		
bifenox	nitrophenyl ether	1.00	2682.70	0.41		
fenolen	non polar narcosis	1.00	138.95	0.50		
indeen	non polar narcosis	1.00	288.77	0.50		
minerale olie	non polar narcosis	1.00	138.95	0.50		
naftaleen	non polar narcosis	1.39	411.42	0.16		
xyleenol	non polar narcosis	1.00	138.95	0.50		
dienochloor	organochlorine	0.03	372.76	0.03		
lindaan	organochlorine	0.17	463.14	0.01	0.44	0.00
MCPA	organochlorine	0.69	0.06	0.50	0.46	0.37
chloorfenvinfos	organophosphate	0.17	130.96	0.04	0.41	0.07
dichloorvos	organophosphate	1.39	27.00	2.88	0.48	0.01
fosethyl-aluminium	organophosphate	1.00	138.95	0.50		
fosfamidon	organophosphate	1.00	5.35	0.29		
glufosinaat-ammonium	organophosphate	1.00	51.79	0.69		
glyfosaat	organophosphate	0.69	5679.18	0.10		
glyfosaat-trimesium	organophosphate	1.00	138.95	0.50		
heptenofos	organophosphate	1.00	33.55	0.50		
mevinfos	organophosphate	1.00	25.45	1.62	0.46	0.34
pyrazofos	organophosphate	1.00	673.86	0.50		
tolclofos-methyl	organophosphate	1.00	673.86	0.16	0.11	0.00
azinfos-methyl	organothiophosphate	0.17	90.01	0.49	0.39	0.01
chloorpyrifos	organothiophosphate	0.09	5568.19	0.08	0.40	0.01
diazinon	organothiophosphate	0.02	227.58	0.12	0.41	0.01
dimethoat	organothiophosphate	0.23	10.68	0.62	0.46	0.30
ethoprofos	organothiophosphate	0.17	56.05	0.50		
etrimfos	organothiophosphate	1.00	1237.31	0.50		
fosalon	organothiophosphate	0.69	179.59	0.23		
malathion	organothiophosphate	0.46	622.71	4.85	0.41	0.09
methidathion	organothiophosphate	1.00	20.48	0.69		
omethoat	organothiophosphate	1.00	0.23	0.50		
oxy-demeton-methyl	organothiophosphate	1.00	29.22	0.50		
parathion-ethyl	organothiophosphate	0.35	553.17	0.35	0.44	0.01
pirimifos-methyl	organothiophosphate	1.00	372.76	0.16	0.43	0.02
thiometon	organothiophosphate	1.00	497.13	0.50		
triazofos	organothiophosphate	1.00	232.12	0.50		
vamidothion	organothiophosphate	1.00	1.36	0.50		
azocyclotin	organotin	1.00	138.95	0.50		
cyhexatin	organotin	1.00	1318.26	0.05		
fenbutatinoxide	organotin	4.62	758.58	0.02		
hymexazool	oxazole	1.00	2.44	0.50		
aldicarb	oxime carbamate	2.31	18.56	0.34		

Active ingredient	TMoA	kW (l/wk)	Kom	kS (l/wk)	VdW (cm/s)	VdS (cm/s)
butocarboxim	oxime carbamate	1.00	10.47	0.50		
methomyl	oxime carbamate	0.17	13.01	0.16		
oxamyl	oxime carbamate	1.00	7.20	0.61		
thiodicarb	oxime carbamate	1.00	337.73	0.23		
perazijnzuur	peroxide	1.00	0.13	0.50		
waterstofperoxide	peroxide	1.00	0.05	0.50		
broomfenoxim	phenoxy	1.00	603.57	0.50		
2,4-D	phenoxyacetic	0.17	23.52	0.59	0.45	0.07
dichloorprop	phenoxypropionic	0.03	776.71	0.50		
dichloorprop-P	phenoxypropionic	1.00	776.71	0.50		
mecoprop-P	phenoxypropionic	1.00	64.35	0.23		
dichlofenthion	phenyl organothiophosphate	1.00	21431.73	0.50		
fenitrothion	phenyl organothiophosphate	0.35	179.59	1.21	0.40	0.03
fonofos	phenyl organothiophosphate	2.31	331.13	0.12		
parathion-methyl	phenyl organothiophosphate	0.69	372.76	0.97		
dichlofluamide	phenylsulfamide	0.12	195.90	0.69		
tolylfluamide	phenylsulfamide	1.00	26.48	0.50		
chloorbromuron	phenylurea	1.00	101.32	0.12		
chloortoluron	phenylurea	1.00	53.88	0.04		
diuron	phenylurea	0.69	128.40	0.05		
isoproturon	phenylurea	0.09	113.79	0.28		
linuron	phenylurea	0.17	232.12	0.08		
metobromuron	phenylurea	1.00	53.88	0.50		
metoxuron	phenylurea	1.00	31.00	0.50		
monolinuron	phenylurea	1.00	63.10	0.08		
pencycuron	phenylurea	1.00	11519.52	0.50		
fenamifos	phosphoramidate	1.00	125.89	0.10		
acefaat	phosphoramidothioate	0.10	1.81	1.76		
tebufenpyrad	pyrazole	1.00	138.95	0.50		
deltamethrin	pyrethroid ester	0.07	167564.82	0.26		
esfenvaleraat	pyrethroid ester	1.00	1543.73	0.81		
fenpropathrin	pyrethroid ester	1.00	138.95	0.50		
fenvaleraat	pyrethroid ester	1.00	1543.73	0.14		
lambda-cyhalothrin	pyrethroid ester	1.00	32253.10	0.16		
permethrin	pyrethroid ester	0.23	13010.25	0.16		
pyrethrinen	pyrethroid ester	1.00	138.95	0.50		
pyridaat	pyridazine	1.00	67324.68	0.50		
chloridazon	pyridazinone	1.00	60.65	0.23		
clopyralid	pyridine	1.00	7.82	0.03		
fluazinam	pyridine	1.00	138.95	0.05	0.38	0.01
fluroxypyr	pyridine	1.00	9.68	0.50		
pyrifenoxy	pyridine	1.00	1311.46	0.50		
triclopyr	pyridine	1.00	16.82	0.11		
imidacloprid	pyridylmethylamine	0.06	138.95	0.02		
bupirimaat	pyrimidine	0.06	305.99	0.04		
fenarimol	pyrimidine	1.00	241.47	0.01		
pyrimethanil	pyrimidine	1.00	138.95	0.50		
fenpiclonil	pyrrole	1.00	1788.82	0.50		
alkyldimethylbenzylammoniumchloride	quaternary ammonium	1.00	138.95	0.50		
alkyldimethylethylbenzylammoniumchloride	quaternary ammonium	1.00	138.95	0.50		
didecyldimethylammoniumchloride	quaternary ammonium	1.00	138.95	0.50		
diquat dibromide	quaternary ammonium	0.69	0.00	0.50		
paraquat-dichloride	quaternary ammonium	1.00	138949.55	0.00		
quinmerac	quinolinecarboxylic acid	1.00	0.91	0.50		
dithianon	quinone	1.00	247.25	0.41		
zilverthiosulfaat	silver	1.00	0.02	0.50		
azoxystrobine	strobil	1.00	138.95	0.50		
kresoxim-methyl	strobil	1.00	138.95	0.50	0.46	0.02
amidosulfuron	sulfonylurea	1.00	138.95	0.50		
metsulfuron-methyl	sulfonylurea	1.00	24.10	0.50		
rimsulfuron	sulfonylurea	1.00	1.72	0.50		
triflusulfuron-methyl	sulfonylurea	1.00	138.95	0.50		
zwavel	sulfur	1.00	138.95	0.50		
piperonylbutoxide	synergists	1.00	51.79	0.97		
etridiazoal	thiazole	1.00	691.36	0.50		
EPTC	thiocarbamate	0.17	109.65	0.81		
prosulfocarb	thiocarbamate	1.00	8283.18	0.50		

Active ingredient	TMoA	kW (1/wk)	Kom	kS (1/wk)	VdW (cm/s)	VdS (cm/s)
tri-allaat	thiocarbamate	1.00	743.75	0.06	0.40	0.00
metamitron	triazinone	1.00	38.52	0.17	0.40	0.09
metribuzin	triazinone	0.17	49.79	0.12		
amitrol	triazole	1.00	1.57	0.24		
bitertanol	triazole	0.35	3201.38	0.12		
bentazon	unclassified	0.02	220.08	0.20	0.48	0.28
lenacil	uracil	1.00	564.19	0.50		
methabenzthiazuron	urea	1.00	256.20	0.04	0.40	0.15
furalaxyl	xylylalanine	1.00	158.25	0.50		
metalaxyl	xylylalanine	1.00	28.65	0.07		

Appendix 2 Mailing list

1. Plv. DG Milieubeheer
2. Ir. J. van der Vlist (DG Milieubeheer)
3. Dr. R. Merckelbach, Alterra, Wageningen
4. R. Kruijne, Alterra, Wageningen
5. R. Smidt, Alterra, Wageningen
6. Dr. T. Brock, Alterra, Wageningen
7. Dr. J. Deneer, Alterra, Wageningen
8. Depot Nederlandse Publikaties en Nederlandse Bibliografie
9. Directie RIVM
10. Prof. Ir. N.D. van Egmond
11. Dr. Ir. R.D. Woittiez
12. Ir. F. Langeweg
13. Drs. J.H. Canton
14. Drs. J. Wiertz
15. Drs. T. Vermeire
16. Drs. R. Wortelboer
17. Ir. M. Vonk
18. Dr. ir. J.R.M. Alkemade
19. Drs. B.J.E. ten Brink
20. Dr. T. Breure
21. Dr. Ch. Mulder
22. Dr. L Posthuma
23. Drs. T. Aldenberg
24. Dr. Ir. D. van de Meent
25. Auteur (Drs. D. de Zwart)
26. SBC / Communicatie
27. Bureau Rapportenregistratie
28. Bibliotheek RIVM
- 29-33 Bureau Rapportenbeheer
- 34-45 Reserve exemplaren (LER)