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**Development of the TOXSWA model for predicting the
behaviour of pesticides in surface water**

**Proceedings of a workshop, held on November 8, 1994 at Wageningen,
The Netherlands**

S.J.H. Crum (ed.)

J.W. Deneer (ed.)

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ABSTRACT

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In an international workshop the state of the art of the aquatic fate model TOXSWA was presented. This report gives an account of the presentations and discussions of the workshop. Model concepts of TOXSWA are explained and preliminary results of the sensitivity analysis are given. Next, the TOXSWA model is compared with the existing SLOOT.BOX model. The leaching model TRANSOL and the spray drift model IDEFICS are presented. They describe two possible entry routes and can be used to generate input data for TOXSWA. Finally, future applications of the TOXSWA model are discussed.

Keywords: aquatic fate model, entry route, leaching, risk assessment, sensitivity analysis, spray drift

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Preface

This report gives an account of the international workshop on the TOXSWA fate model, held at the DLO Winand Staring Centre, Wageningen, the Netherlands, on 8 November 1994. In seven lectures, presented by staff members of the DLO Winand Staring Centre (SC-DLO), the DLO Institute for Environmental and Agricultural Technique (IMAG-DLO, Netherlands) and the National Institute of Public Health and Environmental Protection (RIVM, Netherlands), attention was paid to aquatic fate modelling and related pesticide regulation in the Netherlands. After each lecture a lively discussion took place with the attendants (about 80 persons of about eight different countries).

Within the framework of the Multi-Year Crop Protection Plan (MJP-G) of the Dutch Government the aquatic fate model TOXSWA (TOXic substances in Surface WAters) has been developed at the DLO Winand Staring Centre. The TOXSWA model describes the behaviour of pesticides in small surface waters and its sediment as a function of time and space. Hence it is a tool to make realistic calculations of the Predicted Environmental Concentration for short-term and long-term exposure of organisms in the aquatic environment.

The TOXSWA model is compared to the SLOOT.BOX model, actually in use by the Dutch Board for the Authorization of Pesticides. The model concepts are explained, first results of a sensitivity analysis are shown and a first comparison of model results with experimental data is presented. Two important entry routes of pesticides into surface waters, spray drift and subsurface drainage, are highlighted. Finally future applications of the TOXSWA model are explained.

1 Aquatic fate models: concepts and restrictions

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Abstract

Pesticides behaviour in aquatic systems is of increasing concern to governmental agencies and industrial research has to be performed to answer questions on this item in relation to the possible registration of substances in several countries. In the Netherlands, also as part of the European Union, the item was considered of the utmost importance and therefore The Netherlands had a lead role in the development of a testing system and a decision tool for the aquatic compartment. In the Long-term Crop Protection Plan (MJP-G) the policy of The Netherlands was presented. Some remaining subjects, among which the chronic exposure of waterorganisms to pesticides, were identified as problems to be solved. Shortly, this matter will be mentioned. Also, some basic elements in the modelling process will be discussed, although briefly.

Mathematical modelling of fate and effects of substances in the aquatic environment has become an important tool in the policy of water management. Starting with simple the Biochemical Oxygen Demand and Dissolved Oxygen model of Streeter and Phelps in 1925 to the very complicated computerized models of nowadays the possibilities of models as part of the decision making process have increased enormously. An overview of the historical perspective will be presented. Because a model is always an abstraction of reality, the overlap between measurements in the environment and the results of the model calculation can never match completely. In addition, assumptions are necessary to keep the model comprehensive and within computational limits. This means directly that a model can only be used for the purpose it is developed for.

As there is, thus, a wide variety in models and model concepts a clarification will be presented about the choices leading to the present approach, in which first the SLOOT.BOX model will be treated and from there, looking at the shortcomings of this model, to the future approach: TOXSWA. A comparison of characteristics may serve as an indication of the promises of a more realistic calculation of the Predicted Environmental Concentration for long-term exposure of organisms in the aquatic environment.

2 The TOXSWA model concept

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2.1 Introduction

Since The Netherlands is a country that has many open-watercourses, water quality was an important issue when, in 1975, the Dutch Pesticide Act was extended to include an evaluation of the environmental hazards of pesticides.

Pesticides applied on agricultural fields can partly end up outside these fields. In the Netherlands many of the relatively small agricultural fields are surrounded by field ditches. Originally they have been dug to drain excess water, more recently they are also used for infiltration of water or to prevent the rapid lowering of the water table in the summer season. Next to these water management purposes the watercourses may serve as drinking water reservoirs and as sites for sport fishing. In addition, they host a variety of aquatic communities.

After 1975 preserving these aquatic communities became more important. Stricter rules for admission of pesticides have been formulated in the course of the years. One of the three actual environmental criteria that have to be met, concerns toxicity to aquatic organisms. In the risk assessment procedure the estimated exposure concentration in the field is compared to laboratory toxicity data. With the aid of laboratory tests safe concentration levels have been defined; at these levels no harmful effects can be observed for selected standard aquatic organisms. It is hoped that at these concentration levels the aquatic ecosystems as a whole are protected.

At this moment the Dutch Board for the Authorization of Pesticides uses the relatively simple SLOOT.BOX model to predict short-term exposure concentrations in field ditches. To be able to predict chronic exposure concentrations (up to 28 days) or to differentiate admission of pesticides according to regional characteristics, the Board is interested in a more detailed model, incorporating all relevant processes and other entry routes. So the goal of the TOXSWA model is to provide the Board for the Authorization of Pesticides with an improved tool for the estimation of pesticide concentrations in field ditches.

2.2 Main entry routes

Figure 2.1 shows which entry routes should be taken into account to make realistic estimations of pesticide concentrations in field ditches. When pesticides are sprayed on the crops, a certain proportion can, aided by wind, drift away and land on the water surface of neighbouring ditches. Due to water flow and wind action they may rapidly mix with the water.

Another part of the pesticide-dose applied falls on the soil surface and moves downwards with infiltrating rainwater. This can be capted by drain pipes or trenches that end up in the ditch. The rainwater can also seep into somewhat deeper layers. Water from these layers can be drained to the field ditch and in this way pesticides in the upward flowing water enter the field ditch.

Another possible entry route is surface runoff due to heavy rainfall. By surface runoff pesticides flow directly from the soil surface into the ditch. Generally speaking, this entry route is not very important in the Netherlands. A potentially important entry route may be atmospheric deposition. A considerable amount of pesticides escape to the atmosphere during application and part of this could be deposited in ditches elsewhere. Finally pesticides can also enter the ditch by flow from elsewhere. Input of pesticides into the TOXSWA field ditch system can take place by all these described entry routes. Kroes (Chapter 5) and Holterman (Chapter 6) described two entry routes in more detail. These are transport through the soil to ditches and transport by spray drift to ditches respectively. Both routes can be very important. Although about 20% of the total pesticide consumption in the Netherlands ends up in the atmosphere, this atmospheric entry route will not be treated in this report. Few is known about the wet and dry deposition of pesticides.

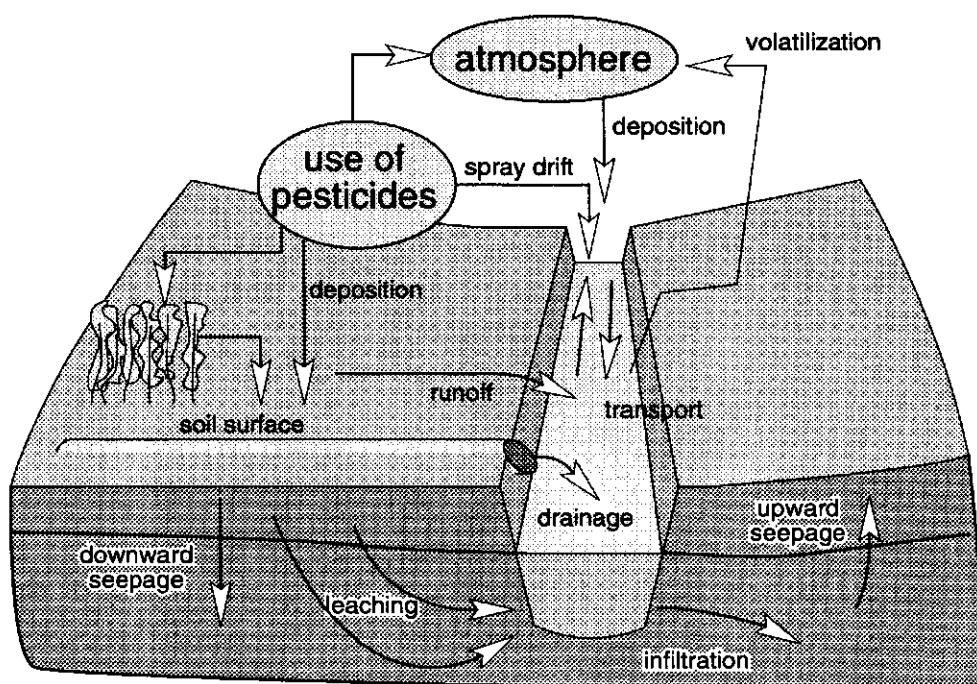


Fig. 2.1 Possible entry routes of pesticides to field ditches

2.3 Structure of field ditch system

In TOXSWA a single field ditch, so without branch-ditches, is modelled (Fig. 2.2). The dimensions of this ditch can be freely chosen as well as other characteristics like amount of suspended solids or macrophytes in the ditch. Discharge and water level can vary in time and space. Up to now calculations have been done for a constant discharge and water level to keep the interpretation of results as simple as possible. The sediment at the ditch bottom has been characterised by porosity, bulk density and organic matter content. These properties vary considerably with depth and therefore they can be introduced into the TOXSWA model as a function of depth in the sediment.

The field ditch system of TOXSWA is been divided into two sub-systems, water column and sediment respectively. In both sub-systems pesticide concentrations are calculated as a function of time and space. The division in two sub-systems is done for two reasons:

1. In each sub-system the pesticide behaviour can be described by a one-dimensional model, so it is not necessary to make a much more complicated two-dimensional model.
2. Partly different processes play a role in both sub-systems.

The sub-systems communicate with each other by exchanging water and pesticide through the wetted perimeter P of the ditch.

In the sediment sub-system the flow of water plus pesticides occurs in principle in a direction perpendicular to the wetted perimeter P , the outline of the ditch. In case of a draining ditch the flow is upward, when water infiltrates the flow is downward. In fact transport takes place in two dimensions, the z -direction downwards, and the y -direction, perpendicular to z . Moreover the transport takes place through a perimeter P , that increases with depth. E.g. perimeter P_3 is larger than perimeter P_1 (Fig. 2.3). In TOXSWA this two-dimensional transport is simplified as a one-dimensional transport in z -direction. This implies that the ditch walls are straightened, so to say, and the flow pattern is simplified to one-dimensional flow in a broadening sediment column (Fig. 2.4).

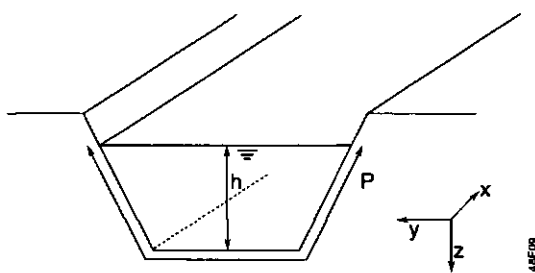
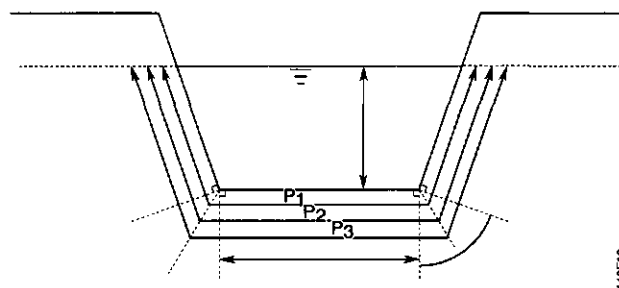


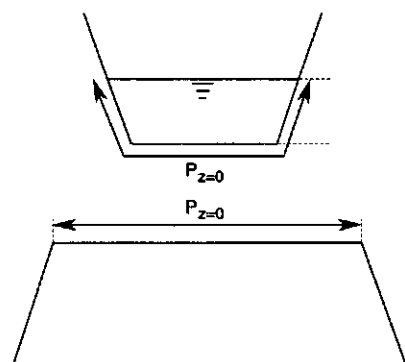
Fig. 2.2 Field ditch modelled in TOXSWA with water level h , wetted perimeter P and defined coordinate system



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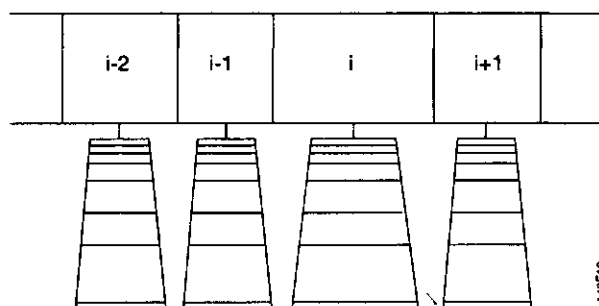
Fig. 2.3 Cross-section of a ditch and its sediment with the shape of stacked trapezia.

Next it is assumed that the exchanging perimeter does not change with a changing water level, but remains constant. In this way the sediment sub-system has constant and not varying dimensions. So water column and sediment are the two sub-systems. In the water column concentration varies with distance and this means that sediment at the beginning of the ditch is influenced by another concentration than sediment located for example halfway. This phenomenon is accounted for by defining a sediment sub-system under each node in the ditch. For the solution of the differential equation for the water column, nodes are defined in the ditch. Each node represents a certain section of the ditch (Fig. 2.5).



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Fig. 2.4 The sediment sub-system lying under an area of constant size $P_{z=0}$ through which exchange of pesticides between water column and sediment occurs



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Fig. 2.5 TOXSWA field ditch system with one water column sub-system and many different sediment sub-systems

2.4 Modelled processes in water column

The diagram of Figure 2.6 displays the modelled processes for the water column in a nutshell. Pesticides can enter the water column by spray drift deposition, surface runoff or any other type of release. The site of input may be located at one point or be evenly distributed along the ditch. The period of input may be instantaneous or the input may happen during a certain period. The pesticides immediately dissolve in the water phase and they are assumed to be ideally mixed over the depth and the width of the ditch. They are also assumed to sorb instantaneously to the suspended solids and to the macrophytes. Dissolved pesticides or pesticides sorbed to suspended solids are subject to flow. This includes advection (simply straightforward flow) and dispersion. Pesticides can escape to the air; for low concentrations this volatilization is often negligible. The sorption to macrophytes has been described by a linear relationship (Fig. 2.7).

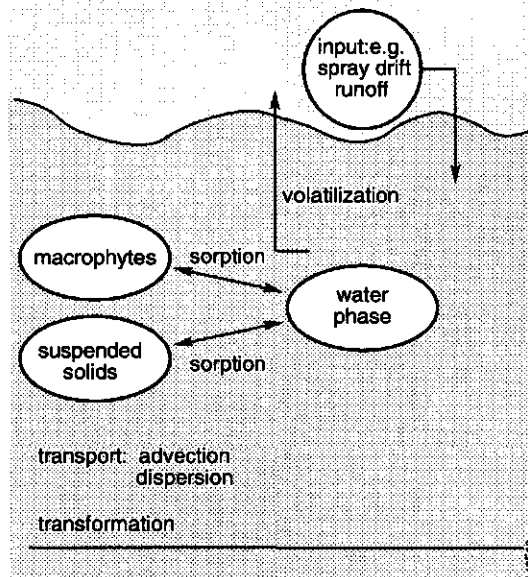


Fig. 2.6 Diagram of modelled processes in the water column.

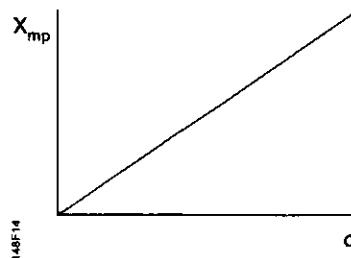


Fig. 2.7 Linear equation describing sorption to macrophytes: $X_{mp} = K_{mp} \cdot c$
 X_{mp} = ratio of the mass of pesticide sorbed divided by the mass of dry macrophytes;
 K_{mp} = distribution coefficient for pesticide between macrophytes and water;
 c = mass concentration of pesticide in the water column.

In fact very few data exist on this process in the literature. Some first calculation results show that the pesticide concentration in water may be heavily influenced by this sorption process. Therefore, we started sorption experiments in our laboratory. Deneer et al. (Chapter 3) give some preliminary results of these experiments. Sorption in soil suspensions is well studied. When you consider wide ranges of concentrations, it generally appears that, with increasing pesticide concentrations in the liquid phase, the pesticide mass sorbed to suspended solids increases proportionally less. A Freundlich equation with a Freundlich exponent smaller than 1 describes this process (Fig. 2.8).

Finally pesticides will degrade. This is described by the equation $-k \cdot c^*$; the transformation rate coefficient, k , is applied to the total mass concentration of pesticide in all its different states in the water column, c^* : dissolved or sorbed to suspended solids or to macrophytes. Transformation includes hydrolysis, biodegradation and photolysis. Metabolites, transformation products, are not considered in TOXSWA.

2.5 Modelled processes in sediment

Figure 2.9 shows the modelled processes in the sediment sub-system. Pesticides can enter the sub-system by upward seeping drainage water. From the pore water pesticides sorb to the solid bottom material. They undergo transformation and they are transported.

Three transport processes occur in the sediment: advection, diffusion and dispersion. The diffusion flux, J_{diff} , is the pesticide mass transported through a unit area and per unit time by diffusion. Diffusion is molecular transport due to the random movement and difference in number of pesticide molecules. It is proportional to the concentration gradient and is directed in opposite direction. In the sediment this flux occurs through the pore volume ϵ (Fig. 2.10).

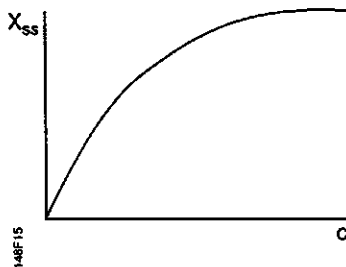


Fig. 2.8 Freundlich equation describing sorption to suspended solids: $X_{ss} = K_{F,ss} \cdot C^{n_{ss}}$
 X_{ss} = ratio of the mass of pesticide sorbed divided by the mass of dry suspended solids;
 $K_{F,ss}$ = Freundlich coefficient for sorption to suspended solids;
 c = mass concentration of pesticide in the water column;
 n_{ss} = Freundlich exponent for sorption to suspended solids

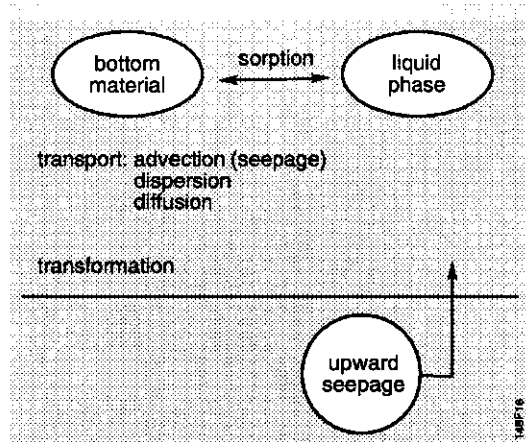


Fig. 2.9 Diagram of modelled processes in sediment

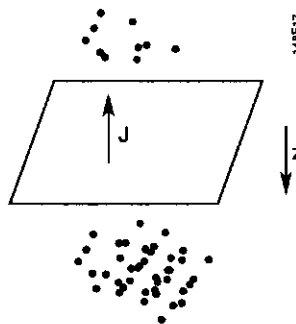


Fig. 2.10 The diffusion process: $J_{diff} = -\epsilon D \frac{\Delta c_{lb}}{\Delta z}$

J_{diff} = mass flux of pesticide by diffusion;

ϵ = volume fraction of pore water;

D = diffusion coefficient of the pesticide in the liquid phase of the sediment;

c_{lb} = mass concentration of pesticide in the liquid phase of the sediment;

z = coordinate indicating depth in the sediment

Dispersion is a process of mixing of substance caused by the advection flow. Due to different flow velocities of the pore water in small and larger pores, sharp concentration fronts become blurred. Although the process is different, the result is comparable to that of diffusion and therefore the mathematical description is analogous to the one for diffusion (Fig. 2.11). E stands for the dispersion coefficient, a measure for proportionality.

There is an instantaneous sorption equilibrium with the solid bottom material. Again this process is described with a Freundlich equation, relating the pesticide mass sorbed to the bottom material to the pesticide concentration in the pore water, the liquid phase of the ditch bottom (Fig. 2.12).

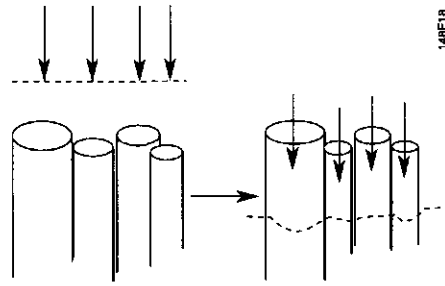


Fig. 2.11 The dispersion process: $J_{disp} = -\epsilon E \frac{\Delta c_{lb}}{\Delta z}$

J_{disp} = mass flux of pesticide by dispersion;

ϵ = volume fraction of pore water;

E = dispersion coefficient in the direction of flow;

c_{lb} = mass concentration of pesticide in the liquid phase of the sediment;

z = coordinate indicating depth in the sediment

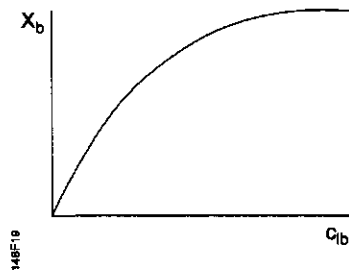


Fig. 2.12 Freundlich equation describing sorption to solid bottom material: $x_b = k_{F,b} \cdot c_{lb}^{n_b}$

X_b = ratio of the mass of pesticide sorbed divided by the mass of dry bottom material;

$K_{F,b}$ = Freundlich coefficient for sorption to bottom material;

c_{lb} = mass concentration of pesticide in the liquid phase of the sediment;

n_b = Freundlich exponent for sorption to bottom material

Transformation is again described by the equation $-k_b \cdot c_b^*$, a transformation rate coefficient, k_b times the total mass concentration in the ditch bottom, c_b^* .

Finally the transport across the interface between water column and sediment is considered. Pesticides can be transported across the interface by means of advection, (upward or downward seepage) and by diffusion, due to the different concentrations of pesticide in the liquid phase of the sediment and the water in the ditch.

In the TOXSWA model it is assumed that the concentration of suspended solids is constant in time and space. So it is assumed that resuspension or sedimentation of suspended solids with pesticides sorbed to them is negligibly small. In turbid, relatively fast-flowing ditches in windy places, which are quite common in the Netherlands, this surely does not hold true. Although, at a first sight, the constant concentration of suspended solids seems a questionable simplification, it will be shown that this assumption is quite acceptable. In fact in field ditches sorption to macrophytes is much more important. This phenomenon will be clarified with a quantified calculation example in Section 2.9.

2.6 Mass balances

With the aid of mass balances all mentioned processes are linked into one formula. Separate mass balances, in one dimension, are made for the sediment and for the water column, resulting in two differential equations. These need to be solved to obtain the total pesticide concentration as a function of time and space. Unfortunately the differential equations are too complicated to be solved analytically. Therefore, they have been solved numerically (by approximations).

2.7 Numerical solution

In the TOXSWA model a simple numerical method, the finite difference method, has been selected (Fig. 2.13). This is based on the principle that a derivative of a function, for example the concentration of pesticide as a function of location, can be approximated with the aid of two function values lying Δx meters apart. With respect to location x this can be done with a forward differential or with a backward differential.

When this principle is applied to the differential equation for the pesticide concentration in the ditch, this implies that the ditch is to be divided in sections of length Δx . In the middle of each section a node is situated, where the concentration is calculated. This concentration represents the concentration in the section.

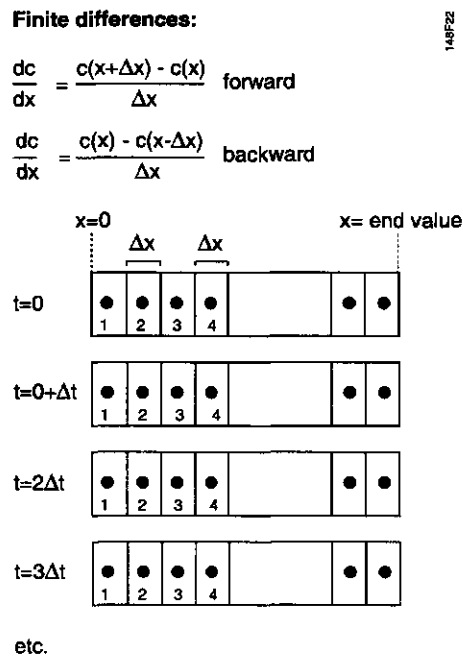


Fig. 2.13 Principles of the finite difference solution method with the approximations of function derivatives and the partitioning into small time and space steps Δt and Δx .

The conservation equation of the ditch contains also derivatives according to time, so this means that the time period also must be divided into small steps, the time steps Δt . Next the initial condition and the boundary conditions need to be known.

The initial condition gives the concentration at all nodes at time $t=0$. The boundary conditions describe the concentrations at the first and last node for all the time steps. The edges of the system are now known and it is now possible to calculate the pesticide concentration at all internal nodes. So this means that the differential equation, the conservation equation, has been solved.

Solving the differential equation by approximations means that deviations from the correct solution have been introduced. These errors depend on two points:

1. The size of the steps in time and space. Smaller Δx and Δt give smaller errors, but this means that the calculation time on the computer can become very high.
2. The type of finite difference scheme selected, this will be clarified with an example (Fig. 2.14). In case of a flow uniquely in one direction, calculation of the pesticide concentration by backward difference is executed with smaller errors than by forward difference. So it is more appropriate to calculate the concentration in node 3 with the concentration in node 2 instead of the one of node 4. When flow might take place in both directions a calculation scheme based on central differences, might be the best. That scheme is in fact a combination of a forward and backward difference scheme.

To which extent the introduced errors are still acceptable depends on the situation. In any case the errors should not accumulate; then the deviation of the true solution will become so large that unrealistic concentrations will be calculated. In general this is easily recognized. Whether smaller, not-accumulating, errors are acceptable depends on the situation (Fig. 2.15). In some cases the introduced errors might be more worrying than in other cases. The upper curves of Figure 2.15 show the concentration profile in a ditch, just after a point-type input of pesticide. Due to small

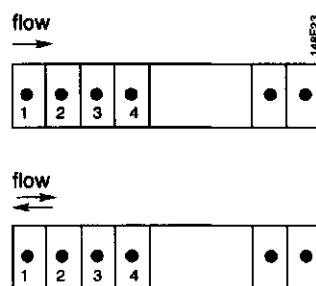


Fig. 2.14 Examples of different water flows in a ditch divided into sections with nodes 1, 2, 3, etc.

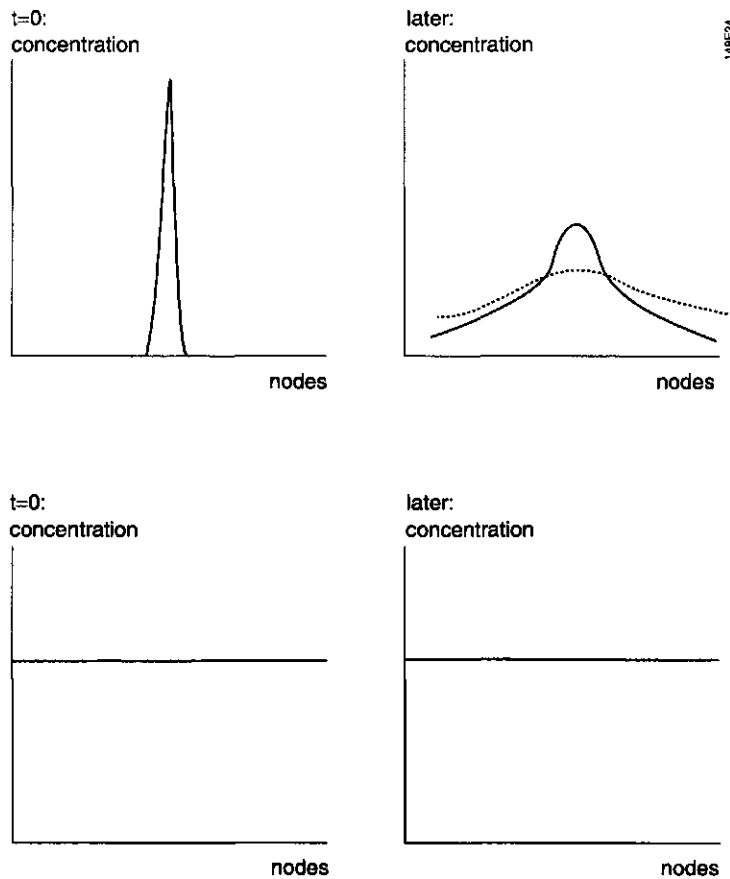


Fig. 2.15 Graphs for concentration against distance (nodes). The upper curves represent a situation with a point-type input, the lower curves with uniform spray drift deposition

flow turbulences the concentration peak will flatten in the course of time. Of course the peak may not flatten too much because of the calculation errors. This situation is represented by the dotted line. In the lower curves, a situation of uniform spray drift deposition, the tendency of the selected calculation scheme to 'mix' concentrations from neighbouring nodes, would not easily lead to wrong concentrations.

So the conclusion concerning numerical solutions is that errors are introduced by solving the two conservation equations numerically. The magnitude of the errors depends on the size of applied time and space steps as well as on the type of calculation scheme selected. In TOXSWA these factors can be freely selected. The size of time and space steps needs to be defined in the input for the model and it is possible to select calculation schemes varying over the entire range from completely backward via somewhere in between, to a completely forward scheme, or from an entirely explicit to an entirely implicit scheme. In this way TOXSWA can handle a variety of situations.

2.8 Verification

A final point in the development of the TOXSWA simulation model concerns the verification. With the aid of the mentioned generalised finite-difference calculation scheme the solution of the two conservation equations has been implemented as the computer program of TOXSWA. After having programmed the computer code it is necessary to verify that the computer program adequately represents the mathematical model, this means the mass balances. For instance checks can be made that the solution obtained with the same numerical solution scheme but halved time and space steps correspond with the solution obtained with the original time and space steps. Also the solution obtained with the numerical solution scheme, so the computer program, should correspond to an analytical solution. For some simplified situations an analytical solution of the conservation equations is possible and both solutions can then be compared.

2.9 Calculation examples

Although the verification of the computer program of TOXSWA is not yet entirely finished some preliminary calculation results are presented. Pesticide concentrations have been calculated for the following situation (Table 2.1). The field ditch is 200 m long and water flows at 10 m.d^{-1} . The water depth is 50 cm and there is an amount of 250 grams of dry macrophytes per m^2 ditch bottom, this corresponds to a moderately-grown ditch in summertime. The suspended solids concentration is 50 g.m^{-3} , a value regularly encountered in the field.

A sediment sub-system halfway the ditch, at about 110 m, has been selected. At this location the pesticide concentrations in the sediment are regarded. The sediment layer in the model is 10 cm thick and the porosity varies from 80% in the upper nodes to 40% in the lower nodes. The organic matter content varies from 8% to 0.5%. There is no seepage, so in the sediment, and across the interface between water column and sediment, pesticides are only transported by means of diffusion.

The calculations have been executed for an imaginary pesticide; an amount corresponding to 0.03 kg.ha^{-1} , for instance due to 3% drift of an application of 1 kg.ha^{-1} , is deposited on the water surface. The pesticide is characterised by a degradation time of 100 days in the water column and 75 days in the sediment. Sorption to suspended solids, macrophytes and the solid bottom material is moderately strong. In a next example the pesticide sorbs very strongly to the suspended solids, macrophytes and sediment material. This example corresponds to the insecticide chlorpyrifos. For this pesticide measurements have been executed at the DLO Winand Staring Centre. The measured values are indicated between brackets in Table 2.1.

Table 2.1 Calculation example for the TOXSWA model for a pesticide with a moderate and high (between brackets) sorption capacity

| Parameter | Value |
|--|--|
| General: | |
| length field ditch | 200 m |
| flow rate water | 10 m.d ⁻¹ |
| water depth | 0.5 m |
| biomass macrophytes | 250 g.m ⁻² |
| biomass suspended solids | 50 g.m ⁻³ |
| spray drift deposition | 0.03 kg.ha ⁻¹ |
| Sediment: | |
| sub system | located at 110 m in the ditch |
| thickness | 10 cm |
| porosity | 0.80 - 0.40 |
| organic matter content | 10 - 0.5 % |
| transport process | no seepage, only diffusion |
| Pesticide characteristics: | |
| half-life (DT ₅₀) in water | 100 days |
| half-life (DT ₅₀) in sediment | 75 days |
| sorption coefficient macrophyte (K _{mp}) | 100 dm ³ .kg ⁻¹ (2000) |
| sorption coefficient organic matter in water and sediment (K _{om}) | 10 dm ³ .kg ⁻¹ (250) |

Figure 2.16 shows the pesticide concentration in the water column and in the sediment at various points of time. In the upper part the distance in the ditch has been set out against the pesticide concentration in the water phase. Due to the deposition of 0.03 kg.ha⁻¹ on the water surface between 20 and 200 m there is a pesticide concentration of 80 µg.l⁻¹. This corresponds to 96% of the total pesticide concentration in the water column; about 4% has been sorbed to the macrophytes and less than 0.01% has been sorbed to the suspended solids. The flow of 10 m.d⁻¹ pushes the pesticide slowly out of the ditch and, because of dispersion, the concentration front flattens. In the mean time pesticide enters the sediment. This is shown in the lower graph. Here the total pesticide concentration in the sediment has been set out against depth, for sediment located at a distance of 110 m from the beginning of the ditch. At the starting time there is no pesticide in the sediment,

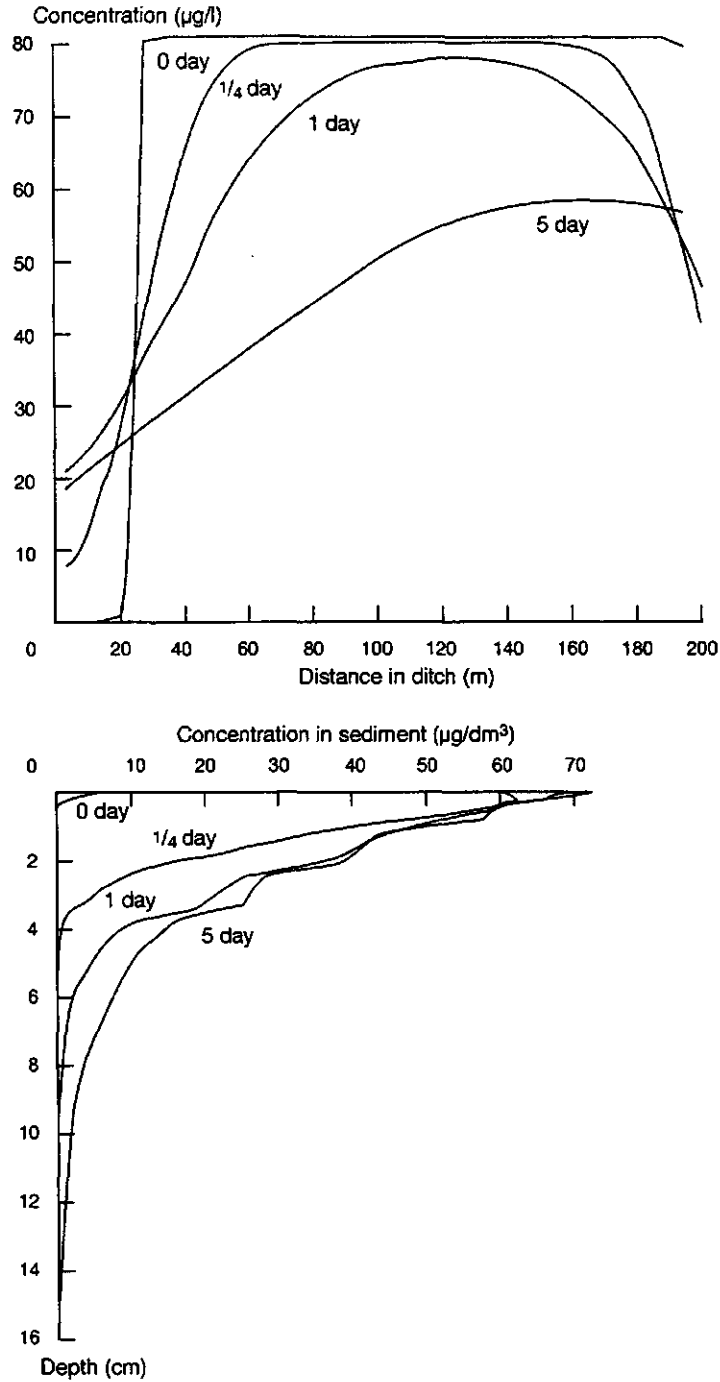


Fig. 2.16 Pesticide concentration curves calculated by TOXSWA for the example of Table 2.1 - Spray drift deposition as input

but forced by the high concentration in the water phase it diffuses inside the sediment and a concentration of about $70 \mu\text{g}\cdot\text{dm}^{-3}$ has been reached there. The next graphs of Figure 2.17 show how the situation is for a point-type input. The same initial deposition took place, but now over 7 m length at 50 m in the ditch. The peak diminishes very quickly due to dispersion and very few pesticide, only up to $4 \mu\text{g}\cdot\text{dm}^{-3}$ diffuses in sediment. The third and last graphs (Fig. 2.18) correspond to

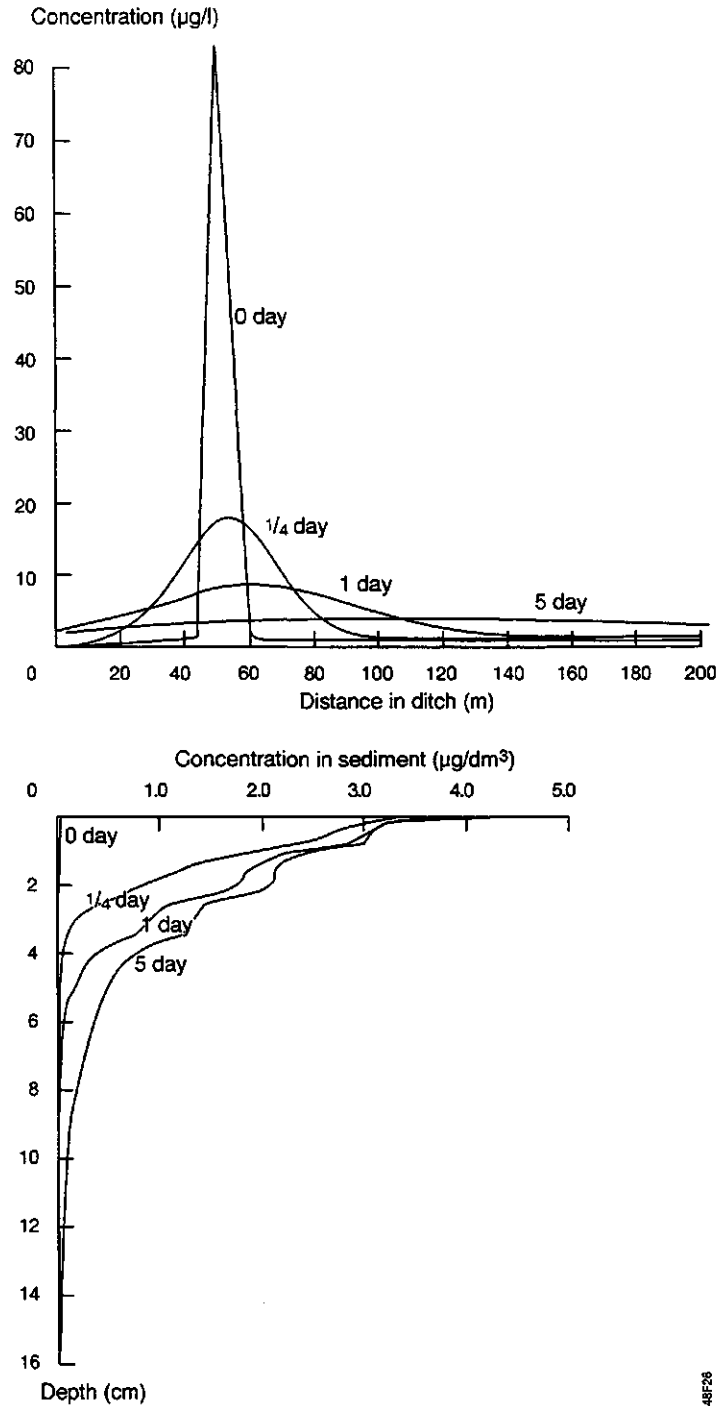


Fig. 2.17 Pesticide concentration curves calculated by TOXSWA for the example of Table 2.1 - Point type input.

the first situation of spray drift deposition between 20 and 200 m, but here it concerns the strongly sorbing pesticide chlorpyrifos. The resulting pesticide concentration in the water phase is much lower than the $80 \mu\text{g.l}^{-1}$ of the first example. Here it reaches about $46 \mu\text{g.l}^{-1}$. Indeed only about 56% of the total pesticide concentration is dissolved in the water. About 44% is sorbed to the macrophytes here and about 0.1% to the suspended solids.

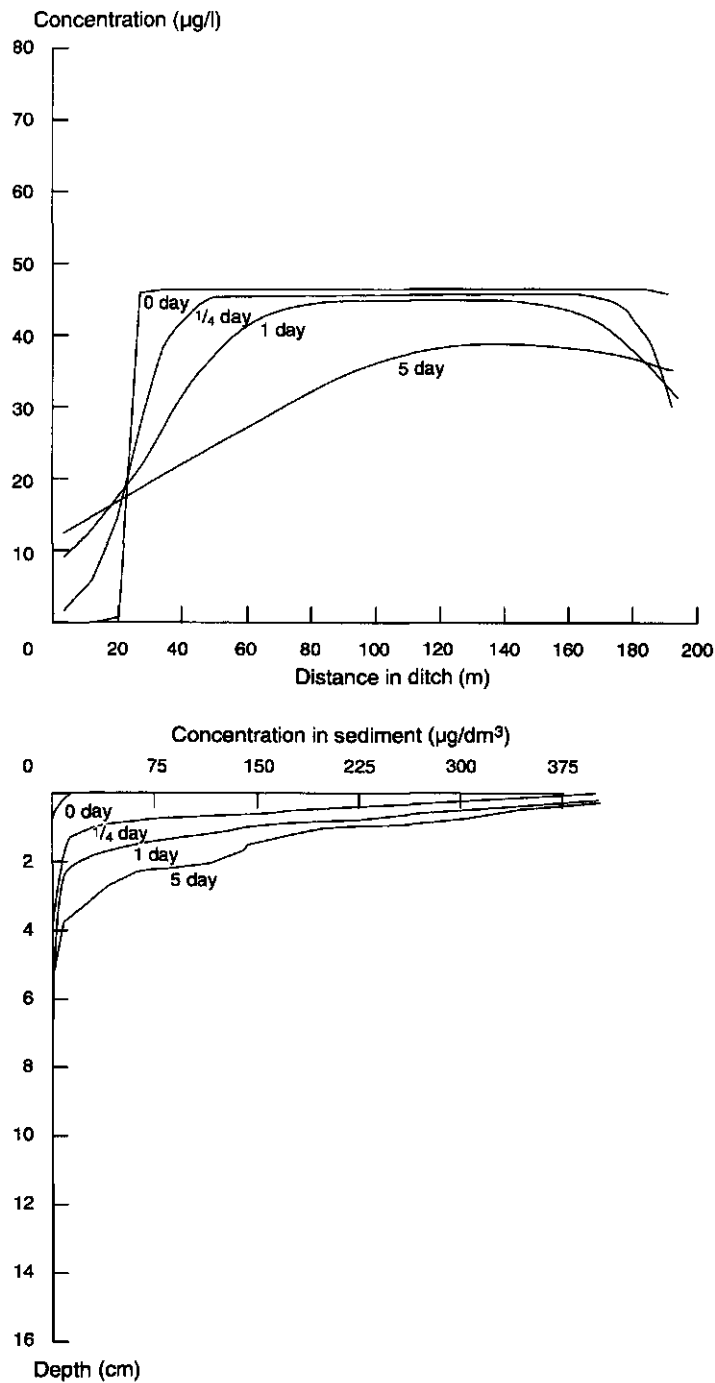


Fig. 2.18 Pesticide concentration curves calculated by TOXSWA for the example of Table 1 - Spray drift deposition as input

Due to the high sorption capacity of chlorpyrifos the total pesticide concentration in the sediment is high and it penetrates more slowly inside. The total pesticide concentration becomes up to about $400 \mu\text{g}\cdot\text{dm}^{-3}$ here.

Table 2.2 compares the calculation results for the pesticide with the moderate and with the high sorption capacity. Of the moderately sorbing pesticide, 96% of the total

amount dissolved in the water and only 4% sorbed to the macrophytes. A negligible part sorbed to the suspended solids. The situation changed for the pesticide with the high sorption capacity. Just after the application, 56% of the amount was dissolved in the water phase and 44% was sorbed to the macrophytes. Only 0.1% sorbed to the suspended solids. So, as stated before, it is indeed justified to maintain a constant concentration of suspended solids in the ditch. Even for this strongly-sorbing substance the amount sorbed to suspended solids is negligible compared to the amount sorbed to macrophytes.

Table 2.2 Comparison of results obtained with TOXSWA for the pesticides of the calculation example of Table 2.1.

| Sorption capacity | Pesticide (% of dose) in water column | | |
|---|---------------------------------------|-------------|------------------|
| | dissolved | macrophytes | suspended solids |
| Moderate $K_{mp} = 100 \text{ dm}^3 \cdot \text{kg}^{-1}$ $K_{om} = 10 \text{ dm}^3 \cdot \text{kg}^{-1}$ | 96 | 4 | <0.01 |
| High $K_{mp} = 2000 \text{ dm}^3 \cdot \text{kg}^{-1}$ $K_{om} = 250 \text{ dm}^3 \cdot \text{kg}^{-1}$ | 56 | 44 | 0.1 |

2.10 Conclusions

The TOXSWA model concept and the type of results it can deliver have been clarified here. The TOXSWA model includes the main processes that affect pesticides in field ditches and it can handle a variety of different situations. It is necessary to finalise its development now and to compare model results with field data. Van der Kolk and Adriaanse (Chapter 4) will give some first results of such a comparison, but a proper validation still has to take place. Only then it has been demonstrated that TOXSWA is a sound tool to predict pesticide concentrations in field ditches.

References

Adriaanse, P.I., 1996. *Fate of pesticides in field ditches: the TOXSWA simulation model*. Report 90. DLO Winand Staring Centre, Wageningen (in press).

Comments and questions

Question (Allen, Hoechst Schering AgrEvo): Many environmental fate-models concerning fate in soil take into account climatic variations that occur following pesticide application, the effective temperature in particular. Does TOXSWA take account of

such variations of temperature with time? If it does not, do you think that this is of concern or is this not an issue for pesticide fate in sediment-water systems?

Answer: I think, generally speaking, it is an issue. When considering for instance degradation, temperature is not necessarily the main environmental parameter since pH and the amount of light may often be more important. At the moment we have chosen to keep things simple, and we have put all of the environmental influences into one degradation rate coefficient. Its value can be freely chosen, which leaves room to incorporate environmental factors.

Question (Allen): So it would be possible in the future to develop more rate constants?

Answer: The interpretation of results becomes more complicated when using more rate constants, since the model in effect gets more complicated. Adding more detail to the model may become important when considering actual field data.

Question (Allen): With soil models much work has been done looking at the actual effect of ambient air temperature on soil temperature. Is such data available for comparing air temperature with actual ditch water temperatures? Are they affected in the same way as soil temperatures are, e.g. on a daily basis?

Answer: An appreciable difference between the effect of air temperature on soil and water temperatures is that soil is immobile, whereas water is moving all the time. Therefore in the water much more mixing will occur. At this moment not very many data are available concerning this phenomenon. According to Leeuwangh (SC-DLO), an appreciable amount of data is available about the relationship between the ambient air temperature and the water temperature in the experimental ditches of the the DLO Winand Staring Centre. The water temperature is influenced heavily by the ambient temperature. Modelling this on the basis of available data should be straightforward. The problem is, however, how to use such data. The half-life of a compound will probably be influenced, but we have only very limited information how the breakdown of a pesticide is affected by temperature. If we actually do have this information it can be used in the model.

Question (De Heer, Dutch Ministry of Agriculture, Nature Management and Fisheries): The model contains separate descriptions of the processes in the water and sediment compartments. Is it possible to use different time-steps for the water and sediment compartments when running the computer program?

Answer: This is possible, although it was not yet fully implemented in the computer program when we carried out the calculations I presented today. Implementation of this feature should not present any great difficulties.

Question (Leeuwangh, SC-DLO): You have shown us two main routes of entry for a chemical: leaching and input by spraydrift. You mentioned that a large amount of the chemical may evaporate into the atmosphere. There is of course the possibility of chemical entering the ditches through wet or dry deposition at a later time. Will it be possible to use that route of entry in the TOXSWA model as well?

Answer: For TOXSWA deposition from the atmosphere into the water compartment can be considered as a distributed input, and it is therefore no problem to include this route of entry. It is treated mathematically very similar to spraydrift. The main problem is to quantify the amount of chemical which enters the system through deposition. Only very limited data are available about this aspect of the environmental fate of pesticides.

Question (Linders, National Institute of Public Health and Environmental Protection): You showed distributions of the chemical in the sediment and in the water column. I noticed that the distribution in the water phase was quite smooth, but there were some irregularities in the sediment profile. Do you have an explanation for this?

Answer: These irregularities correspond to the way that organic matter was distributed in the sediment. We have experimental data on the change of the organic matter content of the sediment with depth, for slices of approximately one centimetre thickness. In the model the organic matter content of the sediment is input on a per millimetre basis. Therefore the organic matter content of intermediate layers was calculated by linear interpolation. Similarly, the porosity and density of intermediate layers of sediment was estimated by interpolation. This interpolation is the cause of the irregularities in the calculated curves.

Question (Hollis, Soil Survey and Land Research Centre): Did I understand correctly that it is not possible to add suspended solids as an input with drainage or run-off?

Answer: At this moment we perform calculations assuming a constant concentration of suspended solids. This implies that a rise of the water level, caused by for example run-off or drain, will automatically be accompanied by an increase of the amount of suspended solids, since the concentration has to remain constant.

Question (Hollis): But it is not possible to add more suspended solids in the input than would be present in the original drain system, thereby effectively increasing the concentration of suspended solids?

Answer: No, this is indeed not possible. If we were to allow this to happen, a mass balance for suspended solids would be necessary, similar to the mass balances for the water column and for the sediment. This would mean that a third differential equation has to be solved, and coupled to the rest of the model.

3 Sensitivity Analysis of TOXSWA

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3.1 Introduction

Developing a model like TOXSWA, one is confronted with the fact that each process takes one or more parameters to describe it. So relatively complicated models, like TOXSWA, will contain many parameters. Not all processes are always of the same importance. Therefore, it is not necessary to know all values for all parameters to the same degree of accuracy. The aim of sensitivity analysis is to provide information about the importance of involved parameters under given circumstances. This may direct the development of estimation and measurement techniques for the model parameters if they are not yet available. In this paper the current state of affairs concerning the sensitivity analysis of the TOXSWA fate model will be presented.

3.2 Methods for sensitivity analysis

There are several techniques to conduct a sensitivity analysis, which all have their advantages and their drawbacks. In this Chapter two examples of quite straightforward methods of analysis are given and compared.

The first method of discussion is the differential sensitivity analysis (DSA) technique. DSA identifies the sensitivity of a model for each parameter in the neighbourhood of some default or median value. All parameters are fixed at their default values, except the parameter to be investigated, whose value is varied slightly around the default. The sensitivity of the output of the model, the target value calculated, is given by the partial differential of this target value and the parameter. The name of the method originates from the fact that differential values or slopes are calculated and used as a measure of sensitivity. An often used related measure of sensitivity is the so called relative sensitivity. The percentage change in the output variable is related to the percentage change in the input variable. This makes it possible to compare the sensitivity of two parameters of which one has a small value while the other takes much larger values. The main advantage of DSA is that it is very simple to carry out. Its main drawback is that it provides information only about the sensitivity of the model in the immediate vicinity of default values.

A less simple method is the response surface analysis (RSA) technique. Within RSA each parameter is assumed to span a certain frequency distribution, and may be more or less characterized by picking some values from this frequency distribution,

for example a minimum, a maximum and a median value. We picked three values for each parameter and the model output was calculated for all possible combinations of these values. All of these output values together span a surface in space, the response-surface, hence the name of the method. Further a simpler model is constructed by which the same response-surface is described. In its simplest form this simpler meta-model consists of a linear model in all parameters, for which the coefficients can be estimated by simple linear regression. These slopes are, of course, the mean sensitivity for that parameter over its entire operating range. Less simple quadratic regression schemes can be used, which account for non-linearity and interactions between parameters. But the basic technique stays the same: least-squares regression.

The main advantage of the RSA method is that it is not limited to the vicinity of some default values. It is aimed towards obtaining a best overall sensitivity for the entire operating range of the variable. Moreover, the study of interactions between parameters is possible. Drawbacks are that a lot of simulation runs are needed to get all possible combinations of parameter values. If for each of the N parameters 3 values are adopted, 3 to the power N simulations are needed. Another drawback is that the output value studied may be time or position dependent. For TOXSWA this would mean that a time and a position in the ditch have to be chosen for which some output variable will be calculated, for example the concentration of the pesticide in the water at that location. Summarising, the response-surface analysis has somewhat more capabilities, but it is also somewhat more complex than differential sensitivity analysis.

3.3 Results of sensitivity analysis

Starting sensitivity analysis, it is always a good idea to start simple, and this is exactly what has been done. In this section some results are given of a relatively simple differential analysis in a very simple ditch. These results are limited but useful to select parameters which can be more fully investigated in a response-surface analysis which will be carried out at a later stage.

The hypothetical ditch we use is very similar to the ditch described by Adriaanse (Chapter 2). This ditch had a length of 200 meters, a width of 1.65 meters and a depth of half a meter. All default values for the remaining parameters are given in Table 3.1. At the time these first calculations were carried out, the implementation of processes occurring in the sediment had not been finished yet. We therefore assumed that no exchange of the pesticide between water and the sediment would occur. Moreover, it has been assumed that no seepage takes place. Water flowing into the ditch at the upper side does not contain pesticides.

Table 3.1 Default values for the parameters used for the differential sensitivity analysis

| Parameter | Default value |
|---------------------------------------|---|
| Molecular mass | 300 Dalton (100-400) |
| Lipophilicity | log P= 3.00 (1.00-5.00) |
| DT ₅₀ | 50 days (2-100) |
| Suspended solids | 50 mg.l ⁻¹ (10-100) |
| Sorption coefficient suspended solids | 400 dm ³ .kg ⁻¹ (1-115000) |
| Biomass macrophytes | 250 g.m ⁻² (50-500) |
| Sorption coefficient macrophytes | 0.2 m ³ .kg ⁻¹ (0.05-2) |
| Henry coefficient | 4.10 ⁻³ (4.10 ⁻⁵ - 4.10 ⁻²) |
| Dispersion coefficient | 10.10 ³ m ² .d ⁻¹ (4.10 ³ -25.10 ³) |
| Flow velocity water | 1000 m.d ⁻¹ |

The output variable that has been used for the differential sensitivity analysis is the concentration of the pesticide in the water compartment at the exact middle of the ditch. The sensitivity of the different parameters we found after differential sensitivity analysis have been given in Table 3.2.

Table 3.2. Results of the least and most sensitive parameters after differential sensitivity analysis

| Least sensitive parameters | Most sensitive parameters |
|--|-------------------------------------|
| transformation rate in water | flow velocity |
| concentration suspended solids | dispersion coefficient |
| sorption coefficient suspended solids | biomass of macrophytes |
| transport coefficient liquid and gas phase | sorption coefficient of macrophytes |
| | Henry coefficient |

In Figure 3.1 the influence of the transformation rate in water on the concentration of the pesticide is shown. The transformation rate in water is an example of a parameter with a lower sensitivity found under those circumstances. In the figure two curves are given, one for the highest DT₅₀, and one for the lowest DT₅₀ considered. It is obvious that the two curves are very similar, although the DT₅₀ values differ fifty-fold. Apparently the transformation rate in water is not a very important parameter, which seems rather surprising. The explanation of this phenomenon is found in the flow velocity of the ditch. The flow velocity was set at 1000 m.d⁻¹. So all pesticide has been washed out of the ditch in approximately four hours. Under these circumstances it is not surprising that a process which takes at least days does not show up in the calculation results. When using TOXSWA for longer term calculations in more stagnant water, however transformation reactions become more important.

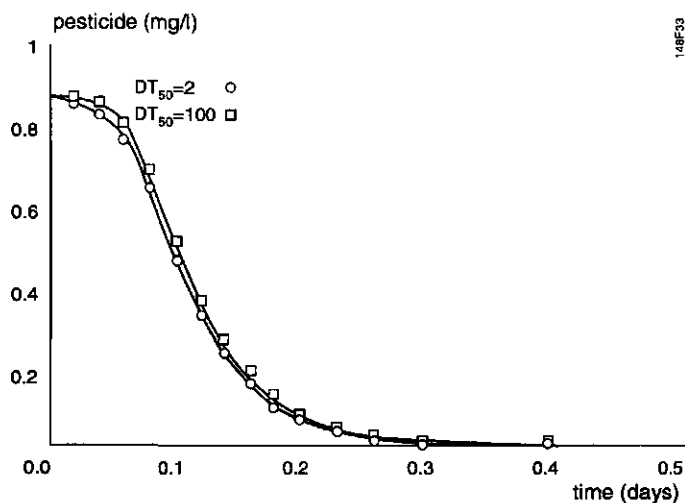


Fig. 3.1 The concentration of a pesticide in the middle (100 m) of the standard ditch. Calculation results with a transformation rate (DT_{50}) of 2 and 100 days respectively

In Figure 3.2 the influence of the sorption coefficient of a pesticide to macrophytes is shown. This sorption coefficient was found to be one of the most sensitive parameters under the given circumstances. In the figure two curves are given, one for the lowest ($0.05 \text{ m}^3 \cdot \text{kg}^{-1}$) and one for highest ($2 \text{ m}^3 \cdot \text{kg}^{-1}$) sorption coefficient considered. A high sorption coefficient for macrophytes leads to a decrease of the pesticide concentration in the water compartment shortly after application. It is obvious that retardation of the pesticide occurs, since the pesticide concentration after some hours is higher for the system where a high sorption coefficient is assumed.

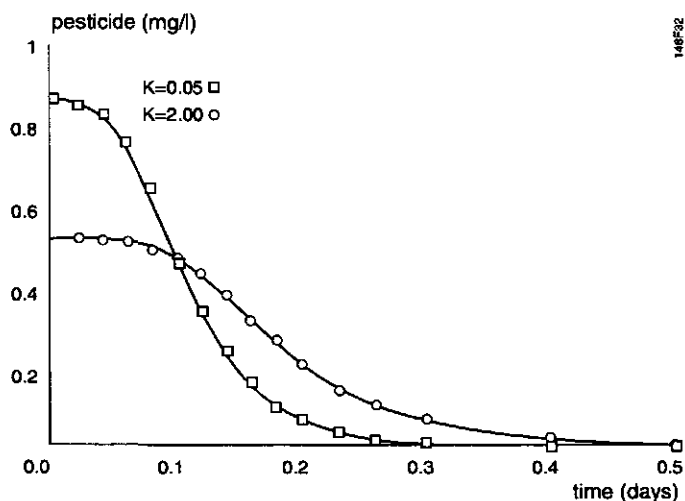


Fig. 3.2 The concentration of a pesticide in the middle (100 m) of the standard ditch. Calculation results with sorption coefficients of 0.05 and $2 \text{ m}^3 \cdot \text{kg}^{-1}$ respectively

3.4 Sorption to macrophytes

As mentioned before sensitivity analysis can be used as a guide in the development of estimation and measurement techniques. As a result of the sensitivity analysis the least and most sensitive parameters are shown in Table 3.2. For the most sensitive parameters in this list, most values can be estimated or at least some information is available. Sorption to macrophytes, however, is a process which has not been studied very much. Only little information can be found in the literature about this process, and most of these studies deal with duckweed. Since we can expect differences in the amounts of macrophytes between ditches, the amount of sorbed material can also differ significantly. Together with the lack of information about the process this was the motive to try to establish a predictive relationship for the sorption of pesticides to macrophytes.

The method used for sorption studies of pesticides to macrophytes was quite straightforward. Macrophytes were immersed in a solution of the pesticide during 24 hours, and the concentration of the chemical was determined in both the plant material and in water. This was repeated for several concentrations of the pesticide. The resulting data are fitted to a Freundlich isotherm ($X = k \cdot c^n$). A typical plot is shown in Figure 3.3, where the sorption of the herbicide linuron to *Elodea nuttallii* has been depicted. Obviously the Freundlich isotherm describes the data quite well.

In Table 3.3 the results of the sorption studies with three different pesticides and three different macrophytes have been given. In this table the calculated Freundlich sorption coefficient and exponent are presented for all possible combinations. It is obvious that the compounds tested differ widely in their sorption behaviour, since both the coefficient and the exponent of the Freundlich isotherms are quite different. The Freundlich exponent for the sorption of chlorpyrifos and ethopofos onto macrophytes is found to be close to the value 1. So the sorption of these pesticides onto macrophytes could be described relatively good by a linear relationship. For the sorption of linuron onto macrophytes the Freundlich exponent ranged from 0.53 to 0.67. This low Freundlich exponent implicates that the calculated sorption coefficients depend on the linuron concentration very much.

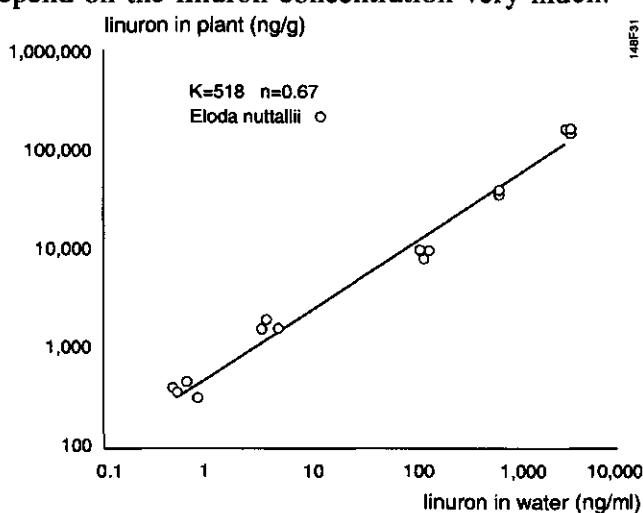


Fig. 3.3 An example of an Freundlich isotherm for the sorption of linuron by the macrophyte *Elodea nuttallii*

Table 3.3. Results of the calculated Freundlich sorption coefficients (in $dm^3.kg^{-1}$) and their related exponents (between brackets) for three different pesticides and three different macrophytes

| Pesticide | Macrophyte | | |
|--------------|-------------------------|--------------------|-------------------------|
| | <i>Elodea nuttallii</i> | <i>Lemna gibba</i> | <i>Chara globularis</i> |
| Linuron | 518 (0.67) | 1023 (0.54) | 831 (0.53) |
| Chlorpyrifos | 1826 (1.02) | 2003 (1.02) | 2175 (1.00) |
| Ethoprofos | 22 (0.94) | 38 (0.81) | 12 (0.98) |

The goal of these experiments is to look whether there is a relationship between sorption coefficients and some other, readily available physico-chemical quantity like for example the octanol-water partition coefficient. If this is the case the relatively important parameter of the macrophyte sorption could be estimated for other compounds.

3.5 Conclusions

Preliminary results of differential sensitivity analysis result in five most sensitive parameters (Table 3.2). These are flow velocity, dispersion coefficient, Henry coefficient, biomass of macrophytes and the sorption coefficient of macrophytes. It is rather surprising that the transformation rate of pesticides in water appears to be one of the least sensitive parameters. This however can be explained by the relatively high flow velocity in the ditch.

First experimental results indicate that no simple relationship exists between sorption coefficients onto macrophytes and other physico-chemical quantities (e.g., octanol-water partition coefficient). This means that up to now for each pesticide sorption to macrophytes should be measured in the laboratory.

Comments and questions

Question (Van Wensem, Technical Soil Protection Committee): Both you and Mrs. Adriaanse told us that the amount of macrophytes in the ditches is very important for the fate of pesticides. Did you consider the role of phyto- and zooplankton?

Answer: Not yet, this has not been incorporated into the model yet.

Question (Van Wensem): The ditches do contain a lot of plankton, and this may play a role comparable to that of macrophytes. Especially when considering that the surface area of the plankton present may be quite large.

Answer: The biomass of large plants is much larger than that of the plankton present. If, however, the surface area is the determining factor for sorption, then the amount of plankton present could indeed be an important parameter. At this moment it is not yet clear whether the mass or the total surface area of the plant material is the best predictor.

Question (Boekhold, Dutch Ministry of Housing, Physical Planning and the Environment): Could you please tell us whether there is a difference between the sorption coefficients of the pesticides to macrophytes which you presented, compared to organic matter?

Answer: The problem is that the sorption coefficients in macrophytes are expressed on a dry weight basis, whereas the sorption coefficients in organic matter are expressed on the basis of organic matter content. They are therefore not directly comparable. We are still trying to find out which parameter at a very low level best describes the actual process of sorption.

Question (Aalderink, Wageningen Agricultural University): You limited your sensitivity analysis to the model parameters. I can imagine that this type of model is also rather sensitive to initial conditions and maybe also to boundary conditions. I expect the model to be especially sensitive to the initial state of the sediment, with respect to the organic matter content of the sediment and with respect to initial concentrations of pollutants. Did you pay any attention to this?

Answer: We will be looking more closely into this when the implementation of the model into a computer program is finished. At the time I did my calculations most of the processes in the bottom layer were not implemented yet. Once those are in the computer program we will also look at things like initial and boundary conditions.

Question (Bügel Mogensen, National Environmental Research Institute, Denmark): I didn't really catch whether there was a difference in sorption capacity between the different types of macrophytes. Not only the mass, but also the surface area of the macrophytes may be an important factor.

Answer: At this point in time we don't yet have a suitable means of measuring the actual surface area of macrophytes, but hopefully we will be able to look into this parameter in the future.

4 Microcosm and mesocosm studies to compare the applicability of the TOXSWA and SLOOT.BOX fate models

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4.1 Introduction

In the registration procedure, pesticides are evaluated with respect to their possible adverse effects on aquatic organisms. Therefore not only their toxic properties need to be regarded, but also the exposure concentration in the surface water system. For predicting this concentration, mathematical models are useful tools.

In the registration procedure in the Netherlands, the SLOOT.BOX aquatic fate model is used to calculate exposure concentrations leading to short term effects on aquatic organisms. This model is less applicable to predict chronic exposure concentrations. The TOXSWA aquatic fate model is more suitable to predict long term concentrations. Therefore this model has been mentioned in the recently changed registration procedure in the Netherlands to calculate exposure concentrations leading to semi-chronic and chronic effects.

Before TOXSWA can be used for registration purposes it is necessary to have insight in the predictive value of the calculated concentrations. Therefore this model needs to be validated. To make a start with this validation, we compared model results of TOXSWA with experimental data. Results of the SLOOT.BOX model are regarded as well in order to establish the difference in output of both models.

4.2 Materials and methods

Models

TOXSWA (Adriaanse, 1996) and SLOOT.BOX (Linders et al., 1990) both simulate the fate of pesticides in a field ditch after one or more applications of the pesticides to the surface water system. The differences between both models have been summarized in Table 4.1.

The most important difference between TOXSWA and SLOOT.BOX is that SLOOT.BOX considers the field ditch as one ideally mixed compartment, whereas in TOXSWA the ditch is divided in a number of compartments. This concept allows TOXSWA to calculate the concentration not only as a function of time, but also as a function of space. This implies as well that TOXSWA can calculate the pesticide

concentration in the ditch not only after diffusive inputs of pesticides (e.g. spray-drift), but also after inputs at one specific point in the ditch (e.g. drain discharge). Another difference between the TOXSWA and SLOOT.BOX model concept is that in TOXSWA more adsorbing materials are included than in SLOOT.BOX, such as macrophytes and sediment.

Table 4.1 Comparison between the aquatic fate models TOXSWA and SLOOT.BOX

| | TOXSWA | SLOOT.BOX |
|--------------------------------------|--|--|
| Entry-routes | <ul style="list-style-type: none"> - spray-drift - atmospheric deposition - soil routes <ul style="list-style-type: none"> • runoff • drainage | <ul style="list-style-type: none"> - spray-drift - atmospheric deposition |
| Output | <ul style="list-style-type: none"> - concentration in <ul style="list-style-type: none"> • water • suspended solids • macrophytes • sediment - function of time and space | <ul style="list-style-type: none"> - concentration in <ul style="list-style-type: none"> • water - function of time |
| Processes in water | <ul style="list-style-type: none"> - volatilization - transformation - sorption to <ul style="list-style-type: none"> • suspended solids • macrophytes | <ul style="list-style-type: none"> - volatilization - transformation - sorption to <ul style="list-style-type: none"> • suspended solids |
| Transport between water and sediment | <ul style="list-style-type: none"> - advection - diffusion | <ul style="list-style-type: none"> - sedimentation/resuspension <ul style="list-style-type: none"> • net sedimentation for short term exposure conc. • equilibrium between sedimentation and resuspension for long term exposure conc. |
| Processes in sediment | <ul style="list-style-type: none"> - sorption to bottom material - transformation | |

Experiments

Model results have been compared with measured concentrations from four experiments.

I chlorpyrifos in microcosms without macrophytes

II chlorpyrifos in microcosms with macrophytes

Experiment I and II were carried out simultaneously in indoor microcosms. The microcosms consisted of a glass aquarium in which a 0.1 m sediment-layer and a 0.5 m column of overlying water were introduced. The fate of chlorpyrifos was studied in two microcosms devoid of macrophytes (experiment I) and two microcosms dominated by the macrophyte *Elodea nuttallii* (experiment II) (Brock et al., 1992). A single dose of chlorpyrifos was applied to the systems simulating spray-drift deposition. The microcosms were kept under constant climatic conditions.

III chlorpyrifos in mesocosms with macrophytes

In this experiment the fate of chlorpyrifos was studied in two outdoor stagnant ditches. In the ditches (length 40 m, width of the water surface approximately 3.4 m) a sediment layer of 0.25 m and a 0.5 m column of overlying water were introduced. The ditches were dominated by submerged macrophytes (e.g., *Elodea nuttallii*, *Chara* spp. and *Ranunculus circinatus*). A single dose of chlorpyrifos was applied to the ditches simulating spray-drift (Leeuwangh et al., 1994).

IV linuron in microcosms with macrophytes

The linuron experiment was carried out in the same indoor microcosms as those described in the experiments I and II. This experiment was set up to study the chronic effect of the herbicide linuron. Therefore the linuron concentration was kept at a constant level during a month time. After that period the fate of linuron was studied in two microcosms (Aalderink & Crum, 1994).

Properties of the insecticide chlorpyrifos and the herbicide linuron were used as input parameters for the two models (Table 4.2). The most important characteristics of the test systems during the four experiments are given in Table 4.3. The suspended solids concentration had not been measured in the test systems and therefore the standard value of 15 g.m^{-3} used in the SLOOT.BOX model has been used as input parameter for both models. During the SLOOT.BOX simulations the standard sedimentation velocity of 3 m.d^{-1} was used.

Table 4.2 Characteristics of the two pesticides used in the experiments

| | Chlorpyrifos | Linuron |
|---|--------------|---------|
| Solubility (mg.l^{-1}) | 0.7 | 81.0 |
| Vapour pressure (Pa) | 0.002 | 0.0025 |
| Sorption coefficient to sediment based at organic matter content ($\text{dm}^3.\text{kg}^{-1}$) | 234.0 | 4.6 |
| Sorption coefficient to macrophytes based at dry weight of macrophytes ($\text{dm}^3.\text{kg}^{-1}$) | 2000 | 200 |
| Transformation coefficient in water as DT_{50} (d) | 75 | 40 |
| Transformation coefficient in sediment as DT_{50} (d) | 115 | 55 |

Table 4.3 Characteristics of the test systems in the four experiments

| | I | II | III | IV |
|---|-------|-------|-------|-------|
| Initial concentration (g.m ⁻³) | 0.035 | 0.035 | 0.043 | 0.015 |
| Water surface area (m ²) | 1.21 | 1.21 | 135.0 | 1.21 |
| Sediment surface area (m ²) | 1.21 | 1.21 | 66.0 | 1.21 |
| Water depth (m) | 0.50 | 0.50 | 0.52 | 0.50 |
| Macrophyte concentration (g.m ⁻²) | 0 | 407 | 529 | 133 |
| Suspended solids concentration (g.m ⁻³) | 15 | 15 | 15 | 15 |
| Thickness sediment layer (m) | 0.1 | 0.1 | 0.25 | 0.1 |
| Average organic matter content in sediment (%) | 2.8 | 2.8 | 2.0 | 3.9 |

4.3 Results and discussion

Simulations were carried out with both the TOXSWA and the SLOOT.BOX model for the described experiments. In Figure 4.1a the simulation results of the chlorpyrifos experiment in the microcosms with no macrophytes and the measured concentrations are shown. Both TOXSWA and SLOOT.BOX gave an overestimation of the measured concentration. All input parameters of the models were determined with great accuracy, except the concentration of suspended solids in the water layer and the sedimentation velocity. In the SLOOT.BOX model, in which suspended solids are the only adsorbing material, model results appeared to be very sensitive for these input parameters. In TOXSWA, pesticides can sorb to the sediment as well, and therefore the TOXSWA simulation results correspond better to the measured concentrations.

In Figure 4.1b the simulation results of the chlorpyrifos experiment in the microcosms with macrophytes (*Elodea nuttallii*) and the measured concentrations are presented. The TOXSWA simulation results appear to start at a concentration less than 40 % of the dose applied. This is due to the fact that TOXSWA assumes instantaneous adsorption equilibria. Therefore immediately after application, a large part of the chlorpyrifos is adsorbed to the macrophytes. SLOOT.BOX simulation results do not correspond very well with the measured concentrations because this model does not include sorption to macrophytes. This sorption appeared to be of major importance in this experiment.

In Figure 4.1c the simulation results of the chlorpyrifos experiment in the outdoor mesocosms and the measured concentrations are shown. The results of this experiment resemble very much to the results of the experiment in the indoor microcosms with macrophytes, although other macrophyte species are present in the mesocosms.

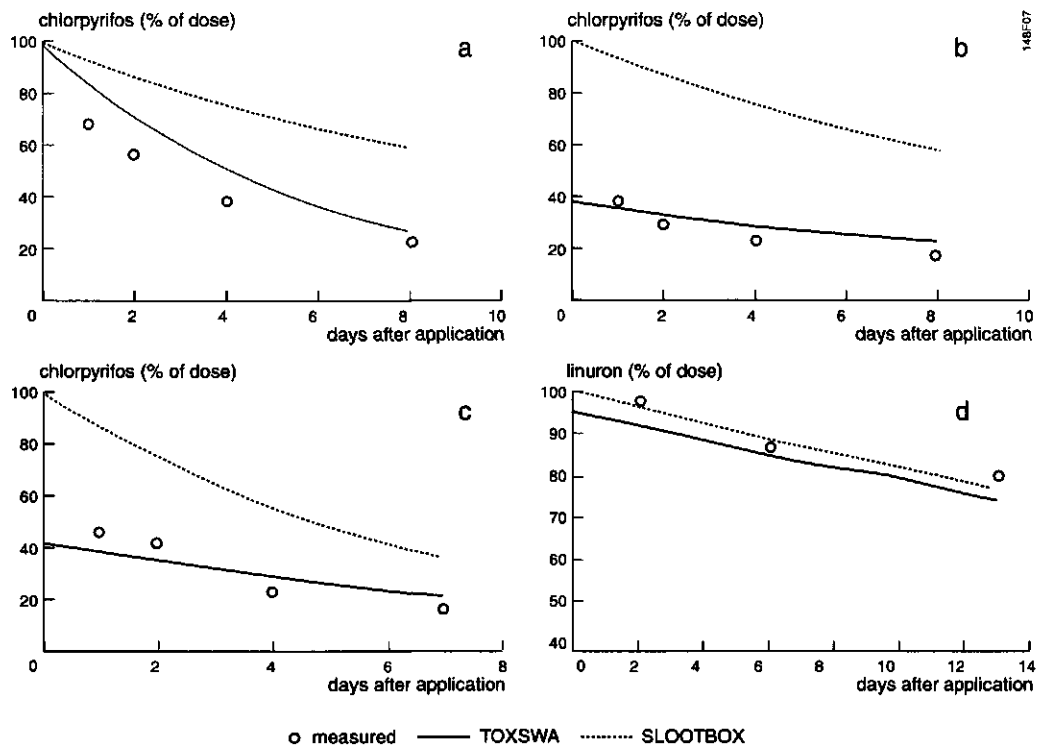


Fig. 4.1 Measured and simulated pesticide concentrations in the test systems; a: chlorpyrifos in microcosms without macrophytes; b: chlorpyrifos in microcosms with macrophytes; c: chlorpyrifos in mesocosms with macrophytes; d: linuron in microcosms with macrophytes.

From sorption experiments to macrophytes of three different species it can be concluded that the sorption coefficient of chlorpyrifos does not differ much between macrophyte species (Van Huffelen, 1993).

In Figure 4.1d the simulation results of the linuron experiment in the microcosms with macrophytes (*Elodea nuttallii*) and the measured concentrations are shown. The simulation results of both models correspond rather well with the measured concentrations. Linuron concentrations calculated by TOXSWA are somewhat underestimated. This is probably due to the fact that the sorption coefficient to macrophytes has been estimated too high. Linuron is a herbicide and application affects the macrophyte biomass. Therefore this sorption coefficient is very difficult to measure. Moreover the macrophytes probably have accumulated linuron during the time that linuron concentration was kept at a constant level. This time-dependent sorption is not included in the TOXSWA model.

4.4 Conclusions

A comparison of the model concepts of TOXSWA and SLOOT.BOX shows that the model concept of TOXSWA is more extensive and therefore TOXSWA can be applied in more situations than SLOOT.BOX.

Results of model simulations show that both TOXSWA and SLOOT.BOX give good predictions of the concentration in water of linuron, a herbicide with low sorption capacity. Simulation results for chlorpyrifos, an insecticide with high sorption capacity, show that TOXSWA calculations correspond better with the measured concentrations. This is mainly due to sorption of chlorpyrifos to macrophytes. This leads to the conclusion that sorption to macrophytes needs to be included in aquatic fate models to give good predictions of exposure concentrations of pesticides with high sorption capacity.

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Comments and questions

Question (Schäfer, Bayer): Did you have to fit some of your model parameters to get the description which you showed us? For example a resistance parameter is used for the transfer from water into air, which was probably not measured. Did you actually measure such values, or did you adjust their values to give an optimal fit of your model to experimental data?

Answer: We did not use any 'fitting'. Parameters for which values were not known and which could not be determined experimentally were estimated. The resistance for volatilization for example was calculated from the diffusion coefficient of the chemical, which in turn was estimated on the basis of the molecular weight of the compound.

Question (Van der Schaaf, ProAgro): What kind of application method did you use for the indoor experiments?

Answer: The application of the pesticide was carried out by spraying the chemical on top of the water surface, which is comparable to the application method used for the outdoor systems.

Question (Van der Schaaf): Is this comparable to spray drift? Especially for poorly soluble compounds the method of application can have large effects on the dispersion of the chemical in the system.

Answer: Of course the distance from the site of application also is important. Since our systems were quite small, the method of application is comparable to the effect of spray drift relatively close to the system. Our goal in these experiments was to get an homogeneous deposition of the chemical on the surface of the water.

Question (Van der Linden, National Institute of Public Health and Environmental Protection): Have the starting concentrations in the microcosms and mesocosms been measured? I didn't see them mentioned on your slides.

Answer: On the slides all concentrations were expressed as a fraction of the starting concentration. For chlorpyrifos the starting concentration was approximately $0.35 \mu\text{g}\cdot\text{l}^{-1}$, and for linuron it was $0.15 \mu\text{g}\cdot\text{l}^{-1}$. The 100% in the slides corresponds to 100% of these measured concentrations.

5 TRANSOL to calculate input for TOXSWA: Transport through the soil to ditches

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5.1 Introduction

One of the entry routes of TOXSWA is the route along which a TOXSWA ditch receives water and pesticides from a neighbouring soil. The TRANSOL model can be used to simulate this route or to be more specific: to calculate the transport from the soil surface through the soil to the ditch. TRANSOL (TRANSport of SOLutes) is a dynamic simulation model which was developed at the DLO Winand Staring Centre to analyse the leaching of solutes like pesticides from the soil surface to groundwater and surface waters. This paper will discuss the schematization of the unsaturated and saturated soil system as it should be applied when using the TRANSOL model to simulate solute discharge to a surface water system. A brief description of the concept of the TRANSOL model will be given followed by some simulation results for the leaching towards groundwater and surface water. Leaching towards groundwater is presented for a standard dataset and for chloride transport in a soil column. Leaching towards the surface waters is presented for an application of the herbicide chloridazon on a bulb field.

5.2 Schematization

The entry route that is simulated with TRANSOL starts with a pesticide application at the soil surface. A precipitation excess forces a downward transport of water and pesticides into the unsaturated and the saturated parts of the soil and towards the neighbouring ditch. The TRANSOL model simulates this entry route by means of transport and processes in a schematized one-dimensional soil column. With this one-dimensional column a mainly two-dimensional groundwater flow to ditches is simulated using the following schematization. Groundwater flow can be divided into a local and a regional flow (Figure 5.1). The regional flow is usually not important for the transport of pesticides from the soil surface to a neighbouring ditch. The local flow however is the essential transport route towards the ditch. To catch this local flow the position of the model profile should be such that it takes account for most of the streamlines that describe the local flow. In the model this is achieved by using an approach formulated by the Dutch hydrologist Ernst (1962), who related the depth of the local flow to the distance between drainage systems or ditches.

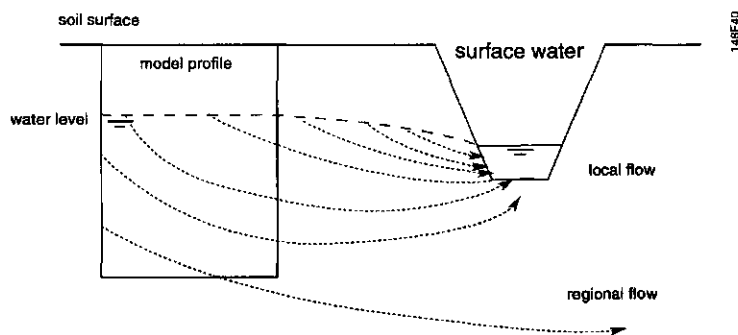


Fig. 5.1 A groundwater system with local and regional flow and the use of a one-dimensional model profile to simulate 2-dimensional flow

He proved that the depth of the local flow stays within 1/4 of the drain distance. If for example the distance between ditches is 20 meter; the position of the lower boundary should be at 5 meter below the soil surface. In this way the model profile covers 90 % of the local flow.

For a situation with a precipitation excess Figure 5.2 shows the main fluxes of a model profile. Boundary conditions at the top of the profile are precipitation and evaporation. Groundwater will be recharged at the groundwater level. At the bottom of the profile water leaches to the regional groundwater flow. The soil profile is divided into a finite number of model layers. The lateral drainage flux is divided proportional to the thickness of the model layers (Figure 5.2 and Figure 5.3 left). This results in a linear decrease of the vertical percolation flux with depth (Fig. 5.3 middle). The residence time of this percolating water is a function of flux and depth and shows a logarithmic increase with depth (Fig. 5.3 right). This implies that water leaving lower parts of the model profile will have a larger residence time, which means: more time to undergo processes like sorption and degradation. The logarithmic relation between residence time variation and depth in the soil profile is similar to the expressions given by Ernst (1973).

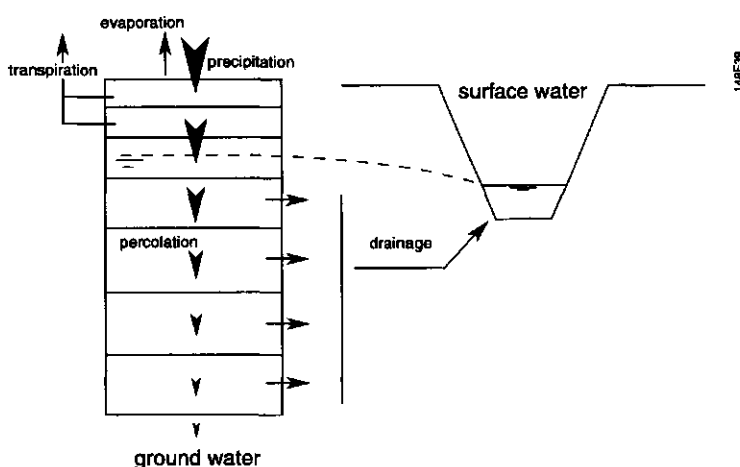


Fig. 5.2 Main fluxes in a one-dimensional model profile

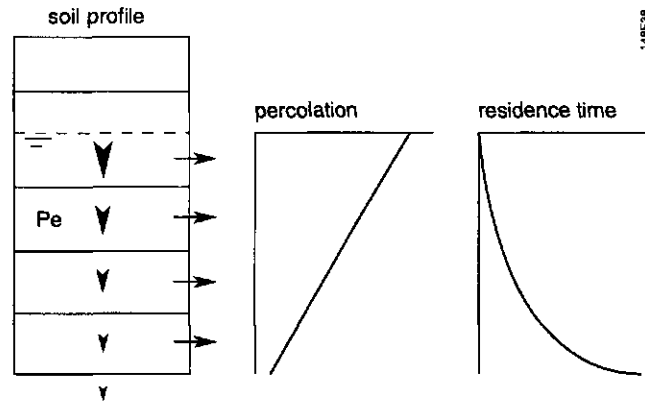


Fig. 5.3 A model profile (left), the percolation flux (middle) and its residence time (right) in a situation with water discharge to a ditch

5.3 Concepts of the TRANSOL model

With the schematization and hydrological data as a given, the TRANSOL model (Kroes and Rijtema, 1995) can be applied to simulate transport and transformation of a pesticide on its way from the soil surface to the ditch. The soil profile is discretised into a finite number of model layers. For each model layer transport and transformation is simulated with the given water fluxes as driving force. The modelling of the processes equilibrium sorption and degradation are derived from the work done by Boesten (1986), who implemented these processes for pesticide leaching and accumulation in the PESTLA model (Boesten and Van der Linden, 1991). Equilibrium sorption is described with a Freundlich sorption isotherm. Degradation is described as a first order process. The degradation products or metabolites can be simulated simultaneously. Environmental influences on degradation are temperature, drought and depth. Crop uptake is modeled as a function of the transpiration water flux and the pesticide concentration in the soil solution. Use can be made of an extended water balance, which includes terms like interception evaporation, soil evaporation, ponding, runoff, and a maximum of 3 surface water systems. Fluxes across all boundaries may be incoming or outgoing which allows flows like upward seepage from deeper soil layers and infiltration from ditches into the soil.

In TRANSOL a combination of analytical solutions and numerical approximations is applied to solve the convection-dispersion equation. Analytical solutions are used to solve the convection-dispersion equation for each distinguished layer. Physical dispersion is simulated by introducing numerical dispersion. A finite differences approximation with a backward scheme is used to solve the convection-dispersion equation for the whole model profile. With this scheme the calculation procedure follows the direction of the water flow.

5.4 Leaching towards groundwater using a standard data set

The leaching towards the groundwater was simulated using a standard dataset and had two main objectives. The first objective was to test the TRANSOL model on its ability to simulate the leaching of pesticides from the soil surface to the groundwater. The second objective was to prove that the results of TRANSOL do not differ significantly from the results of PESTLA version 1.1 (Boesten and Van der Linden, 1991). The PESTLA model is well tested and validated against analytical solutions. PESTLA combined with a standard dataset is used for pesticide registration purposes in the Netherlands. The models TRANSOL and PESTLA have the following agreements: i) both are dynamic simulation models, ii) equilibrium sorption can be described with a Freundlich isotherm, iii) degradation is regarded as a first order process, with a similar correction for the environmental influences of temperature, drought, and depth. The main differences between both models are: i) TRANSOL uses hydrological input from another model, whereas PESTLA has its own hydrological model. This results in a variable groundwater level in TRANSOL and a fixed groundwater level in the PESTLA version that was regarded for this comparison. ii) Simulations in the saturated zone and leaching to surface waters is included in TRANSOL, whereas PESTLA only regards the saturated layer from 1 to 2 meter below the soil surface. iii) Physical dispersion is simulated in TRANSOL by means of an introduced numerical dispersion; in PESTLA this is explicitly simulated. iv) Soil temperature in TRANSOL is simulated using a sinus wave with a phase shift and a damping depth. In PESTLA measured temperatures are used as input. The dataset that was used for the simulations has the following characteristics: i) a maize crop on a sandy soil, ii) a spring pesticide application of $1 \text{ kg}\cdot\text{ha}^{-1}$, iii) meteorological data from De Bilt, the 72% wet year 1980, iv) measured soil temperatures at four different depths under a grassland field in De Bilt.

An important difference seemed to be the simulation of soil temperatures. In PESTLA measured values are used and in TRANSOL soil temperature is simulated using a sinus model. Figure 5.4 shows the soil temperatures used in both models at a depth of 5 cm below the soil surface.

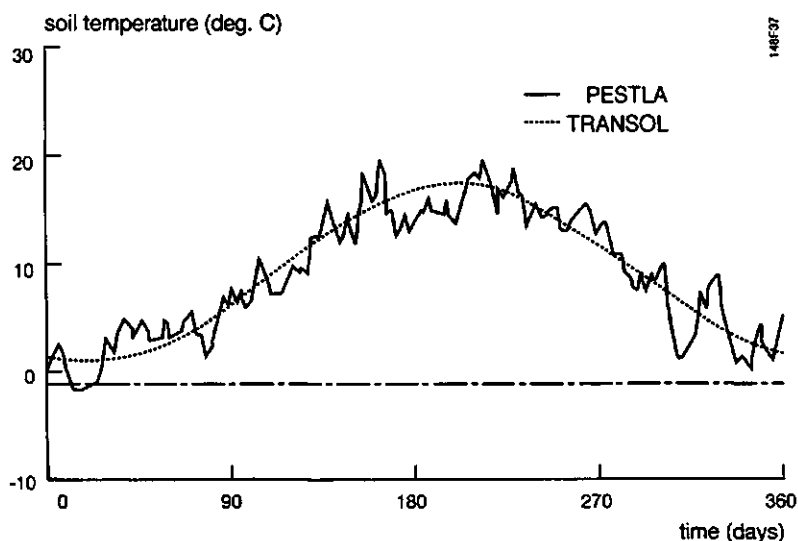


Fig. 5.4 Simulated and measured soil temperatures at 5 cm below the soil surface

With the dataset 168 combinations of different sorption and transformation or degradation were simulated (Kroes and Boesten, 1993). The results that were regarded are: i) the leaching at 1 m below the soil surface in % of the applied dose and ii) the maximum pesticide concentration in the layer 1 - 2 meter below the soil surface. From the simulations it was concluded that the results agree well (Figure 5.5). Only at very low concentrations and at very low leaching fractions both model results showed a difference which as maximally a factor 2. A larger agreement could probably be achieved but would demand a relatively high investment. Both models turned out to be sensitive to temperature. For PESTLA this was shown in an article published by Boesten (1991). A sensitivity analysis for TRANSOL showed that a temperature change of 1 °C caused a 13 % change in both the leaching fraction and the maximum concentration. In spite of the sensitivity of both models to temperature the results are satisfying, from which we concluded that both temperature descriptions are acceptable.

5.5 Leaching towards groundwater in a soil column

Tracer experiments (Hendriks, 1993) in soil columns were carried out to verify the transport concept used in the TRANSOL model. The soil columns were 120 cm long and had a diameter of 25 cm. Chloride was used as a tracer. The columns were sampled in the field and contained a certain amount of chloride at the start of the experiment. This initial chloride profile showed an increase in the concentration level with increasing depth. In the laboratory the transport of chloride through the columns was induced by means of an infiltrating water flux on top of the soil column. The experiment was executed in two periods: a stationary and a leaching period, both about 8 months long. During the stationary period just enough water was supplied at the top of the column to compensate the loss by sampling. During the leaching period a constant high water flux infiltrated on top of the column. This infiltrating

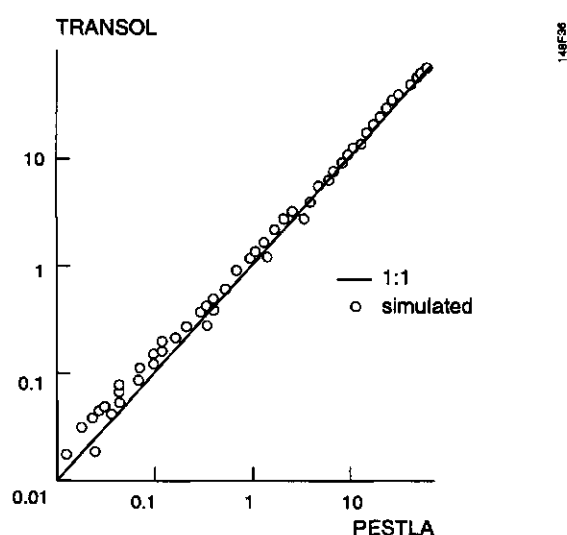


Fig. 5.5 Simulation results of TRANSOL and PESTLA: maximum concentration in the layer 1-2 meter below the soil surface

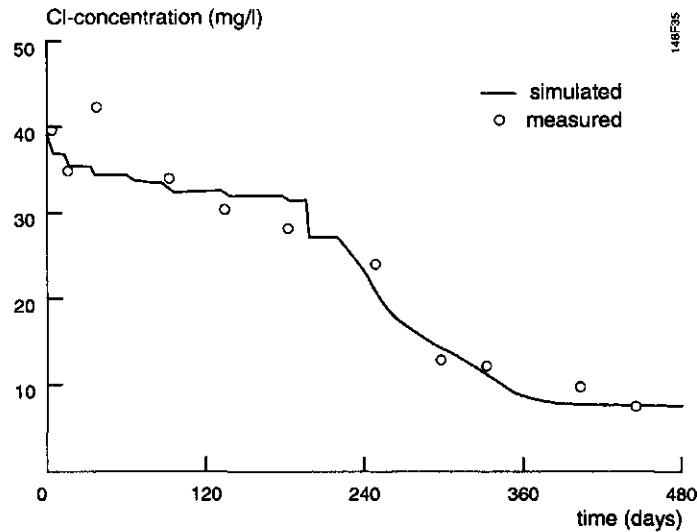


Fig. 5.6 Chloride concentration (mg.l^{-1}) at a depth of 110 cm in the groundwater of a soil column

water contained a low chloride concentration of 8 mg.l^{-1} . Experimental results were used to compare simulated and measured values at different depths and in columns with different concentration levels. Results of one column are given for a depth of 110 cm (Figure 5.6). During the stationary period a slight decrease in the concentration level is caused by evaporation and sampling. As the leaching period starts around daynumber 220 a gradual decrease in the concentration level occurs until at daynumber 380 the concentration level is equal to the concentration of the infiltrating water on top of the soil column. The simulation results were regarded as satisfying and considered as a successful test of the transport concept applied in the TRANSOL model.

5.6 Leaching towards surface water

Experiments were executed on drained bulb fields in the western part of the Netherlands (Dijkstra et al, 1995). These experiments had two objectives: i) quantify the actual discharge of pesticides to the surface water system, and ii) perform scenario analysis for alternative soil types, and hydrological conditions. One of the pesticides that was used in the experiments is the herbicide chloridazon. It is frequently used in the Netherlands and in one of the experiments it was applied in early spring on a bulb field which discharges water by means of drains to a neighbouring ditch. Drained amounts of water were measured and analyses of chloridazon concentrations were executed in the drainage water. Special measuring equipment was used to collect field data about water and pesticide discharge proportional to the totally discharged volumes. Water discharge was simulated using the model SWATRE (Feddes, 1978). The drains discharged continuously over the experimental period of two and a half years (1992-1994). Drain water discharge during winter was caused by a precipitation excess and during summer by an irrigation water excess. The simulated drain water discharges were calibrated against measured data. The TRANSOL model was applied

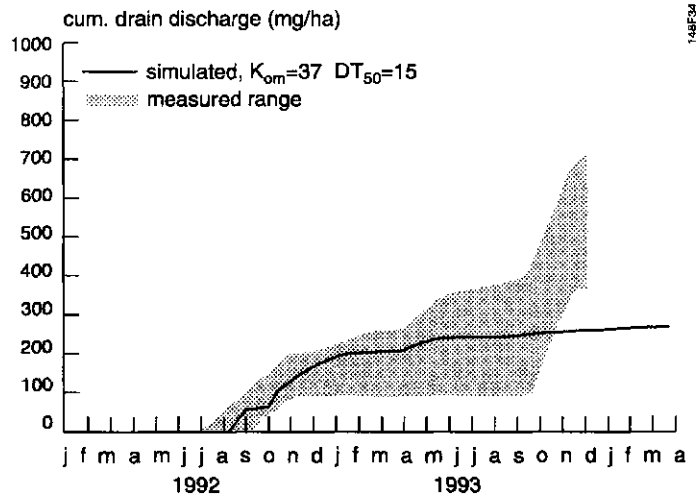


Fig. 5.7 Cumulative discharge of chloridazon ($\text{mg}\cdot\text{ha}^{-1}$) in drainage water from a bulb field

to simulate the addition of chloridazon at the soil surface, the transport and transformation in the unsaturated/saturated parts of the soil and the leaching of chloridazon towards drains. Chloridazon was applied in early spring at a dosage of $1 \text{ kg}\cdot\text{ha}^{-1}$. Chloridazon is a herbicide with a moderate sorption and a high degradation rate. Measured chloridazon concentrations in the discharged drainage water were very close to the detection limit. This minimized the amount of reliable data for a comparison between simulated and measured values. It seemed appropriate to compare simulated values with a range of measured data (Figure 5.7). The maximum in the measured range was determined by the detection limit or by measured values; the minimum in the measured range was zero (no discharge).

5.7 Conclusions

It is important to use a residence time concept for pesticide transport to surface waters. Conceptual differences between TRANSOL and PESTLA are small. Simulation results of both models agree well. Depending on type and scale of application the TRANSOL model can be used to simulate the entry route from the soil surface to the ditch and in that way generate input data for TOXSWA.

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Comments and questions

Question (Leeuwangh, SC-DLO): Considering the residence time of compounds in soil, which can be years, how can the output of TRANSOL be handled in the TOXSWA model where much shorter times are used?

Answer: The residence time is of course dependent on the sorption coefficient and transformation rate of the compound, but in general the timescale in TRANSOL is much longer than what is used for TOXSWA. In most cases the input into the

TOXSWA system will consist of pesticides which were applied a year or so ago. The delay in pesticide leaching to surface water should be considered when defining initial conditions in TOXSWA.

Question (Smelt, SC-DLO): You mentioned that TRANSOL can also model run-off. Can you give an indication of the amounts of chemical we should consider?

Answer: Run-off is basically a hydrological problem. Since TRANSOL does not include a hydrological model, it can not model run-off itself. If you can model run-off in a hydrological model detailed enough, then in TRANSOL you can simulate it as a solute flow coming from three directions.

Question (Sarafin, BASF): I have one remark, and one question. In the first presentation by Mr. Linders, we were told that we have as many models as problems. Now we know that we have more models than problems. Would you agree with my feeling that if we consider ecotoxicological effects an input by spray drift is much more relevant than leaching?

Answer: It depends on your situation. Maybe spray drift is a problem which is easier to control than a diffuse process like the leaching through soil. At this moment you may be right, but when low spray drifts have been achieved you may be wrong.

Question (Hollis, Soil Survey and Land Research Centre): You mentioned that the hydrology is external to TRANSOL. Can you just explain that a little bit?

Answer: There is an option in the model. You can link it to a two-layer model, and then you use the internal concepts. Your hydrology is then simplified to a hydrology for the root zone and the subsoil. A submodel in TRANSOL then uses the residence time concept. You can also use hydrological data originating from some other hydrological model, like for example Swatre.

Question (Hollis): The hydrology in the external models calculates the residence time which is then fed into TRANSOL?

Answer: That's correct.

Question (Van der Schaaf, ProAgro): You mentioned that the PESTLA model has already been accepted and validated. As far as I know PESTLA has only been validated for a very limited number of situations, so there we may have a difference of opinion. You also stated that the output of TRANSOL corresponds very well to the results achieved with PESTLA, but that this similarity breaks down at very low concentrations of the pesticide. I think that this is especially the range of

concentrations that we are very interested in, because this is where we run into problems with the presence of pesticides. Any comments on this?

Answer: There is of course a boundary to the use of each model. If you go below $0.01 \mu\text{g}\cdot\text{l}^{-1}$ PESTLA also starts to show deviations from the analytical solutions. Apparently this is the region where the limits of such models and mathematical techniques are reached. Part of the deviation between PESTLA and TRANSOL is due to the fact that PESTLA uses real, measured, temperatures, whereas the calculations with TRANSOL assume temperatures changing in time according to a sine function. Therefore TRANSOL deviates somewhat from the actual data. Both models are very sensitive to temperature deviations, 1°C causes a deviation in the model output of 13%. This may be the main reason for the deviations at these small concentrations.

6 IDEFICS: a computer model to quantify spray drift from field sprayers

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6.1 Introduction

Application of pesticides in field crops usually takes place using a boom sprayer. A conventional boom sprayer is provided with hydraulic spray nozzles, through which the spray liquid is forced at a constant pressure. The liquid stream leaving the nozzle rapidly breaks up into a spray, containing a wide variety of drop sizes: from very small droplets up to very large ones. While large drops follow ballistic rules, small droplets are very susceptible to wind and turbulence and therefore may easily drift away.

'Drift' can be defined in several ways. Here we will define drift as 'all drops containing pesticide that deposit outside the sprayed area or stay airborne'. The main problem regarding drift can be explained as follows. To reach the target area (usually a crop and frequently its lower leafsides) and to obtain a good distribution of drops over this area, small drops are needed. However, to prevent drift the production of small drops must be avoided. This reflects the basic dilemma in crop spraying. To optimize the spraying process (i.e. to obtain an effective spray distribution over the crop, as well as to minimize drift as much as possible) an insight into the essential parameters involved is necessary, both qualitatively and quantitatively. Consequently, this leads us to the question how to obtain such information. The first solution is by doing field trials. The advantage of a direct comparison of the results to farming practice is opposed by several important disadvantages: (1) weather conditions cannot be planned or controlled, (2) field trials are labour-intensive, (3) due to the large number of parameters many trials are necessary, and (4) varying just one parameter while keeping the others at a fixed value is hardly possible in practice. Computer simulation of the spraying process can overcome all of these disadvantages, although, almost ironically, it demands field trials for verification of all its essential settings. The IMAG program for Drift Evaluation from Field sprayers by Computer Simulation (IDEFICS) was developed to simulate drift from conventional boom sprayers. The IDEFICS model computes the downwind deposition of drifting spray drops onto the ground or surface water (if present). It is ideally fit to assess all parameters independently regarding their effect on drift. It can also be used to estimate drift hazards, or to recommend optimal sprayer settings, given a certain situation. As a special case, IDEFICS can supply input data for the TOXSWA model.

6.2 Modelling the spraying process

IDEFICS is a 2D random-walk model which basically computes the trajectory of a drop leaving the spray nozzle down to the place where it deposits on the ground (see Figure 6.1). Downwind from the crop a field of cut grass is assumed, optionally containing a ditch or a canal with adjustable geometry.

The trajectory along which a drop moves through the air depends on two forces acting upon the drop:

- gravity;
- drag force due to air resistance experienced by the moving drop.

The gravitational force is proportional to the drop mass, and therefore slightly diminishing due to evaporation during flight. The drag force due to air resistance comprises the contributions of local wind velocity and the head wind opposite to the drop velocity.

The essential parameters involved are divided into three categories:

1. crop related parameters:
 - essentially only crop height is important;
2. application technique related parameters:
 - nozzle type;
 - liquid pressure;
 - height of the sprayer boom over the crop;
 - forward speed of the sprayer;
3. environmental parameters:
 - average wind velocity;
 - turbulence intensity;
 - relative humidity;
 - air temperature.

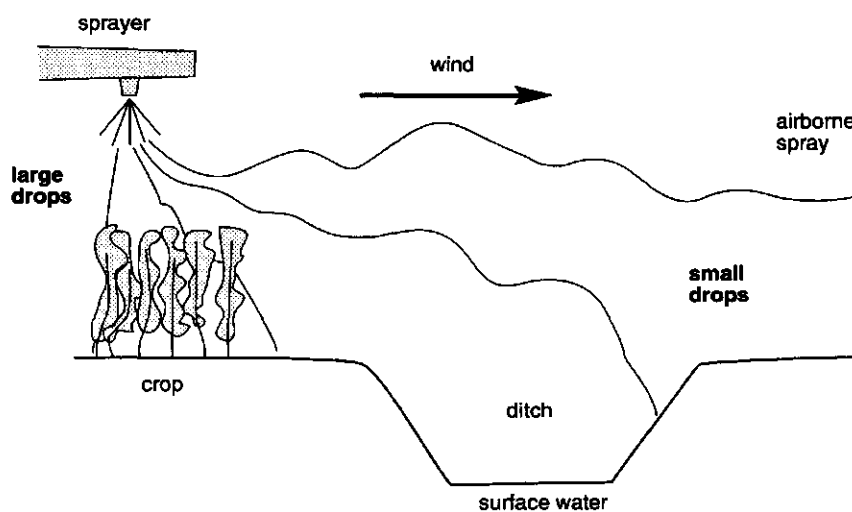


Fig. 6.1 Schematic field layout of IDEFICS simulation model

Crop density, however important to distribution of chemicals inside the crop, does not affect downwind spray drift. Nozzle type and liquid pressure determine the drop size distribution of the spray and the initial drop velocity at the nozzle outlet. As stated above small drops are more susceptible to drift than large ones. Table 6.1 gives a qualitative impression of drift susceptibility depending on drop diameter. It is widely accepted that drops up to 200 μm diameter are biologically the most effective. Unfortunately their drift potential is moderate to high. Using a technique producing large drops (to avoid drift) will not only result in a poor coverage but also may give rise to run-off to the ground (especially drops $>350 \mu\text{m}$ diameter). Generally, hydraulic nozzles produce drops of all drop sizes (see Figure 6.2). Air turbulence intensity is related to local wind velocity and atmospheric stability. Relative humidity and air temperature, together with drop size and relative drop velocity, determine the rate of evaporation. Usually only the smallest drops show significant evaporation, affecting far-field deposition ($>10 \text{ m}$) only. Intuitively it is expected that drop size distribution, wind velocity, and boom height above the crop are the major parameters affecting spray drift.

Table 6.1 Drop size and drift susceptibility

| Drop size [μm] | Drift susceptibility |
|-----------------------------|----------------------|
| < 100 | high |
| 100 - 200 | moderate |
| 200 - 350 | low |
| >350 | very low |

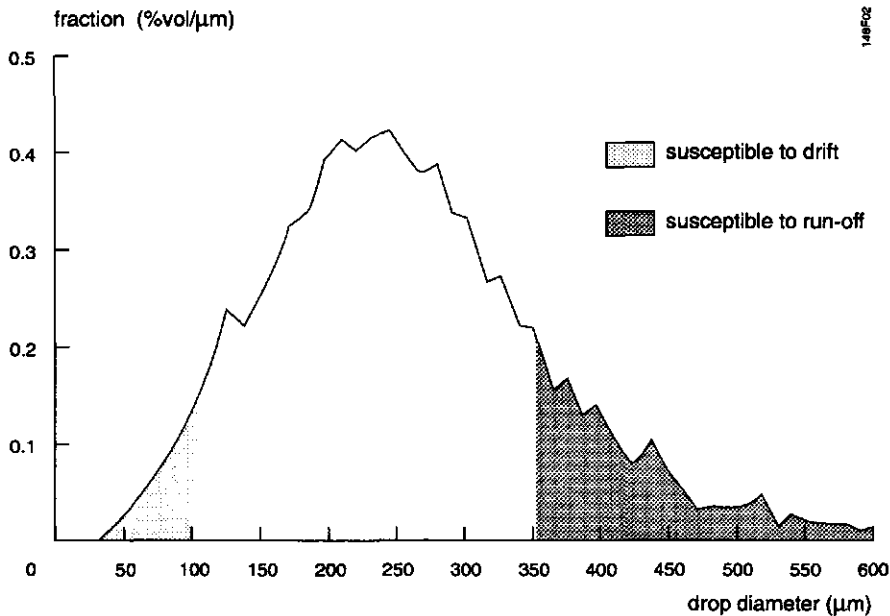


Fig. 6.2 Typical drop size distribution of a medium sized hydraulic spray nozzle

6.3 Results

In experimental single-nozzle field trials on cut grass sprayer boom height (4), nozzle type (3), liquid pressure (3) and forward speed (4) were varied independently. The number in brackets represent the number of settings used. The results show that IDEFICS predicts downwind droplet deposition well. Downwind ground deposits less than about 1% of the applied dosage appear to be slightly overestimated by IDEFICS. However, this does not affect the total amount of drift. Measured deposition of drift using a conventional sprayer agreed well with simulations results (Figure 6.3). The peak at about 0.5 m reflects the shielding effect of the crop (height 0.5 m in this example) towards drift. The precise form of the curve strongly depends on sprayer settings and weather conditions.

The major factors affecting spray drift are average wind speed, sprayer boom height and the volume fraction of small drops. Figure 6.4 gives an example of the relative deposition of drift to the ground (0-5 m downwind) using a conventional sprayer depending on wind speed and boom height. The front corner is set to 1.

Figure 6.5 shows the effect of drop size distribution on drift from a conventional field sprayer. It is clear that a 'coarse' spray (containing only few small drops) will give much less drift than a 'fine' spray (many small drops). In this example, at 2 m downwind a coarse spray appears to give a deposit of only about 1/3 of that of a fine spray. At larger distances downwind the difference in deposits from a coarse and fine spray becomes still more pronounced.

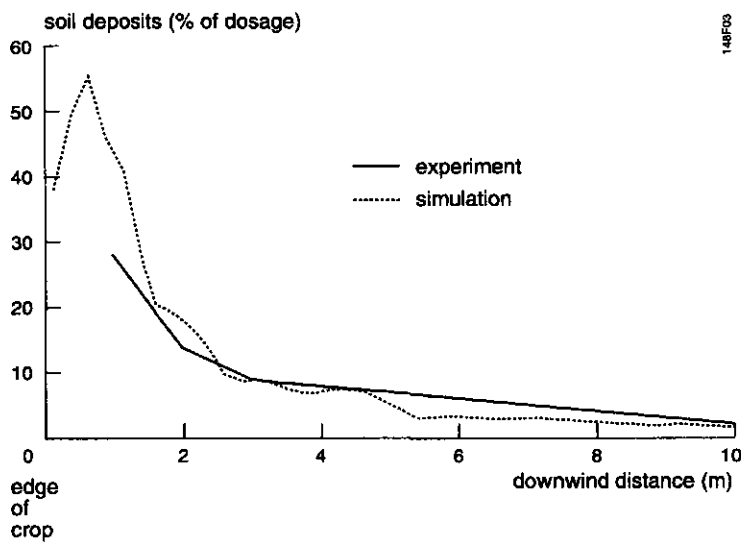


Fig. 6.3 Typical downwind drift using a conventional sprayer

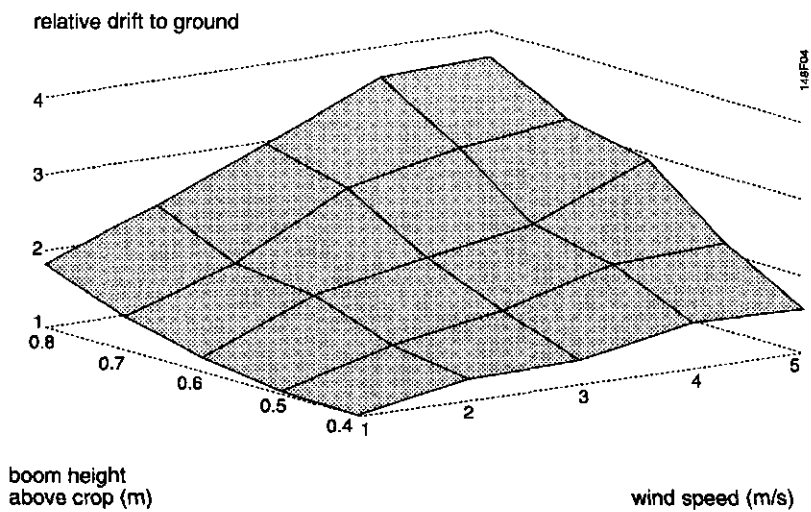


Fig. 6.4 Relative drift to ground (0-5 m)(simulation results)

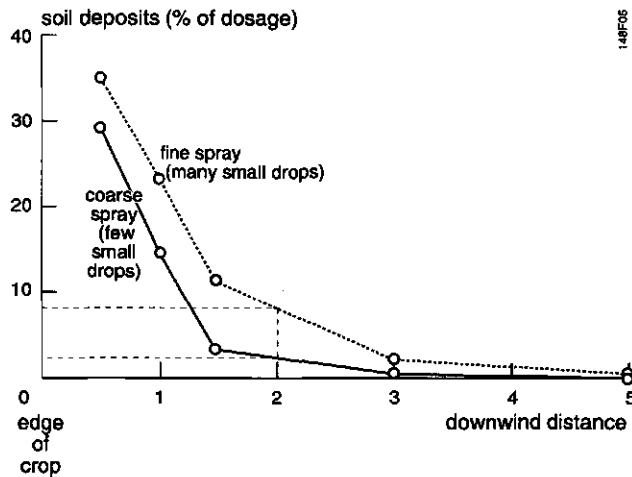


Fig. 6.5 Effect of drop size distribution on drift (simulation results)

6.4 Discussion

IDEFICS is particularly suited to predict nearby (0-10m) distribution of chemicals as a function of downwind distance. The model can also be used to assess potential drift reducing methods quantitatively. In contrast with field trials the model can rapidly assess the effect of a single parameter on drift. With IDEFICS a database can be set up to estimate spray drift hazards or to recommend the optimal sprayer settings, given certain meteorological conditions. Also, in view of the TOXSWA workshop, IDEFICS offers a good opportunity to quantify spray drift to surface water to be used as input data for the TOXSWA model.

Comments and questions

Question (Schäfer, Bayer): You showed us that there are two points which are of importance for the distribution of the droplet size, which where the nozzle and the pressure. Don't you think that surface tension is important as well? And I would like to know what you actually use as input for the model. Is the droplet size distribution an input for the model, or do you calculate it?

Answer: Indeed, surface tension is important as far as droplet size is concerned. The input of the model is based on measurements of the drop size distribution of actual nozzles. The size distribution is measured and input into the model.

Question (Klein, Fraunhofer-Institut für Umweltchemie und Ökotoxikologie): You mentioned that crop density is not an important parameter for spray drift. Is this not only true for specific situations, e.g. spraying from the top to the bottom? If you spray to e.g. appletrees then you will spray parallel to the soil surface and then crop density is a very important parameter, would not you agree? Can IDEFICS only be used for spraying from top to bottom?

Answer: Yes, it's only intended for aerable crops as were shown here.

Question (Leeuwangh, SC-DLO): Most of you, and especially the people from the Netherlands, will know that until now the percentage emission to the surface water is taken from a table. This table was constructed several years ago from experimental emission data. You are telling us about IDEFICS as a possible model to predict the emission into surface water. Have you compared the output of IDEFICS to data in the table?

Answer: The model, as well as experiments which were carried out at our institute, seems to indicate that the table generally underestimates the amount of drift into surface water. What the model shows is that you should not simply use a single number for the deposition into surface water, because it strongly depends on the type of nozzle, weather conditions etc.

Question (Schäfer): How do you handle the energy balance of the droplets? Do you calculate the actual temperature of your droplet? You calculate the evaporation from the droplet, which will diminish the droplet size. This evaporation will have an effect on the temperature of the droplet.

Answer: In the model it is assumed that the droplet takes on its lowest temperature, which is the 'wet bulb' temperature. According to theory this should be a quite good approximation. Only close to the nozzle, where evaporation has to start, temperature will be somewhat lower. During most of the trajectory the droplet has a constant temperature, depending on relative humidity and air temperature.

Question (Van der Kolk, SC-DLO): Has this model been validated for various situations, or just for the one you presented here?

Answer: It has been validated for different situations as well, and usually the agreement between model and experimental data is quite good.

Question (De Heer, Dutch Ministry of Agriculture, Nature Management and Fisheries): I would like to point out that we need validated databases for good and bad weather conditions. In previous experiments we observed up to 1% deposits on the surface of ditches. We noticed, however, that the shape of the ditch is very important. Do you use realistic shapes in your simulations? The graph you showed us did not seem to be very representative of a real ditch?

Answer: The model has the possibility to shape the ditch like I showed in the picture. Because of the relatively low wind velocity in the ditch area most drops, especially the smallest, will not be influenced by the geometry of the ditch. Only when the ditch is very close to the crop, which it usually is, the big drops may deposit differently.

Question (Rijtema, SC-DLO): The presence of the ditch can cause turbulences, especially when dealing with low water levels. This might affect your results considerably. Did I understand correctly that you measured deposits on soil surfaces, and not on actual ditches?

Answer: During the past two years we have also measured the deposition in ditches. These did not observe considerable differences between the deposition in the ditch and on the surface above the ditch.

7 Future applications of TOXSWA

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Abstract

A tiered strategy is proposed for the use of TOXSWA in the registration procedure. For a quick scan of the potential environmental risk, it is suggested that TOXSWA is used in a standard setting of environmental conditions. Several standard settings, reflecting different Dutch situations, will be identified under which TOXSWA will be used. To enable a quick scan, it is intended to present TOXSWA in the form of tables. In case a more refined risk assessment is needed, the specific conditions have to be identified and implemented in the model. It is recommended that TOXSWA should be validated under various environmental conditions before using the model in the registration of pesticides.

7.1 Introduction

The placing of a pesticide on the market requires among others that the product is evaluated for the degree of short term and long term risk to be expected for aquatic organisms after use of the pesticide according to the proposed conditions of use. If the concentration of the active substance to be expected in surface water has an impact considered unacceptable on non-target species, no authorization should be granted. Since environmental risk is defined as the exposure divided by toxicity, it is essential to have a good measure of either. The TOXSWA calculation model may provide estimates of the exposure concentrations in water and sediment.

In this paper a tiered strategy is proposed for the use of TOXSWA in the registration procedure. For a quick scan of the potential environmental risk, TOXSWA may be used in a standard setting of environmental conditions. In case a more refined risk assessment is needed, the specific conditions should be identified under which TOXSWA should be used. In the last part of this paper attention is given to future studies to validate the model.

7.2 Environmental Risk Assessment

In environmental risk assessment exposure concentrations in the environment are compared to the toxicity of the pesticide for susceptible organisms. The risk is defined as the Predicted Environmental Concentration (PEC) divided by the No Effect Concentration (NEC) that was measured in laboratory test organisms.

Since toxicity depends on time of exposure, the PEC and NEC should be based on the same time interval. Generally in toxicity studies there is a differentiation between short term exposure (acute toxicity) and long term exposure (chronic toxicity). In the risk assessment procedure for aquatic organisms it is assumed that effects due to acute toxicity generally occur within 1 to 4 days, while chronic toxicity is demonstrated within 4 to 28 days of exposure. Considering the very short life cycle of algae, we can study chronic toxicity within 4 days. With the waterflea *Daphnia magna*, a crustacean, we have several generations within 21 days. So with this species we should relate 21 days of exposure in the field to the concentration in laboratory that did not produce any toxic effect in 21 days. With fish, in so-called early life stage tests, chronic toxicity is studied in 28 days. The TOXSWA model should predict chronic exposure concentrations that would result in agricultural ditches after 4, 21 and 28 days.

7.3 Use of Models in Risk Assessment

In general, any model used for estimating the exposure concentration in the environment is based on a simplification of reality. In models that predict exposure concentrations in ditches, generally assumptions are made regarding the environmental and hydrological conditions, the design and characterization of the ditch and the agricultural area. The consequence of the standardized situation is that any variation in time and space is neglected. For instance, variation in hydrology, biomass of macrophytes, and biotransformation of the pesticide is not dealt with in the model. At this point, one has to realize that the use of a standardized TOXSWA model must be seen as a first step in risk assessment. It may be that the risk quotient indicates there is no risk at all, or that the risk is high. At this decision point the need may arise to refine the exposure assessment. For instance, international developments in the EU leave open the possibility of adequate risk assessment according the 'unless' statement.

In the first tier of risk assessment registration authorities as well as the applicants can check the level of risk in a standardized situation. As a result, for some of the pesticides it will be possible to decide upon registration, upon risk management, or upon withdrawal of the request for registration. For other pesticides a more sophisticated risk assessment may be needed. By defining environmental and hydrological conditions that are more appropriate for a specific pesticide application, the TOXSWA model will provide more relevant estimates. It should be pointed out that such a 'made to measure' exposure estimate requires much more effort and the input of expert judgement from applicants for registration as well as from regulators.

It should be pointed out that the use of exposure models need not be the final step in risk assessment. Considering the EU guidelines it is possible to negate the exposure estimate by the model. In case the issue of concern is the estimate of exposure, a relatively simple field study may provide the information that is needed.

7.4 Implementation of TOXSWA

It is planned that from 1995 TOXSWA will be used as a decision making tool. Implementation of the calculation model itself does not seem to be the best idea. As with any model, it is essential to be aware of sources of errors and uncertainties associated with its use. A lack of understanding of the structure of the model, its assumptions, and its limitations may lead to faulty results and interpretation. These drawbacks can be avoided when for various combinations of substance-specific parameters tables could be produced. These tables should indicate concentration in water at 4, 21 and 28 days after pesticide use. The tables should be a function of those parameters that have a major influence on the pesticide concentration in water. For instance, the tables should indicate the effects of the pesticide sorption coefficient to macrophytes, and the dispersion of the pesticide in the ditch. Since the TOXSWA model is still being developed, it is too early to demonstrate how the TOXSWA derived tables could look like. The idea behind of the use of tables, however, can be demonstrated by the way the PESTLA model is used.

The Pesticide Leaching and Accumulation model was developed in collaboration between the National Institute of Public Health and Environmental Protection, and the DLO Winand Staring Centre. PESTLA estimates the accumulation of pesticides in the uppermost soil layer one year after pesticide application, as well as the maximum concentration in groundwater between 1 to 2 m depth below the soil surface. Sensitivity analysis showed that accumulation in soil and maximum concentration in groundwater strongly depends on sorption coefficient based on the organic matter content in soil (K_{om}) and on the half-life of the pesticide in soil (DT_{50}).

For various combinations of K_{om} and DT_{50} accumulation in soil and the maximum concentration in groundwater were calculated for a standard environment. This resulted in a table of K_{om} and DT_{50} values and the concurrent maximum concentration in groundwater, the percentage of the dose leached below a depth of 1 meter, and the percentage of the dose still present in topsoil after a year. Only a small part of the table is presented here (Table 7.1). It can be seen that K_{om} and DT_{50} have fixed values. For these values calculations were made of the maximum concentration in groundwater (C_dmax), the percentage of the dose leached below a depth of 1 m (%PER), and the percentage of the dose still present in topsoil (%ACC). The values presented should be multiplied by the actual dose rate since the calculations are based on a dose rate of $1 \text{ kg} \cdot \text{ha}^{-1}$. For any pesticide, that is, for any substance-specific K_{om} and DT_{50} the maximum concentration in groundwater, the percentage of the dose leached below a depth of 1 m, and the percentage of the dose still present in topsoil can be calculated.

Table Table 7.1 For several combinations of K_{om} and DT_{50} the concurrent maximum concentration in groundwater (C_dmax), the percentage of the dose leached below a depth of 1 meter (%PER), and the percentage of the dose still present in topsoil after a year accumulation in soil (%ACC) were calculated for a standard environment (part of table from Emans et al., 1992).

| DT_{50} -soil | K_{om} | C_dmax | %PER | %ACC |
|-----------------|----------|----------|-------|-------|
| 300 | 0.0 | 60.8 | 24.8 | 0.001 |
| 400 | 0.0 | 64.5 | 26.3 | 0.001 |
| 500 | 0.0 | 66.8 | 27.2 | 0.001 |
| 10 | 10 | 0.007 | 0.003 | 0.000 |
| 20 | 10 | 0.8 | 0.3 | 0.000 |
| 40 | 10 | 9.0 | 3.9 | 0.17 |
| 60 | 10 | 20.4 | 9.1 | 0.44 |
| . | . | . | . | . |
| 400 | 10 | 83.4 | 43.4 | 2.2 |
| 500 | 10 | 87.6 | 46.0 | 2.3 |

DT_{50} -soil half life pesticide in soil
 K_{om} sorption coefficient based on organic matter content
 C_dmax maximum concentration in groundwater
 %PER percentage of dose leached below 1 m
 %ACC percentage of dose still present in topsoil

However it is more simple and quicker to interpolate from the table instead. The interpolation is made easy by a computer program. This program has been implemented in USES prototype 2.

From the table iso-lines of equal accumulation and equal maximum concentration in the groundwater between 1 to 2 meter below the soil surface can be constructed. As an example the graph with iso-lines of equal concentration in groundwater is shown (Fig. 7.1). The maximum concentration in groundwater for a pesticide with a sorption coefficient K_{om} of 100 ($l.kg^{-1}$) and with a half-life in soil of 100 days is between 0.1 and 1 $\mu g.l^{-1}$. One of the advantages of this graph is that it visualises the influence of the sorption coefficient K_{om} and DT_{50} in soil on concentration in groundwater. The graph also gives an indication of the maximum concentration in groundwater to be expected for a given pesticide. However, since that the iso-lines indicate the concentrations on a log-scale, visual interpolation only provides a rough estimate.

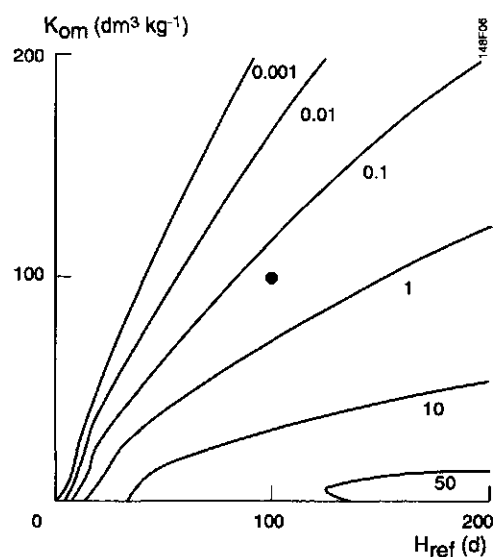


Fig. 7.1 Iso-lines of equal maximum concentration in groundwater between 1 to 2 meter below the soil surface (Boesten & Van der Linden, 1991)

For the TOXSWA model it is the intention to follow a similar procedure. Maximum concentrations in water will be calculated for a standard ditch in a standard environment under standardized hydrological conditions. The calculation must be based upon the base set of data provided in the notification of pesticides, similar to the situation for PESTLA. From a scientific point of view the available base set is rather limited. However, this view is not shared by those who have to provide the data. As a consequence extrapolation methods or best estimates have to be used to generate the unknown parameters. For instance, the sorption to macrophytes, half-life in water based on half-life due to hydrolysis or photolysis, and so on. In choosing standard conditions, 'realistic worst case' conditions will be assumed. This implies that realistic values will be chosen for variables and parameters. Part of these conditions already have been described for SLOOTBOX. For TOXSWA, however, more than one set of conditions will be identified under which TOXSWA will be used. These sets will apply for typical Dutch situations.

7.5 Validation

Before TOXSWA can be used as an instrument in environmental risk assessment its predictions should be corroborated by comparing experimental results with measured datasets. TOXSWA will be presented in the surface water working group of FOCUS, an international regulatory modelling workgroup. In this workgroup the suitability of models will be critically examined. Elements to be discussed will be model capability, deficiencies, and recommendations for calibration and validation.

Validation of the present TOXSWA model was started by using datasets for the microcosms and mesocosms. The experimental set-up of the microcosm and mesocosm studies only in part reflect the so-called standard conditions defined in

TOXSWA. For instance, so far all studies were carried out in stagnant water. Therefore only part of the processes in TOXSWA could be validated. In order to show the predictive power of the integral TOXSWA model it would be best to have datasets that are measured in agricultural practice. However, datasets of sufficient quality do not, or do hardly, exist.

7.6 Implementation of TOXSWA in USES

Harmonisation of models is thought to be essential since the use of different methods for evaluating chemicals can lead to inconsistencies in national and international policy. It therefore is foreseen that TOXSWA will be implemented in USES, the Uniform System for the Evaluation of Substances. USES is a harmonized system for making a rapid general risk evaluation for a wide range of chemicals, among which pesticides.

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Emans, H.J.B., M.A. Beek & J.B.H.J. Linders (1992) Evaluation system for pesticides (ESPE). *I. Agricultural pesticides*. National Institute of Public Health and Environmental protection, Report nr. 679101 004, 80 pp.

Comments and questions

Question (Adams, Monsanto Europe): Did I understand that we have had a discussion here today of a model that is not yet finished, and when it is finished you will give us tables that we can use, because we are not up to using the model properly ourselves? Is that correct?

Answer: The way you describe it is not completely correct, since it suggests that we don't trust you working with the model. That certainly is not true. What we propose is an easy method for people to use the model. We would like to make available tables or graphs, in a similar way as we did for PESTLA, giving you a first indication without going into much deeper detail. As a first step this approach should probably suffice for initial risk assessment. It is of course possible that on the basis of this first step you decide that a more detailed examination of the data is needed, e.g. when looking at a specific compound under specific conditions. For these situations you will have to know the ins and outs of the model. This offers

the possibility to review the exposure concentrations calculated by the model. The model is only a reflection of reality.

Question (Adams): If I am trying to develop a new pesticide I need to understand the tools which are going to be used in its approval process. I want to do that now for something in six years time. Do I need to take a driving test to use this model? If I have a car I understand how to drive it. If I don't I get a chauffeur. Do I have to hire a chauffeur to be able to use this model? If so, is that a sound approach? Could it not just be available for everybody to learn to use properly and add to the debate in a meaningful way?

Answer: The comparison with the drivers license is not completely correct. When you make a mistake during driving harm may occur to someone else. When making a mistake in the use of the model harm will probably occur to yourself only. I agree with you, however. The model will be made available for those who want to work with it. The process used in a hazard assessment must be completely clear. You are right that you want insight in the method of hazard assessment before starting to develop a pesticide. You should therefore have the necessary instruments at the most early stage. The first version of TOXSWA will be 'user friendly'. On the other hand you should be aware that some knowledge is needed to use the model.

Question (Allen, Hoechst Schering AgrEvo): We in the agrochemical industry provide the regulator generally with data which could be described as how fast the compounds break down and how strongly they are adsorbed. An evaluation is then made based on these two parameters. Models like PESTLA are very sensitive to these parameters. The data that I have seen today suggest that TOXSWA is not very sensitive towards these two parameters in the evaluation of the fate of a compound. The key parameters were a flow velocity and the amount of macrophytes in the ditch. Your approach will use a standardized ditch, and look at the variables we give you, whereas really it is the other way around. You have probably got in the Netherlands different ditches with different flow rates, different velocities and different quantities of macrophytes than in the rest of Europe. It doesn't seem to matter what the properties of a molecule are in terms of influencing its fate. The key issues are: how much of a compound is applied in grams per hectare, and how much of it is going to drift into the ditch. There doesn't seem to be much benefit in using the type of data we provide for the purpose of evaluation. It just seems to come down to environmental factors, and the rate at which the compound is applied.

Answer: I agree that we may have given this impression, although it's not completely true. For the first step in the evaluation we will not receive more data than those which are already asked. For scientists that is a pity, because asking for the right data to be used in a model would be much better. In the present situation we will have to manage with the available data. On the other hand we are aware that we need more data, which are not presented by the companies applying. John Deneer indicated our present ideas of how we will try to get the important data from open literature and from estimation techniques bases on molecular properties. Considering your

remark about differences between ditches across European countries, I agree. What I outlined was the situation for the Netherlands. For a first risk assessment we have to standardize the Dutch ditch. I also indicated that at a later stage we may look at other realistic conditions that result from the use of a specific pesticide under specific conditions. This is a second step in risk assessment. When considering a different region in Europe it might be necessary to define the standard surface water different from the standard used for the Netherlands. In my opinion the way in which we developed the TOXSWA model it will also be of use in situations differing from Dutch conditions. I do not want to imply that the standard conditions for using TOXSWA in the Netherlands should be used for situations outside of the Netherlands, regardless of the local situation.

Question (Schneider, Ciba Geigy): I don't know anything about Dutch ditches, and I'm only a pedestrian, so please apologize my simple point of view, but if you would ask me to do a simple exposure assessment, I would assume that the highest concentration you will find in a ditch will be observed immediately after the application of the pesticide. If you add all possible routes of input of a chemical into a ditch, and accumulate this amount of chemical into a standard ditch of e.g. 0.3 meters depth, it should be possible to calculate the maximum concentration that can be observed in the ditch. This may be compared to the No Effect Concentration of the most sensitive organism, resulting in a safety factor which you may be happy about or not. Under such circumstances I do not think that the TOXSWA model is needed. From a scientific point of view, such a model may be a useful tool to study the behaviour of a chemical once it has entered the system. But I doubt its usefulness for comparing exposure and effect concentrations.

Answer: Maybe we should make a clearer distinction between acute and chronic toxicity. You mainly addressed acute toxicity. When dealing with chronic toxicity the No-Effect Concentration will generally be much lower than acute toxic concentrations. Acute toxic effects will usually only occur near the site of application of the pesticide. Chronic toxicity will sometimes also occur at sites not directly located near the site of application. TOXSWA is being developed with these sites of chronic toxicity in mind. That is what we are aiming at: chronic toxicity and long-term exposure. This of course implies that input through drift is not the only entry route, leaching and input through drains will also contribute to the exposure of organisms to pesticides. This is what mostly differentiates TOXSWA from simpler calculation schemes which are suitable only for the estimation of exposure concentrations shortly after application of the pesticide.

Question (?): It was mentioned that you would like to perform your calculations for a 'realistic worst case' situation. I was wondering how you will decide what circumstances can be used for such a situation, and what criteria you will use to select these circumstances.

Answer: It is not our intention to decide upon such standard circumstances ourselves. Representatives of several Dutch ministries should be involved in selecting one or more standardized scenarios. We have inquired after possible standard conditions, and have already received some useful suggestions. A complete picture has not emerged yet, however. What we intend to do is to propose standard conditions, in addition to the conditions already defined for the SLOOT.BOX model, and henceforth ask representatives of the various ministries involved whether they can agree with these conditions or not.

Question (Guyot, Rhône-Poulenc): I am a little concerned about the standardization process. I think it could be very valuable for the people who design TOXSWA to provide a tool which could be applicable to many different situations rather than only standard conditions. I cannot believe that modelling is a standard exercise. If you want the companies to provide reliable information of good quality on the fate of pesticides, I think you will have to leave a lot of freedom to conduct the right experiments. We really know how difficult it is to extract useful information from field and laboratory experiments. The final decision should be based on all information extracted from experiments and modelling efforts, but I strongly believe that it is a scientific exercise rather than a standard experiment. I appreciated that in the presentations this morning it became obvious that the critical parameters in TOXSWA were mostly environmental rather than compound related characteristics. This shows that reality cannot be really standardized. I would like to use TOXSWA as a very global tool, applicable to many situations in France or other countries, rather than to standard experiments only. I do not think it is very efficient to restrict its use to standard scenarios.

Answer (1): In risk assessment it is essential to have a quick and efficient method to determine whether pesticide use will lead to environmental problems or not. That is what we intend to use TOXSWA for in combination with standardized conditions. Of course the model is open for use by anyone who wants to do so. The first step is only a relatively quick check. A more thorough examination can always be carried out later.

Answer 2 (Adriaanse, SC-DLO): I would like to answer to the remark concerning the sensitivity analysis. There may have arisen a misunderstanding about the type of parameters to which TOXSWA is sensitive. It should be remembered that the results up till now only apply to the water column. Sorption to bottom material has not yet been investigated, and this will probably be an important parameter. Sorption to the sediment is governed to a large extent by properties of the pesticide. Another property of the pesticide to which the model is quite sensitive is the sorption coefficient of the compound to macrophytes. This coefficient also is largely governed by properties of the compound, and not by the environment. The observation that the model was not very sensitive to degradation rates, i.e. DT_{50} , is caused by the fact that the sensitivity analysis was carried out for a very short time-span, which was approximately 0.4 days. The half-time used in the sensitivity analysis was appreciably longer than the space of time investigated, which implies that degradation will not be very important. This may of course change when investigating longer

lengths of time. Not only environmental parameters are important, some properties of the pesticide itself are equally important as well.

Question (Hollis, Soil Survey and Land Research Centre): Most of what has been said seems to me to be pointing to how difficult it is to define a realistic worst case scenario. The very complex interactions that go on seem to me to suggest that such a scenario will be different depending on the characteristics of the compound. The environmental characteristics that give you a worst case situation for one particular compound will not be the same for another compound. And they will also vary according to different environmental characteristics. That is why I agree very much with Dr. Guyot, that you need to use modelling in its true environmental context, where you can look at the variation of environmental parameters across the landscape. You need to interpret the results of models very carefully in that respect, and I am a little worried about this realistic worst case scenario.

Answer (1): I agree with your reservations. However, the registration authorities want to deal with a problem quickly, especially during the first step of the procedure. The use of standardized scenarios is more or less common practice when dealing with the estimation of aqueous concentrations of pollutants. It would be more acceptable if we could indicate ranges instead of just a single estimated concentration of the chemical. Very broad ranges would usually imply that the second step in the risk assessment, i.e. more detailed calculations, are necessary. For compounds where the initial calculations show that no risk is involved the assessment could stop there, which would considerably quicken the process of risk assessment.

Answer 2 (Van der Linden, National Institute of Public Health and Environmental Protection (RIVM): I would like to add to Dr. Leeuwangh's explanation that from the point of view of the government, it takes lots of time to model the behaviour of compounds on the basis of data supplied by companies. This process can take more than three months per compound, and we simply don't have this time available for each compound. This is the reason that we have to standardize, simply to speed up the assessment.

Question (Rijtema, SC-DLO): I have a question for Mr. Linders, concerning the decision trees he presented. In the schemes used in the European Union there is usually an 'unless clause'. Does this also apply to the schemes for risk assessment which you presented? When you calculate expected concentrations for a standardized ditch using TOXSWA, you will use the ratio between this expected concentration and a No Observed Effect Concentration to carry out risk assessment. Do you also introduce an 'unless clause' into your decision trees?

Answer: (Linders, RIVM): Yes, indeed. In the current situation in the Netherlands there is no such 'unless clause' when calculating expected concentrations and comparing them to toxic concentrations. In relation to the European Union such a clause is introduced. This can be reached during the initial risk evaluation if the first

cut-off criteria are not met. In this respect one can use TOXSWA by varying characteristics of the model in a situation where no risk is indicated. You might change the application technique, or the application amount. If it has enough efficacy, you can e.g. change the dosage of the pesticide. Models like TOXSWA give you the ability to experiment with such changes.

Question (Mattaar, Rhône-Poulenc): Mr. Linders explanation worries me somewhat. As a first step you develop a model. You then standardize the environment which is used in the calculations with this model. The result is that you get tables or graphs, which are used as a first step in screening chemicals. On the other hand you say that we can use the results of such calculations to adapt the use of the product. We might look at the dose-rate e.g. to find a compromise between best performance of the product and safety to the environment. My feeling is that there is a general misunderstanding that an excess of products is used in normal agricultural use. Normally a minimum dose-rate is already used, and is already applied for in the registration process. It is not a maximum dose-rate that the company wants to sell, it's already a minimum dose which is still effective. At the most you might be able to reduce the dose-rate with a factor of 1.5 or 2. On the other hand, if we look at the standardization process the differences in concentrations caused by differences in scenarios will be much larger. I have the feeling that using the model for the finer calibration of the use of the product is probably not one of the best uses for it. With the PESTLA model a similar process occurred as has now been advocated for TOXSWA. The model was developed and graphs were produced. These graphs were intended for use as a first screening instrument. However, somewhere along the way this seems to have been forgotten by people dealing with registrations of pesticides. When working with the model myself, I often encounter large difficulties when trying to change one or more of the parameters involved. Are not you afraid that this will also happen to TOXSWA if you only supply graphs, and that people will use the model in ways for which it was never intended? I feel there is some responsibility on the part of the people who produced the model. They cannot simply put it on the road and wait who picks it up.

Answer: I have witnessed this process before, not only with PESTLA, and I hope that it will not occur with TOXSWA. I think it shows that when we introduce the model, or the tables or graphs, we will have to make it very clear that this is only to be used for a first check, as I said before. This first check may not yield conclusive results. That is why I am happy that the assessment procedure of the European Union leaves the possibility to negate the results of such a first check with a second made-to-measure check like e.g. a field study. I agree with you that it is the responsibility of the people who are working on the model, and who are trying to introduce it for risk assessment, to indicate that the model is a reflection of reality and that its results may be way off the mark when dealing with a specific situation in the environment.

General conclusions

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We have finally reached the end of this meeting. I think that we can draw a few conclusions at least. The first one is that the addition of the sorption of pesticides to macrophytes in surface water is essential. A conclusion which was not explicitly presented, but which I have drawn for myself, is that sorption to floating organic material is in TOXSWA considered in combination with sorption to suspended sediments. This morning there was a question about the influence of temperature on transformation rates. An important conclusion which we can draw from the presentation given by Joop Kroes is that temperature is an important parameter. When modelling chronic exposures over relatively long periods of time it will probably be essential to incorporate the influence of temperature. This might be achieved by adapting some modelling approach, e.g. by assuming a sine-wave course of temperature with time over a 24 hour period, in order to introduce at least some effect of temperature on the transformation rate of a compound in surface water. When studying chronic toxicity over periods of e.g. 28 days, one might imagine an application of the pesticide in spring where the mean temperature of the surface water at the end of the 28 day period is considerably higher than immediately after the application.

A request was made for making experimental data available for further validation of the TOXSWA model. We are at this moment preparing to generate new data in micro- and mesocosms ourselves. This is obviously very time consuming and costly. Any data available and suitable for validating TOXSWA are therefore most welcome.

We have had a long discussion about the use of models such as TOXSWA for risk assessment. TOXSWA is suitable as a tool in risk assessment, but great care should be taken to define realistic conditions in the model. Especially the definitions of initial and environmental conditions should be chosen very carefully. Whether the ditch receives its water only from neighbouring fields, or also takes water from adjoining ditches e.g. can make a large difference. In the latter case we would need much more information about the use of the compound in other parts of the region, since these might contribute directly to the load in our ditch through transport of contaminated water into our model ditch.

I will not close this meeting before a word of thanks to the speakers today for the material presented. Our main aim was to let you have a look at the state that the development of TOXSWA has reached up till now. Sometimes it is more interesting to have a look at a product still under development than to only see the finished result. I would also like to thank the organizers of this day, and of course the participants of the workshop. The day gave an exchange of ideas and viewpoints, and we will try to use these in the further development of TOXSWA.

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