

Pesticide leaching in Polders

Field and model studies on cracked clays and loamy sand

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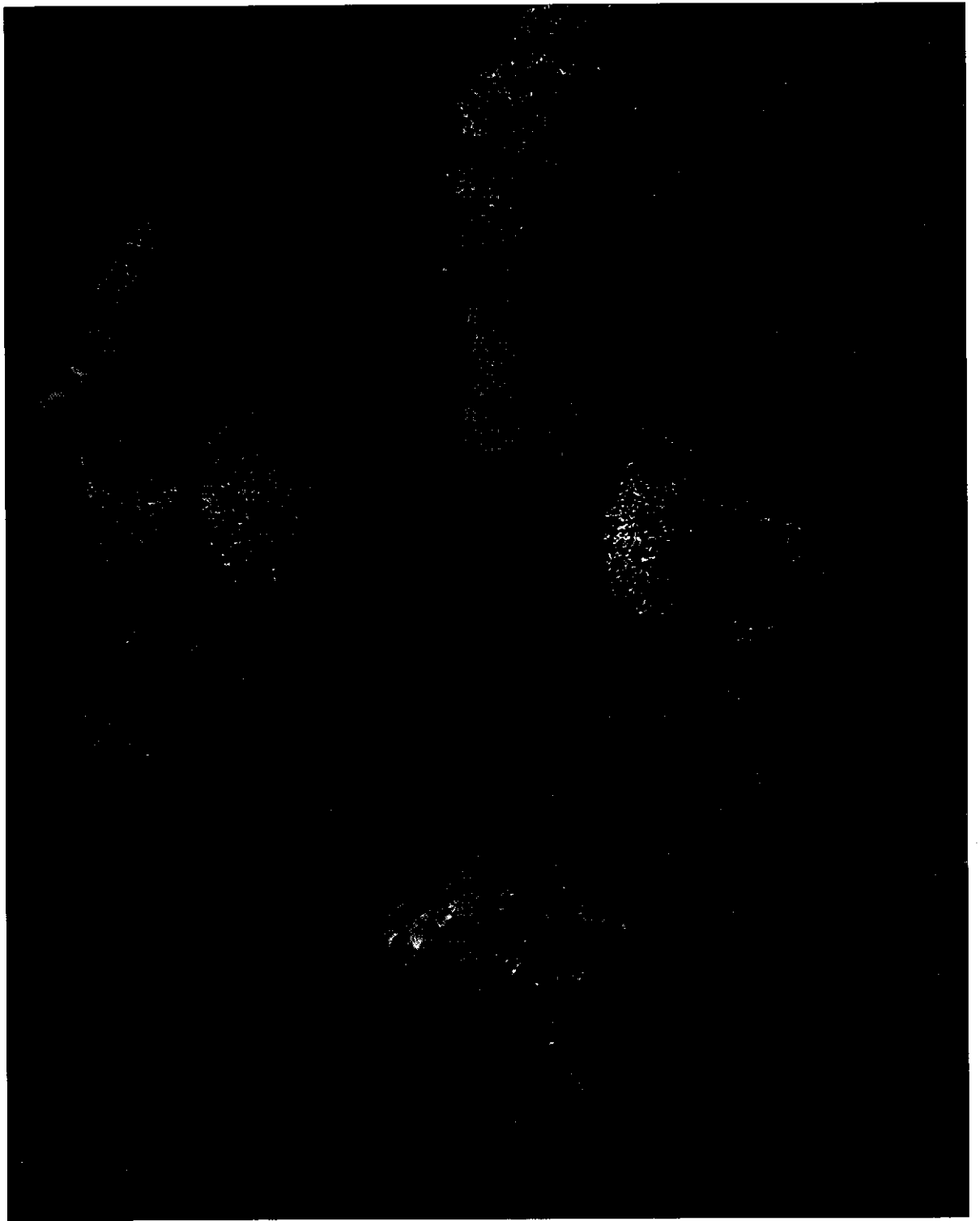
BIBLIOTHEEK
LAND-EN WATERBODEN
WAGENINGEN

Stellingen

1. Het gebruik van een standaard hydrologisch jaar in het toelatingsbeleid van bestrijdingsmiddelen dient te worden verlaten.
 - *Van de Veen, J.R. and J.J.T.I. Boesten. 1996. DLO-SC report 117.*
 - *Dit proefschrift*
2. Preferent transport van bestrijdingsmiddelen door kleigronden met een gescheurde ondergrond onder de bouwvoor kan op eenvoudige wijze beschreven worden door een imaginaire drain aan te nemen op de grenslaag van bouwvoor en ondergrond.
 - *Dit proefschrift*
3. Landsdekkende berekeningen naar de uitspoeling van bestrijdingsmiddelen naar het grondwater zijn weinig zinvol zolang niet meer bekend is over het effect van de heterogeniteit van de bodem op de uitspoeling.
4. Bij gebruik van het grondontsmettingsmiddel 1,3-dichloorpropeen heeft vervroeging van het tijdstip van toediening meer effect op de beperking van de emissie via de drains naar het oppervlaktewater dan een verkleining van het toegepaste volume.
 - *Dit proefschrift*
5. De gemeten uitspoeling van bestrijdingsmiddelen in laboratoriumopstellingen (kolomproeven) vertoont voor eenzelfde grondsoort weinig overeenkomst met gemeten uitspoeling in het veld.
6. In modelstudies naar de emissie van bestrijdingsmiddelen ten behoeve van het toelatingsbeleid dient in tegenstelling tot de huidige praktijk doorgaans rekening te worden gehouden met preferent transport.
 - *Dit proefschrift*
7. Informatie over het gebruik en de karakteristieken van individuele bestrijdingsmiddelen dient voor iedereen toegankelijk te zijn.
 - *Geenen, J.P.W. en G.M. van der Geest. 1995. CUWVO V. Bestrijdingsmiddelen-rapportage 1992/1993*

8. Uitstel van de aanleg van de Markerwaard betekent een versnelde aanslag op de beperkte open ruimte in de randstad Holland, die met de droogmakerijen van de vorige eeuw is gecreëerd.
9. Normoverschrijding van bestrijdingsmiddelen in het aquatisch milieu houdt niet in dat er ook daadwerkelijke effecten zullen optreden.
10. Ongewenst gedrag van kinderen wordt door buitenstaanders veelal toegeschreven aan de opvoeding, door ouders veelal aan de genetische aanleg.
11. Discriminatie in al zijn vormen is te veroordelen, ook positieve.
12. Het instellen van een objectieve index voor het predikaat "deskundige" in dagbladen en/of televisierubrieken, zou het inschatten van het belang van een geventileerde opinie voor de lezer en/of kijker verbeteren.
13. "De privatiseringsdwang zal de geschiedenis ingaan als grote maatschappelijke misser".

- *Huisman, P.E. NRC. 20-8-1997*



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Abstract

Pesticide leaching in polders/Field and model studies on cracked clays and loamy sand/ Klaas P. Groen - Lelystad: Rijkswaterstaat, Directie IJsselmeergebied (RWS, RDIJ), 1997 - 296 p.: 149 fig. 51 tab.; 24 cm - (Van Zee tot Land, 62: ISBN 90-369-1209-1). Thesis Wageningen. - Ref. - ISBN 90-369-1209-1 (LUW)

This thesis reports on a study of pesticide leaching in polder areas. The study comprises two aspects: a data collection program and the development, calibration and application of the model *SWACRO* for the simulation of pesticide transport.

Field data were collected at three experimental fields, all situated in the IJsselmeerpolders. The experimental fields were situated on loamy sands and cracked clay soils. Four different pesticides were incorporated in the research program: 1,3-dichloropropene, metarnitron, aldicarb and simazine. The inert ion bromide was used as a tracer and applied with the pesticides. The soil physical properties of the experimental fields and the characteristics of the pesticides involved were determined in laboratory experiments.

The model *SWACRO* was selected to describe water and solute flow in the (un)saturated zone. The model was extended to transport of pesticides and preferential flow. Preferential flow was calculated according to the mobile/immobile concept (loamy sand) or the imaginary drain concept, conceivably extended with segmentation of the upper boundary conditions (cracked clays). Calibration of the model was performed in three steps: (1) calibration of soil water fluxes, (2) calibration of the concentration of conservative solutes in drainage water and the concentration profiles of conservative solutes, (3) calibration of the concentration of pesticides in drainage water and transformation of pesticides. The model was calibrated for the three experi-

mental fields. Generally, soil water fluxes and the concentration levels of bromide and pesticides in drain pipes could be reasonably well simulated.

The extended model *SWACRO* was used to formulate design and management criteria for polder areas in order to develop an integrated pest management. With the calibrated model the effects of several design and management scenarios have been evaluated. Generally, scenario analysis showed that pesticide characteristics, time of application of the pesticide, soil characteristics, lateral boundary conditions and weather conditions define the concentration of the pesticide in the drain pipes and thereby the fraction of the dosage leached. Generally, the fraction of the dosage leached is higher for cracked clay soils than for loamy sands. Sensitivity for leaching is low to moderate for areas without preferential flow and a high organic matter content and high to very high for areas with preferential flow and a low organic matter content. For cracked clay soils it was calculated that leaching is mainly caused by preferential flow through cracks. The scenario studies showed that several measures can be taken in order to reduce leaching: (1) Reduction of leaching by allowing pesticide application only during a certain period (2) Introduction of new drainage criteria with increasing drain depth (3) Decreasing preferential flow by increasing the ploughing depth.

For the IJsselmeerpolders the present legislation for the registration of pesticides should be adapted, taking into account that: (1) Leaching may contribute significantly to the presence of pesticides in surface waters (2) Leaching is highly influenced by preferential flow.

Keywords: pesticide, leaching, simulation model, drained soils, cracked clays, loamy sand, field experiments, calibration, IJsselmeerpolders.

Voorwoord

Bij het gereedkomen van dit proefschrift wil ik iedereen bedanken die aan de totstandkoming heeft bijgedragen. Allereerst wil ik mijn promotoren prof. Feddes, prof. Schultz en dr. Boesten bedanken voor hun betrokkenheid, waarbij een ieder een eigen karakteristieke rol heeft gespeeld. Mijn promotor Reinder Feddes ben ik erkentelijk voor zijn kritische en opbouwende inzet in de begeleiding. Als geen ander wist hij gedurende het onderzoek en het bespreken van de concepten de vinger op de zere plek te leggen. Mijn voormalige chef en promotor Bart Schultz was degene met de onderzoeksvraag, die de aanleiding was voor het ontstaan van dit proefschrift. Gedurende de duur van het onderzoek heeft hij gezorgd voor de organisatorische randvoorwaarden waarbinnen het onderzoek kon plaatsvinden. Mijn co-promotor Jos Boesten wil ik bedanken voor de wijze waarop hij mij heeft begeleid en geadviseerd op het gebied van simulatiemodellen, laboratoriumproeven en bestrijdingsmiddelen. Meer dan de anderen zag hij de grote hoeveelheid werk die op mij afkwam.

Het tweemaandelijks overleg met de begeleidingscommissie, waarin naast de bovengenoemde personen ook Ruurd Koopmans en Jos van Dam zitting hadden, heb ik altijd als zeer prettig ervaren. Ruurd wil ik bedanken voor zijn bijdrage op het gebied van de agrohydrologie. Jos heeft een grote bijdrage geleverd aan de ontwikkeling van de computer-programmatuur, waarvoor ik hem zeer erkentelijk ben. Ook hebben wij, vaak in driemanschap met Gé van den Eerthweg, over het onderzoek gediscussieerd en veldproeven verricht. Ik heb jullie graafkunsten mogen aanschouwen en wacht in spanning op jullie dissertaties.

De Rijksdienst voor de IJsselmeerpolders, later Rijkswaterstaat Directie Flevoland, vervolgens Directie IJsselmeergebied en het huidige RIZA ben ik

zeer erkentelijk voor de geboden mogelijkheden tot de start en afronding van dit proefschrift. De verschillende hoofden, waarbij ik speciaal wil noemen de heren Fokkens en Pinkers, wil ik bedanken voor het vertrouwen dat zij altijd hebben gehad in de goede afloop en de ruimte die zij mij hebben geboden.

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Chapter 1

Introduction

Introduction

General

During the last decades a tremendous increase in agricultural productivity has been created in many parts of the world. Together with fertilizers, improved crop varieties, more efficient machinery and management practices, pesticides are one of the main contributors to this development. In modern agricultural practices, pesticides have become indispensable for insect, weed and disease control. In general, pesticides are very effective in controlling or preventing pests, even when they are applied in very small quantities. Within the European Community, some 800 different types of active ingredients are in use (Teunissen-Ordelman and Schrap, 1996), which can be subdivided in groups, according to the function for which they are being used: fungicides, herbicides, insecticides, fumigants and other organic chemicals used for related functions (Royal Society of Chemistry, 1987).

The adverse effects of the use of pesticides on environmental quality have been recognized for some time. Trace amounts of pesticides are present on non-agricultural land, in the atmosphere and in water. Many examples show that pesticides have a strong impact on aquatic ecosystems and form a potential ecological threat (Stortelder et al., 1989; Faasen, 1995). Moreover, it is indicated that groundwater and surface water used for drinking water purposes is polluted with pesticides (e.g. Hopman et al., 1992; Dogterom et al., 1995). In some cases monitoring data showed that concentration levels of pesticides are well above the standard set for drinking water by the Council of European Communities (1988). It may be expected that the actual situation is worse than can be deduced directly from monitoring data, as an analytic determination method at the level of $0.1 \mu\text{g l}^{-1}$ is still lacking for a large group of pesticides. Only recently more extensive

monitoring programs became available indicating that traces of pesticides are found in drainage systems, lakes and coastal waters (e.g. Wauchope, 1978; Faasen, 1992; Van Steenwijk et al., 1992; Van Meerendonk et al., 1994).

Pesticide use in the Netherlands

In the Netherlands, some 300 different types of pesticides are permitted and applied for agricultural purposes. These pesticides control an estimated number of 6,000 different diseases and pests. Dutch agriculture is vulnerable to diseases and pests and highly dependent on the use of pesticides. This is among other reasons caused by the climatological circumstances, specialized organization with a limited crop rotation and market demands for high quality. The use of pesticides in the Netherlands amounts to approximately 10 kg ha^{-1} , which is very high compared to other countries in the world (Ministry of Agriculture, Nature Management and Fisheries, 1991; Brouwer et al., 1994). During the period 1984 - 1988 the pesticide use expressed as kg active ingredients stabilized. The total sales of pesticides during this period amounted to approximately 20,000 tons of active ingredients. The sale of pesticides has been falling since 1988 (mainly insecticides, herbicides and fumigants). For 1994 it is expected that total sales under normal weather conditions approximate 15,500 tons, which is roughly equal to an average use of 8 kg ha^{-1} . During the period 1988 - 1994 the percentage of the amount of the various groups of pesticides used annually altered slightly: fumigants (52% - 42%), fungicides (20% - 26%), herbicides (19% - 19%), insecticides/acaricides (3% - 4%) and remaining pesticides (6% - 9%) (NEFYTO, 1995). In the Netherlands fumigants are used in large quantities in the growing of potatoes, vegetables and bulbs.

The Dutch National Environmental Policy Program shows that nowadays more attention is being given to environmental issues (Ministry of Housing, Regional Development and the Environment, 1988). For the use of pesticides the strategic objectives as stated in the Multi year plan on crop protection (Ministry of Agriculture, Nature Management and Fisheries, 1991) are:

- *reduction of the dependency.* This should be achieved by a wider crop rotation plan, an alteration of plant material which is less susceptible to diseases, increasing attention for hygiene and biological pest control;
- *reduction of the use.* It is assumed that reduction of the use will automatically lead to a proportional decrease of the emission of pesticides to ground-water, surface water and air;
- *reduction of the emission of pesticides to ground-water, surface water and air.* Transport routes of pesticides to the environment may occur by aerial drift of pesticides, volatilisation and atmospheric transport, wind erosion, runoff, leaching and inaccurate use.

The IJsselmeerpolders

The surface area of the Netherlands is 3,400,000 ha. Approximately 25% of this area is below mean sea level and even 65% would be flooded if there were no dikes. The history of land reclamation in the Netherlands has resulted in the following polder areas (Schultz, 1983): low lying lands (1,335,000 ha), drained lakes (315,000 ha) and land gained from the sea (350,000 ha).

The most recent and at the same time biggest project regarding reclamation of land out of water, is the closing off and partial reclamation of the Zuider Zee, a former estuary in the central part of the Netherlands (figure 1.1). The Zuider Zee project, which started in 1918, includes the construction of a Barrier dam and the reclamation of five polders. The Zuider Zee became an inland lake, the IJsselmeer, by 1932, when the Barrier dam was closed. At the same time the Wieringermeer (1929: 20,000 ha) was reclaimed. Subsequently the North-East Polder (1942: 48,000 ha),

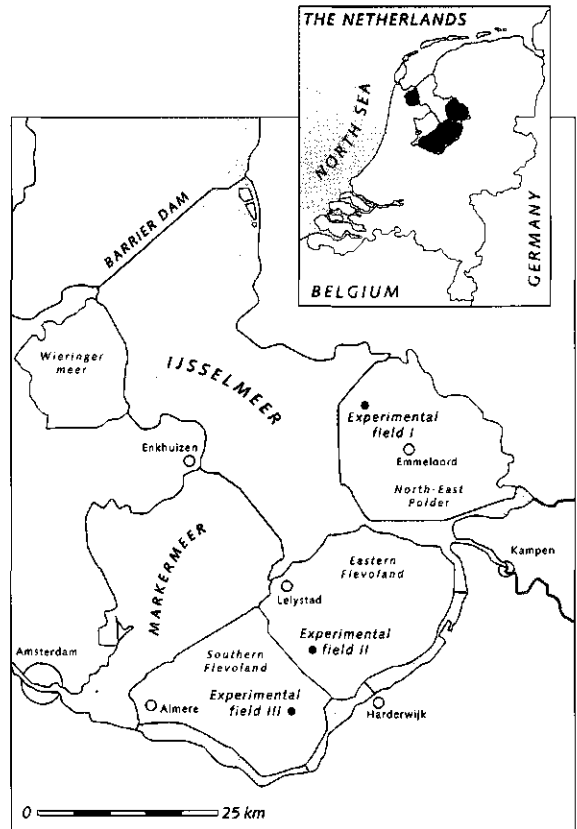


Figure 1.1. The IJsselmeerpolders.

Eastern Flevoland (1956: 54,000 ha) and Southern Flevoland (1968: 44,000 ha) were reclaimed from the IJsselmeer (Van Duin and De Kaste, 1990).

In 1980 the government announced its plan for the reclamation of the last polder in the Zuider Zee project, the Markerwaard (roughly 41,000 ha). In 1975 it was already decided that the "procedure for crucial decisions on town and country planning (PKB)" should be applied to the Markerwaard. As part of the PKB procedure, relevant government departments have been working on various aspects (such as planning, geohydrology, costs/benefits) related to the reclamation of the Markerwaard. In 1990 the Government decided to postpone the reclamation of the Markerwaard, due to a number of reasons such as lack of finances, agricultural overproduction, environmental issues (Ministry

of Transport, Public Works and Water Management, 1990).

Characteristics of the IJsselmeerpolders

The IJsselmeerpolders comprise an area of 166,000 ha, of which 96,000 ha is used as cultivated land. The greater part of the cultivated land is used for agricultural products, like cereals (17%), potatoes (24%), sugar-beet (16%) and dairy farming (14%). Beside these agricultural products, a considerable part of the polder is used for horticulture (e.g. orchards (3%), bulb growing (2%) and vegetable growing (3%)) (Centraal Bureau voor de Statistiek, 1993). In general, pesticide loads are low (less than 1 kg ha⁻¹) on grass and green fodder, except for fodder maize. Pesticide loads between 1 and 5 kg ha⁻¹ are encountered in maize, cereals and oil plant crops. The average load per hectare is high in fruit cultures, bulbs, potatoes and sugar beet. All these crops are grown in the IJsselmeerpolders.

The soil profile in the IJsselmeerpolders can be roughly characterised as a layer of Holocene, with a thickness from nearly nil to over 7 m, underlain by Pleistocene sands. The Holocene includes approximately ten soil types of which clayey soils with a clay content above 25% and loamy soils comprise the mayor part of the area. As the research was restricted to three experimental fields, not every soil type could be tested for the leaching of pesticides. A selection of the various soil types was made based on the sensitivity to leaching and representativity (covering a large part of the area). Besides the soil type, the way the drain pipes were installed (variations in depth and distance) played an important role in the selection.

The water management system inside the IJsselmeerpolders consists of the following items: subsurface drain pipes, collector drains, submain drains, main drains and pumping stations. In general the precipitation surplus runs through the unsaturated zone into the saturated zone. From there it enters the subsurface drain pipes, which drain off into the collector drains. The length and distance between the drain pipes is mainly based upon topography, soil conditions and on

agricultural economy. The maintenance of the drains pipes and collector drains is the responsibility of the farmers. From the collector drains, the water is drained into the submain drains and from there into the main drains. The main drains are connected to the pumping stations (figure 1.2). The maintenance of the submain drains, main drains and pumping stations is the responsibility of the Water-Board.

Objectives of the present research

In the development plans for the Markerwaard, considerable areas of the sandy and loamy sandy soils (the Enkhuizerzand area) were planned to be used for bulb cultivation. At this point in time pesticides are essential for this type of cultivation and are normally applied in considerable amounts. During the decision-making process concern increased for the potential threats of pesticides on human health and environmental quality. In future the drainage water of the newly reclaimed areas would be drained off to the lakes surrounding the Markerwaard, which are also used for water supply purposes and have high natural and recreational values. In order to formulate design and management criteria for the Markerwaard and estimate the quantity of pesticides to be drained off to the lakes surrounding the Markerwaard, a research project was started. Since concern is mostly associated with the presence of pesticides in the soil environment and surface waters (such as collector drains, submain drains and main drains), it is essential that the processes affecting the transport of pesticides are understood clearly.

As the knowledge with regard to different aspects of the processes affecting the transport of pesticides was limited, a field experiment was introduced on a tulip field, with the intention to calibrate and validate a future transport model. Because the future areas for bulb cultivation are still under water, the selected experimental field was situated in the already existing North-East Polder (figure 1.1: experimental field I). Here climatic conditions and soil characteristics are comparable with the possible future bulb areas in the Markerwaard. The field experiment started in the autumn of 1989 and continued until the spring of 1992. Although in 1990 the reclamation of the Markerwaard

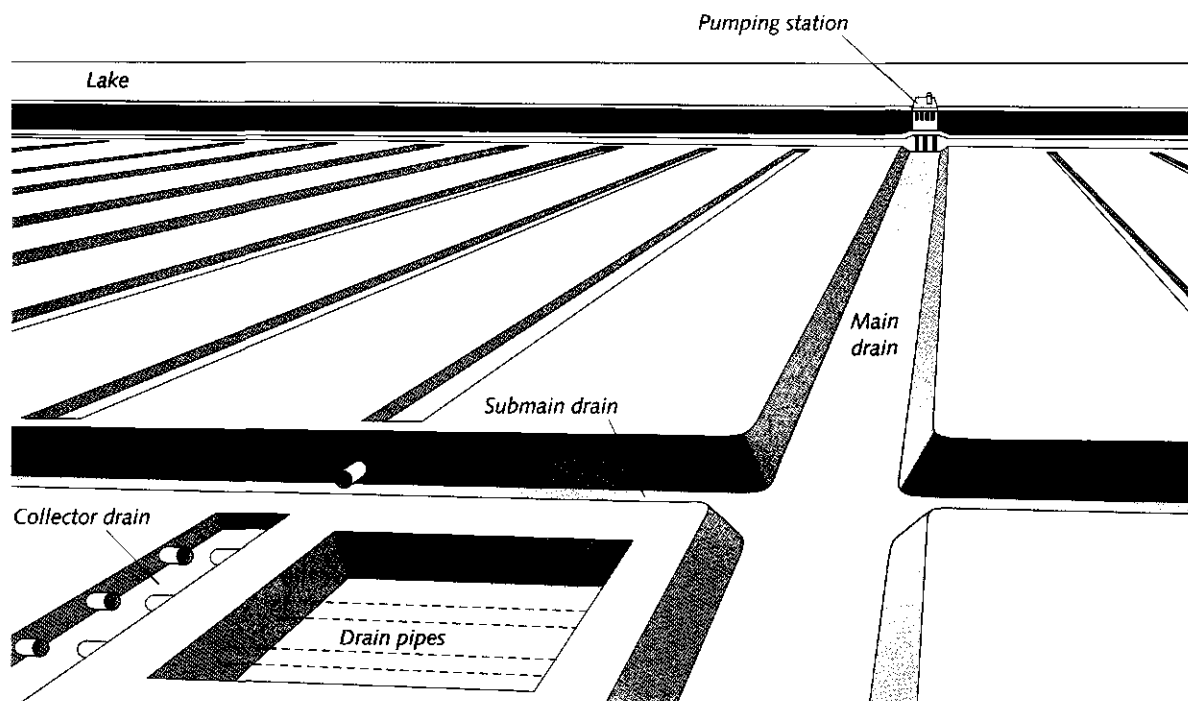


Figure 1.2. Schematic lay out of the drainage system.

was postponed, the results of the field experiment in the North-East Polder are still very important for other areas with similar soils where pesticides are applied.

During the years of the field experiment in the North-East Polder, the government's policy towards the admission of new pesticides became stricter. The reduction of the emission of pesticides into groundwater and surface water became one of the strategic headlines of the government's policy. In order to formulate measures to reduce the emission of pesticides, it is essential that the processes affecting the transport of pesticides are understood clearly. For clay soils in polder areas these processes were unknown. Therefore the research project was extended with two new field experiments. Both are situated in the Flevopolders on clay soils. One experimental field is situated in Eastern Flevoland (figure 1.1: experimental field II), the other experimental field is situated in Southern Flevoland in an orchard (figure 1.1: experimental field III). In experimental field II a potato crop was grown. At both experimental

fields the measurements started in 1992 and ended in 1994.

The research project focuses on the last objective of the Multi year plan on crop protection (Ministry of Agriculture, Nature Management and Fisheries, 1991). The basic problem for many cases of pollution has been the lack of knowledge of the processes affecting emission to air, groundwater and surface water. The objective of this research is to formulate design and management criteria for polder areas in order to develop an integrated pest management: effective and controlled application with little adverse effects on the surrounding environment. This includes the formulation of measures to reduce the emission of pesticides. Due to the enormous variety in different types of pesticides, crops, hydrological and soil conditions and the application time of pesticides, the use of computer simulation models is indispensable. Therefore an additional objective is the development, calibration and validation of a computer simulation model.

The research project is limited to the IJsselmeerpolders, newly reclaimed polder areas in the central part of the Netherlands. No attention will be paid to the transport of pesticides due to wind erosion and runoff, as these processes hardly occurred at the site of the research and thus the contribution was of minor importance to pollution of the environment. Pollution of the environment due to inaccurate use could be considerable, but is incidental and difficult to quantify and therefore also left out of consideration.

Four pesticides were incorporated in the research program. These pesticides were selected on the basis of leachability, representativity, demonstrability and application specifics. The representativity is defined by the quantity applied and the presence of various functional groups (e.g. fungicides, herbicides, insecticides, fumigants) and chemical families (e.g. organophosphorus, carbamate, triazine, organotin, nitro-com-

pounds, urea, dithiocarbamate, organochlorine, phenoxy) in the research program. For the pesticides in the research program, a chemical analysis method at the level of $0.1 \mu\text{g l}^{-1}$ should be available. To reduce the complexity, only soil-applied pesticides were incorporated in the research program.

This thesis

The model concepts of a computer simulation model for solute and pesticide transport are discussed in chapter 2. The model concepts are calibrated and validated extensively with the help of laboratory and field experiments, which are discussed in chapter 3. Chapter 4 gives the results of the calibration and verification of the simulation model for the three experimental fields. Scenario analyses with the models are presented in chapter 5.

Chapter 2

Water flow and solute transport in the unsaturated zone

Klaas Groen

Water flow and solute transport in the unsaturated zone

2.1 Water flow

In order to evaluate the fate of pesticides in the unsaturated zone and to determine mobility and persistence, it is essential to have a good description of the soil water flow as a function of time and depth. Soil water flow in the unsaturated zone is a complex physical process. Dynamic, deterministic models are based on the basic laws of soil water flow: conservation of mass and Darcy's law. The combination of both laws leads to a non-linear partial differential equation. The flow equations can be solved either analytically or by numerical methods. Analytical solutions can sometimes be found for more simple cases, but generally numerical methods are required. Numerical solutions to the flow equations offer a powerful tool in approximating the real nature of the unsaturated zone for a wide variety of soil systems and external conditions (Feddes et al., 1988-1). Once numerical models have been tested with field experiments and parameters have been derived, computer simulations can be performed.

Numerical methods divide the flow region into a network of elements. The numerical solution results in an approximate set of values at discrete nodal points. One criterium to classify models is time dependency. Here stationary (e.g. *CAPSEV* (Wesseling, 1984)), pseudo-stationary (e.g. *MUST* (De Laat, 1980)) and non-stationary models (e.g. *SWATRE* (Belmans et al., 1983)) can be distinguished. The accuracy of the model directly depends on the scheme of discretization used. For some hydrological situations stationary models give nearly the same result as pseudo- or non-stationary models. However for more complex hydrological situations non-stationary models should be used.

Various dynamic, deterministic models have been developed to describe water flow in the unsaturated zone. These models can be subdivided into one-dimensional

and two-dimensional models. Examples of the first type are *RFQSM* (Shaffer and Ribbens, 1974), *DRAINMOD* (Skaggs, 1980), *DEMGEM* (Abrahamse et al., 1982), *ONZAT* (Van Drecht, 1983), *SOMOF* (Gilding, 1983), *SWATRE* (Belmans et al., 1983), *OPDRAS* (Shopsky et al., 1984) and *HYSWASOR* (Dirksen et al., 1993). Examples of the second type are *UNSAT2* (Neuman et al., 1974), *DRAINET* (Hundertmark et al., 1991), *FUSSIM2* (Heinen and de Willigen, 1992) and *SWMS_2D* (Simunek et al., 1992). Despite the increasing number of two-dimensional models, the greater part of the models to simulate soil water flow are one-dimensional. One of the main reasons is the limited availability of input parameters for two-dimensional models. The one-dimensional, non-stationary, numerical models differ according to the type of boundary conditions, mathematical approach and model input-output. The differences generally depend on the major objectives of the model.

Of the above mentioned models, the model *SWATRE* is one of the most extended models (e.g. maximum number of compartments and soil layers and different options for boundary conditions). Feddes et al. (1978) developed a numerical model for the transient unsaturated soil moisture flow in a heterogeneous soil-root system under the name *SWATR* (Soil-Water-Actual-Transpiration). A new version of this model, *SWATRE* (extended), was made by Belmans et al. (1983). In this version a different numerical solution scheme was applied and the model was extended to different types of conditions at the bottom of the soil system. Feddes et al. (1978) developed the model *CROPR*, which calculates the potential and actual growth rate of a potato crop having an optimal nutrient supply. This model and the model *SWATRE* have been combined in the model *SWACRO*, which is a numerical model that combines the transient one-dimensional soil moisture flow and the crop production that follows

from the calculated transpiration rate (Feddes, 1985). A review of the principles underlying the modelling of the soil water dynamics in general and with reference to the model *SWACRO* has been presented by Feddes et al. (1988-1).

Adaptations to the model, concerning the numerical scheme and upward seepage will be discussed in section 2.1. Extension of the model with the transport of solutes and with transport, transformation and sorption of pesticides will be discussed in section 2.2. In section 2.3 solutions for modeling preferential flow in loamy sands and cracked clay soils are presented.

2.1.1. Basic flow equations

The model *SWACRO* is based on the one-dimensional water balance equation for a soil profile. If surface runoff can be neglected, the change in water storage ΔW (L) for a given period of time (Δt) can be written as:

$$\Delta W = [I + P + Q - (E_s + E_i + E_t)] \Delta t \quad 2.1$$

where:

I	= irrigation rate	(L T ⁻¹)
P	= (gross) precipitation rate	(L T ⁻¹)
Q	= net upward flow rate through the bottom	(L T ⁻¹)
E_s	= actual soil evaporation rate	(L T ⁻¹)
E_i	= interception rate	(L T ⁻¹)
E_t	= actual transpiration rate	(L T ⁻¹)
Δt	= time period estimated	(T)

E_s , E_i and E_t should be expressed as m³ per m² per unit of time. Although each component may be active only over a part of the total area, E_s , E_i and E_t are expressed in units of length over time as if they occur over the total surface area.

Conservation of mass for one-dimensional vertical flow requires that the change of water storage with time is equal to minus the divergence of the soil water flux density, minus the root water extraction:

$$\frac{\delta \theta}{\delta t} = - \frac{\delta q}{\delta z} - S \quad 2.2$$

where:

θ	= volumetric water content	(-)
q	= macroscopic soil water flux density	(L T ⁻¹)
z	= vertical coordinate taken positive upwards	(L)
S	= sink term for root water extraction	(T ⁻¹)

To describe the flow of water in the soil, Darcy's law is used. For one-dimensional vertical flow, the soil water flux density can be written as:

$$q = -K \left(\frac{\delta h}{\delta z} + 1 \right) \quad 2.3$$

where:

h	= pressure head	(L)
K	= hydraulic conductivity	(L T ⁻¹)

Richards (1931) was the first to present the differential equation for unsaturated soil water flow in porous media. Richards' equation is a combination of equation 2.2 and 2.3 and is usually written as (Feddes, 1978):

$$C(h) \frac{\delta h}{\delta t} = \frac{\delta}{\delta z} \left[K(h) \frac{\delta h}{\delta z} + 1 \right] - S \quad 2.4$$

where the differential soil moisture capacity $C(h)$ (L⁻¹) is equal to:

$$C(h) = \frac{\delta \theta}{\delta h} \quad 2.5$$

In equation 2.4 the coefficients C and K are functions of the pressure head. Equation 2.4 is the basic equation for predicting soil water movement in heterogeneous soils.

2.1.2 Numerical method

Richards' equation is solved by an implicit finite-difference scheme as proposed by Haverkamp et al. (1977) (Belmans, 1983). It can be written as:

$$C_i^j (h_i^{j+1} - h_i^j) = \frac{\Delta t^j}{\Delta z_i} \left[K_{i-\frac{1}{2}}^j \left(\frac{h_{i-1}^{j+1} - h_i^{j+1}}{\Delta z_{i-1/2}} \right) + K_{i+\frac{1}{2}}^j \right] - \frac{\Delta t^j}{\Delta z_i} \left[K_{i+\frac{1}{2}}^j \left(\frac{h_i^{j+1} - h_{i+1}^{j+1}}{\Delta z_i} \right) + K_{i+\frac{1}{2}}^j \right] - \Delta t^j S_i^j \quad 2.6$$

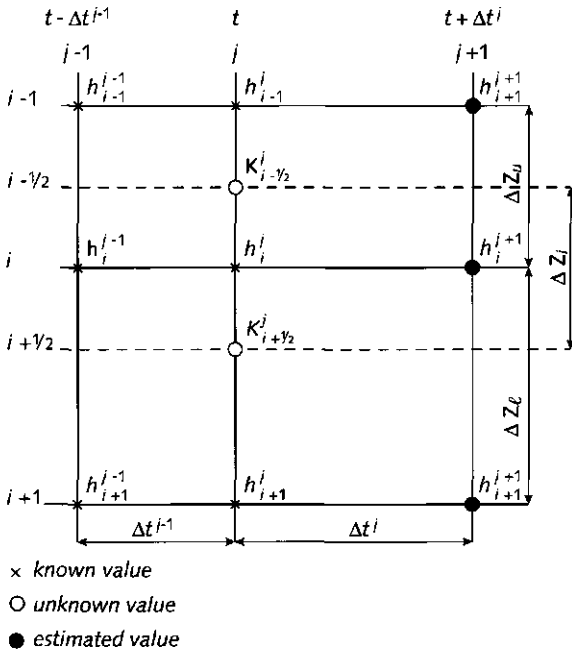


Figure 2.1 Depth (index i) - time (index j) region under consideration.

where $\Delta t^j = t^{j+1} - t^j$, $\Delta z_u = z_{i-1} - z_i$, $\Delta z_l = z_i - z_{i+1}$ and $\Delta z_i = (\Delta z_u + \Delta z_l) / 2$. The indexes i refer to discretization in space and j to discretization in time. K and S are established at time level j . The mean K between the nodes is calculated as the arithmetic mean. The one-dimensional flow domain is divided into compartments named Δz_i , which may be unequal in size. Equation 2.6 is valid for all nodal points except the top and bottom node of the soil column. The values of the hydraulic conductivity K and differential moisture capacity C are obtained by explicit linearization, which implies that K and C are taken at the previous time level j .

Rearrangement of equation 2.6 to a linear equation has been presented by Belmans et al. (1983). If the fluxes or pressure heads at the bottom and top of the defined profile are known, a system of $(i_n - 2)$ linear equations with an equal number of unknowns results. To solve the system of equations, a direct method known as the

Thomas (tridiagonal) algorithm is used (e.g. Remson et al., 1971).

However, due to the highly non-linear character of the differential moisture capacity, solution of Richards' equation with the proposed finite-difference scheme, induces mass balance problems at high infiltration rates. During these periods, the time step must be reduced strongly to avoid errors in the soil water balance. Particular for a whole growing season, this leads to a long calculation time (Van Dam and Feddes, 1997). A simple but effective solution was proposed by Celia (1990), who suggested to express the change of volumetric water content no longer as:

$$\theta_i^{j+1} - \theta_i^j = C_i^j (h_i^{j+1} - h_i^j) \quad 2.7$$

but as:

$$\theta_i^{j+1} - \theta_i^j = C_i^{j+1,m} (h_i^{j+1,m+1} - h_i^{j+1,m}) + \theta_i^{j+1,m} - \theta_i^j \quad 2.8$$

where m stands for the number of iterations. In this way, C is not averaged over a time step, but over an iteration step. When convergence is reached, the change of h has become negligible and consequently the effect of non-linearity in C has become negligible.

The original finite-difference scheme is extended with a second calculation step. In the first calculation step the linearized, implicit scheme is applied:

The mass balance is improved in the second calculation step with $m = 1$ (Celia, 1990):

$$C_i^j (h_i^{j+1,1} - h_i^j) = \frac{\Delta \theta^j}{\Delta z_i} \left[K_{i-1/2}^j \left(\frac{h_{i-1}^{j+1,1} - h_{i-1}^{j+1,1}}{\Delta z_u} \right) + K_{i+1/2}^j \right] - \frac{\Delta \theta^j}{\Delta z_i} \left[K_{i+1/2}^j \left(\frac{h_{i+1}^{j+1,1} - h_{i+1}^{j+1,1}}{\Delta z_l} \right) + K_{i+1/2}^j \right] - \Delta \theta^j S_i^j \quad 2.9$$

$$C_i^{j+1,1}(h_i^{j+1,2} - h_i^{j+1,1}) + (\theta_i^{j+1,1} - \theta_i^j) =$$

$$\frac{\delta t^j}{\delta z_i} \left[K_{i-\frac{1}{2}}^j \left(\frac{h_{i-1}^{j+1,2} - h_{i-1}^{j+1,1}}{\delta z_u} \right) + K_{i+\frac{1}{2}}^j \right]$$

$$- \frac{\delta t^j}{\delta z_i} \left[K_{i+\frac{1}{2}}^j \left(\frac{h_i^{j+1,2} - h_i^{j+1,1}}{\delta z_l} \right) + K_{i-\frac{1}{2}}^j \right] - \delta t^j S_i^j$$
2.10

The second calculation step is repeated until a defined stop criterium has been reached. The pressure head is taken as a variable and estimated as (Van Dam and Feddes, 1997):

$$\Delta h_{max} = reltol |h| + abstol \quad 2.11$$

where *reltol* = relative tolerance and *abstol* = absolute tolerance are parameters, which should be declared in the input file. Due to the rapid change of soil water fluxes near the soil surface, the distance between the nodes should be small here.

2.1.3 Soil physical properties

In the model *SWACRO* the soil system is divided into a number of compartments, with variable height. One or more compartments form a soil layer with specific soil physical properties. These soil physical properties consist of the soil-moisture retention curve $h(\theta)$ and the unsaturated hydraulic conductivity curve $K(h)$.

SWACRO offers the alternative to describe the soil-physical relationships as analytical functions (Mualem, 1976; Van Genuchten, 1980; Van Genuchten and Nielsen, 1985). In the Netherlands the soil-physical relationships are usually presented by the Staring-series, a collection of tables (and parameters) representing the most frequently occurring soil types in the Netherlands (Wösten et al., 1987). However, these relationships can also be obtained by measuring the soil hydraulic functions in the laboratory.

The most recent empirical formula to describe the soil moisture retention curve is (Van Genuchten and Nielsen, 1985):

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m} \quad 2.12$$

with:

$$m = 1 - \frac{1}{n} \quad 2.13$$

where:

- θ_r = residual volumetric water content (-)
- θ_s = saturated volumetric water content (-)
- α = shape parameter (L^{-1})
- n, m = shape parameters (-)

The relation between the hydraulic conductivity and pressure head $K(h)$ is represented by:

$$K(h) = K_s \frac{[(1 + |\alpha h|^n)^m - |\alpha h|^{n-1}]^2}{(1 + |\alpha h|^n)^{m(\lambda+2)}} \quad 2.14$$

where:

- K_s = saturated hydraulic conductivity ($L T^{-1}$)
- λ = shape parameter depending on dK/dh (-)

Various methods, such as the needle method (Freyer and Lange, 1990), the crust method (Stolte, 1989) and the evaporation method (Veerman, 1989) have been presented for measuring the soil hydraulic functions. Generally these methods require restrictive initial and boundary conditions and are very time consuming. To avoid this, a new technique has recently been developed to determine the soil hydraulic functions. It combines limited measurements, concepts of unsaturated flow and numerical computer techniques to determine in a transient flow process the unknown soil properties (Kool et al., 1987). The unknown parameters of the soil hydraulic functions ($\alpha, \lambda, n, \theta_r, \theta_s, K_s$) are estimated by minimizing deviations between observed and model-predicted output. The laboratory outflow method is an example of this technique (Kool et al., 1985; Van Dam et al., 1990-2). The advantage of this approach is that no restrictive initial and boundary conditions are needed. However, this method cannot be used for shrinking/swelling clay soils. For these soils the evaporation method is applied.

2.1.4 Upper boundary conditions

The condition of the upper boundary of the soil profile is determined by evapotranspiration and infiltration.

Maximum evapotranspiration rate is defined as the highest possible evapotranspiration rate from a wet cropped surface under the prevailing meteorological conditions. E_{max} can be divided in potential soil evaporation rate (E_{sp}), potential transpiration rate (E_{tp}) and interception rate (E_i):

$$E_{max} = E_{sp} + E_{tp} + E_i \quad 2.15$$

If the interception rate is equal to zero, E_{max} is reduced to the *potential evapotranspiration rate* (E_p) according to:

$$E_p = E_{sp} + E_{tp} \quad 2.16$$

Equations 2.15 and 2.16 imply that potential evapotranspiration rate is defined as a function of soil cover as encountered in the field. Unlike earlier definitions it means that E_p is defined as the maximum possible evapotranspiration rate from an area partly covered by a crop, which is dry at the outside. The model SWACRO offers four alternatives for the calculation of the daily potential evapotranspiration rate. At the experimental fields the Makkink equation was used to calculate the reference crop evapotranspiration rate (Makkink, 1957, 1960). A slightly adjusted equation of Makkink is presented by Hooghart and Lablans (1988):

$$E_r = 0.65 \frac{s}{s + \gamma} \frac{K^\downarrow}{\lambda_w} \quad 2.17$$

where:

E_r	= reference evapotranspiration rate	($L T^{-1}$)
K^\downarrow	= global solar radiation flux density	($M T^{-3}$)
s	= saturated vapour pressure	($L^{-1} M T^{-2} \Theta^{-1}$)
γ	= psychrometric coefficient	($L^{-1} M T^{-2} \Theta^{-1}$)
λ_w	= latent heat of vaporization of water	($L^{-1} M T^{-2}$)

To calculate the reference evapotranspiration rate, the global solar radiation flux density (K^\downarrow) and the mean daily air temperature have to be measured. Reference evapotranspiration rate is multiplied by a crop factor, f ,

to obtain the potential evapotranspiration rate of the concerned crop:

$$E_p = f E_r \quad 2.18$$

The crop factor f contains the influence of partly soil cover and is therefore a function of time. It depends on the characteristics of the crop, its development stage and the prevailing meteorological conditions. The f factor is usually given as average decade values during the growing season. They have been determined experimentally.

Potential soil evaporation rate is calculated according to Belmans et al. (1983):

$$E_{sp} = E_p \exp(-0.6 LAI) \quad 2.19$$

where:

$$LAI = \text{Leaf Area Index} \quad (-) \quad 2.19$$

The exponential function in equation 2.19 varies from 0 to 1. If LAI is equal to 0, E_{sp} equals E_p . On the other hand, if LAI is large (> 5), E_{sp} approximates 0. The leaf area index is calculated as:

$$LAI = a S_c + b S_c^2 + c S_c^3 \quad 2.20$$

where:

a, b, c	= regression coefficients	(-)
S_c	= soil cover	(-)

The regression coefficients a , b and c differ for each crop. Accordingly, the LAI (and consequently the potential soil evaporation) may be different for each crop for the same soil cover. This is illustrated in figure 2.2.

As E_p (equation 2.18) and E_{sp} (equation 2.19) are known, the *potential transpiration rate* (E_{tp}) is calculated using equation 2.16. The actual flux density through the soil surface (q_s) is presented by:

$$q_s = E_s - (P - E_i) \quad 2.21$$

where:

E_s	= actual soil evaporation rate	($L T^{-1}$)
E_i	= interception rate	($L T^{-1}$)
P	= (gross) precipitation rate	($L T^{-1}$)

Actual soil evaporation rate is described according to

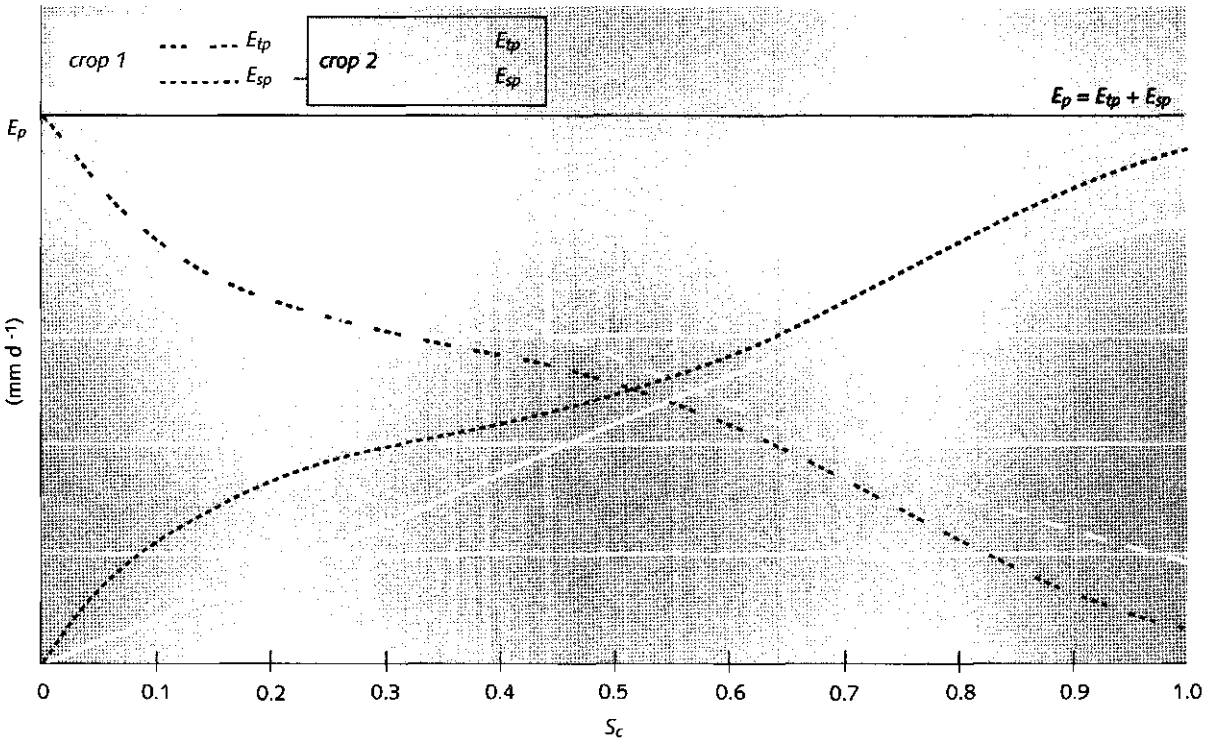


Figure 2.2 Partitioning of the potential evapotranspiration E_p (constant value) in potential transpiration E_{tp} and potential evaporation E_{sp} as a function of the soil cover S_c for two illusory crops with different values for the regression coefficients a , b and c (equation 2.20). The lines show that partitioning depends on the regression coefficients a , b and c .

Ritchie (1972) and Boesten (1986) and may be distinguished in two stages. In the first stage the soil is wet and the actual volume flux of evaporation is equal to the potential flux. In the second stage the soil surface is gradually drying out and the actual evaporation flux is rapidly decreasing. At the end the actual volume flux is very low and relatively constant. The sum of the actual soil evaporation during a drying cycle according to Boesten (1986) can be represented by:

$$\begin{aligned} \text{STAGE 1: } \sum E_s &= \sum E_{sp} \quad \text{for } \sum E_{sp} \leq \beta^2 \\ \text{STAGE 2: } \sum E_s &= \beta \sqrt{\sum E_{sp}} \quad \text{for } \sum E_{sp} > \beta^2 \end{aligned} \quad 2.22$$

where:
 β = soil dependent parameter $(L^{0.5})$

Interception rate (E_i) is estimated as (Braden, 1985):

$$E_i = a_i LAI \left(1 - \frac{1}{1 + \frac{P S_c}{a_i LAI}} \right) \quad 2.23$$

where:

a_i = parameter representing the crop dependent saturation value $(L T^{-1})$

Actual evapotranspiration rate (E_a) is the sum of the actual soil evaporation rate (E_s), interception rate (E_i) and the actual transpiration rate (E_t), thus:

$$E_a = E_s + E_i + E_t \quad 2.24$$

Actual transpiration rate is the flux of water through the canopy of the leaves. The water needed for transpiration is extracted from the soil by the plant roots.

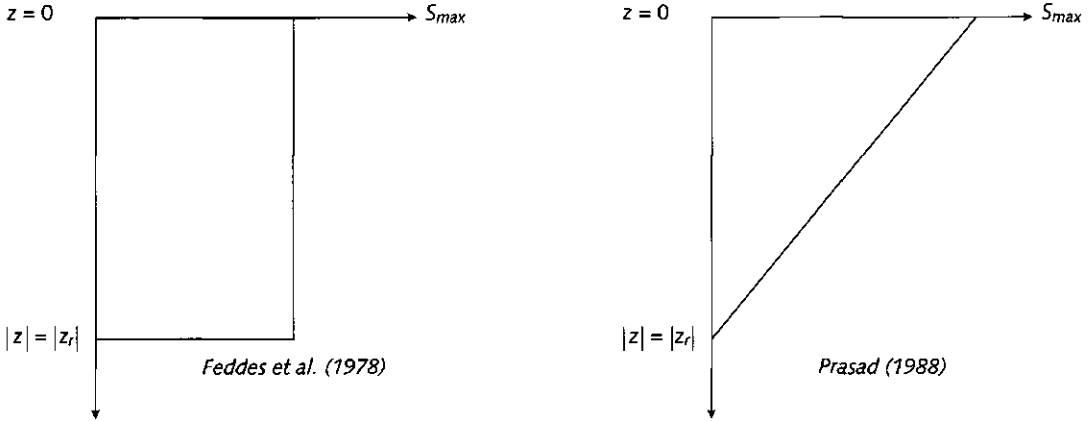


Figure 2.3 Schematic view of different water uptake functions under optimal soil water conditions S_{\max} as a function of $|z|$, as proposed by various authors.

The distribution of water extracted from the soil is a function of the root developing stage, the root water uptake function and the soil water pressure head. Water uptake by roots is represented by a volumetric sink term (S) which is added to the continuity equation (equation 2.4). The function for S depends on the pressure head and is defined as (Feddes, 1978):

$$S(h) = \alpha(h) S_{\max} \quad 2.25$$

where:

- $\alpha(h)$ = reduction factor (-)
 S_{\max} = maximum possible water extraction rate by roots (T^{-1})

Various expressions for S_{\max} have been presented. Feddes et al. (1978) assume a homogenous distribution of S_{\max} with depth, according to (figure 2.3):

$$S_{\max} = \frac{E_{tp}}{|z_r|} \quad 2.26$$

where:

- z_r = lower limit of the root zone (L)

As roots can extract most water from the upper soil layers, and proportionally less water from the deeper layers, another linear relationship was proposed, according to (Prasad, 1988; figure 2.3):

$$S_{\max} = 2 \frac{E_{tp}}{|z_r|} \left(1 - \frac{|z|}{|z_r|} \right) \quad 2.27$$

Under non-optimal conditions, i.e. either too dry or too wet, S_{\max} is reduced by means of the pressure-head dependent reduction factor $\alpha(h)$ (equation 2.25; Feddes et al., 1978). The shape of this function is shown in figure 2.4. Water uptake below $|h_1|$ (oxygen deficiency) and above $|h_4|$ (wilting point) is set equal to zero. Between $|h_1|$ and $|h_2|$ and between $|h_3|$ and $|h_4|$ a linear variation is assumed. The value of $|h_3|$ is dependent on the transpiration demand and thus varies with E_{tp} . The values of $|h_1|$, $|h_2|$, $|h_3|$ and $|h_4|$ are dependent on the type of crop.

2.1.5 Lower boundary conditions

The model *SWACRO* contains different hydrological options for the bottom boundary condition. The different options used, are:

- there is no flux at the bottom of the profile (e.g. due to an impermeable layer at the bottom of the defined profile);
- the flux is a linear function of the height of the phreatic surface.

The model *SWACRO* is extended to an option for upward as well as for downward seepage, describing the

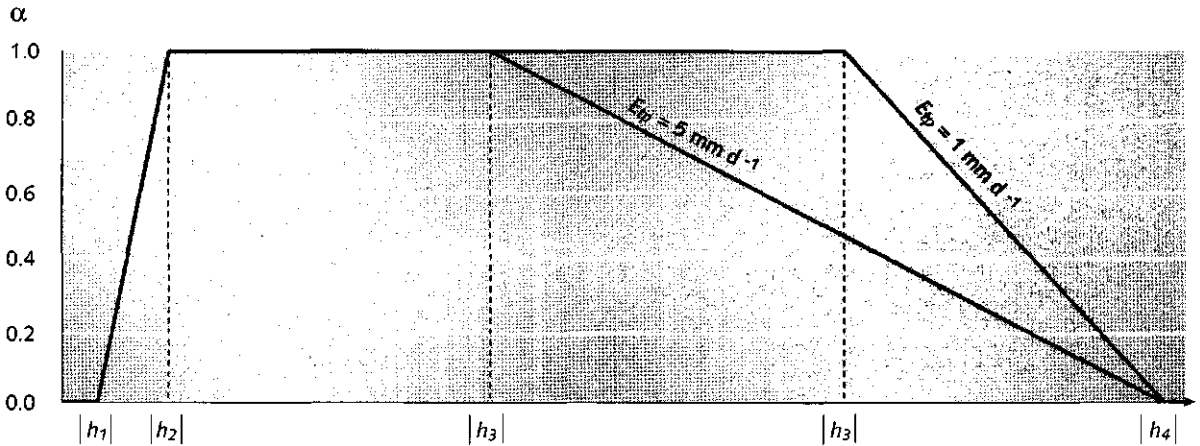


Figure 2.4 Dimensionless sink term variable, α , as a function of the absolute value of the soil water pressure head, $|h|$ (after Feddes et al., 1978).

situation in polder areas, which are surrounded by lakes with higher water levels. The quantity of upward seepage is dependent on the hydraulic head and the permeability of the subsoil. The deep upward seepage may appear as outflow of a subsurface drainage system, as extra evapotranspiration or as upward flow through the bottom of a ditch or canal. When the canal bottom cuts into the more permeable aquifers, upward seepage will occur through the bottom of the canal. The amount of seepage water upwards through the bottom of a ditch is hard to quantify. A schematic profile of the hydraulic head in the Pleistocene profile is given in figure 2.5. The fluxes at the bottom of the profile are a linear function of the phreatic surface, given by:

$$q_b = \frac{h_{pl} - h_{phr}}{\Upsilon} \quad 2.28$$

where:

- Υ = drainage resistance (T)
- h_{pl} = hydraulic head in the Pleistocene subsoil (L)
- h_{phr} = height of phreatic surface (L)
- q_b = flux at the bottom of the soil profile (L T⁻¹)

The flux through the bottom of the defined profile will be negative (downward) if the height of phreatic surface is above the hydraulic head in the Pleistocene subsoil (downward seepage). The flux will be positive if the height of the phreatic surface is below the hydraulic head in the Pleistocene sand (upward seepage).

2.1.6 Lateral boundary conditions

In the unsaturated zone the movement of soil water is supposed to occur only in a vertical direction, while for the saturated zone or at perched water tables, both

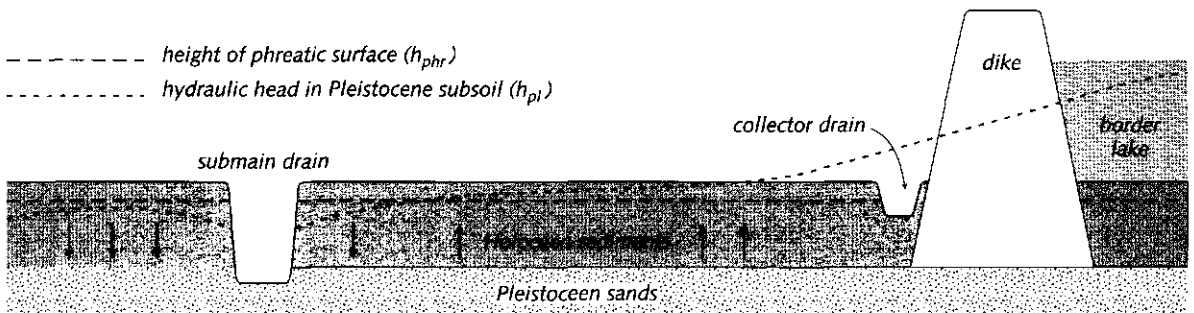


Figure 2.5 Schematic profile of the hydraulic head in the Pleistocene subsoil (h_{pl}) in a cross-section perpendicular to a dike.

horizontal and vertical groundwater flow is taking place. The horizontal flux of the groundwater flux is calculated with the steady-state equations of Hooghoudt or Ernst. Whether the Hooghoudt or the Ernst equation is selected, depends on the soil profile and relative position of the subsurface drain pipes. Appropriate solutions indicating which of the two formulas should be used in various situations, are presented by Ritsema (1994). These solutions were also applied in the model *SWACRO*.

The Hooghoudt formula is based on Darcy's law, the continuity principle and the Dupuit-Forchheimer theory, the last also known as the assumption of horizontal flow (Dupuit 1863; Forchheimer, 1886; Hooghoudt, 1940). If the subsurface drain pipes are situated above or on top of an impervious layer and the hydraulic conductivity of the soil is homogeneous, the drain discharge rate can be calculated with:

$$q_d = \frac{8 K_b d_{eq} h_m + 4 K_i h_m^2}{L^2} \quad 2.29$$

where:

- q_d = drain discharge rate per unit surface area (L T⁻¹)
- K_b = hydraulic conductivity of the layer below the drain pipes (L T⁻¹)
- d_{eq} = equivalent depth (L)
- h_m = height of the phreatic surface midway between the drain pipes above the water level in the drain pipes (= total hydraulic head loss) (L)
- K_i = hydraulic conductivity of the layer above the drain pipes (L T⁻¹)
- L = drain spacing (L)

If the drain pipes are situated on top of the impervious layer, the equivalent depth is equal to zero. If the drain pipes are situated above the impervious layer, the equivalent depth is calculated according to exact solutions as presented by Van der Molen and Wesseling (1991). The concept for the calculation of the equivalent depth is presented by Ritsema (1994).

If the interface between the layers does not coincide with the level of the drain pipes and the flow of water

is not considered to be only horizontal, the Ernst formula applies (Ernst; 1956, 1962). The Ernst formula is particularly useful if the upper soil layer has a considerably lower hydraulic conductivity than the lower layer. The flow to the drains is divided into vertical, horizontal and radial flow. Total hydraulic head loss (h_m) may be given by:

$$h_m = q_d \frac{D_v}{K_v} + q_d \frac{L^2}{8 \Sigma (KD)_{hor}} + q_d \frac{L}{\pi K_r} \ln \left(\frac{a_r D_r}{u} \right) \quad 2.30$$

where:

- D_v = thickness of the layer in which vertical flow is considered (L)
- K_v = hydraulic conductivity in the layer with vertical flow (L T⁻¹)
- $(KD)_{hor}$ = transmissivity of the soil layers through which horizontal flow is considered (L² T⁻¹)
- K_r = hydraulic conductivity in the layer with radial flow (L T⁻¹)
- a_r = geometry factor for radial flow depending on the flow conditions (-)
- D_r = thickness of the layer in which radial flow is considered (L)
- u = wet perimeter of the drain (L)

The drain discharge rate may be restricted by the discharge capacity of the drain pipes. How much submerged drain flow occurs depends on the drain discharge rate, the wetted perimeter of the drain pipes, pipe length, pipe roughness and area drained. Submerged drain flow may strongly influence the height of the phreatic surface.

2.2 Solute transport

Water is the primary carrier for the transport of solutes. In most deterministic models, the actual movement of solutes in the soil is a result of three processes: convective transport in the liquid phase, diffusive transport in the liquid phase and diffusive transport in the gas phase. Convective transport of solutes in the soil results

in dispersion. It is caused by variation of the effective pore water velocity.

Water movement may be distinguished in two particular systems, the unsaturated zone and the saturated zone. In the unsaturated zone, the water movement is assumed to be one-dimensional in the vertical direction. The solutes percolate downwards as a result of irrigation or precipitation surplus. For sorbing compounds, the actual rate of displacement in the profile may be much less than for non-sorbing compounds. For volatile compounds, which evaporate in the gas phase, the transport is dependent on pressure and concentration gradients. However, in both cases the movement is still considered to be one-dimensional in the vertical direction. In the saturated zone, the flow of solutes is assumed to take place in the general direction of groundwater flow. For a soil with a subsurface drainage system, the groundwater flow is assumed to be horizontal (see subsection 2.1.6).

Various models that describe pesticide fate in the unsaturated zone have been presented in the literature (e.g. Davidson and Chang, 1972; Van Genuchten, 1974; Van Genuchten and Wieringa, 1976; Leistra, 1978, 1979; Rao et al., 1979; Nicholls et al., 1982-1, 1982-2; Boesten, 1986; Wagenet and Hudson, 1989). These models are based on a deterministic concept, including physical and chemical processes of solute transport in soils. Various models have been reviewed by Wagenet and Rao (1990). Generally, a distinction is made between management-oriented and research-oriented models.

Research-oriented mathematical models for pesticide fate in the unsaturated zone have been developed by for example Hudson and Wagenet (1992, *LEACHM*) and Boesten and Van der Linden (1991, *PESTLA*: version 1.1). The model *PESTLA* is a modified version of the model described by Leistra and Dekkers (1977). With respect to pesticide behaviour in the soil, *PESTLA* and *LEACHM* are based on the same basic concept: convection/dispersion equation for solute transport, non-linear sorption according to the Freundlich equation, temperature dependent first-order transformation rates, and passive plant uptake. However, some differences between these models can be distinguished. *LEACHM*

incorporates the prediction of the transport and transformation of the pesticide as well as up to two intermediates (transformation products). Furthermore *LEACHM* provides the prediction of the volatilization losses.

The soil water flow in both models is based on a relatively simple concept (e.g. simple bottom boundary conditions (*PESTLA*, *LEACHM*), evapotranspiration on a weekly basis (*LEACHM*). For this reason an extended version of the model concept of *PESTLA* for pesticide fate has been adapted and implemented as a subroutine in the model *SWACRO* (Feddes et al., 1988-1). The extended model can describe soil water flow, crop water use, crop yield and pesticide fate (Work Group *SWAP*, 1997).

The concept for pesticide fate as presented by Boesten (1986, 1991-1) has been extended to describe transport of pesticides in the gas phase and microbiological transformation. The program does account for preferential flow of water and solutes in macro-pores and the presence of mobile and immobile soil-water domains. The concepts for pesticide fate in the extended model *SWACRO* will be presented in this section.

2.2.1 Mass conservation and transport

The one-dimensional mass conservation equation for pesticides in the soil system can be presented as:

$$\frac{\delta c^*}{\delta t} = - \frac{\delta J}{\delta z} - R_t - R_u - R_d \quad 2.31$$

where:

c^*	= total solute concentration in all phases	(L ⁻³ M)
t	= time	(T)
J	= total solute flux density	(L ⁻² M T ⁻¹)
z	= vertical coordinate taken positive upwards	(L)
R_t	= sink term for transformation	(L ⁻³ M T ⁻¹)
R_u	= sink term for root water uptake	(L ⁻³ M T ⁻¹)
R_d	= sink term for lateral drainage	(L ⁻³ M T ⁻¹)

Total pesticide concentration in the soil system, c^* , can be subdivided in:

$$c^* = \rho X + \theta c_l + \varepsilon c_g \quad 2.32$$

where:

ρ	= dry soil bulk density	($L^{-3} M$)
X	= sorbed-phase content	(-)
θ	= volumetric water content	(-)
c_l	= concentration in the liquid phase	($L^{-3} M$)
ε	= volumetric air content	(-)
c_g	= concentration in the gas phase	($L^{-3} M$)

Combination of equation 2.31 and 2.32 gives:

$$\frac{\delta}{\delta t} (\rho X + \theta c_l + \varepsilon c_g) = - \frac{\delta J}{\delta z} - R_t - R_u - R_d \quad 2.33$$

Equation 2.33 is the basic one-dimensional mass conservation equation for pesticide fate in a soil system. It includes pesticide transport in the liquid and gas phase, sorption, transformation, lateral drainage and plant uptake. Each of these processes will be considered in the following subsections.

The total solute flux is represented as:

$$J = J_{dl} + J_{cl} + J_{dg} \quad 2.34$$

where:

J_{dl}	= diffusive flux density in the liquid phase	($L^{-2} M T^{-1}$)
J_{cl}	= convective flux density in the liquid phase	($L^{-2} M T^{-1}$)
J_{dg}	= diffusive flux density in the gas phase	($L^{-2} M T^{-1}$)

Convective transport in the gas phase, resulting from pressure gradients caused by groundwater table fluctuations, air pressure fluctuations or a temperature gradient in the soil, is left out of consideration. This is allowed only if diffusion has a much greater effect on the spreading of vapour than convection. The convective transport in the gas phase has recently been studied in more detail and is considered to be of some consequence in the transport of extremely volatile chemicals (Wagenet, et al. 1989) and in the transport of volatile chemicals in dry, coarse soils or in loosely tilled top soils containing large air voids (Van den Berg, 1992).

However, in homogeneous soils of medium or fine texture, convective transport in the gas phase does not seem to contribute much to the transport of volatile chemicals such as fumigants.

Diffusion in the liquid phase of porous media can be described according to Fick's law (e.g. Wagenet, 1984):

$$J_{dl} = - D_{dif,\theta} \frac{\delta c_l}{\delta z} \quad 2.35$$

where:

$D_{dif,\theta}$ = effective diffusion coefficient for the liquid phase ($L^2 T^{-1}$)

The diffusion coefficient through the soil can be calculated from:

$$D_{dif,\theta} = D_{dif,w} \tau_l \theta \quad 2.36$$

where:

$D_{dif,w}$ = diffusion coefficient in water ($L^2 T^{-1}$)
 τ_l = tortuosity factor for diffusion in the liquid phase (-)

One-dimensional flux density due to diffusive transport in the gas phase of the soil system in the vertical direction is represented as:

$$J_{dg} = - D_{dif,\varepsilon} \frac{\delta c_g}{\delta z} \quad 2.37$$

where:

$D_{dif,\varepsilon}$ = vapour diffusion coefficient in the gas phase ($L^2 T^{-1}$)

The vapour diffusion coefficient in the gas phase depends on the gas-filled pore volume of the soil system and the tortuosity of the pore system. It is given by:

$$D_{dif,\varepsilon} = D_{dif,air} \tau_g \varepsilon \quad 2.38$$

where:

$D_{dif,air}$ = vapour diffusion coefficient in air ($L^2 T^{-1}$)
 τ_g = tortuosity factor for diffusion in the gas phase (-)

The tortuosity factor depends on the volume fraction of the gas phase in the soil system. Values of the tortuosity factor can be derived by using the experimental factors compiled by Leistra (1972) or the Millington-Quirk model (Sheare et al., 1973).

The vapour diffusion coefficient in air is to some extent dependent on the soil and air temperature. It can be calculated using estimation methods presented by Reid and Sherwood (1966) or Cohen et al. (1988). The influence of the temperature on the coefficient is comparatively small for the pesticides 1,3-dichloropropene (Van den Berg, 1992) and is therefore neglected.

The one-dimensional vertical convective-dispersive transport in the liquid part of the soil is described by:

$$J_{cl} = qc_l - \theta D_{dis} \frac{\delta c_l}{\delta z} \quad 2.39$$

where:

q = macroscopic soil water flux density ($L T^{-1}$)
 D_{dis} = dispersion coefficient ($L^2 T^{-1}$)

The mechanical dispersion coefficient (D_{dis}) describes mixing between large and small pores as a result of local variations of the effective pore water velocity. It can be calculated as:

$$D_{dis} = L_{dis} |v_e| \quad 2.40$$

where:

L_{dis} = dispersion length (L)
 v_e = effective pore water velocity (q/θ) ($L T^{-1}$)

Combining equation 2.35, 2.37 and 2.39 into equation 2.34 gives:

$$J = -D_{dif,\theta} \frac{\delta c_l}{\delta z} + qc_l - \theta D_{dis} \frac{\delta c_l}{\delta z} - D_{dif,g} \frac{\delta c_g}{\delta z} \quad 2.41$$

The effective diffusion coefficient for the liquid phase ($D_{dif,\theta}$) can be written as:

$$D_{dif,\theta} = D_{dif} \theta \quad 2.42$$

where:

D_{dif} = diffusion coefficient ($L^2 T^{-1}$)

Equation 2.41 can finally be rewritten as the general equation:

$$J = qc_l - \theta (D_{dis} + D_{dif}) \frac{\delta c_l}{\delta z} - D_{dif,g} \frac{\delta c_g}{\delta z} \quad 2.43$$

The combination of the mechanical dispersion coefficient and the diffusion coefficient through the liquid phase is often referred to as the hydrodynamic dispersion coefficient. When the soil water flux is of any importance ($q > 1 \text{ mm d}^{-1}$), the contribution of the diffusion coefficient can be neglected (Bolt, 1979). For non-volatile pesticides, equation 2.43 can be even more simplified by neglecting the third term.

The partial differential equations for pesticide behaviour were solved numerically using an explicit finite difference method. The solution was based on central difference approximations of the derivatives with respect to depth in soil. Derivatives with respect to time were integrated by assuming that the time derivative is constant over the time step (rectangular method). In order to guarantee stability, the maximum time step, dt_{max} is defined as:

$$dt_{max} = \frac{(dz_i)^2 \theta}{2(D_{dis} + D_{dif})} \quad 2.44$$

This stability criteria is valid for non-sorbing and non-volatile solutes. However, sorption increases stability. For gas diffusion stability was tested by running the program assuming that the solute is not transformed. Normally dt_{max} exceeds the maximum time step admissible for the solution of Richard's equation. However, if dt_{max} is smaller, the time step is adjusted according to equation 2.44.

2.2.2 Transformation

Transformation of pesticides can take place along microbiological or chemical pathways. Different concepts have been presented to describe the transformation of pesticides (e.g. Linders, 1983;). In most

pesticide fate models (e.g. *LEACHM*, *PESTLA*) transformation is described by simple first-order kinetics. However, in many cases transformation takes place along more complicated pathways (e.g. Hamaker, 1972; Munnecke et al., 1982; Alexander and Scow, 1989) and thus cannot be described mathematically by first-order kinetics.

The model *SWACRO* contains two different options for the transformation of pesticides. In the first option transformation is described by first-order kinetics. The rate of transformation is characterized in terms of a half-life, which allows the possibility of comparing different types of pesticides. If first-order kinetics are used, it is usually not specified whether transformation takes place along microbiological or chemical pathways. Microbial transformation can be described by first-order kinetics if cometabolism is involved. Cometabolism is a process in which the pesticide is transformed by metabolic reactions but does not serve as an energy or nutrient source for the microorganism. A concept for first-order transformation will be presented in subsection 2.2.2.1.

In the second option, transformation is described by Monod's kinetics (Scow, 1990). Biodegradation is the predominant process, in which a pesticide serves as a substrate for growth. The microorganisms obtain their requirements for growth and energy from the pesticidal molecules. The biological transformation rate reflects both microbial activity and microbial population density. Microbiological transformation caused by biodegradation can be identified by rapid transformation after a period of time (e.g. hours, days, weeks) (Simkins and Alexander, 1984; Vink and Groen, 1992). Usually, more complex microbiological processes, such as biodegradation, are predominant in the root zone (Simkins and Alexander, 1984). A concept for microbiological transformation will be presented in subsection 2.2.2.2. In both cases soil temperatures often have a strong impact on the rate of transformation. Therefore, the calculation of soil temperatures will be discussed in subsection 2.2.2.3.

2.2.2.1 First-order transformation

In most models pesticide transformation is represented by first-order transformation (e.g. Bolt, 1979; Boesten,

1986; Wagenet and Hudson, 1989) as:

$$R_t = k_t c^* \quad 2.45$$

where:

$$k_t = \text{first-order transformation rate coefficient} \quad (\text{T}^{-1})$$

The resulting equation is a simple linear model that can easily be tested by regression analysis and the half-life time can then be calculated from the slope. According to Walker (1974) and Leistra and Dekkers (1977) both water content and temperature of the soil have a large influence on the transformation rate. Boesten and van der Linden (1991) proposed the addition of the influence of soil depth on the rate of transformation with a numerical function.

The first-order transformation rate coefficient is calculated from:

$$k_t = f_T f_\theta f_z k_{t,ref} \quad 2.46$$

where:

$$\begin{aligned} f_T &= \text{coefficient for the influence of soil temperature on the rate of transformation} & (-) \\ f_\theta &= \text{coefficient for the influence of soil moisture content on the rate of transformation} & (-) \\ f_z &= \text{coefficient for the influence of soil depth on the rate of transformation} & (-) \\ k_{t,ref} &= \text{reference coefficient for first-order transformation} & (\text{T}^{-1}) \end{aligned}$$

This equation assumes that the effects of soil temperature, moisture content, and soil depth on the transformation rate are independent from each other. Some experimental evidence on this simple approach was provided by Walker (1974). Normally the reference coefficient for first-order transformation gives the rate of transformation for a pesticide in a soil sample, taken from the plough layer as reference depth, with a reference soil moisture content at a matrix pressure of -10 kPa (i.e. $h = -100$ cm) and a reference soil temperature of 20 °C.

The influence of soil temperature on the rate of transformation is given by:

$$f_T = \exp [\gamma_a (T - T_{ref})] \quad 2.47$$

where:

$$\begin{aligned} \gamma_a &= \text{coefficient} & (\Theta^{-1}) \\ T &= \text{soil temperature} & (\Theta) \\ T_{ref} &= \text{reference temperature} & (\Theta) \end{aligned}$$

Equation 2.47 can be considered as a numerical approximation of the Arrhenius equation (Boesten, 1986, 1991-1):

$$f_T = \exp \left[\frac{E}{R T_{ref} T} (T - T_{ref}) \right] \quad 2.48$$

where:

$$\begin{aligned} E &= \text{molar activation energy} & (\text{L}^2 \text{M N}^{-1} \text{T}^{-2}) \\ R &= \text{universal gas constant} & (\text{L}^2 \text{M N}^{-1} \text{T}^{-2} \Theta^{-1}) \end{aligned}$$

Because T and T_{ref} are absolute temperatures (Kelvin) the quotient $E / (R T_{ref} T)$, which is equal to parameter γ_a , never differs more than 5% if T varies from 5 to 35 °C (i.e., from 278 to 308 K). Therefore, equation 2.48 may be simplified to equation 2.47, using a γ_a value equal to this quotient measured at a temperature of 20 °C (Boesten, 1986).

The influence of the soil moisture content on the rate of transformation f_θ may vary from 0 to 1. It is calculated from (Walker, 1974):

$$f_\theta = \left(\frac{\theta}{\theta_{ref}} \right)^{b_l} \quad 2.49$$

where:

$$\begin{aligned} \theta_{ref} &= \text{soil moisture content at a reference level} & (-) \\ b_l &= \text{parameter} & (-) \end{aligned}$$

The coefficient for the influence of soil depth on the rate of transformation (f_z) is given for each soil compartment. It is related to the reference coefficient for first-order transformation in the plough layer, which is set at 1. The factor f_z is not described by a formula but with a numerical function.

For some pesticides transformation can be described mathematically by first-order kinetics preceded by an

initial phase (Stryer, 1988). Basically, this approach is a mathematical simplification of biodegradation, which can be identified by rapid transformation after a period of time (subsection 2.2.2.2). During the initial phase, no transformation is observed, thus $k_i = 0$. The length of the initial phase can be determined by many factors such as adaptation of soil due to previous applications, soil moisture content, soil depth and soil temperature. If the soil is already adapted and the soil moisture content is constant, the length of the initial phase in the plough layer is a function of the soil temperature. After the initial phase the first-order transformation rate coefficient is calculated from equation 2.45.

2.2.2.2 Microbiological transformation related to microbial activity

Microbiological transformation related to microbial activity is presented by (Vink et al., 1994):

$$R_t = - \frac{1}{\gamma_b} \frac{\mu_{max} c^*}{K_M + c^*} \frac{1}{1 + \left(\frac{c^*}{K_L} \right)^{a_m}} M \quad 2.50$$

$$\frac{dM}{dt} = \frac{\mu_{max} c^*}{K_M + c^*} \frac{1}{1 + \left(\frac{c^*}{K_L} \right)^{a_m}} M - \alpha_m (1 + \beta_m M) M \quad 2.51$$

and

where:

$$\begin{aligned} c^* &= \text{total solute concentration in all phases} & (\text{L}^{-3} \text{M}) \\ M &= \text{microbial activity} & (\text{L}^{-3} \text{M}) \\ \gamma_b &= \text{gain factor for biomass production} & (-) \\ \mu_{max} &= \text{maximum rate of growth} & (\text{T}^{-1}) \\ K_M &= \text{saturation constant of Monod's equation} & (\text{L}^{-3} \text{M}) \\ K_L &= \text{critical concentration level for microbial growth} & (\text{L}^{-3} \text{M}) \\ a_m &= \text{constant} & (-) \\ \alpha_m &= \text{microbial mortality rate} & (\text{T}^{-1}) \\ \beta_m &= \text{microbial mortality constant} & (\text{L}^3 \text{M}^{-1}) \end{aligned}$$

At concentrations far below the critical pesticide concentration for microbial development, equations 2.50 and 2.51 reduce to:

$$R_t = \frac{1}{\gamma_b} \frac{\mu_{max} c^*}{K_m + c^*} M \quad 2.52$$

and

$$\frac{dM}{dt} = \frac{\mu_{max} c^*}{K_m + c^*} M - \alpha_m (1 + \beta_m M) M \quad 2.53$$

If the microbial transformation only takes place in the liquid phase, c^* in equation 2.50 - 2.53 can be replaced by the concentration in the liquid phase, c_l . However, the parameters used will then change.

Transformation rates of pesticides depend upon soil factors such as soil temperature, soil moisture content, strength of sorption and soil microbial biomass. The influence of temperature on the transformation of substances are usually presented by classical physical-chemical response functions such as the Arrhenius equation (see subsection 2.2.2.1). This equation can only be applied at temperatures below 20 °C and at very low pesticide concentrations (Nörtersheuser, 1993). Biological activity depends upon temperature in a different way. Firstly, elementary reaction rates increase with temperature. Secondly, biochemical reactions are mediated by enzymes which function only if a complex secondary structure is maintained. A rise in temperature leads to an enhanced decay rate of the secondary structure. Between a minimum threshold temperature (T_{min}) and a maximum threshold temperature (T_{max}) the two effects are superimposed. It is assumed that outside this range no microbial activity occurs. This gives the empirical equation (O'Neil, 1969; O'Neil et al., 1972):

$$\mu(T) = \mu_{max} \left(\frac{T_{max} - T}{T_{max} - T_{opt}} \right)^a e^{\frac{a(T - T_{opt})}{(T_{max} - T_{opt})}} \quad \text{for } T_{min} < T < T_{max} \quad 2.54$$

$$\mu(T) = 0 \quad \text{for } T \leq T_{min} \wedge T \geq T_{max}$$

with

$$a = \frac{\left[b \left(1 + \sqrt{1 + \frac{40}{b}} \right) \right]^2}{400} \quad 2.55$$

$$b = (Q_{10} - 1) (T_{max} - T_{opt})$$

where:

$\mu(T)$ = rate of a microbial temperature dependent reaction (T⁻¹)

μ_{max} = maximum rate (T⁻¹)

T = soil temperature (T)

T_{max} = lethal temperature for micro-organisms (T)

T_{min} = minimum temperature for microbial activity (T)

T_{opt} = optimum temperature for maximum microbial activity (T)

Q_{10} = increase of decay rate by increase of temperature of 10 °C (T⁻¹)

Due to the complexity of the equations, statistical packages are used to estimate the various parameters. Generally, some parameters are fixed during the estimation process.

2.2.2.3 Soil temperatures

For both first-order transformation as well as for microbiological transformation the soil temperature has a considerable impact on the rate of transformation. During the laboratory and field experiments it was demonstrated that the rate of transformation can easily rise by a factor ten if soil temperatures rise from 5 °C to 20 °C. An empirical way to describe soil temperatures as a function of depth and time has been presented by Van Wijk and De Vries (1963). For a homogeneous soil, the soil temperature is a distribution with depth $|z|$ and time t given by:

$$T(|z|, t) = T_m + T_a \exp\left(\frac{|z|}{d}\right) \sin\left(\omega t - \frac{|z|}{d}\right) \quad 2.56$$

where:

$T(|z|, t)$ = estimated temperature of the soil at depth $|z|$ and time t (Θ)

T_m = average soil temperature over a year (Θ)

T_a	= yearly amplitude of the temperature at the soil surface	(Θ)
d	= damping depth over a year	(L)
ω	= angular frequency of the temperature wave	(T^{-1})

where:

$c_{l,ref}$	= reference concentration in the liquid phase	($L^{-3} M$)
K_F	= Freundlich coefficient	($L^3 M^{-1}$)
$1/n$	= Freundlich exponent	(-)

The amplitude of the soil temperature will decrease with increasing depth. Especially at the soil surface, the effect of the diurnal variation of the soil temperature can be considerable. The diurnal amplitude is influenced by soil cover, soil type, soil moisture content and weather factors such as solar radiation and precipitation. The average diurnal soil temperature can be calculated as a function of the annual soil temperature, if time (day number) and soil depth are known.

2.2.3 Sorption

Sorption is a dynamic process in which pesticides are continually exchanged between the liquid phase and solid surface. Main adsorptive surfaces in soils are provided by clay minerals and organic matter. Different bonding mechanisms occur between the solid surface and the pesticides. The most important interactions are physical bonding due to London - Van der Waals forces, electrostatic bonding by ion exchange, hydrogen bonding, dipole - dipole interactions or coordination bonding. These bonding mechanisms do not necessarily occur separately, but will usually be a combination of two or more interactions (Bailey and White, 1970; Young et al., 1992).

One of the main assumptions in the sorption of pesticides is the instantaneous attainment of an equilibrium between the pesticide in solution and that adsorbed on the soil surface. The sorption of pesticides has been mathematically presented in literature by linear (e.g. Leistra, 1972; Wagenet and Rao, 1990), Langmuir (e.g. Cohen et al., 1988) and Freundlich equations (e.g. Calvet, 1980; Boesten, 1986, 1991-2). The Freundlich isotherm equation has been most frequently used to describe pesticide sorption on soils. It is given by (e.g. Boesten and van der Linden, 1991):

$$X = K_F c_{l,ref} \left[\frac{c_l}{c_{l,ref}} \right]^{1/n} \quad 2.57$$

The value of $c_{l,ref}$ should be in the same order of magnitude at which pesticide sorption measurements are usually made. In pesticide/soil systems various sorption mechanisms operate and the properties of sorption sites can be expected to be heterogeneous. Therefore the equation for the Freundlich sorption isotherm is to be preferred a priori to the equation for the Langmuir sorption isotherm. The Freundlich equation accounts in a certain way for surface heterogeneity, whereas the Langmuir sorption isotherm assumes uniform sorption sites (Boesten, 1986). If the Freundlich exponent equals unity, the equation becomes similar to the linear equation. Thus, the linear equation is a special case of the Freundlich equation.

In the model *SWACRO*, sorption takes place according to the Freundlich isotherm equation. It is assumed that an equilibrium of the partitioning between the sorbed and liquid phase is reached instantaneously. However, sorption experiments that were continued for weeks, months or years, have shown that in many cases sorption does not reach equilibrium on a time scale of minutes or hours, but continues on a longer time scale (e.g. Boesten and Van der Pas, 1983; Walker, 1987; Pignatello and Huang, 1991). Furthermore, in the Freundlich equation reversible bonding of the pesticide to the soil is assumed. However, hysteresis effects on the adsorption and desorption are often observed. These effects make sorption to the soil even more complex. Generally hysteresis effects are less important than the long term sorption (Van Genuchten and Cleary, 1982). As the model *SWACRO* uses the Freundlich isotherm equation, neither of these aspects are taken into account.

2.2.4 Distribution between gas and liquid phase

Volatilization is the process by which a pesticide evaporates in the vapour phase to the atmosphere from another environmental compartment (Thomas, 1990). Especially for pesticides sprayed on a crop, this may be an important mechanism for the loss of the pesticide

(Wagenet et al., 1989). The rate at which a pesticide volatilizes is strongly dependent on the chemical properties of the pesticide and the environmental conditions. For most pesticides directly applied to the soil, the contribution of volatilisation to the loss of the pesticide is negligible and therefore not taken into account. However for pesticides with a high vapour pressure, such as fumigants, volatilization cannot be ignored. These pesticides are principally applied below the soil surface.

For some pesticides, such as fumigants, a significant fraction is present in the gas phase of the soil system. The relation between the concentrations of the pesticide present in the liquid and gas phase can be described by:

$$c_l = K_g c_g \quad 2.58$$

where:

- K_g = ratio for partitioning of the fumigant between liquid and gas phases (-)
 c_g = concentration in the gas phase ($L^{-3} M$)

In this equation K_g equals the inverse of the non-dimensional Henry's law constant. Generally, the partitioning over the liquid and gas phases proceeds rapidly (e.g. Brusseu et al., 1991; Cho and Jaffe, 1990).

K_g is a function of the soil temperature. Generally, K_g decreases when the soil temperature rises. For fumigants like 1,3-dichloropropene, the relation between the soil temperature and K_g can be described by:

$$K_g = b_2 \exp(-b_3 T) \quad 2.59$$

where:

- b_2 = parameter (-)
 b_3 = parameter (Θ^{-1})
 T = soil temperature (Θ)

The effect of the temperature on the partitioning of the fumigant between the solid, liquid and gas phase is rather complex. It is a combination of the effect of the soil temperature on the sorption of the fumigant onto the solid phase, on the solubility of the fumigant in the liquid phase and on the saturated vapour pressure of

the fumigant. As the soil temperature and the soil moisture content change in time and with depth, partitioning of the fumigant between the soil phases will therefore change in time and with depth.

2.2.5 Plant uptake of solutes

Water needed for transpiration is extracted from the soil by the plant roots. The pesticides, dissolved in the liquid phase, will to some extent enter the root system. As this process is irreversible, the extraction of pesticides by plant roots may be looked upon as a sink term.

It is assumed that the plant uptake of pesticides is a function of the concentration of dissolved pesticides in the liquid phase in the soil and of actual transpiration. The uptake of pesticides is considered to be a sink term. If the pesticide is not transformed within the plant system, it will accumulate. Total uptake depends on the type of pesticide, the concentration of the pesticide in the liquid phase, the rooting depth, the root water uptake function and actual evapotranspiration.

The plant uptake of pesticides is given by:

$$R_u = F S c_l \quad 2.60$$

where:

- F = transpiration stream concentration factor (-)
 S = sink term for water extraction (T^{-1})
 c_l = concentration in the liquid phase ($L^{-3} M$)

Equation 2.60 implies passive uptake as found for a number of pesticides (e.g. Briggs et al., 1982). Plant uptake of water also has a direct impact upon the movement of water through the soil, as it retards the movement of a pesticide through the root zone. For accurate simulation of the fate of mobile pesticides in the root zone, knowledge on rooting depth at different times of season, root density distribution with depth and time, and the relation between soil-water stress and plant extraction is indispensable.

2.2.6 Lateral drainage of solutes

In the unsaturated zone the movement of soil water predominantly takes place in a vertical direction. In the

saturated zone or below perched water tables, groundwater flow may be horizontal, radial and vertical. Lateral flow of water to drain pipes is calculated with the formula of Hooghoudt or Ernst, which has been discussed in subsection 2.1.7.

In the model *SWACRO* the one-dimensional soil profile is situated between the defined drainage system (e.g. drain pipes, open field drains, collector drains or main drains). The soil profile is divided into a number of nodal compartments with variable height and soil physical properties. The calculated lateral drainage flux is subdivided between the compartments situated above the impervious layer of the defined profile and beneath the phreatic surface, as presented in figure 2.6. The lateral flux of solutes of each compartment R_d ($L^3 M T^{-1}$) is a function of the thickness and saturated permeability, formulated as:

$$R_d = q_d c_{l,n} \frac{dz_n}{d_m^2} \frac{K_{s,n}}{K_{s,avg}} \quad 2.61$$

where:

- q_d = drain discharge rate per unit of surface area ($L T^{-1}$)
- $c_{l,n}$ = concentration of the liquid phase for compartment n ($L T^{-1}$)
- dz_n = thickness of soil compartment n (L)
- d_m = distance between phreatic surface and impervious layer midway between the drains (L)
- $K_{s,n}$ = saturated permeability of soil compartment n ($L T^{-1}$)
- $K_{s,avg}$ = average saturated permeability for the compartments between phreatic surface and impervious layer ($L T^{-1}$)

2.3 Preferential flow

Preferential flow paths in the soil can cause an accelerated movement of solutes (including pesticides) in the unsaturated-saturated soil system. Rapid transport of solutes can be caused by flow through cracks in struc-

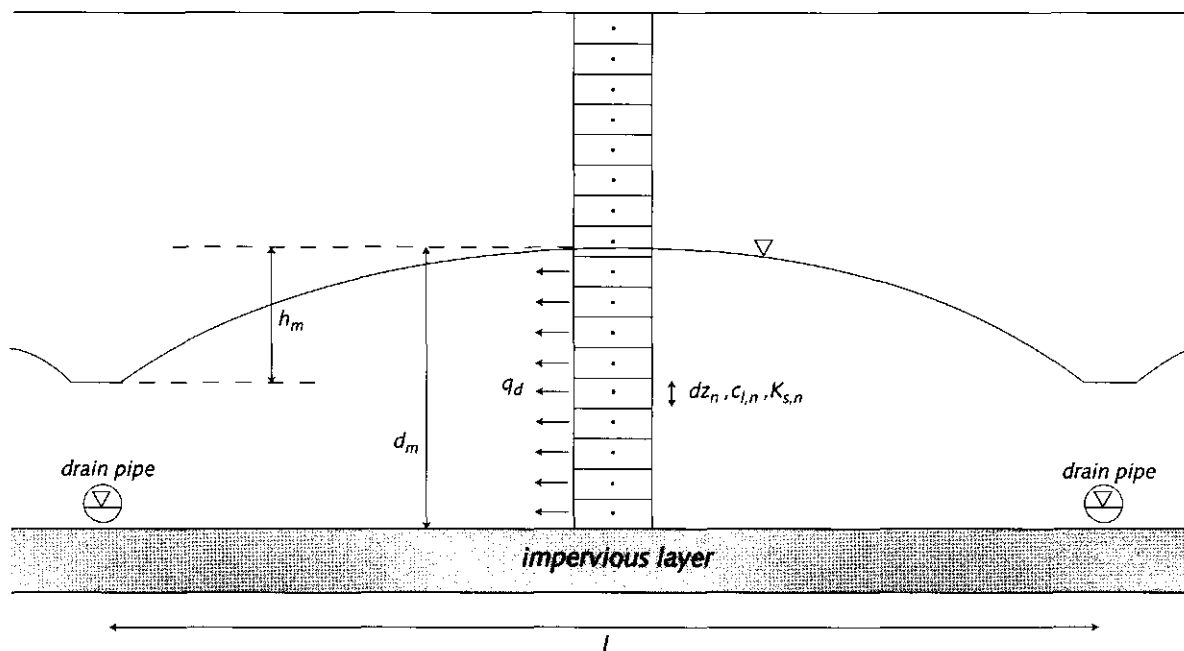


Figure 2.6 Schematic reproduction of the flow of solutes to drain pipes for a case where the drain pipes are situated on an impervious layer.

tured soils, unstable wetting fronts and funnel flow (e.g. Beven and Germann, 1982; Kamra et al., 1991; Bronswijk, 1991; Gerke and Van Genuchten, 1993; Booltink et al., 1993; Steenhuis et al., 1994; Flury et al., 1994). The preferential stream paths can short-circuit the biological active root zone reducing time for the transformation of pesticides before they reach the drain pipes. The transport of pesticides to drain pipes is therefore often more rapid and the concentrations of pesticides in the drainage water higher than what would normally be expected for homogeneous soils (e.g. Van der Zee and Boesten, 1991).

Most deterministic simulation models for water and solute flow in the unsaturated zone assume the soil to be homogenous and isotropic. The solute transport is described by the convection-dispersion equation. However, for many soils, such as water repellent soils, aggregated soils, soils with preferential stream paths (cracks and fissures, pores formed by soil fauna or plant roots) the presented convection-dispersion equation will be inadequate in describing the leaching process. If preferential flow paths are present in the soil, models for solute transport based on the Richard equation and the convection-dispersion equation are unable to predict this fast transport. In that case, processes which describe preferential flow should be included in the model.

In this section concepts for preferential flow of water, and transport of solutes and pesticides are discussed. These concepts are restricted to the description of preferential flow at the experimental fields North-East Polder, Eastern Flevoland and Southern Flevoland.

2.3.1 Mobile and immobile transport

Among the alternatives for modelling preferential flow is the concept of a mobile and immobile phase. This alternative is often used for soils with unstable wetting fronts, when only part of the soil matrix actively participates in the flow process. As part of the soil water flows along the stream paths, the stagnant water of the immobile liquid zones stays relatively undisturbed (Van Genuchten and Wagenet 1989; Van Dam et al., 1990-1).

The mobile-immobile concept differentiates soil water

in mobile and immobile fractions. The average concentration of the solute is defined as:

$$\theta c_l = \theta_m c_{l,m} + (1 - f_m) \theta_i c_{l,i} \quad 2.62$$

where:

- θ_m = volumetric water content in mobile soil domain (-)
- $c_{l,m}$ = concentration in the mobile fraction of the liquid phase ($L^{-3} M$)
- f_m = fraction of the liquid phase present in the mobile region (-)
- θ_i = volumetric water content in immobile soil domain (-)
- $c_{l,i}$ = concentration in the immobile fraction of the liquid phase ($L^{-3} M$)

While θ is defined with respect to the total soil volume (mobile + immobile region), θ_i is defined with respect to the immobile soil volume only. The fraction of the solute phase in the mobile region equals f_m , the fraction of the solute phase in the immobile region equals $(1 - f_m)$.

Assuming first-order transformation and the balanced distribution of sorption between the mobile and immobile phase, the mass conservation equation for the mobile part is now defined as:

$$\begin{aligned} & \frac{\delta \left(\theta_m c_{l,m} + f_m \varrho K_F c_{l,ref} \left[\frac{c_{l,m}}{c_{l,ref}} \right]^{1/n} \right)}{\delta t} = \\ & \frac{- \delta \left(q c_{l,m} - \theta_m [D_{dis} + D_{dif}] \frac{\delta c_{l,m}}{\delta z} \right)}{\delta z} \\ & - k_l \left(\theta_m c_{l,m} + f_m \varrho K_F c_{l,ref} \left[\frac{c_{l,m}}{c_{l,ref}} \right]^{1/n} \right) \\ & - F S c_{l,m} - q_d c_{l,m} - E_{ex} \end{aligned} \quad 2.63$$

and for the immobile part as:

$$\frac{\delta (1 - f_m) \left(\theta_i c_{l,i} + \varrho K_F c_{l,ref} \left[\frac{c_{l,i}}{c_{l,ref}} \right]^{1/n} \right)}{\delta t} = - (1 - f_m) k_l \left(\theta_i c_{l,i} + \varrho K_F c_{l,ref} \left[\frac{c_{l,i}}{c_{l,ref}} \right]^{1/n} \right) + E_{ex} \quad 2.64$$

where:

E_{ex} = exchange rate between the mobile and immobile fraction ($L^{-3} M T^{-1}$)

Solutes and pesticides may slowly diffuse from the mobile into the immobile region or reversely. The relation between the mobile and immobile fraction is a function of soil depth. The interaction between the mo-

bile and immobile fraction is given by:

$$E_{ex} = a_{ex} (c_{l,m} - c_{l,i}) \quad 2.65$$

where:

a_{ex} = exchange coefficient (T^{-1})

More detailed information on the concept of mobile/immobile transport is presented by the Working Group SWAP (Van Dam et al., 1997). The concept of mobile/immobile transport was applied at the experimental field North-East Polder for solute transport of non-volatile compounds.

2.3.2 Preferential flow through cracks in clay soils

The soil profiles of the experimental fields Eastern and Southern Flevoland can be classified as heavy non-swelling clay soils with cracks. A schematic drawing of the ripened, heavy clay soils in Flevoland is presented in figure 2.7. The soil can be subdivided verti-

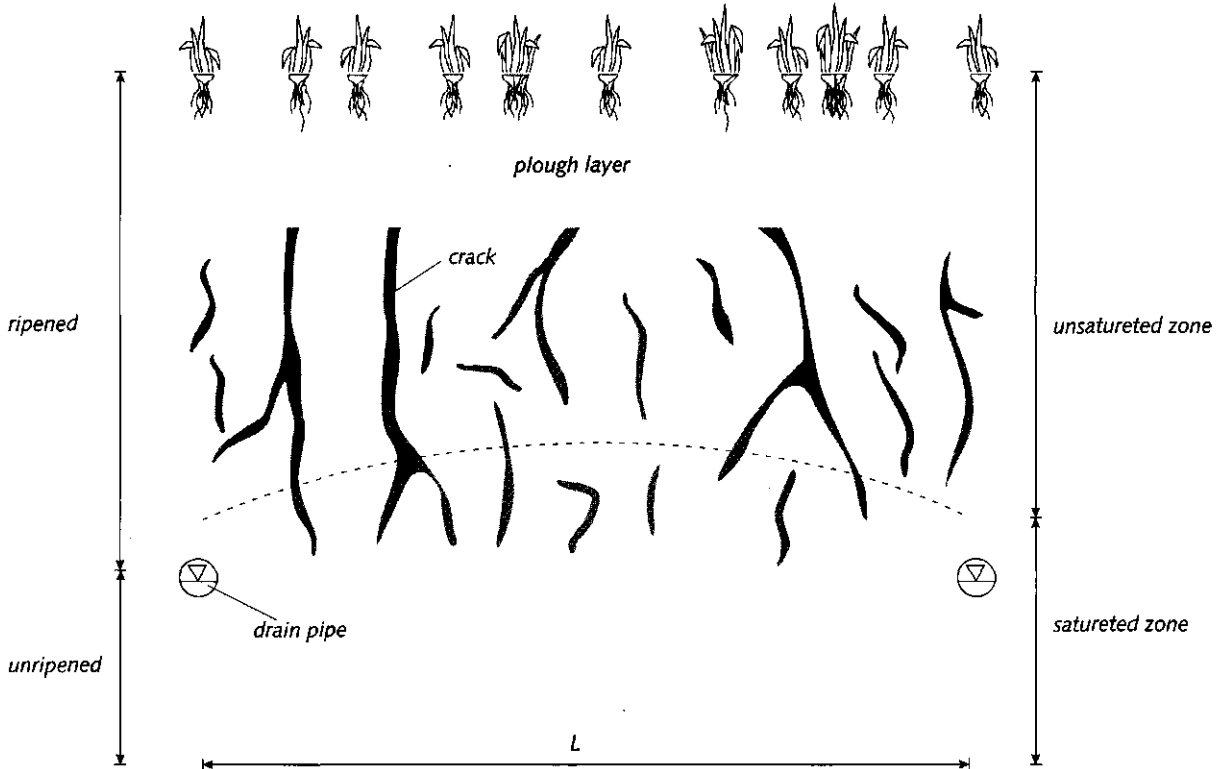


Figure 2.7 General profile of the ripened, heavy clay soils in the IJsselmeerpolders (L = distance between the drain pipes).

cally in a plough layer (0 - 0.35 m - soil surface), basalt like structure elements with cracks (0.35 - >1.10 m - soil surface) and an unripened subsoil (>1.10 m - soil surface). The depth of the unripened subsoil depends strongly on the depth of the drain pipes, the appearance of seepage and the type of crop. More detailed information on the soil characteristics of the heavy clay soils and the physical soil-ripening process will be provided in the next chapter (subsections 3.1.1.2: Experimental field Eastern Flevoland and subsection 3.1.1.3: Experimental field Southern Flevoland). For these soils a new concept is applied to describe the flow of water, solutes and pesticides through cracks.

Figure 2.8 presents the schematisation of the soil profile of the experimental field Eastern Flevoland. When rainfall occurs, net precipitation will reach the top of the soil profile. If net precipitation rate does not exceed the infiltration capacity at the top of the soil profile, it will flow into the plough layer (figure 2.8 - left (I)). Otherwise ponding or surface runoff will occur (figure 2.8 - left (II)). Under moderate wet conditions, water will flow into the unsaturated subsoil (figure 2.8 - left (III)). If the flux of water from the top soil to the subsoil exceeds the infiltration capacity of the basalt struc-

ture elements, water will be stored in the top layer until the pressure head near the plough layer becomes zero (perched water table). At this moment water starts to flow into the cracks (figure 2.8 - left (IV)). The water flows along the walls of the clay columns. The width of the individual cracks will be no obstruction to the flow of water during extreme precipitation events. The soil moisture content of structure elements is hardly affected by the film flow and remains practically unchanged.

The distribution between the water flowing into the cracks and the water infiltrating into the clay columns, depends on the infiltration rate of the clay columns. For the simulation of the water, solute and pesticide flow in cracked clay soils, without leaving the concept of one-dimensional flow, imaginary drains are installed at a depth of 0.35 m (figure 2.8 - right). These drains represent the effects of the cracks on the water movement in the plough layer. In the model *SWACRO*, the distribution between the water flowing into the cracks and the water infiltrating into the clay columns is determined by the saturated conductivity of the semi-permeable layer just below the plough layer (0.35 - 0.40 m - soil surface). If the flux of water from the plough layer to the subsoil exceeds the infiltration capacity, the super-

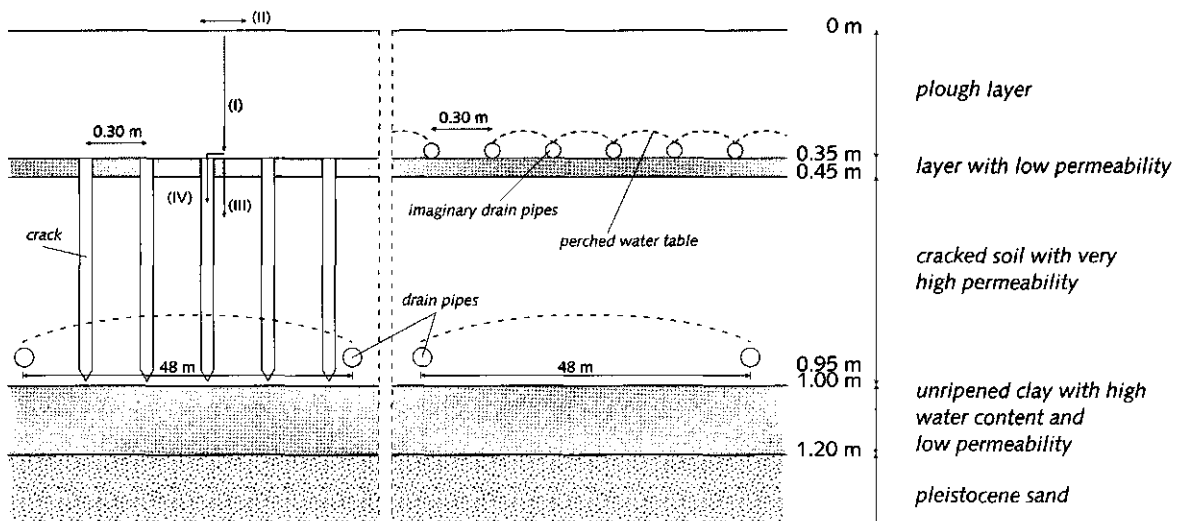


Figure 2.8 Schematic profile of ripened clay soil in the IJsselmeerpolders and lateral boundary conditions as implemented in the model *SWACRO*. The reported values in this figure correspond to observed values at the experimental field *Eastern Flevoland*.

fluos water will run into the imaginairy drains (the so-called short-circuiting).

Thus, two drainage levels can be distinguished. The total lateral solute flux is equal to:

$$R_d = R_{d,1} + R_{d,2} \quad 2.66$$

where $R_{d,1}$ and $R_{d,2}$ are calculated according to equation 2.61. In this equation the concentration in the liquid phase (c_l) for the first drainage level originates from the perched water tables in the plough layer. For the first drainage level, the semi-permeable layer is situated just below the plough layer and d_m gives the distance between the perched groundwater level and the semi-permeable layer.

The residence time of the solutes and pesticides is very short as the observed saturated permeability of the cracked soil at the experimental fields Eastern and Southern Flevoland amounted to 300 - 500 m d⁻¹. Therefore, transformation in the saturated zone during transport towards the drain pipes may be neglected.

2.3.3 Spatial inhomogeneity of the precipitation

Most deterministic simulation models for water flow and solute transport in the unsaturated zone assume homogenous distribution of the precipitation at the top of the soil. However, vegetation may strongly influence the redistribution of the precipitation. Generally, the actual flux through the top of the soil is equal to the actual soil evaporation plus the intercepted precipitation minus the precipitation, as presented in equation 2.21.

However, in some situations a significant part of the precipitation will flow along the stem (e.g. trees) or leaves (e.g. sugar beets) of the vegetation. On the other hand, the vegetation (e.g. apple trees) may behave as an umbrella; a significant part of the precipitation will flow along the leaves and drop amidst the trees. In both cases the vegetation induces a strong redistribution of the precipitation, which causes a considerable spatial variability of the actual flux through the soil. In this case, the one-dimensional deterministic simulation models for water and solute flow in the unsaturated zone can still be applied if the field is subdivided in a number of sections. The net precipitation and area will

then vary for each section (figure 2.9). This concept can only be used if the variation in the actual flux through the bottom of the soil is known. For the experimental field in Southern Flevoland the above-mentioned concept was applied.

If the vegetation strongly redistributes the precipitation, the actual flux through the soil surface as presented by equation 2.21 is rewritten to:

$$q_{s,k} = E_{s,k} - (a_k P - E_l) \quad 2.67$$

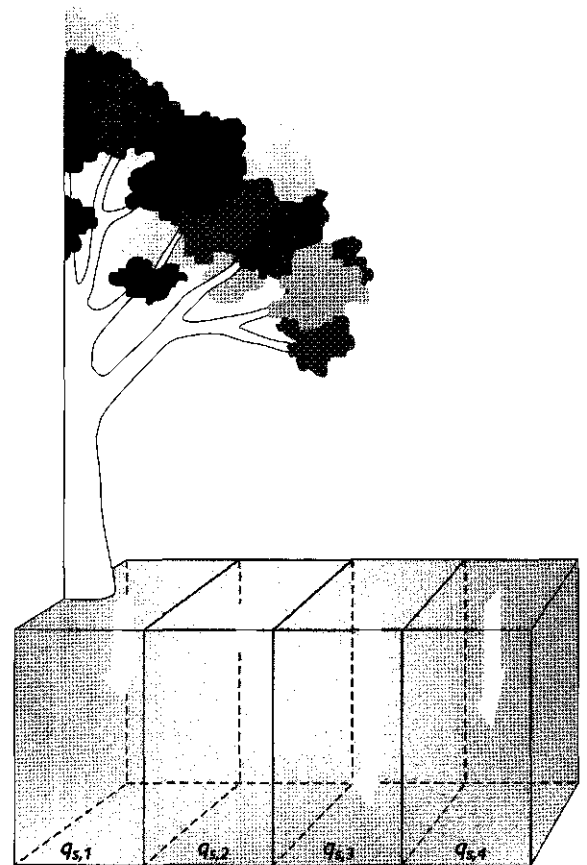


Figure 2.9 Schematic overview of the effect of redistribution of the precipitation on the actual flux density through the soil surface. In this particular case four sections of equal surface area have been distinguished.

where:

$q_{s,k}$ = actual flux density through the soil at section k (L T⁻¹)

$E_{s,k}$ = actual soil evaporation rate at section k (L T⁻¹)

a_k = parameter representing the segmentation of the precipitation (-)

precipitation rate should be equal to the weighted average of the daily precipitation rate per section. Thus, if the surface area is equal for each section:

$$\sum_{k=1}^n a_k = n \quad 2.68$$

where:

n = number of sections (-)

In order to maintain a correct water balance, the daily

Chapter 3

Laboratory and field experiments

Klaas Groen

Laboratory and field experiments

Computer simulation models are attractive tools for evaluating the behaviour of pesticides. However, the results of calculations with simulation models can be very deceiving, if the models are not calibrated properly. To obtain reliable results, simulation models need to be tested carefully against accurate laboratory and field data.

Data to determine the fate of water, solutes and pesticides were collected at three experimental fields, all situated in the IJsselmeerpolders. Four different pesticides were incorporated in the research program: 1,3-dichloropropene and metamitron (experimental field North-East Polder), aldicarb (experimental field Eastern Flevoland) and simazine (experimental field Southern Flevoland). The inert ion bromide was used as a tracer. The location and general characteristics of the experimental fields and collected field data are presented in section 3.2.

The soil physical properties of the experimental fields i.e. soil-moisture retention curve and the hydraulic conductivity curve, as well as the characteristics of the pesticides involved i.e. transformation and sorption were determined in laboratory experiments. Methods of analyses and results of these laboratory experiments are presented in section 3.1. Furthermore, some information on the general soil properties and the formation of the soil profile are presented.

3.1. Laboratory experiments

3.1.1 Soil characteristics

All three experimental fields are situated in the IJsselmeerpolders, which were reclaimed from the former Zuider Zee. The top layers consist of Holocene sediments, deposited during the last 20 centuries. The

thickness of these sediments varies from nearly zero up to four metres. They are predominantly underlain by Pleistocene sandy sediments (figure 3.1).

The Holocene sediments can be distinguished in Flevomeer deposits, Almere deposits, Zuider Zee deposits and IJsselmeer deposits. The Flevomeer deposits were laid down in lakes, surrounded by bog peat. The bog peat was eroded by the wave action of the lakes. During this era (from 750-0 B.C.) gyttja-like sediments were deposited with high contents of organic matter (15-30%). Afterwards the supply of mineral parts increased as the main part of the bog peat area had already been destroyed. Therefore, from 0-1600 A.D. sediments with lower content of organic matter were deposited, named Almere deposits.

In the Almere deposits different layers can be distinguished. The organic matter decreases as the mineral parts increase from the oldest to the youngest layers. The Flevomeer and Almere deposits were sedimented under fresh and afterwards under increasing brackish conditions. Around 1600 A.D. the salinity of the water increased abruptly. Under these saline conditions a marine sediment was deposited, with clay contents varying from 10-40% (Zuider Zee deposits). In 1932 the Zuider Zee was separated from the North Sea. The water of the IJsselmeer became fresh within a few years. In this fresh water reworked Zuider Zee deposits were laid down, called IJsselmeer deposits.

Directly after reclamation of the polders, the loamy and clayey Holocene sediments were very soft, had a high water content, were practically impermeable and had a very low bearing capacity.

After reclamation, water was withdrawn from the soil during successive growing seasons which induces a

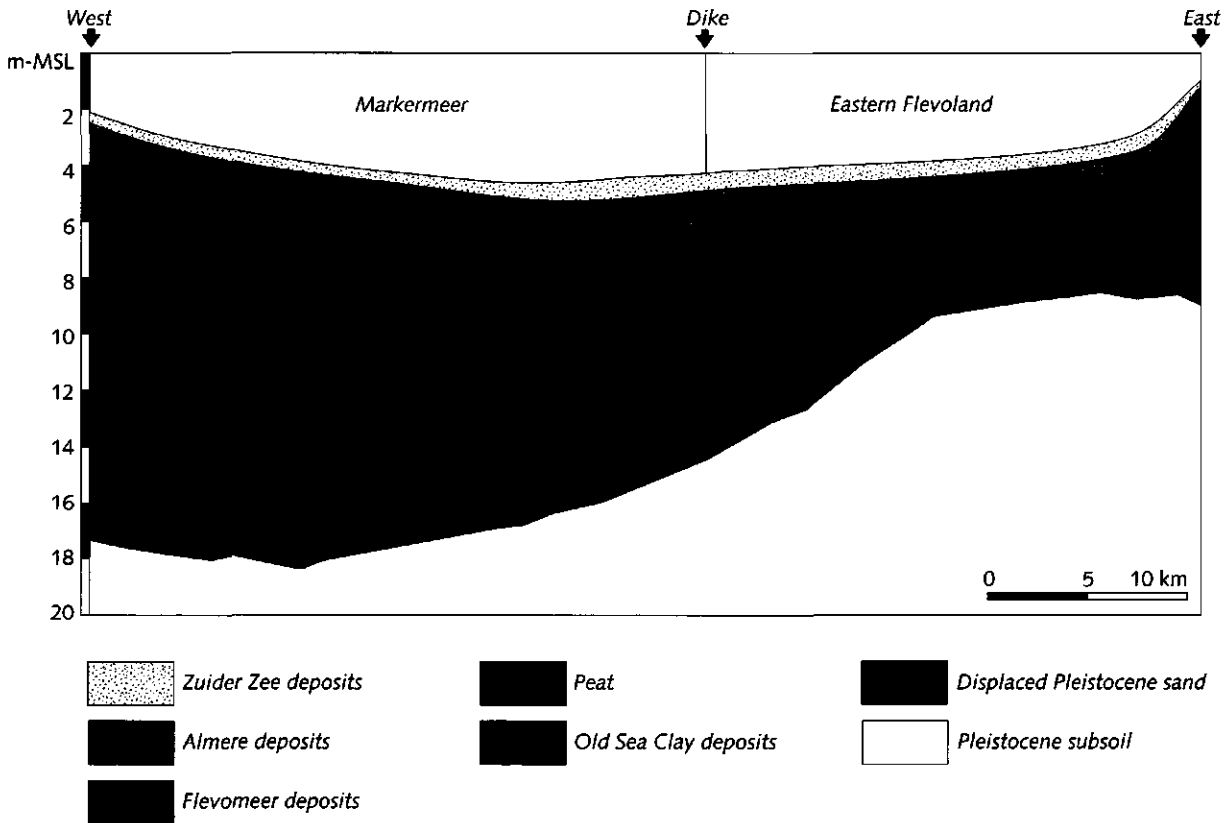


Figure 3.1. Simplified composition of the Holocene deposits in the former Zuider Zee area. The cross-section leads from West (Schardijk - North Holland) over Lelystad to East (Elburg - Gelderland) (De Glopper, 1973). See also figure 1.1.

physical soil-ripening process. This process changes the soil structure: it converts the soil from waterlogged and reduced materials into more compact, aerated and permeable materials (Rijniersce, 1983).

For heavy clay soils this process is accompanied by subsidence, cracking and the formation of structure elements. As the process is practically irreversible, a system of macropores formed by cracking remains practically unchanged, due to structural changes inside the soil matrix. However, the formed structure of the top soil is destroyed by tillage operations, resulting in a homogeneous plough layer. Beneath the plough layer the formed basalt-like structure elements remain unchanged. Normally the soil-ripening process proceeds as far as the depth of the drain pipes.

Swelling and shrinkage of ripened clay soils in the IJsselmeerpolders is limited. The reason is that two out of three main types of clay minerals, kaolinite (20%) and illite (60%), are non-swelling clay minerals. Only drying and rewetting of montmorillonite (20%) causes volume changes.

3.1.1.1 Experimental field North-East Polder

The soil profile of the experimental field North-East Polder is classified as a calcareous fluvisol of the Formation of Duinkerke (photo 3.1). The 0.4 m topsoil is a fine textured loamy sand (Zuider Zee-deposits). The subsoil consists of a loamy sand with fine layers of sandy loam (Almere deposits; in the North-East Polder these deposits are named Sloef deposits). In this subsoil the former root channels of reed can be recog-

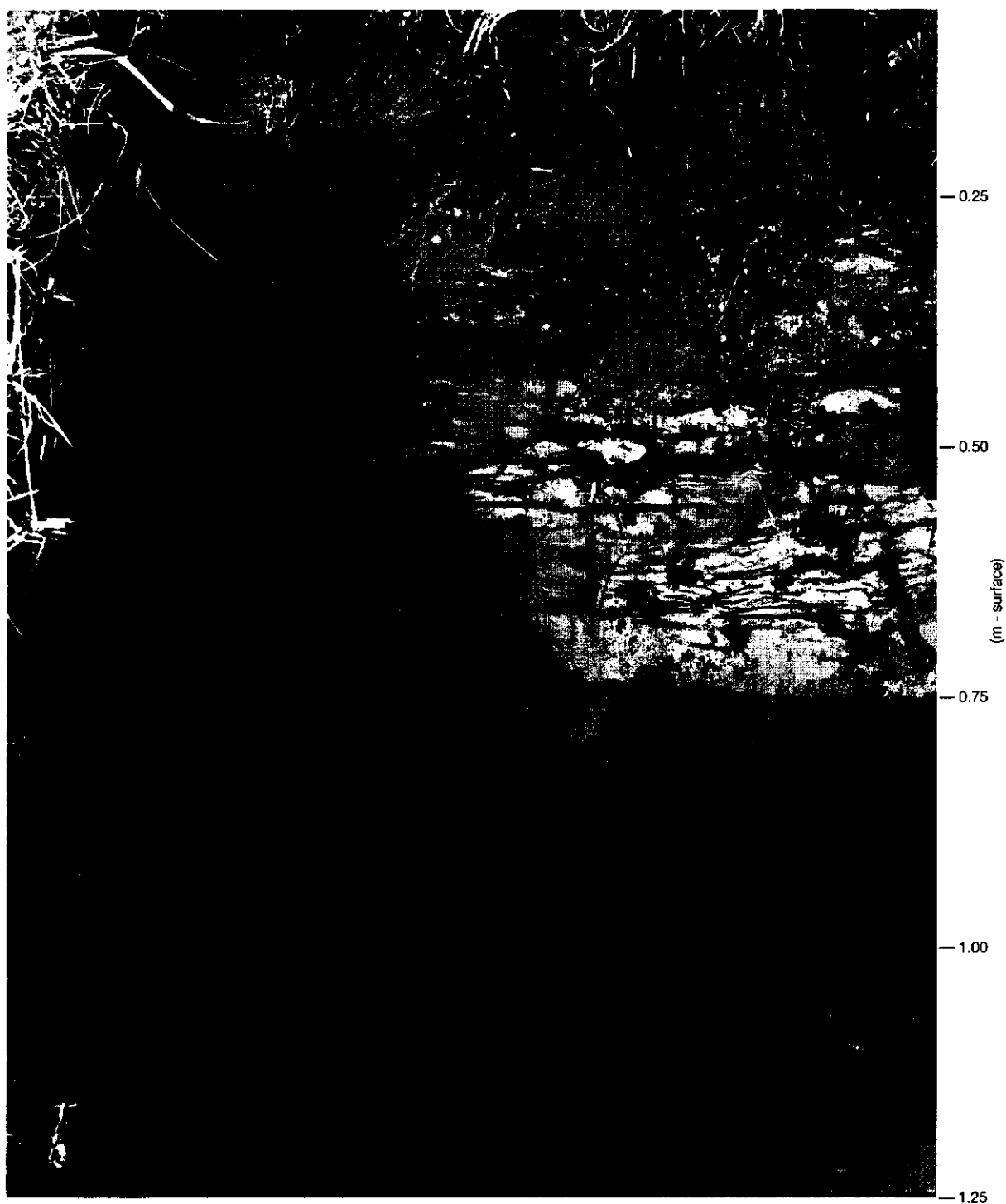


Photo 3.1. Soil profile of the experimental field *North-East Polder*.

Table 3.1. Measured soil properties of the experimental field *North-East Polder*.

Soil depth (m)	Fraction < 2 μ m (%)	Specific surface area (m ² kg ⁻¹)	Bulk density (kg m ⁻³)	K_s (cm d ⁻¹)	Organic matter (%)	CaCO ₃ (%)	pH _{H2O}
0.05-0.15	6.4	33.9	1430	55	1.9	5.90	7.8
0.25-0.35	6.6	41.9	1530	28	1.7	5.20	7.8
0.45-0.55	6.3	54.7	1470	12	1.6	5.45	7.8
0.65-0.75	4.8	55.6	1430	3.3	1.6	6.85	7.8

Table 3.2. Fitting parameters for the soil water retention curve $\theta(h)$ (equation 2.12) and the hydraulic conductivity curve $K(h)$ (equation 2.14) for the experimental field *North-East Polder*.

Soil depth (m)	θ_r (-)	θ_s (-)	α (cm ⁻¹)	n (-)	m (-)	λ (-)	K_s (cm d ⁻¹)
0.00 - 0.30	0.000	0.415	0.0102	1.577	0.366	1.000	28.1
0.30 - 0.90	0.000	0.457	0.0039	1.443	0.307	1.123	2.83
0.90 - 1.20	0.000	0.750	0.0043	1.211	0.174	-1.000	1.63

nized. Beneath a depth of roughly 0.4 m, active roots are not normally distinguished. About 0.9 m below the surface, a nearly impermeable layer of detritus-gytta of about 0.2-0.3 m thick occurs (Flevomeer deposits). Underneath the detritus-gytta layer Pleistocene sands are found. The saturated hydraulic conductivities K_s of the detritus-gytta layer and the Pleistocene sands were recorded with the Kopecky method (De Roo and Beemster, 1989) and amounted to 0.04 ± 0.03 cm d⁻¹ and 18.5 ± 10.1 cm d⁻¹ respectively. The organic matter and clay content of the detritus-gytta is approximately 40% and 20%. The calcium-content of the gytta layer is very low (< 1%). If water is withdrawn from the detritus-gytta layer (e.g. the groundwater table 1.1 m below the surface), it causes an irreversible physical soil-ripening process. This process is accompanied by subsidence and cracking, which may strongly influence the permeability.

Based on morphological and chemical characteristics, soil samples were taken at 10 sides (descending from plot I and II - see figure 3.19) at 0.05-0.15, 0.25-0.35, 0.45-0.55 and 0.65-0.75 m depth (figure 3.19: Experimental field North-East Polder - Plot I). Some physical and chemical characteristics are presented in table 3.1. The water retention and hydraulic conductivity func-

tions were computed from laboratory experiments. The method used is known as the multi-step outflow method (Kool et al., 1985, Van Dam et al., 1994). In this method an undisturbed soil sample is placed in a pressure cell on top of a ceramic plate. The sample is saturated from below until equilibrium in the burette is reached. The outflow experiment starts by increasing the pneumatic pressure at the top of the sample. This induces unsaturated flow in the soil sample, while the ceramic plate stays saturated. The cumulative outflow of water is registered in the burette. This cumulative outflow is used to derive the soil hydraulic parameters with the program *MULSTP* (Van Dam et al., 1990-2).

Parameters concerning residual θ_r and saturated moisture content θ_s , the saturated conductivity and the empirical parameters are presented in table 3.2. Some deviation can be observed between the measured and computed K_s (tables 3.1 and 3.2). One of the reasons is that the optimized K_s is affected by unsaturated conditions. However, the differences are relatively small.

3.1.1.2 Experimental field Eastern Flevoland

From the soil surface down to a depth of 0.35 m IJsselmeer and Zuider Zee deposits are found (photo 3.2). The IJsselmeer deposits cannot be distinguished from

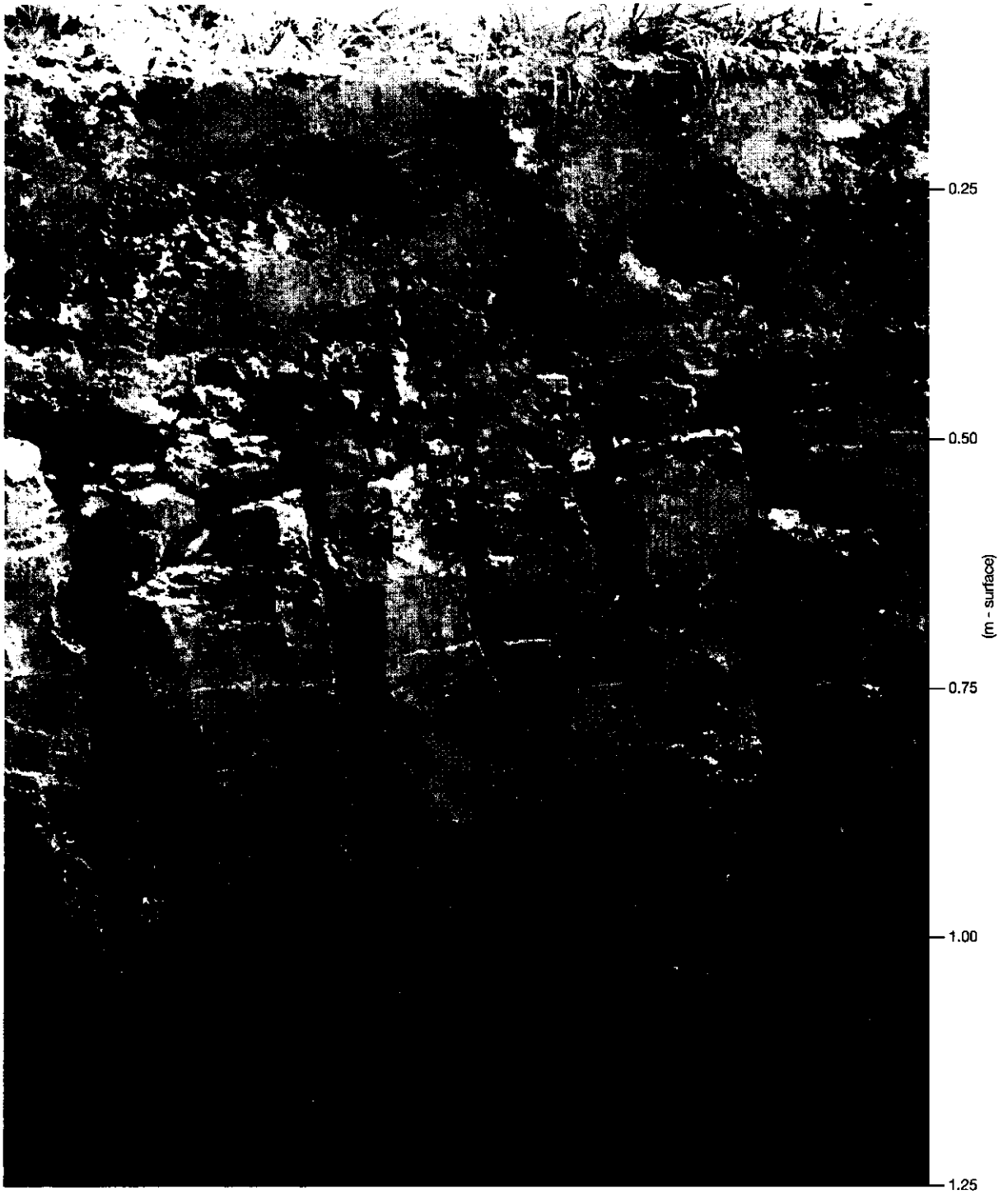


Photo 3.2. Soil profile of the experimental field Eastern Flevoland.

Table 3.3. Measured soil properties of the experimental field *Eastern Flevoland*.

Soil depth (m)	Fraction < 2 μ m (%)	Bulk density (kg m ⁻³)	K_s (cm d ⁻¹)	Organic matter (%)	CaCO ₃ (%)	pH _{H2O}
0.15-0.25	26.4	1288	14	1.9	8.00	8.0
0.30-0.40	28.8	1198	7.4	2.6	7.50	8.0
0.45-0.55	31.2	1077	5.1	4.1	8.50	8.0

Table 3.4. Fitting parameters for the soil water retention curve $\theta(h)$ (equation 2.12) and the hydraulic conductivity curve $K(h)$ (equation 2.14) for the experimental field *Eastern Flevoland*.

Soil depth (m)	θ_r (-)	θ_s (-)	α (cm ⁻¹)	n (-)	m (-)	λ (-)	K_s (cm d ⁻¹)
0.00 - 0.35	0.010	0.470	0.0091	1.155	0.134	-5.000	0.261
0.35 - 0.40	0.010	0.510	0.0106	1.144	0.126	-2.576	0.089
0.40 - 1.00	0.010	0.580	0.0021	1.168	0.144	-5.000	0.050
1.00 - 1.20	0.010	0.737	0.0028	1.189	0.159	-0.000	0.050
1.20 - 1.70	0.010	0.360	0.0224	1.507	0.336	-0.140	13.21

Zuider Zee deposits due to ploughing. The clay content of the plough layer amounts to 26%. Beneath a depth of 0.35 m up to 1.8 m Almere deposits are present. The organic matter content decreases from the oldest (approximately 7%) to the youngest layers (approximately 4%). In the Almere deposits, irreversible cracks are found. The cracks have a width varying from 2.5 to 4.5 cm and are interconnected. The basaltic structures have a diameter of 0.2 to 0.3 m. Approximately 0.1 m beneath the subsurface drainage system (1 m below the soil surface) the clay is unripened, indicating a very low hydraulic conductivity. Here no detritus-gytta was found between the Almere deposits and Pleistocene sands. Some physical and chemical characteristics are presented in table 3.3.

Due to shrinkage of the soil at low water contents, the multi-step outflow method was not suitable for the measurements of the water retention and hydraulic conductivity functions. Here the evaporation method was applied. In soil samples of 8 cm height and 10.3 cm in diameter Time Domain Reflectometry-sensors were installed at four depths.

After saturation the samples were placed on a balance. The soil water evaporates from the top of the sample.

During the experiment the total weight of the samples and the soil water pressure head was measured. The water retention curve was calculated from the measurements. As the flux at the bottom boundary is zero, the flux at the upper boundary is equal to the loss in weight. The gradients in hydraulic head were obtained from the TDR-sensors. Unsaturated conductivity can be calculated with Darcy's law. An extended review of this method is presented by Veerman (1989). Results are given in table 3.4.

Measurements were carried out in duplicate. Deviation can be observed between the fitted saturated hydraulic conductivity (table 3.4) and the saturated hydraulic conductivity which was measured with the Kopecky method (table 3.3). As is the case with the multi-step method, the fitted K_s from the evaporation method is affected by unsaturated flow conditions. The soil characteristics are only valid for the basaltic structures. Due to the interconnecting cracks in the subsoil, the saturated permeability of the soil is very high and amounts to 300-500 m d⁻¹.

3.1.1.3 Experimental field Southern Flevoland

From the soil surface down to a depth of 0.25 m Zuider Zee deposits are found (photo 3.3). Here, no IJsselmeer

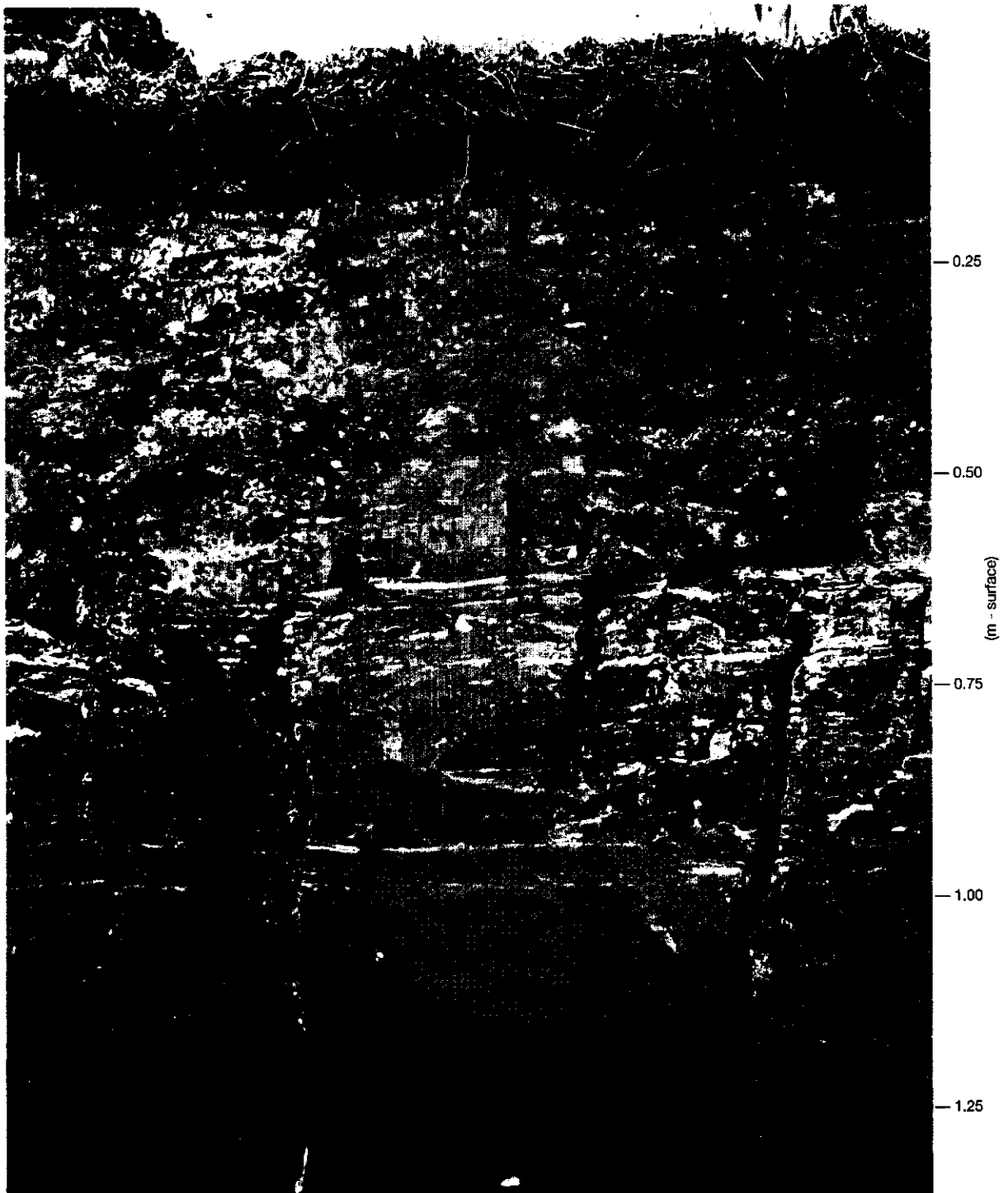


Photo 3.3. Soil profile of the experimental field *Southern Flevoland*.

deposits are present on top of the Zuider Zee deposits. Beneath a depth of 0.25 m down to approximately 2.5 m Almere deposits are found. The organic carbon content decreases from the oldest (approximately 15%) to the youngest layers (approximately 3%). In the top-layer (Zuider Zee deposits) as well as in the subsoils below the Zuider Zee deposits, irreversible cracks are present.

The cracks have a width varying from 1.0 to 3.5 cm and are mostly interconnected. Beneath the drain pipes (1.1 m below the soil surface) the clay is unripened, indicating a very low hydraulic conductivity. Due to the high water content (unripened soil) and the increasing organic matter content the bulk density decreases with depth. No detritus-gytta was found between the Almere-deposits and Pleistocene sands. Table 3.5 gives some characteristics of the soil properties.

Due to shrinkage of the soil at lower water contents, the multi-step outflow method was not suitable to measure the water retention and hydraulic conductivity functions. Instead the evaporation method was applied (see subsection 3.1.1.2). Results are presented in table 3.6. Some deviations can be observed between the fitted K_s (table 3.6) and the K_s measured with the Kopecky

method (table 3.5). The soil characteristics are only valid for the basaltic structures. Due to the interconnecting cracks in the subsoil, the saturated permeability of the soil is high and amounts to 150-350 m d⁻¹.

At the experimental field Southern Flevoland the soil-ripening process is still in progress. Both the soil water retention curve and the hydraulic conductivity curve are influenced by the stage of soil ripening (Rijniersce, 1983). The stage of soil ripening depends on the withdrawal of water from the soil during successive growing seasons.

The experimental field Southern Flevoland consists of rows of apple trees alternated by grass strips (section 3.2). As the grass extracted less water from the soil than the apple trees, the physical soil ripening showed less progress beneath the grass strips. For the grass strip the same soil layers can be distinguished. The soil physical functions below the grass strip were not determined in the laboratory. Therefore, the parameters for the soil water retention curve $\theta(h)$ and the hydraulic conductivity curve $K(h)$ of the soil layer below the grass strip are estimated. It is assumed that the K_s diminishes by 20% and q_s increases by 10%.

Table 3.5. Measured soil properties of the soil below the apple trees at the experimental field *Southern Flevoland*.

Soil depth (m)	Fraction < 2 μ m (%)	Bulk density (kg m ⁻³)	K_s (cm d ⁻¹)	Organic matter (%)	CaCO ₃ (%)	pH _{H2O}
0.05-0.15	35.2	1200	32	2.8	8.7	8.1
0.15-0.25	34.5	1170	23	2.9	8.0	8.2
0.50-0.60	37.7	1029	1.7	3.2	7.8	8.2
1.00-1.10	32.0	579	0.8	14.0	5.1	8.2

Table 3.6. Fitting parameters for the soil water retention curve $\theta(h)$ (equation 2.12) and the hydraulic conductivity curve $K(h)$ (equation 2.14) for the soil below the apple trees at the experimental field *Southern Flevoland*.

Soil depth (m)	θ_r (-)	θ_s (-)	α (cm ⁻¹)	n (-)	m (-)	λ (-)	K_s (cm d ⁻¹)
0.00 - 0.35	0.010	0.486	0.0154	1.111	0.100	-1.704	2.185
0.35 - 0.40	0.010	0.510	0.0106	1.144	0.126	-2.576	0.089
0.40 - 1.00	0.010	0.580	0.0035	1.173	0.147	-0.000	0.087
1.00 - 1.70	0.010	0.737	0.0028	1.189	0.159	-0.000	0.050

3.1.2 Pesticide-soil properties

After application, the pesticide is subjected to various processes, such as partitioning between the soil phases, transformation and transport processes. In order to calculate the movement of pesticides in the soil, many parameters have to be estimated. Laboratory experiments are used to establish parameters related to sorption and transformation. Other parameters, such as parameters related to volatilization were derived from the literature. In the laboratory, experiments were set up to determine the rate of transformation and the sorption capacity for the pesticides involved in the research program. A list of the laboratory experiments is presented in table 3.7.

For the loamy sand of the North-East Polder, laboratory experiments were executed for four soil layers up to the depth of the drain pipes. Due to irreversible cracking in the subsoil (subsection 3.1.1), leaching of pesticides in the heavy clay soils of Eastern and Southern Flevoland is mainly determined by sorption and transformation processes in the plough layer. Thus, laboratory experiments on transformation and sorption

were executed for this layer only. The transformation experiments in the laboratory were executed at various temperatures, depending on the soil temperature observed in the field experiments in the first month after application. For 1,3-dichloropropene the temperature range was 6 to 22 °C, for simazine 13 to 18 °C. Soil moisture content was kept at field capacity for all transformation experiments.

3.1.2.1 Metamitron

Metamitron (4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one; trade name Goltix (Bayer)) belongs to the chemical family of the triazines (figure 3.2). It is a selective systematic herbicide, adsorbed predominantly by the roots, but also by the leaves and inhibits photosynthesis (Royal Society of Chemistry, 1987).

The soil used for the laboratory experiments was collected at the experimental field North-East Polder. For each layer (table 3.7) soil was taken from 20 different spots and transported to the laboratory. Here the soil of each layer was mixed thoroughly and divided among

Table 3.7. List of laboratory experiments concerning transformation and sorption for different soil depths and temperatures of the pesticides involved in the research program.

Pesticide	Type of soil and site	Sub-section	Transformation		Sorption	
			Temperature (°C)	Soil depth (m)	Temperature (°C)	Soil depth (m)
Metamitron	Loamy sand of North-East Polder	3.1.2.1	5 / 15	0.05 - 0.15	5	0.05 - 0.15
				0.25 - 0.35		0.25 - 0.35
				0.45 - 0.55		0.45 - 0.55
				0.65 - 0.75		0.65 - 0.75
1,3-Dichloropropene	Loamy sand of North-East Polder	3.1.2.2	5 / 10 / 20	0.05 - 0.15	10 / 20	0.05 - 0.15
				0.25 - 0.35		0.25 - 0.35
				0.45 - 0.55		0.45 - 0.55
				0.65 - 0.75		0.65 - 0.75
Aldicarb	Heavy clay of Eastern Flevoland	3.1.2.3	5 / 15	0.05 - 0.30	5	0.05 - 0.30
Simazine	Heavy clay of Southern Flevoland	3.1.2.4	15	0.05 - 0.30	5	5

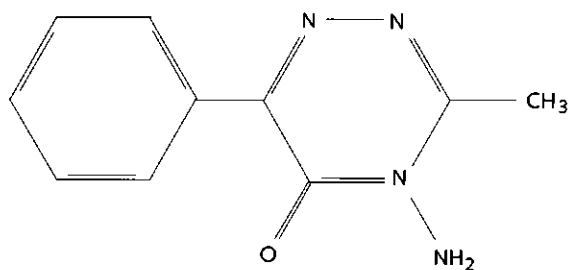


Figure 3.2. Chemical structure of metamitron.

26 flasks. The period between the collection of the samples and the laboratory experiments amounted to approximately 2 weeks. During this period the samples were stored in a darkroom at 5 °C.

Transformation: For each layer, the influence of the soil temperature on the rate of transformation was established at a temperature of 5 and 15 °C. The highest observed content of each soil layer at the field experiments was taken as starting-point of the experiments (0.05-0.15 m: 2 mg kg⁻¹, 0.25-0.35 m: 1 mg kg⁻¹, 0.45-0.55 m: 0.5 mg kg⁻¹, 0.65-0.75 m: 0.5 mg kg⁻¹).

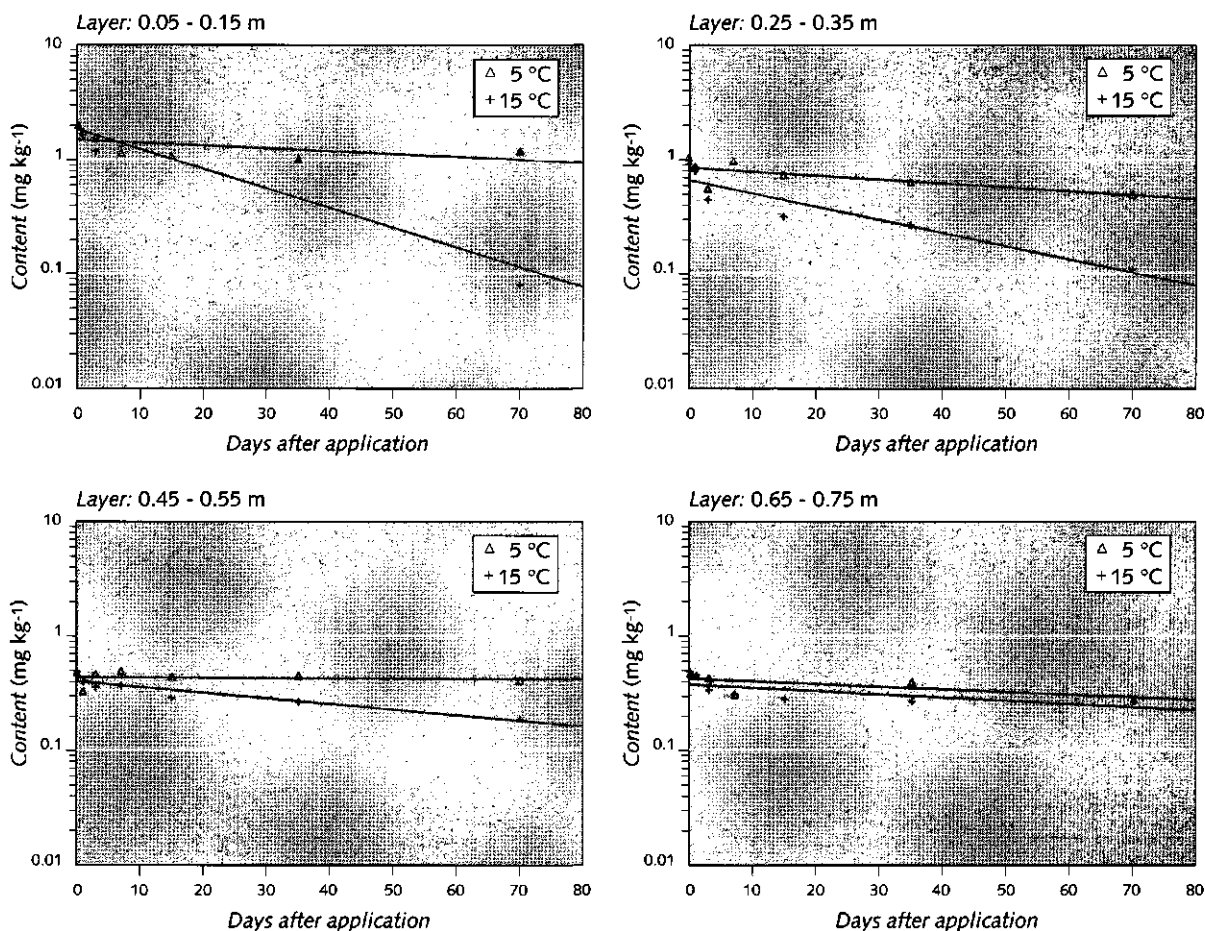


Figure 3.3. Observed (Δ and +) and calculated (—) remaining contents of metamitron at two different temperatures (5 °C and 15 °C) for four different soil layers (0.05-0.15; 0.25-0.35; 0.45-0.55 and 0.65-0.75 m) for the loamy sand of the experimental field *North-East Polder* as determined in laboratory incubations. The lines are calculated for first-order transformation (equation 2.45).

To prevent inactivation of micro-organisms by methanol (which may influence the half-life time of metamitron), 100 μl standard solution (in methanol) was diluted with water to 1 ml. Approximately 1 kg soil of each layer was divided among 14 flasks (150 ml) and the standard solution of metamitron was added to each of the flasks. A specified amount corresponding to the desired initial content was added to the soil samples with a gastight syringe. The maximum amount of methanol applied amounted to 0.15 cm^3 / 100 g soil. The soil was mixed carefully with a spoon. The soil moisture content was replenished to field capacity (water content = 0.25 kg kg^{-1}). The flasks were not sealed (open incubation) and stored in the dark at 5 and 15 $^{\circ}\text{C}$ respectively. In order to keep soil moisture content at field capacity, the flasks were weighted two times a week. Extra water was added if necessary.

The flasks were put in a thermos-cupboard and one flask per treatment was sampled at seven times: one hour, one, three, seven, fifteen, thirty-five and seventy days after application. The flasks were shaken with 50 ml methanol added to the glass jars and shaken for 30 minutes on a reciprocating shaker with a frequency of 160 motions per minute.

The samples were centrifuged for 10 minutes at 2000 g (3000 rpm). An extract was pipetted from the sample and shaken for 30 seconds in a separating funnel with water and dichloromethane. Part of the dichloromethane extract was dried with sodium sulphate and afterwards evaporated to dryness with nitrogen gas (125 ml min^{-1} at a temperature of 30 $^{\circ}\text{C}$). The residue was dissolved in 0.5 ml ethyl-acetate and 4.5 ml hexane. Metamitron was analyzed with a HP 5880 gas-chromatograph. Helium was used as a carrier gas ($\bar{u} = 30 \text{ cm s}^{-1}$: volume rate/inner diameter) and nitrogen as a make-up gas. The length and diameter of the capillary column (Wall Coated Open Tubular) amounted to 50 m and 0.0025 m respectively. The temperatures of the injector, column and detector were 170, 90 and 250 $^{\circ}\text{C}$ respectively. The detection limit amounted 0.01 $\mu\text{g l}^{-1}$. Recovery of metamitron was found to be $65 \pm 7\%$. The results of the analysis were corrected for recovery.

Results of the experiment are presented in figure 3.3.

Table 3.8. Calculated first-order transformation rate coefficient (k_1) of metamitron at two different temperatures (5 $^{\circ}\text{C}$ and 15 $^{\circ}\text{C}$) for four different soil layers (0.05-0.15; 0.25-0.35; 0.45-0.55 and 0.65-0.75 m) for the loamy sand of the experimental field *North-East Polder*. The coefficient for the influence of soil depth on the rate of transformation (f_z) was calculated from k_1 at 15 $^{\circ}\text{C}$ (equation 2.46). The soil moisture content is constant at field capacity

Soil layer (m)	k_1 (d^{-1})		f_z (-)
	5 $^{\circ}\text{C}$	15 $^{\circ}\text{C}$	
0.05 - 0.15	0.011	0.048	1.00
0.25 - 0.35	0.009	0.040	0.83
0.45 - 0.55	< 0.007	0.015	0.31
0.65 - 0.75	< 0.007	0.010	0.21

The observed values have been converted into first-order transformation rate coefficients using linear regression after log-transformation. Results are presented in table 3.8. Average standard deviations of k_1 values amounted to 0.003 d^{-1} for 5 $^{\circ}\text{C}$ and 0.006 d^{-1} for 15 $^{\circ}\text{C}$. The influence of temperature on the first-order transformation rate (f_T) was described with equation 2.47. The estimation of the coefficient γ_a (equation 2.47) was based on the results for the 0.05 - 0.15 m layer, which resulted in $\gamma_a = 0.15 \text{ }^{\circ}\text{C}^{-1}$.

The coefficient for the influence of soil depth on the rate of transformation (f_z) is calculated from k_1 at 15 $^{\circ}\text{C}$, according to equation 2.46. Values for f_z are presented in table 3.8. The table shows that f_z decreases with depth. The reference coefficient for first-order transformation ($k_{1,\text{ref}}$), as presented in equation 2.46 was calculated to be 0.10 d^{-1} . Figure 3.4 shows that the results of the transformation rate studies with metamitron can be described reasonably well with equations 2.46 and 2.47 using the selected parameter values.

Allen and Walker (1987) studied the transformation of metamitron in 18 different top soils ($T = 20 \text{ }^{\circ}\text{C}$ and $h \approx -2.4 \text{ m}$). They found that transformation of metamitron could be best described by the first-order kinetics. Their first-order transformation rate coefficient ($k_{1,\text{ref}}$) was on average 0.023 d^{-1} and the maximum value amounted to 0.065 d^{-1} . Thus, the transformation rate at 20 $^{\circ}\text{C}$ derived from the present study was much faster

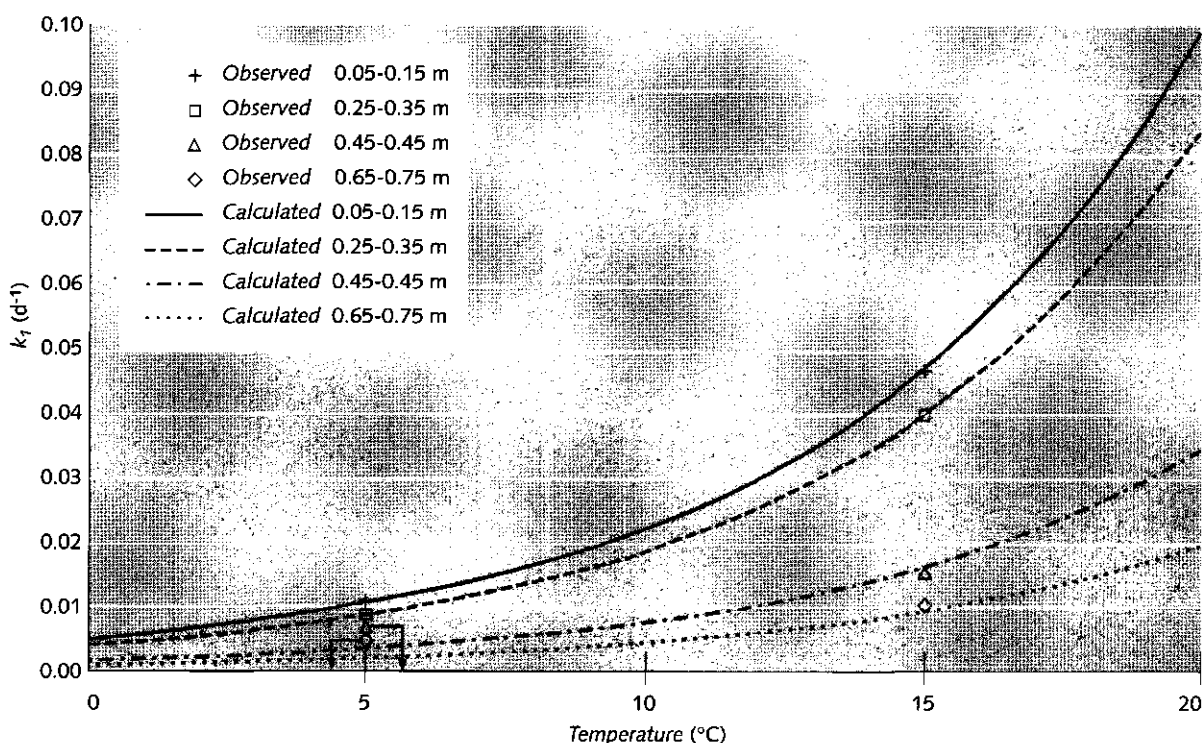


Figure 3.4. Observed and calculated influence of the temperature on the first-order transformation rate of metamitron (k_1) at a depth of 0.05-0.15 m, 0.25-0.35 m, 0.45-0.55 m and 0.65-0.75 m with soil moisture content at field capacity for the loamy sand of the experimental field *North-East Polder*. The lines were calculated with equations 2.46 and 2.47 ($k_{1,ref} = 0.10 \text{ d}^{-1}$ at $T_{ref} = 20 \text{ °C}$ and $\gamma_a = 0.15 \text{ °C}^{-1}$). The arrows indicate that the figures are upper limits.

than in all soils from the study of Allen and Walker.

Boesten (1986) collected data on the effect of soil temperature on the transformation coefficient of approximately 50 different combinations of soils and pesticides. He observed an average γ_a value of 0.08 °C^{-1} with an standard deviation of 0.02 °C^{-1} . This demonstrates that the parameter γ_a for metamitron derived from the present study is extremely high (equation 2.47). This may be caused by the methanol used in the experiment. At a temperature of 5 °C volatilization of methanol will be smaller than at a temperature of 15 °C . A higher concentration of methanol may have retarded transformation at 5 °C . In consequence of this, the difference between the transformation rate coefficient at 5 and 15 °C will increase.

Sorption: Standard solutions were made (by dissolving

metamitron crystals with a purity of 99%) with 5, 10, 100, 500 and $1000 \mu\text{g l}^{-1}$ metamitron in 0.01 M CaCl_2 and cooled to a temperature of 5 °C . 100 ml of the standard solution was added to 50 g of soil (soil/solution-ratio = 0.5) in glass jars and shaken for 6 hours at 5 °C on a reciprocating shaker with a frequency of 160 motions per minute. For each concentration, measurements were carried out in duplicate. The glass jars with soil were stored for 16 hours at 5 °C . Afterwards the glass jars with soil were shaken for 1 hour at a temperature of 5 °C . Next, the soil samples were centrifuged at 2000 g (3000 rpm) for 15 minutes. A sample was taken from the supernatant and shaken for 30 seconds in a separating funnel with dichloromethane (water/dichloromethane = 1/2). Part of the dichloromethane extract was dried with sodium sulphate and afterwards treated with nitrogen gas (125 ml min^{-1} at a temperature of 30 °C). The residue was dissolved in 0.5 ml

ethyl-acetate and 4.5 ml hexane. Metamitron was analyzed with a HP 5880 gas-chromatograph. Helium was used as a carrier gas ($u = 30 \text{ cm s}^{-1}$) and nitrogen as a make-up gas. The length and diameter of the capillary column (Wall Coated Open Tubular) amounted to 50 m and 0.0025 m respectively. The temperatures of the injector, column and detector were 170, 90 and 250 °C respectively.

The detection limit amounted to $0.1 \mu\text{g l}^{-1}$. It was assumed that the recovery of the procedure for extraction of water was 95%. Furthermore, it was assumed that the measured difference in concentration between standard solutions and glass jars with soil was due to adsorption.

Figure 3.5 and table 3.9 present the observed sorption

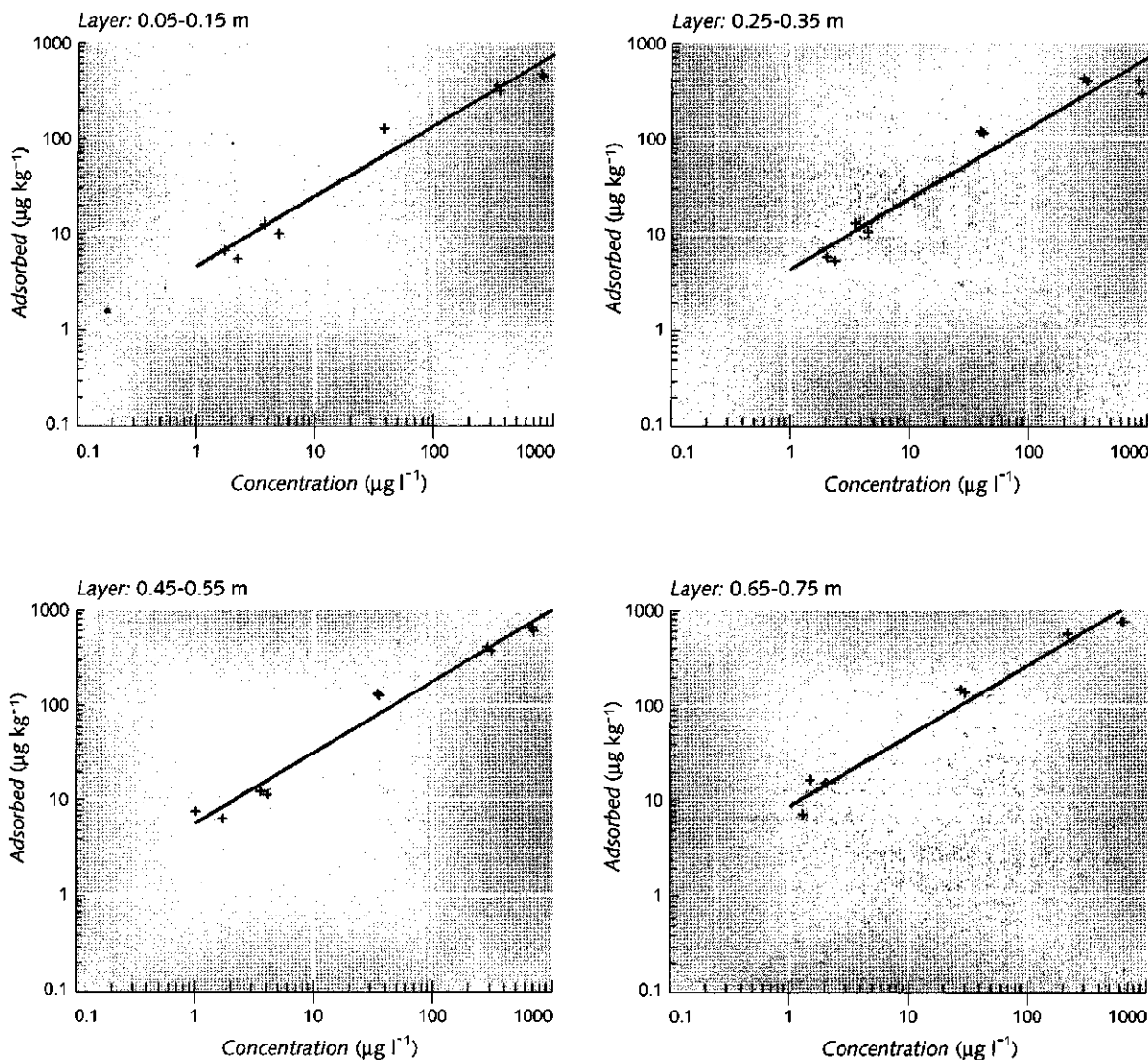


Figure 3.5. Sorption isotherms of metamitron for four different soil layers at 5 °C for the loamy sand of the experimental field *North-East Polder*. The observed values are presented as +. The lines were calculated with the Freundlich equation (equation 2.57: $c_{L,ref} = 10 \mu\text{g l}^{-1}$).

Table 3.9. Freundlich parameters for the sorption isotherms of metamitron for the experimental field in the North-East Polder calculated with equation 2.57 ($c_{l,ref} = 10 \mu\text{g l}^{-1}$).

Soil layer (m)	K_F ($\text{cm}^3 \text{g}^{-1}$)	(1/n) (-)
0.05 - 0.15	2.50	0.74
0.25 - 0.35	2.45	0.74
0.45 - 0.55	3.35	0.75
0.65 - 0.75	4.80	0.74

of metamitron and the corresponding Freundlich parameters. At high concentration levels observed concentrations strongly deviate from calculated concentration levels (especially for the layer 0.25-0.35 m). The results for all soil depths show similar deviations from the fitted line. This may be due to systematic errors. Table 3.9 shows that the Freundlich coefficient K_F increases with depth. Depending on concentration and soil depth, the K_{om} -value (Freundlich coefficient K_F divided by the organic matter content) varied from 42-91 $\text{cm}^3 \text{g}^{-1}$ ($c_{l,ref} = 1 \text{ mg l}^{-1}$). Allen and Walker (1987) reported values for the adsorption of metamitron on 18 different mineral soils. K_{om} -values which could be extracted from their values, varied from 45 up to 225 $\text{cm}^3 \text{g}^{-1}$ with an average value of 112 $\text{cm}^3 \text{g}^{-1}$. So our results corresponded reasonably well with those of Allen and Walker (1987).

3.1.2.2 1,3-Dichloropropene

1,3-Dichloropropene belongs to the chemical family of the organochlorines which are predominantly used for pre-planting control of most species of nematodes (Royal Society of Chemistry, 1987). At the experimental field North-East Polder 1,3-dichloropropene was injected as DD95, a liquid which contained more than 95% of an approximate equal mixture of the (Z)-isomer and the (E)-isomer. The chemical structure of the (Z) and (E) isomer are presented in figure 3.6.

Transformation. Based on morphological and chemical characteristics, soil samples were taken at a 0.05-0.15, 0.25-0.35, 0.45-0.55 and 0.65-0.75 m depth at 10 sites for each of the three plots (subsection 3.2.1). At the laboratory the samples of each layer were mixed thoroughly and moisture content was adjusted to field

capacity (moisture content $\approx 0.25 \text{ kg kg}^{-1}$). The samples were stored in a refrigerator at a temperature of 5 °C. Incubations started within a week after collecting the soil.

For each soil layer, 36 flasks were prepared in duplicate for 3 temperatures at 6 time intervals. To each flask (volume = 500 ml) within the series, 100 g of mixed moist soil was added. A standard solution of 50 μl methanol with dichloropropene was diluted with water to 1 ml. The amount of dichloropropene in methanol varied for each soil layer. The amounts of (Z) and (E)-1,3 dichloropropene added to each flask corresponded with an initial content of approximately 15 mg kg^{-1} for the 0.05-0.15 m layer, 5 mg kg^{-1} for the 0.25-0.35 m layer, 0.3 $\mu\text{g kg}^{-1}$ for the 0.45-0.55 m layer and 30 mg kg^{-1} for the 0.65-0.75 m layer. The dichloropropene/methanol/water solution was added with purger syringes and injected at different points. The maximum amount of methanol applied amounted 0.02 $\text{cm}^3 / 100 \text{ g soil}$. After addition the soil was mixed carefully with a spoon. The flasks were sealed (gastight seal) and stored in the dark at 5, 10 and 20 °C respectively. Initial contents in the laboratory experiments approximated the highest contents in the field for each soil layer. After 1h, 3, 7, 14, 35 and 70 days, 24 flasks (3 different temperatures and 2 flasks per soil layer) were taken for extraction.

Dichloropropene was extracted from soil by heating the flasks to 100 °C for 30 min after adding 150 ml water and 10 ml hexane. After condensation, the hexane and 1,3-dichloropropene were collected in a

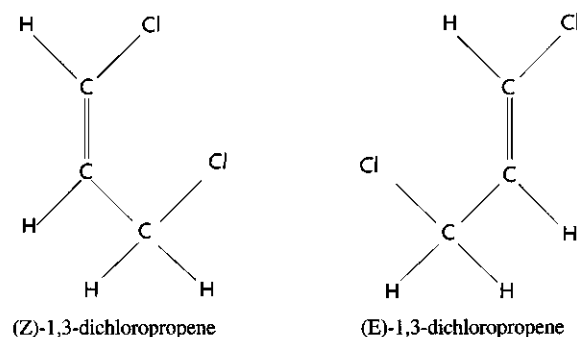


Figure 3.6. Chemical structure of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene.

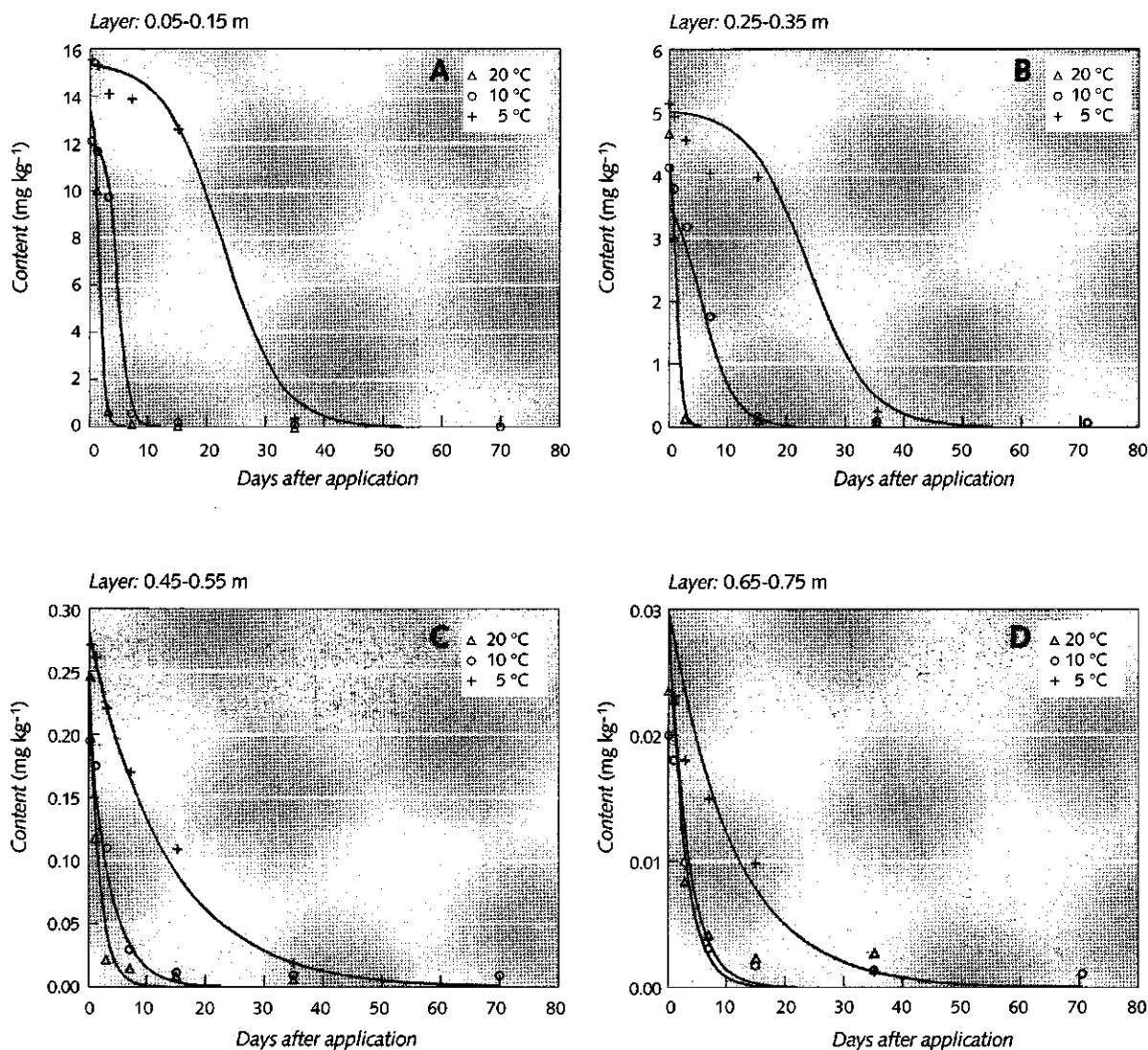


Figure 3.7. Observed (Δ , \circ and +) and calculated (—) remaining contents of (Z) 1,3-dichloropropene at various temperatures for different soil layers of the loamy sand of the experimental field *North-East Polder* as determined in laboratory incubations. The lines were calculated with equation 2.50 for parts A and B and with equation 2.45 for parts C and D. Note the difference in scale of the vertical axes.

Daen and Stark receiver. Analyses of the hexane solution were performed with Perkin-Elmer 8500 gas chromatograph. Helium was used as a carrier gas ($\bar{u} = 25 \text{ cm s}^{-1}$). Two capillary columns (CPsil5/13CB) of 25 m length, 0.0032 m internal diameter, were used in combination with an ECD Nickel-63 detector at 300 °C. A step-wise temperature program led to an oven temperature of 250 °C. The temperature of the in-

jector and column were 150 °C and 45 °C respectively. Retention time was 5 minutes. The detection limit amounted to $0.05 \mu\text{g l}^{-1}$. Recovery for this method for (E) and (Z) 1,3-dichloropropene applied in hexane was $70 \pm 5\%$. Results were corrected for recovery.

The results are presented in figure 3.7 (Z-isomer) - 3.8 (E-isomer) and show considerable differences in trans-

formation rates for different soil layers containing different initial contents and different soil temperatures. However, differences between the (Z) and (E)-isomer are small. For the highest concentrations (layers: 0.05-0.15 m and 0.25-0.35 m) a lag-time was observed during which concentration levels remained constant. The duration of the lag-time amounted to approxi-

mately 12, 3 and 1 days for soil temperatures of respectively 5, 10 and 20 °C. After the lag-time transformation of 1,3-dichloropropene accelerated, followed by decreasing transformation rates at low residual concentrations.

This phenomenon can be recognized as biological

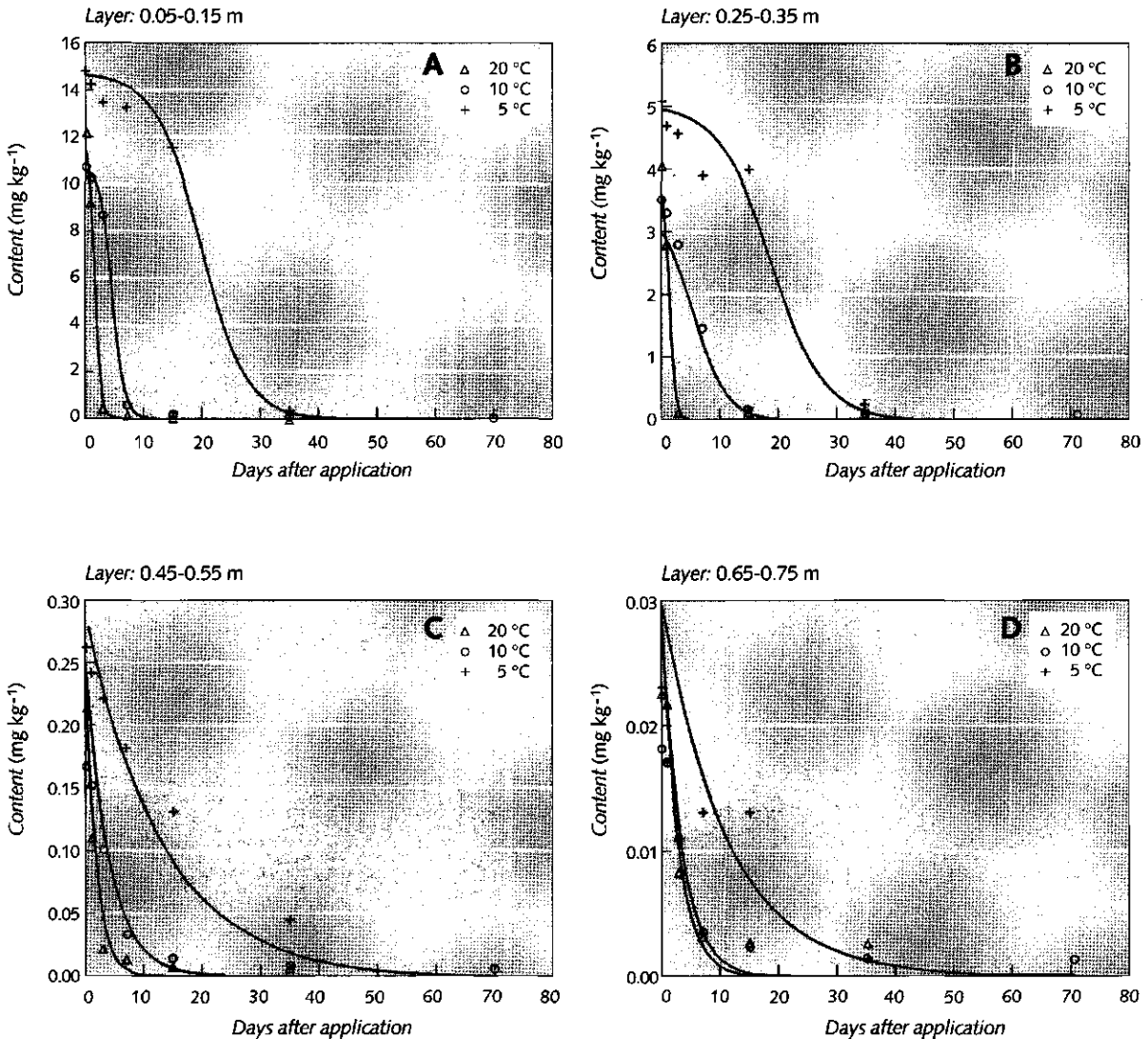


Figure 3.8. Observed (Δ , \circ and $+$) and calculated (—) remaining contents of (E) 1,3-dichloropropene at various temperatures for different soil layers of the loamy sand of the experimental field *North-East Polder* as determined in laboratory experiments. The lines were calculated with equation 2.50 for parts A and B and with equation 2.45 for parts C and D. Note the difference in scale of the vertical axes.

Table 3.10. Optimized parameter set for microbial transformation in the top layers of the loamy sand of the *North-East Polder* (layers: 0.05-0.15 m and 0.25-0.35 m) for both (E) and (Z) 1,3-dichloropropene according to Vink et al., 1994.

Symbol	Parameter	Value	Equation
α_m	Microbial mortality rate	0	2.51
β_m	Microbial mortality constant	0	2.51
γ_b	Gain factor for biomass production	0.56 d ⁻¹	2.51
K_M	Saturation constant of Monod's equation	0.64 mg kg ⁻¹	2.51
Q_{10}	Increase of transformation by increase of temperature of 10 °C	3.22	2.55
T_{opt}	Optimum temperature for maximum microbial activity	15.6 °C	2.54
T_{max}	Lethal temperature for micro-organisms	40.0 °C	2.54
T_{min}	Minimum temperature for microbial activity	0 °C	2.54
μ_5	Rate of microbial reaction at 5 °C	0.05 d ⁻¹	2.54
μ_{10}	Rate of microbial reaction at 10 °C	0.23 d ⁻¹	2.54
μ_{20}	Rate of microbial reaction at 20 °C	0.25 d ⁻¹	2.54

transformation (Vink and Groen, 1992). The microbial population is linked to substrate concentration by Monod's approach. For the top layers the results of the laboratory experiment were used to optimize the parameters as presented in subsection 2.2.2.2. (Vink et al., 1994). The optimisation procedure is presented by Vink et al. (1994). Because the experimental results for the 0.05-0.15 and 0.25-0.35 m layers for both isomers were very similar, it was attempted to describe the results of these studies with a single parameter set.

The lines in the figures 3.7 A and B and 3.8 A and B show the calculated results with the optimized parameter set for both layers and both isomers combined, which is presented in table 3.10.

The transformation of 1,3-dichloropropene in the deeper soil layers can be well described with the first-order transformation (equation 2.45). The lines in figure 3.7 (layer C: 0.45-0.55 m; layer D: 0.65-0.75 m) and 3.8 (layer C: 0.45-0.55 m; layer D: 0.65-0.75 m) show the calculated concentration with the optimized parameter set, which is presented in table 3.11. The first-order transformation rate coefficient of (E) and (Z) 1,3-dichloropropene for the soil layers 0.45-0.55 m and 0.65-0.75 m was obtained by linear regression. Differences between the first-order transformation rate coefficient for the (E) and (Z) isomer are very small. Figures 3.7 and 3.8 show that the last few percent of the dose is transformed at much slower rate.

For the determination of the parameter γ_a (equation 2.47), which is valid for the soil layers 0.45-0.55 m and 0.65-0.75 m, the average first-order transformation rate coefficients k_f of (E) and (Z) 1,3-dichloropropene for different depths and temperatures (table 3.11) were used. The parameter γ_a was calculated (as an average over both layers) by linear regression after logarithmic transformation and amounts to 0.10 °C⁻¹. The influence of the soil depth on the rate of transformation for the layer 0.45-0.55 m and 0.65-0.75 m was calculated as the quotient of the first-order transformation rate coefficients at different temperatures for the layer 0.65-0.75 m and 0.45-0.55 m and amounts to 0.9. Figure 3.9 present the relationship between the soil temperature, soil depth and k_f .

Table 3.11. First-order transformation rate coefficient k_f of (E) and (Z) 1,3-dichloropropene for the soil layers 0.45-0.55 m and 0.65-0.75 m at field capacity ($h \approx -2.4$ m) as a function of soil depth and temperature for the loamy sand of the *North-East Polder*.

Soil layer (m)	k_f (d ⁻¹)					
	5 °C		10 °C		20 °C	
	(E)	(Z)	(E)	(Z)	(E)	(Z)
0.45 - 0.55	0.10	0.10	0.25	0.21	0.49	0.53
0.65 - 0.75	0.08	0.09	0.29	0.24	0.44	0.39

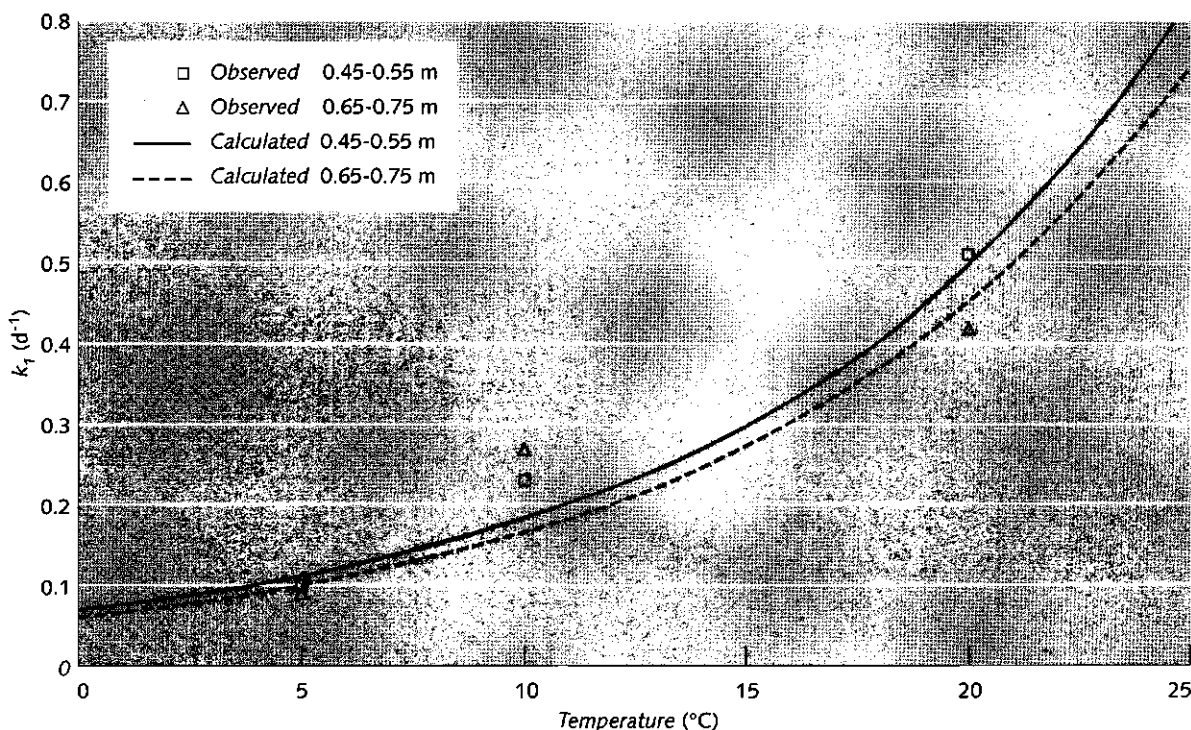


Figure 3.9. Influence of the soil temperature on the first-order transformation rate coefficient k_1 of (Z) 1,3-dichloropropene at a depth of 0.45-0.55 m and 0.65-0.75 m for the loamy sand of the experimental field *North-East Polder*. The lines are calculated according to equations 2.45 and 2.47 ($h \approx -2.4$ m, $k_{1,ref} = 0.51$ d⁻¹, $f_{0.45-0.55m} = 1$, $f_{0.65-0.75m} = 0.9$, $\gamma_a = 0.10$ °C⁻¹).

Sorption: Soil samples were taken at a 0.05-0.15, 0.25-0.35, 0.45-0.55 and 0.65-0.75 cm depth at 10 sites for each of the three plots (subsection 3.2.1). In the laboratory samples of each layer were mixed thoroughly and moisture content was adjusted to field capacity ($h \approx -2.4$ m).

The samples were stored in a refrigerator at 5 °C. The experiments started within a week after collecting the soil.

Standard solutions (from colourless liquid with 96% (E) and (Z) 1,3-dichloropropene) were produced with (1.1; 5.6; 11.1; 111; 1,113; and 11,130 µg l⁻¹ (Z)-isomer) and 1.0; 5.0; 10.0; 100; 1,007 and 10,070 µg l⁻¹ (E)-isomer) in 0.01 M CaCl₂ at a range of concentrations which are approximately known. Required amounts of 1,3-dichloropropene were added to the soil

using punger syringes. 100 ml of the standard solution was added to 50 g moist soil (soil/solution-ratio = 0.5). The glass jars with soil and standard solution were sealed with Teflon™ lined caps and shaken for 6 hours on a reciprocating shaker with a frequency of 120 motions per minute. Half of the glass jars were shaken at a temperature of 20 °C; the other half at a temperature of 10 °C. Both were preserved for 16 h at the same temperature (half at a temperature of 20 °C; the other half at a temperature of 10 °C). Afterwards, half the glass jars were shaken for 10 minutes at 10 °C; the other half at 20 °C. For each combination of temperature and concentration level, the experiment was executed in duplicate. Controls were produced in glass jars with standard solutions, without soil and with 10 ml air. The controls were sealed with Teflon™ lined caps and stored for 1 day at a temperature of 10 °C and 20 °C. Afterwards the controls were analyzed.

Due to small amount of air present in the glass jars (approximately 10 ml), effects of volatilization of 1,3-dichloropropene to the air may occur. For all soil layers losses due to volatilization were measured for the (Z) 1,3-dichloropropene, which is the most volatile isomer. Losses ranged from 3 - 14%, with an average of 7% at 10 °C and 9% at 20 °C. It was assumed that the per-

centage volatilised from the glass jars with soil was equal to the percentage volatilised from the glass jars without soil at the same temperature and same initial concentration level. Assuming that the percentage volatilized in the glass jars without soil equals the percentage lost in the glass jars with soil is theoretically not completely correct (equal percentages lost from the

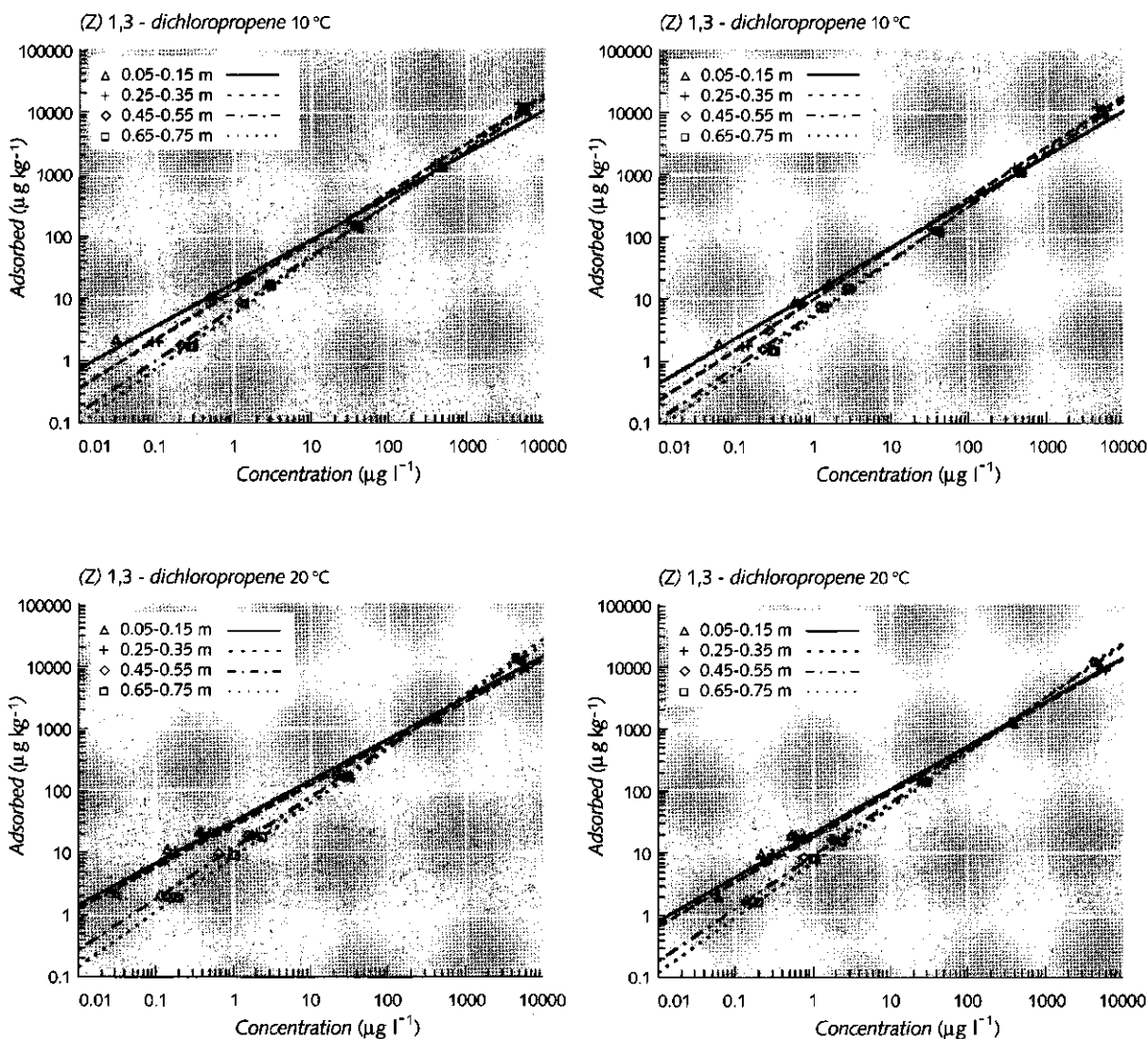


Figure 3.10. Sorption isotherms of 1,3-dichloropropene of four soil layers at 10 °C and 20 °C for the loamy sand of the experimental field *North-East Polder* as determined in laboratory incubations. The observed values are presented as Δ , +, \square and \diamond . The lines were calculated with the Freundlich equation (equation 2.57: $c_{l,ref} = 10 \text{ mg l}^{-1}$).

Table 3.12. Freundlich parameters K_F and $1/n$ of (E) and (Z) 1,3-dichloropropene for different soil temperatures and soil layers at the loamy sand of the experimental field *North-East Polder* calculated with equation 2.57 ($c_{l,ref} = 10 \text{ mg l}^{-1}$).

Soil layer (m)	Temperature °C	(Z) 1,3-dichloropropene		(E) 1,3-dichloropropene	
		K_F ($\text{cm}^3 \text{ g}^{-1}$)	($1/n$) (-)	K_F ($\text{cm}^3 \text{ g}^{-1}$)	($1/n$) (-)
0.05-0.15	10	1.0	0.69	1.0	0.73
0.25-0.35	10	1.8	0.78	1.6	0.81
0.45-0.55	10	2.0	0.84	1.7	0.85
0.65-0.75	10	2.0	0.88	1.7	0.89
0.05-0.15	20	1.9	0.67	1.2	0.71
0.25-0.35	20	1.7	0.67	1.2	0.72
0.45-0.55	20	1.6	0.82	2.3	0.85
0.65-0.75	20	1.6	0.88	2.4	0.88

fraction present in the liquid phase would be more appropriate). However, the difference between the two approaches is small because sorption did lead to decreases in the concentration in the liquid phase that were usually not larger than 50% under our experimental conditions.

Both soil samples and controls were centrifuged at 2000 g (3000 rpm) for 15 minutes and a known volume of the liquid phase was pipetted from the sample. The content of 1,3-dichloropropene was measured with a HP 5880A gas-chromatograph, using the Purge and Trap method. Helium was used as a carrier gas ($\dot{v} = 25 \text{ cm}^3 \text{ s}^{-1}$) and 2,6-diphenyl-*p*-phenyloxide as an adsorbate. The temperatures of the injector, column and detector were 150 °C, 45 °C and 300 °C respectively. Retention time was 5 minutes. The detection limit amounted to $0.05 \mu\text{g l}^{-1}$. It was assumed that recovery was 100% for both (Z) 1,3-dichloropropene and (E) 1,3-dichloropropene. The results are presented in figure 3.10 and table 3.12.

Results show that differences between the (E) and (Z)-isomer are small. For higher temperatures the sorption of 1,3-dichloropropene is a little stronger. However, the dependency of the Freundlich coefficient and exponent to a change in temperature is small. The Freundlich exponent ($1/n$) increases with increasing depth. The absolute values of the Freundlich exponent proved to

be low. Standard deviations of the Freundlich coefficient K_F amounted to $0.05\text{--}0.12 \text{ cm}^3 \text{ g}^{-1}$. Depending on the temperature, concentration and soil depth, the K_{om} -value (Freundlich coefficient divided by the organic matter content) varied from $52\text{--}156 \text{ cm}^3 \text{ g}^{-1}$ ($c_{l,ref} = 10 \text{ mg l}^{-1}$). Leistra (1972) reported K_{om} -values which varied from $14\text{--}15 \text{ cm}^3 \text{ g}^{-1}$ ($c_{l,ref} = 100 \text{ mg l}^{-1}$). So our results indicate stronger sorption than those of Leistra (1972). It can be derived from data from his study that the Freundlich coefficient increases with increasing soil temperatures, so the same trend as found in table 3.12.

3.1.2.3 Aldicarb

Aldicarb (figure 3.11; 2-methyl-2(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime; trade name Temic (Union Carbide)) belongs to the chemical family of the carbamates. It is a systemic pesticide for controlling certain insects, mites and nematodes. Normally, aldicarb is applied as granules and either applied before planting or simultaneously with planting.

After application aldicarb is rapidly oxidised to aldicarb sulphoxide; 2-methyl-2(methylsulphilyn)propionaldehyde *O*-(methylcarbamoyl)oxime, which then slowly oxides to aldicarb sulphone; 2-methyl-2(methylsulpholyn)propionaldehyde *O*-(methylcarbamoyl)oxime. Various oximes, nitriles, amides, acids, and alcohols are also formed depending on environmental parameters (Royal Society of Chemistry, 1987;

figure 3.11). Aldicarb and its oxidation products, sulphoxide and sulphone seem to be the only highly toxic compounds: the other transformation products are much less toxic or not toxic to aquatic organisms (Lightfoot et al., 1987).

Transformation experiments: In October 1993 soil was collected at the experimental field Eastern Flevoland. The soil was taken from the plough layer of a plot which had been treated with aldicarb three years previously. In 1993 wheat was grown on the field. Approximately 10 kg of soil from different locations was taken to the laboratory and stored in the dark at 10 °C. Incubations started roughly 1 month after collecting the soil. The soil was mixed thoroughly and moisture content was adjusted to field capacity (moisture content 0.30 kg kg⁻¹). For the plough layer, 28 glass jars were analyzed. To 16 glass jars of 200 ml, 50 g of mixed soil was added. Aldicarb (with water as solvent) was added with microlitre syringes and carefully mixed with a spoon. The concentration directly after application approximated 75 mg kg⁻¹ dry soil. The glass jars were sealed and stored in the dark at 5 °C. At intervals of 1 hour, 3, 7, 14, 28, 42, 56 and 84 days dur-

ing incubation, the glass jars were taken for extraction.

Three weeks after the start of the first experiment a second experiment was initiated. To 12 glass jars of 200 ml, 50 g of mixed soil was added. Aldicarb (with water as solvent) was added with microlitre syringes and carefully mixed with a spoon. The concentration directly after application approximated 110 mg kg⁻¹ dry soil. The glass jars were sealed and stored in the dark at 15 °C. At intervals of 1 hour, 3, 7, 14, 30 and 50 days during incubation, the glass jars were taken for extraction.

After addition of 50 ml acetone, the sealed glass jars were shaken for half an hour on a reciprocating shaker with a frequency of 175 motions per minute at a temperature of 20 °C. The samples were put through a centrifugal machine at 900 g (2000 rpm). Part of the acetone extract (± 0.5 ml) was pipetted from the sample and the acetone was evaporated with nitrogen gas (100 ml min⁻¹ at a temperature of 25 °C). The residue was dissolved in 1 ml eluents (95% water and 5% Acetonitrile) and filtrated (0.2 µm membrane). The content of aldicarb, aldicarb sulphoxide and aldicarb sulphone

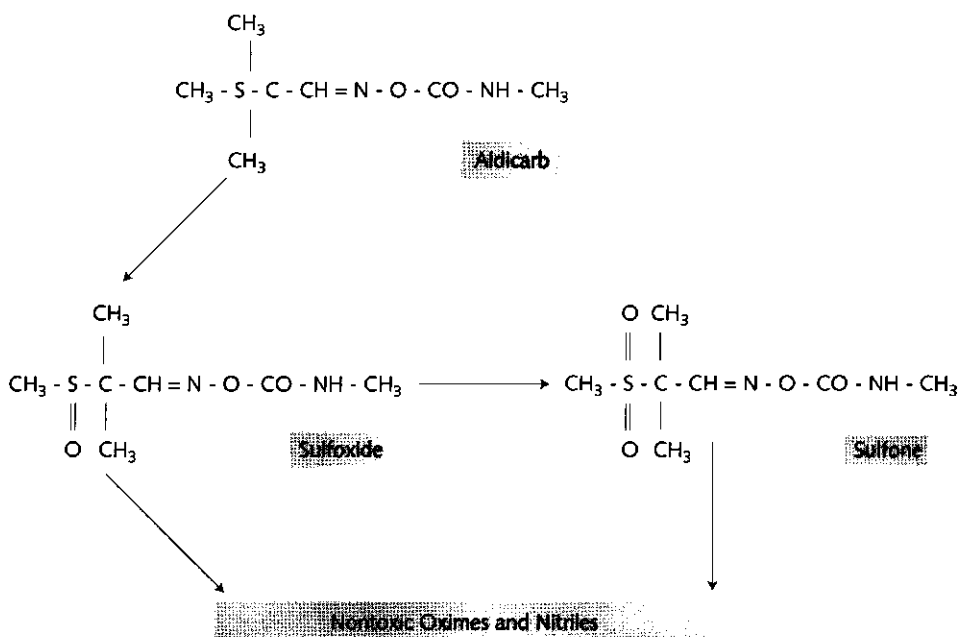


Figure 3.11. Transformation pathways of aldicarb.

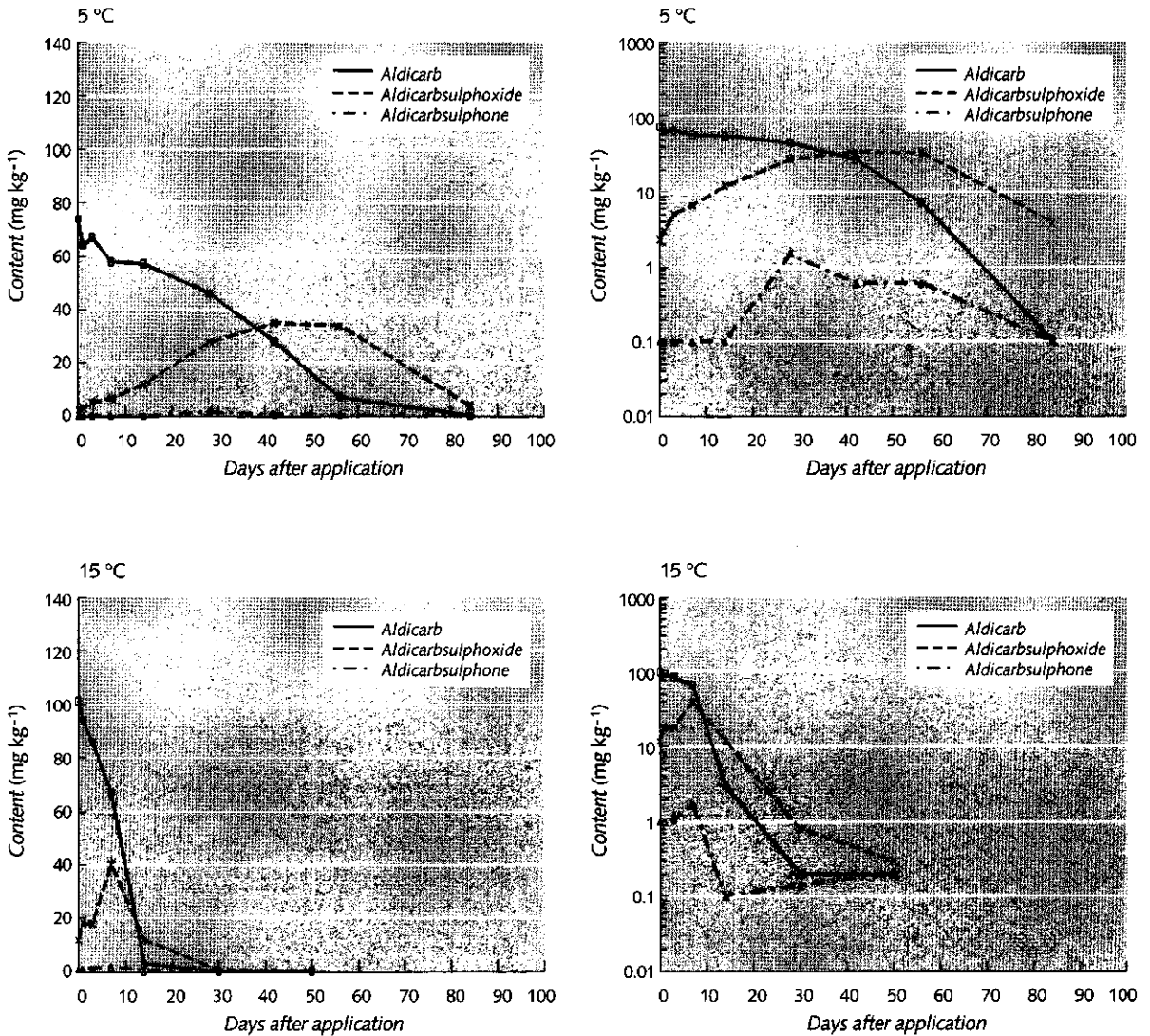


Figure 3.12. Content of aldicarb, aldicarb sulphoxide and aldicarb sulphone as a function of time in laboratory incubations at 5 and 15 °C with soil from the plough layer of the experimental field *Eastern Flevoland* ($h \approx -2.4$ m). The only difference between the left and right figure is the vertical axes (linear and logarithmic respectively).

were measured with a HPLC (Waters) by injecting 50 μ l of the filtrated extract. The HPLC analysis was executed by Vydac machine (column: C18-TP54) with UV detection (214 nm) at a flow rate of 0.6 ml min⁻¹ and acetonitrile as carrier gas. The detection limit amounted to 0.1 μ g l⁻¹ both for aldicarb sulphoxide and aldicarb sulphone. Analytic recovery amounted to ap-

proximately $90 \pm 5\%$ for aldicarb, $65 \pm 7\%$ for aldicarb sulphoxide and $80 \pm 5\%$ for aldicarb sulphone. The results were corrected for recovery.

The results of the experiment are presented in figure 3.12 both on a vertical linear and logarithmic scale. The figure shows that roughly half of the amount of

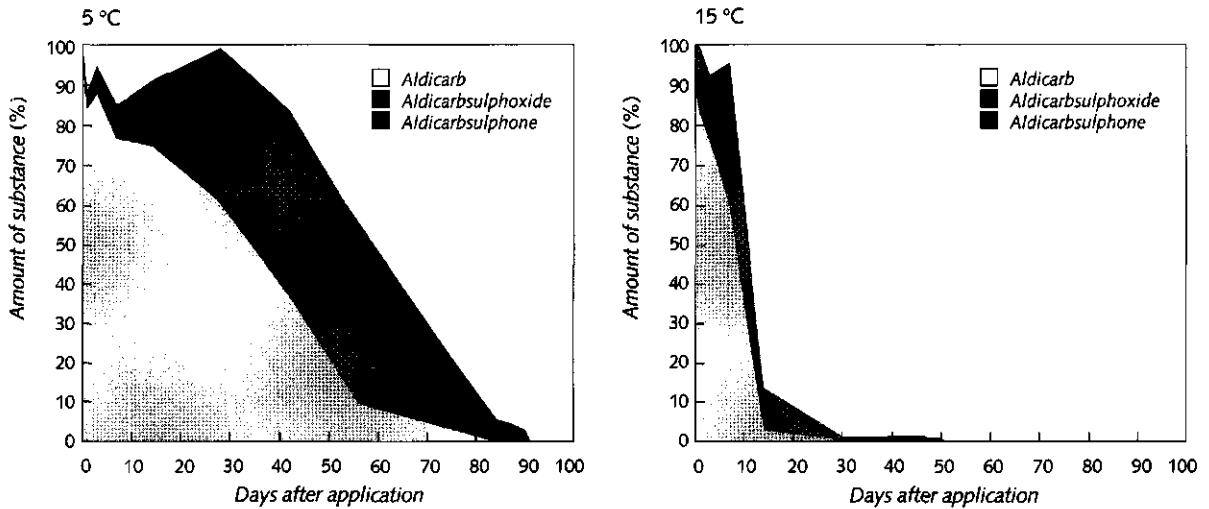


Figure 3.13. Cumulative sum of contents of aldicarb, aldicarb sulphoxide and aldicarb sulphone in time as percentage of doses applied (75 mg kg^{-1} at 5°C and 110 mg kg^{-1} at 15°C) in the plough layer of the experimental field *Eastern Flevoland* as determined in laboratory incubations with a temperature of 5 and 15°C and $h \approx -2.4 \text{ m}$.

aldicarb is transformed into aldicarb sulphoxide. However, less than 3% of the original amount of aldicarb is transformed into aldicarb sulphone. In order to simplify the complex transformation of aldicarb, the content of aldicarb and aldicarb sulphoxide were added up and the formation of aldicarb sulphone was neglected. Figure 3.13 shows cumulative sum of contents of aldicarb, aldicarb sulphoxide and aldicarb sulphone in time as percentage of dose applied. The sum of the contents is approximately equal to the amount of the substance, as the relative differences in molecular weight between aldicarb, aldicarb sulphoxide and aldicarb sulphone (190, 206 and 222 respectively) are small.

As presented in figure 3.14, an initial phase and transformation of aldicarb/aldicarb sulphoxide can be distinguished. Both the initial phase and the rate of transformation depend on the soil temperature. The initial phase amounted to 8 and 42 days at soil temperatures of 15 and 5°C respectively (figure 3.14). Linear regression was applied for different soil temperatures. After the initial phase, the half-live time value amounted to 4 days ($k_{1,15} = 0.17 \text{ d}^{-1}$) for 15°C and to 14 days ($k_{1,5} = 0.05 \text{ d}^{-1}$) for 5°C . From these values it can

be calculated that the coefficient γ_a is equal to 0.12°C^{-1} and $k_{1,\text{ref}} = 0.30 \text{ d}^{-1}$ at a temperature of 20°C .

The procedure to consider only the sum of aldicarb/aldicarb sulphoxide is of course a strong simplification. It can be derived from figure 3.12 that the transformation of aldicarb does not follow first-order kinetics. It would have been very difficult to develop a transformation sub-model that describes the conversion patterns in figure 3.12 adequately.

Transformation of aldicarb and its oxidation products in soils has already been studied frequently (e.g. Coppedge et al., 1977; Smelt et al., 1978-2; Bromilow et al., 1980-1 and 1980-2; Smelt et al., 1983; Hansen and Spiegel, 1983). Results of these studies differed greatly. Besides, transformation of aldicarb and its oxidation products in soil at the experimental field *Eastern Flevoland* differed from these studies. This may be caused by microbial adaptation. Frequent application of aldicarb may cause microbial adaptation and result in accelerated transformation (e.g. Smelt et al., 1987).

As the accelerated transformation of aldicarb has not been observed on heavy clay soils before, transforma-

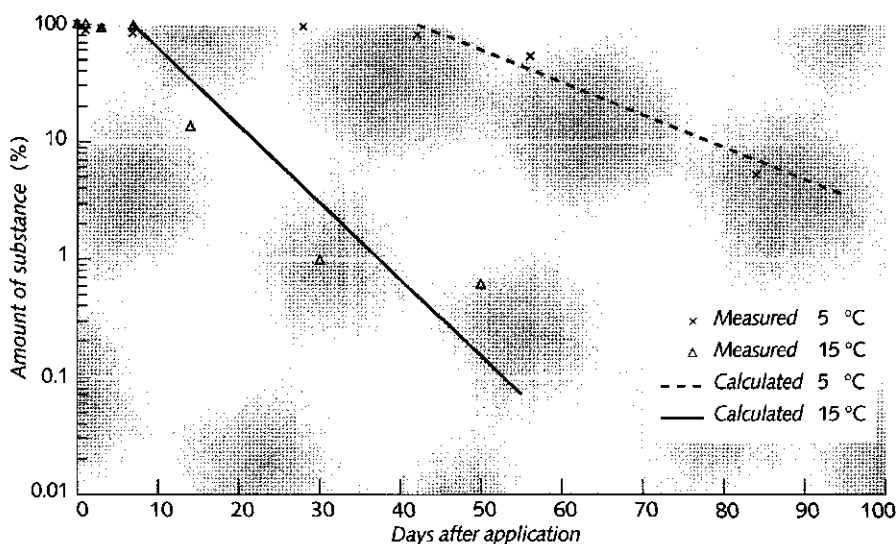


Figure 3.14. Observed (∇ and \times) and calculated (—) remaining sum of contents of aldicarb/aldicarb sulphone as percentage of doses applied (75 mg kg^{-1}) in laboratory incubations of the plough layer of the experimental field *Eastern Flevoland* at a temperature of 5 and 15°C and $h \approx -2.4 \text{ m}$. The initial phase amounted to 8 (15°C) and 42 days (5°C). First-order transformation was calculated with equation 2.45.

tion experiments were repeated at 15°C with soil from the plough layer of the experimental field *Eastern Flevoland*. The moisture content amounted to 0.35 kg kg^{-1} and the initial content of aldicarb at the start of the experiment was 25 mg kg^{-1} (Smelt, 1996). The results of this experiment were similar to the results presented in the figures 3.13 and 3.14. Again, transformation of aldicarb sulphoxide into aldicarb sulphone could not be observed. The calculated first-order transformation rate coefficient at 15°C for the sum of aldicarb and aldicarb sulphoxide amounted to 0.09 d^{-1} . However, no initial phase was observed.

Sorption experiments: In October 1993 soil was collected at the experimental field *Eastern Flevoland*. The samples were taken from the plough layer of a plot which had not been treated with aldicarb before. Approximately 5 kg of soil were collected from different locations and mixed thoroughly. Incubations started directly after collecting the soil. Standard solutions (from crystals with 99% aldicarb) were made with 50, 100, 500, 1000 and $3500 \mu\text{g l}^{-1}$ aldicarb in 0.01 M CaCl_2 and cooled to a temperature of 5°C . 100 ml of the standard solution was added to 50 g of soil (soil/solution ratio = 0.5) united in glass jars and shaken for 6 hours at 5°C

on a reciprocating shaker with a frequency of 190 motions per minute.

The glass jars with soil were stored for 16 hours at 5°C . Afterwards the glass jars with soil samples were shaken for 1 hour (175 motions per minute) at a temperature of 15°C . The glass jars with soil were put through a centrifugal machine at 900 g (2000 rpm). Approximately 70 ml water was extracted from the sample and put in a jar together with 10 g sodium sulphate. This sample was extracted twice with 20 ml dichloromethane. The extract was dried with 2 g sodium sulphate, filtrated and concentrated with a rotary evaporator. Part of the extract ($\pm 0.5 \text{ ml}$) was concentrated with nitrogen gas (100 ml min^{-1} at a temperature of 25°C). The residue was dissolved in 1 ml eluens (95% water and 5% Acetonitrile) and filtrated ($0.2 \mu\text{m}$ membrane). The content of aldicarb was measured with a HPLC (Waters: Vydac machine (column: C18-TP54)) by injecting $50 \mu\text{l}$ of the filtrated extract. The HPLC analysis was executed with UV detection (214 nm) at a flow rate of 0.6 ml min^{-1} and acetonitrile as carrier gas. The detection limit amounted to $0.1 \mu\text{g l}^{-1}$. Analytic recovery amounted to approximately $90 \pm 5\%$. The results were corrected for recov-

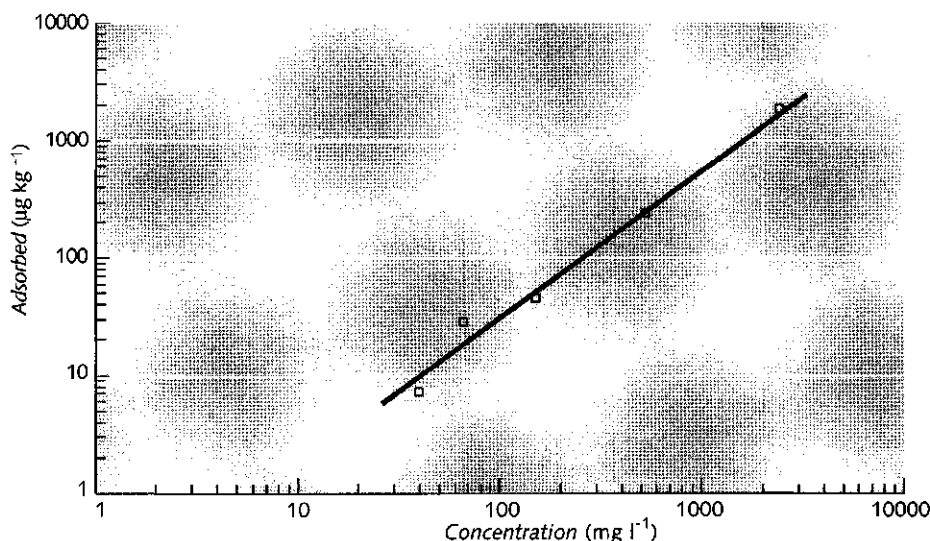


Figure 3.15. Sorption isotherm of aldicarb for the plough layer of the experimental field *Eastern Flevoland* at 20 °C as determined in laboratory incubations. The observed values are presented as □. The calculated values (according to equation 2.57) are presented as lines ($K_F = 0.41 \text{ cm}^3 \text{ g}^{-1}$, $(1/n) = 1.0$, $c_{l,ref} = 100 \text{ µg l}^{-1}$).

ery. It was assumed that the decrease in concentration in the liquid phase was due to sorption.

Results of the laboratory experiments are presented in figure 3.15. The best fit was obtained if the Freundlich coefficient (K_F) was taken as $0.41 \text{ cm}^3 \text{ g}^{-1}$. The Freundlich exponent ($1/n$) is equal to 1.00 (linear sorption). The standard deviation of the coefficient amounted to $0.10 \text{ cm}^3 \text{ g}^{-1}$. A K_F value of $0.41 \text{ cm}^3 \text{ g}^{-1}$ corresponds to a K_{om} value $21.6 \text{ cm}^3 \text{ g}^{-1}$. This K_{om} value is higher than observations in previous studies (e.g. Bromilow et al., 1980-1, 1980-2). Bromilow observed K_{om} values of 4.7 and $9.3 \text{ cm}^3 \text{ g}^{-1}$ for two different sandy loam soils.

3.1.2.4 Simazine

Simazine (2-chloro-4,6-bisethylamino-1,3,5-triazine) belongs to the chemical family of triazines (figure 3.16). It is a selective systemic herbicide, absorbed through roots with translocation acropetally in the xylem, accumulating in the apical meristems and leaves, where it inhibits photosynthesis (Royal Society of Chemistry, 1987). The use of simazine includes the control of germinating annual grasses and broad-leaved weeds.

Transformation experiments: The rate of transformation of simazine depends on the soil temperature and the soil moisture content (Walker, 1976). For the experimental field Southern Flevoland, the transformation of simazine was only analyzed for the top layer at a temperature of 15 °C and with soil moisture content at field capacity.

In March 1994 soil was collected at the experimental field Southern Flevoland. Soil was taken from the top layer of the soil, directly beneath the apple trees. The soil was treated with simazine during the spring and summer period with a frequency of two to three times

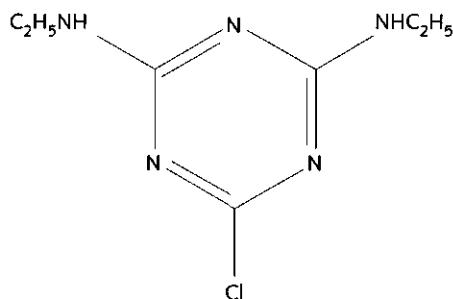


Figure 3.16. Chemical structure of simazine.

The flasks were centrifuged for 15 minutes at 2000 g (3000 rpm).

An extract was pipetted from the sample and shaken for 30 seconds in a separating funnel with water and dichloromethane. The dichloromethane phase was dried with 5 g sodium sulphate and filtrated into a 50 ml flask, where it was treated with nitrogen gas (125 ml min^{-1}) until 5 ml supernatant. This was supplemented with dichloromethane (1:1) and 250 μl of the solution was evaporated. The residue was further treated with 500 μl iso-octane/ethylacetate (9:1). Simazine was analyzed with a Perkin Elmer 8500 gas-chromatograph using CP sil 5 CB column (50 length, 320 mm diameter, $0.42 \mu\text{m}$ film thickness) in combination with a NP-detector. Helium was used as a make-up gas at 80 kPa. The temperature was increased gradually to 300°C . It was assumed that the recovery of the procedure for extraction of water was 90%. Detection limit amounted to $0.5 \mu\text{g l}^{-1}$. Sorption was calculated as the decrease in concentration between controls and glass jars with soil.

Results of the laboratory tests are presented in figure

3.18. The best fit was obtained if the Freundlich coefficient and exponent are equal to $4.0 \text{ cm}^3 \text{ g}^{-1}$ and 0.77 respectively with $c_{l,ref} = 10 \mu\text{g l}^{-1}$. If $c_{l,ref} = 1000 \mu\text{g l}^{-1}$, the Freundlich coefficient and exponent are equal to $1.4 \text{ cm}^3 \text{ g}^{-1}$ and 0.77 respectively. This corresponds to a K_{om} value of $50 \text{ cm}^3 \text{ g}^{-1}$. Gustafson (1988) and Ahlsdorf et al. (1987) reported K_{om} values which are higher (81 and 83 respectively).

3.2 Field experiments

Data collection, data handling and data analysis are presented in this section. Data were collected at the experimental fields North-East Polder, Eastern Flevoland and Southern Flevoland both manually and by automatic (digital) operating devices. The method of data collection was a very important part of the research. This was influenced by the frequency, the spatial variability of the measurements and the costs. In general, automatic measurements were performed to collect data at high frequencies and at moments when on-site visits were impossible. For variables reflecting dynamic processes with fluctuations of less than a day,

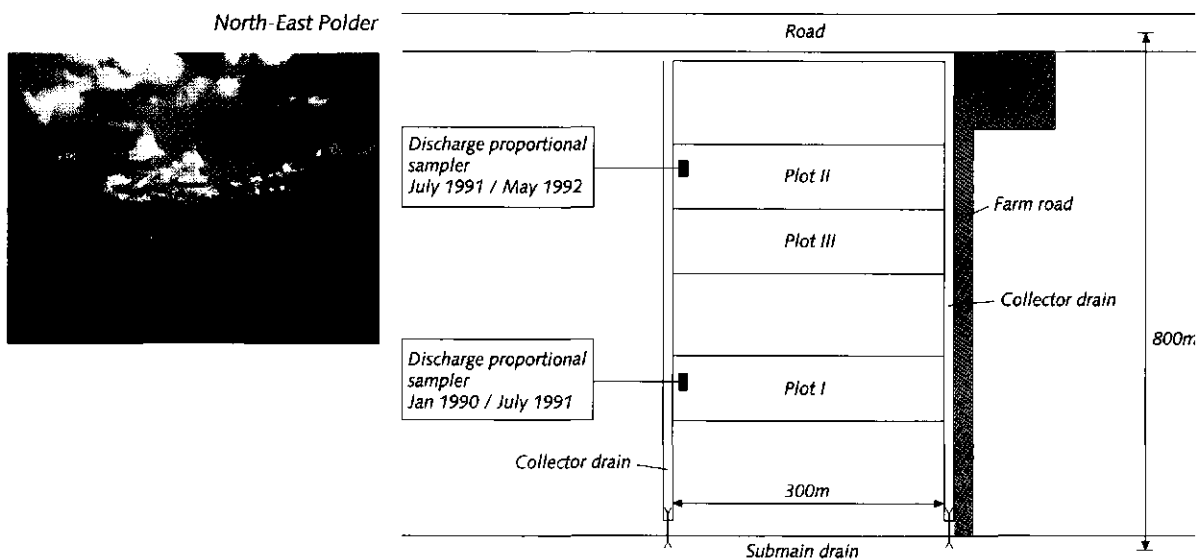


Figure 3.19a General impression and outline of the experimental field North-East Polder.

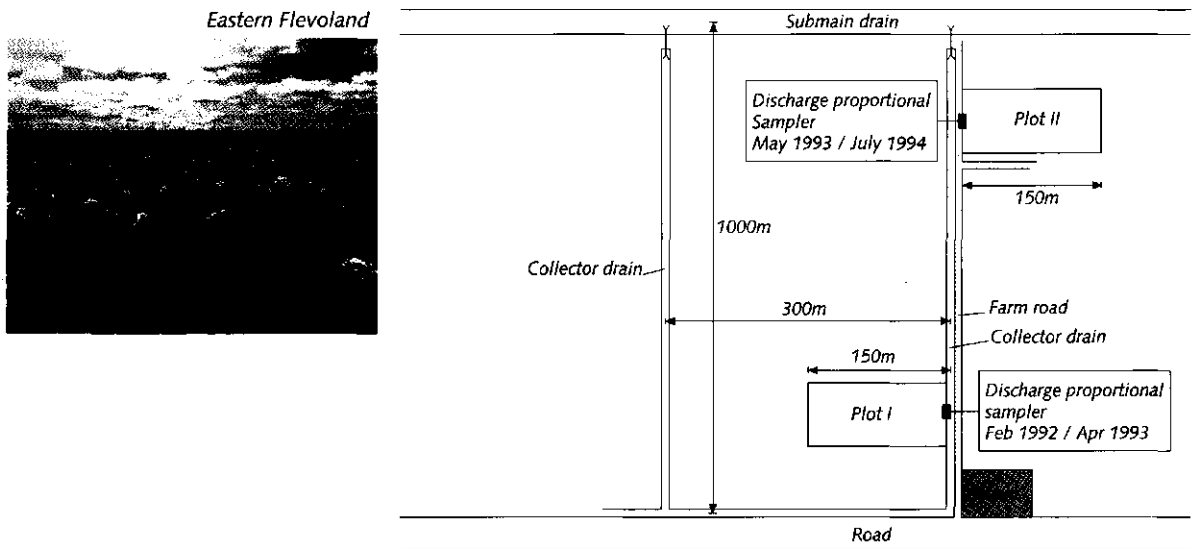


Figure 3.19b General impression and outline of the experimental field *Eastern Flevoland*.

automatic measurements were often the only way to obtain sufficient data. When data collection could be performed at low frequency or when automatic sampling became too expensive, manual collection of data was used as an alternative.

Sometimes problems occurred during the data collection. These problems were connected with malfunctioning of automatic operating devices often resulting in a loss of valuable information. At the time the data were being processed, it was often impossible to recollect missing data.

Special attention was paid to the quality of the monitoring program for the concentration of solutes and pesticides in the drainage water and the content of solutes and pesticides in the soil. For water quality monitoring, it is important to keep the time interval between sampling in the field and laboratory analyses in the field as short as possible. Especially at high temperatures, loss of pesticides, due to volatilization and transformation, can be considerable. Due to spacial variability of the movement of solutes in the soil, it was important to collect sufficient data for the monitoring of the content of solutes and pesticides in the soil in order to obtain a correct statistical mean.

3.2.1 Location and general characteristics of the experimental fields

A general impression and outline of the experimental fields is presented in figure 3.19. At the first experimental field in the North-East Polder collection of field data took place from September 1989 until May 1992. Due to crop rotation, the sampling sites had to be relocated every year; data were collected at various plots at which tulips were grown (plot I, II and III). The tulips were planted in ridges of approximately 0.8 m width. At the second experimental field in Eastern Flevoland the collection of field data took place from February 1992 until July 1994. Again, the sampling sites had to be relocated after one year; data were collected at two plots at which potatoes were grown (plot I and II). The potatoes were planted in ridges of 0.35 m width. At the third experimental field in Southern Flevoland the collection of field data took place from April 1992 until July 1994. The orchard consisted of Elstar apple trees, planted in rows, interspersed by grass strips. The distance between the apple trees within a row amounted to 1.2 m. The width of the strip with apple trees and the grass strip amounts to roughly 1.5 m.

The experimental fields differ in soil characteristics, crops and drainage conditions (table 3.13). One of the

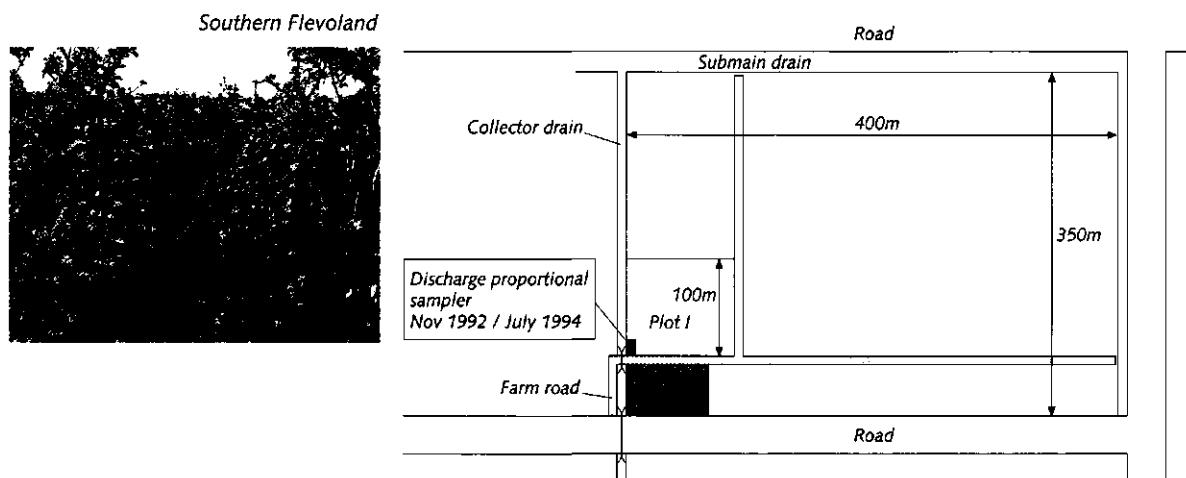


Figure 3.19c General impression and outline of the experimental field *Southern Flevoland*.

selection criteria was the fact that an impermeable layer is situated directly beneath the drain pipes, resulting in a zero seepage flux. Because of this situation, the precipitation surplus runs through the drain pipes into the collector drains. However, some seepage occurred at the experimental fields in the North-East Polder and Eastern Flevoland.

The soil of the experimental field in the North-East Polder is classified as a loamy sand. At approximately 1 m below the surface, a semi-permeable layer of detritus gyttja is found (photo 3.1). The drain pipes are situated on top of the detritus layer. Due to the low permeability, the spacing between the drain pipes is only 4 m. Both the experimental fields Eastern Flevoland and Southern Flevoland consist of heavy clay soils (photo 3.2 and 3.3). At the experimental plot in Eastern Flevoland the drain pipes are situated at a depth of ap-

proximately 1.0 m below the soil surface. The drain spacing amounts to 48 m. At the experimental plot in Southern Flevoland the drain pipes are situated at a depth of approximately 1.1 m below the soil surface. The drain distance amounts to 24 m. Beneath the drain pipes the clay is unripened, causing a very low hydraulic conductivity. More detailed information on soil characteristics of the experimental fields North-East Polder, Eastern Flevoland and Southern Flevoland has already been presented in subsection 3.1.1.

3.2.2 Application of pesticides and tracers

Four pesticides were incorporated in the research program; 1,3-dichloropropene, metamitron, aldicarb and simazine. Bromide was applied as a tracer. For each experimental plot, an overview on date of application, quantity applied and period of field measurements for the selected pesticide(s) and the tracer bromide is pre-

Table 3.13. Some characteristics of the experimental fields

	Area of the plots (ha)	Soil type	Crop	Drain pipes	
				Depth (m)	Spacing (m)
North-East Polder	0.85	Loamy sand	Tulips	0.85	4
Eastern Flevoland	2.16	Heavy clay	Potatoes	0.95	48
Southern Flevoland	2.40	Heavy clay	Apple trees	1.10	24

Table 3.14. Date of application, quantity applied and period of field measurements for selected pesticides.

	Pesticide	Date of application	Quantity Applied (kg ha ⁻¹)	Period of field measurements
North-East Polder				
Plot I	1,3-Dichloropropene	06-09-1989	170.0	06-09-1989/31-12-1989
Plot I	Metamitron	23-02-1990	2.2	23-02-1990/13-07-1990
Plot I	Bromide	23-02-1990	33.0	23-02-1990/13-07-1990
Plot II	1,3-Dichloropropene	13-09-1990	170.0	13-09-1990/31-12-1990
Plot III	1,3-Dichloropropene	07-11-1990	170.0	07-11-1990/15-05-1991
Plot II	Metamitron	14-03-1991	0.8	14-03-1991/07-05-1992
Plot II	Bromide	14-03-1991	26.5	14-03-1991/07-05-1992
Eastern Flevoland				
Plot I	Aldicarb	14-04-1992	0.5	14-04-1992/30-03-1993
Plot I	Bromide	19-05-1992	7.7	19-05-1992/30-03-1993
Plot II	Aldicarb	30-03-1993	3.0	30-03-1993/01-07-1994
Plot II	Bromide	14-04-1993	11.7	14-04-1993/01-07-1994
Southern Flevoland				
Plot I	Simazine	11-04-1992	0.50	11-04-1992/21-04-1993
Plot I	Simazine	09-06-1992	0.25	09-06-1992/21-04-1993
Plot I	Bromide	09-06-1992	16.8	09-06-1992/21-04-1993
Plot I	Simazine	21-04-1993	0.75	21-04-1993/01-07-1994
Plot I	Bromide	21-04-1993	33.6	21-04-1993/01-07-1994

sented in table 3.14.

North-East Polder: Two different pesticides were examined at the experimental plots; 1,3-dichloropropene (trademark DD95) and metamitron (trademark Goltix). DD95 consists of 1,3-dichloropropene (> 95%) and a number of diverse compounds of which 1,3-dichloropropane is the most prominent ($\pm 2\text{-}3\%$). Technical 1,3-dichloropropene is an equal mixture of the (E)- and (Z)-isomers (both $\pm 48\%$).

On 6 September 1989 the field experiment started with the injection of 170 kg ha⁻¹ 1,3-dichloropropene at a depth of approximately 0.2 m. Dichloropropene was injected with a horizontal blade injector containing four injector blades with spray nozzles under the blades. In order to obtain an equal distribution of dichloropropene, flow rate and tank pressure were regularly tested during application. The dose was calculated by reading the level in the tank and by measuring the surface area treated. After application the soil sur-

face was compressed with a roller. The measurements on the concentration of 1,3-dichloropropene in the drain pipes at plot I ended on 31 December 1989. After this period, samples of the drainage water were taken at random to verify if traces of 1,3-dichloropropene could still be measured.

Metamitron was applied in the early spring (plot I: 23 February 1990 - 2.2 kg ha⁻¹). Approximately 1 l metamitron was dissolved in 150 l water and sprayed at the field through fissure nozzles. The speed of the tractor amounted to 5 km h⁻¹. The dose was controlled by reading the level in the tank and by measuring the surface area treated. Bromide was used as a tracer and was applied together with metamitron (33 kg ha⁻¹). Measurements on the concentration of metamitron and bromide in the drainage water at plot I continued until July 1990.

After this period the discharge proportional sampling process was transferred to plot II (figure 3.19a). Here

measurements on the concentration of dichloropropene in the drain pipes started on 13 September with the injection of 170 kg ha^{-1} 1,3-dichloropropene and ended on 31 December 1990. In order to examine the effect of a winter application of 1,3-dichloropropene on leaching, the experiment was repeated on another plot (figure 3.19a: plot III). Here measurements on the concentration of dichloropropene in the drain pipes started on 7 November with the injection of 170 kg ha^{-1} 1,3-dichloropropene and ended in the spring at 15 May 1991. Sampling of the pipe drains was executed manually. Five drain pipes were sampled three times a week (Monday, Wednesday and Friday). During discharge peaks sampling was intensified. The method of application at plot II and plot III corresponded to plot I.

As in the preceding year, metamitron was applied in the early spring (plot II: 14 March 1990). Due to a relatively warm winter period the tulips were already above the soil surface. Metamitron was applied in a similar manner to the previous year. However, metamitron could only be applied in a small amount (0.8 kg ha^{-1}) in order to prevent damage. Again bromide was applied at the same time as metamitron (26.5 kg ha^{-1}). The field measurements on metamitron and bromide in the drainage water at plot II continued until July 1990.

An experiment was undertaken to establish the deviation in the quantity of metamitron applied per m^2 . During the spraying of metamitron at plot II, 12 plates were scattered over the experimental field to determine the amount of metamitron which reached the soil surface. According to these plates the applied dose was equal to $0.75 \pm 0.17 \text{ kg ha}^{-1}$. The standard deviation amounted to approximately 20%. The observed amount of metamitron which reached the soil surface corresponded well with the quantity applied (0.8 kg ha^{-1}) according to the farmer and the content of metamitron in the soil one day after application ($0.70 \pm 0.18 \text{ kg ha}^{-1}$).

Eastern Flevoland: At the experimental field Eastern Flevoland the pesticide aldicarb and its transformation products aldicarb-sulphone and aldicarb-sulphoxide were examined at two experimental plots. At the first plot the field measurements on the concentration levels

of aldicarb-sulphone and aldicarb-sulphoxide in the drainage water started on 14 April 1992 and continued until April 1993. At plot I aldicarb was applied at the ridges (5 kg with 10% active material, which is equal to 0.5 kg ha^{-1}) through a plastic tube simultaneously with the planting of potatoes. Aldicarb was applied to approximately 15% of the surface area. Bromide, which was used as a tracer, was applied approximately 1 month after application of aldicarb at 15 May 1992. Bromide was dissolved in 400 liter water and sprayed at the field through fissure nozzles. The dose was controlled by reading the level in the tank and measuring the surface area treated.

After approximately one year the discharge proportional sampling process was transferred to another plot (figure 3.19b: plot II). Measurements started on 30 March 1993 and continued until July 1994. In 1993 aldicarb was applied before the planting of the potatoes as a full-field application (30 kg ha^{-1} with 10% active material = 3.0 kg ha^{-1}), using a fertilizer distributor. After application aldicarb was interacted in the soil up to a depth of 0.1 m. Deviation in application of aldicarb was controlled and amounted to less than 10%. Again bromide was used as a tracer and applied 14 days after application of aldicarb on 14 March 1993. The method of application and control of the dose applied at plot II corresponded to plot I.

Southern Flevoland: At the experimental field Southern Flevoland the pesticide simazine was examined. Generally simazine is applied in the spring at the strip where the apple trees are planted. The width of this strip amounts to 1.5 m. As the width of the spray beam amounts to 0.75 m, simazine is applied in two drives. The applied quantity of simazine is dissolved in a tank containing 400 l water. Simazine is sprayed at the field through fissure nozzles. The field measurements on the concentration levels of simazine in the drainage water started on 11 April 1992 and continued until July 1994. During this period simazine was applied three times (11 April 1992, 0.5 kg ha^{-1} ; 9 June 1992, 0.25 kg ha^{-1} ; 21 April 1993, 0.75 kg ha^{-1} , calculated as an average over the whole plot but applied only in the strips). Bromide was applied simultaneously with simazine on 9 June 1992 (16.8 kg) and 21 April 1993 (33.6 kg ha^{-1}).

3.2.3 Data collection program

The field data collection program is summarized in table 3.15. Basically two types of data can be distinguished:

- *data related to soil water fluxes*: precipitation, irrigation, groundwater levels, drain discharges, soil moisture content, evapotranspiration, interception;
- *data related to solute (pesticide) fluxes*: preferential flow, concentration of solutes and pesticides in drainage water, concentration profiles of solutes and pesticides.

Data were collected both manually (M) and automatically (A) at all the experimental fields. The frequency of the measurements was either proportional (P), incidental (I), hourly (H), daily (D) or weekly (W). The number of spatial distributed measurements (called Numbers) varied from 1 to 15 plots per experimental field.

The experimental fields in Eastern and Southern Flevoland were not irrigated. At the experimental fields in the North-East Polder and Eastern Flevoland, the reference evapotranspiration (according to Makkink) was computed with data from a nearby

Meteorological Station. At the experimental field in Southern Flevoland the data were collected on site. Data on interception of tulips for the experimental fields in the North-East Polder and of potatoes for the experimental field Eastern Flevoland were obtained from literature (Braden, 1985).

Sampling on concentrations of solutes and pesticides in drainage water and concentration profiles was undertaken "automatically/manually" and "manually" respectively. The samples were taken to the laboratory for analysis. Equipment, sampling strategies, sampling methods and results will be discussed in more detail in the next subsections.

3.2.4 Precipitation and irrigation

On-site measurements of precipitation are a necessity, due to spatial differences in precipitation. This makes precipitation data from other sources unreliable, especially when these data are used for the calculation of drain discharges.

On each experimental field at least one KNMI (Royal Dutch Meteorological Service) standard rain gauge was installed. The standard rain gauge has a circular

Table 3.15. Summary of the field data collection program.

	Experimental field North-East Polder			Experimental Field Eastern Flevoland			Experimental Field Southern Flevoland		
	Type	Freq.	Number	Type	Freq.	Number	Type	Freq.	Number
Precipitation	A / M	P / D	1 / 2	A / M	P / D	1 / 2	A / M	P / D	1 / 1
Irrigation	M	I	4						
Groundwater levels	A / M	H / W	2 / 10	A / M	H / W	2 / 15	A / M	H / W	2 / 15
Drain discharges	A / M	P / I	1	A	P	1	A	P	1
Soil moisture content	M	I	5	M	W	2	M	D	2
Evapotranspiration	A	D	1	A	D	1	A	D	1
Interception							M	D	20
Preferential flow	M	I	1	M	I	1	M	I	1
Concentration of solutes and pesticides in drainage water	A / M	P / I	1 / 3	A	P	1	A	P	1
Concentration profiles of solutes and pesticides	M	I	5	M	I	5	M	I	5

Type:

Frequency of the measurements:

Number:

A = Automatic

H = Hourly

P = (Discharge) Proportional

Number of spatial distributed measurements

M = Manual

D = Daily

I = Incidental

per experimental field

W = Weekly

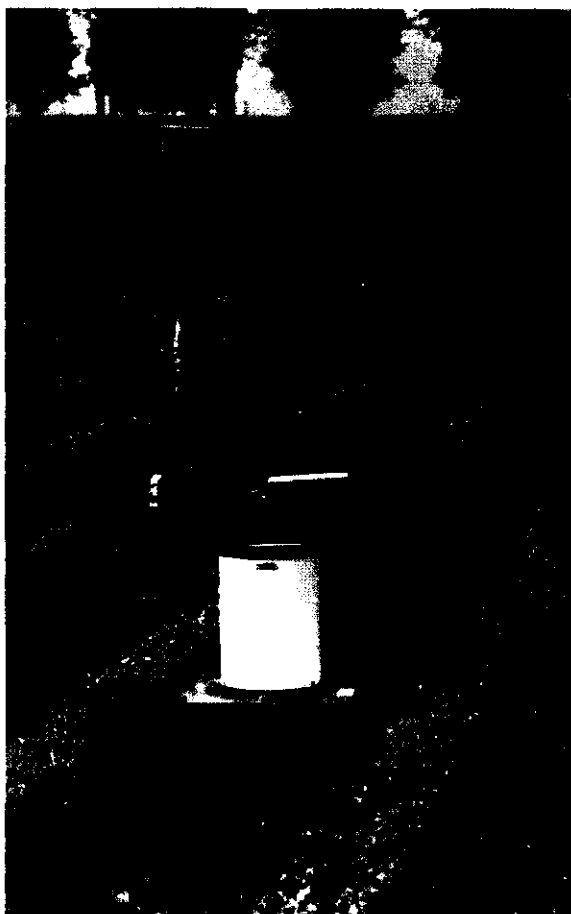


Photo 3.4. Tipping bucket connected to a skipper data logger and a standard rain gauge.

catch funnel with a surface of 200 cm^2 and is placed 40 cm above the surface (photo 3.4). The amount of precipitation was manually measured as well as automatically registered every day.

For automatic recording a tipping bucket rain gauge was used. The tipping bucket rain gauge is based on the divided bucket mechanism, a predetermined amount of water is collected in a 4 ml bucket, which when full, tips over discharging the collected water. The circular catch funnel of the tipping bucket is 200 cm^2 , thus every 0.2 mm precipitation a tilt is registered. The collected count of tilts is transmitted to a data logger. As

with the standard rain gauge, the tipping bucket is placed 40 cm above the surface (photo 3.4).

Due to problems with the data loggers some time series of the automatic recorded precipitation are fragmentary. During some periods the catch funnel of the tipping bucket had to be cleaned every week, but in general this part of the automatic recording showed no malfunctioning.

Uninterrupted series of daily precipitation are available for all experimental fields. However, some data which were derived from the tipping bucket rain gauge are not reliable. This was mainly caused by the fact that while the tipping bucket should stand exactly at water-level, during some periods this was not the case.

For all experimental fields, the differences in the observed amount of precipitation between the standard gauge and the tipping bucket were negligible on an annual basis, but could be considerable per rain shower. The average deviation per shower amounted to approximately 20%, but differences of more than 50% and more were not uncommon. An example of variations in the measured precipitation is presented in figure 3.20. Tipping Bucket I and II are identical and were placed 40 cm above the surface. The distance between the Tipping Bucket I and Tipping Bucket II from the standard rain gauge was respectively 2 and 100 m.

At the experimental field in the North-East Polder sprinkler irrigation was applied during the months of April, May and June. The quantity of applied water, which depended on the precipitation deficit during these months, amounted to approximately 50 - 75 mm. The spatial variability of the applied irrigation water was measured with a number of buckets distributed over the experimental field. The average deviation per bucket amounted to approximately 25% (Brongers and Groen, 1993).

3.2.5 Evapotranspiration

At the experimental fields North-East Polder and Eastern Flevoland, the reference evapotranspiration rate was obtained from a nearby meteorological station in Lelystad. At the experimental field Southern Flevoland the global radiation and the air temperature were mea-

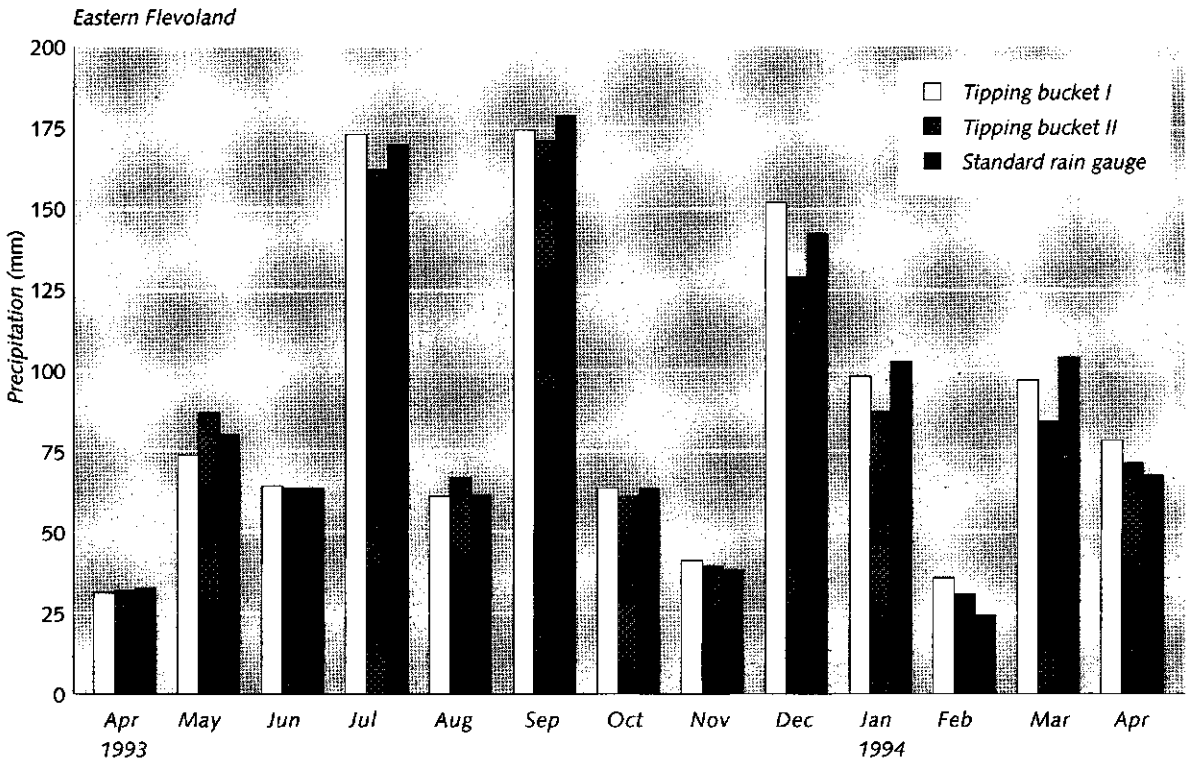


Figure 3.20. Example of variations in the observed precipitation between the tipping buckets and the standard gauge at the experimental field Eastern Flevoland.

sured on-site. With these figures, the reference evapotranspiration rate was calculated (equation 2.17).

To acquire the potential evapotranspiration rate, the reference evapotranspiration rate is multiplied by a dimensionless crop factor f . Examples of potential evapotranspiration rate and precipitation for the experimental fields North-East Polder, Eastern Flevoland and Southern Flevoland are presented in figure 3.21.

The actual evapotranspiration rate is defined as the sum of the actual evaporation rate, the actual transpiration rate and the interception rate (equation 2.24). The extent and distribution of the actual evapotranspiration rate is derived from the potential evapotranspiration rate and is dependent on factors such as the pressure head, type of crop, planting distances, developing stage, rooting characteristics and soil characteristics.

Most facts and figures needed for the calculation of the actual transpiration and the actual soil evaporation were derived from literature data and not measured at the experimental fields. As few literature data were available on the interception of apple trees and the contribution of the interception to the water balance was assumed to be considerable, an experiment was set up at the experimental field Southern Flevoland to study the interception by apple trees. Roughly 25 rain gauges were placed underneath the trees to establish the interception rate and redistribution of precipitation (photo 3.5). The interception was studied during a period of 15 months. Part of the precipitation is intercepted by the trees. Another part flows along the stem of the trees. The remaining precipitation will reach the soil strongly redistributed. Redistribution of the throughfall will be discussed in subsection 3.2.11.

The interception is strongly dependent on the Leaf Area Index and will be insignificant during the winter period and considerable during the summer period (figure 3.22). However, interception does not only depend on the Leaf Area Index, but also on the precipitation intensity rate. This is illustrated in figure 3.23. As the precipitation intensity grows, the relative part of interception rate to the water budget becomes smaller.

3.2.6 Groundwater levels

Each plot of the three experimental fields consisted of two rows of piezometers, each row containing 10-20

piezometers. Two additional piezometers were installed containing pressure sensors (PDCR 900 series; Druck Limited, Great Britain). In order to measure the total hydraulic head loss, one pressure sensor was located on a drain pipe (water level in the drain pipe), the other was located midway between the drain pipes (height of phreatic surface). The continuous measurements of the groundwater levels were carried out with a frequency of one reading per hour. The data were recorded on a Skipper data logger (internal memory 32 kb, external RAM-memory-card 64 kb, with 6 differential or 12 single ended ports: Van Essen Instruments bv, The Netherlands).

Groundwater levels of all piezometers were collected three times a week on Monday, Wednesday and Friday. These data were used to evaluate the spatial distribution and to control and (if necessary) to correct the automatic measurements. Calibration of the pressure sensors is essential, due to zero-displacement in time. In the period 1989-1990 only fragmented time series of the automatic registered groundwater levels are available, due to problems with the Skipper data loggers and pressure instruments. These problems were caused by air humidity (deregulating the electronic devices), battery problems, disconnection of cables. Furthermore, equipment had to be removed during tillage operations and harvesting periods.

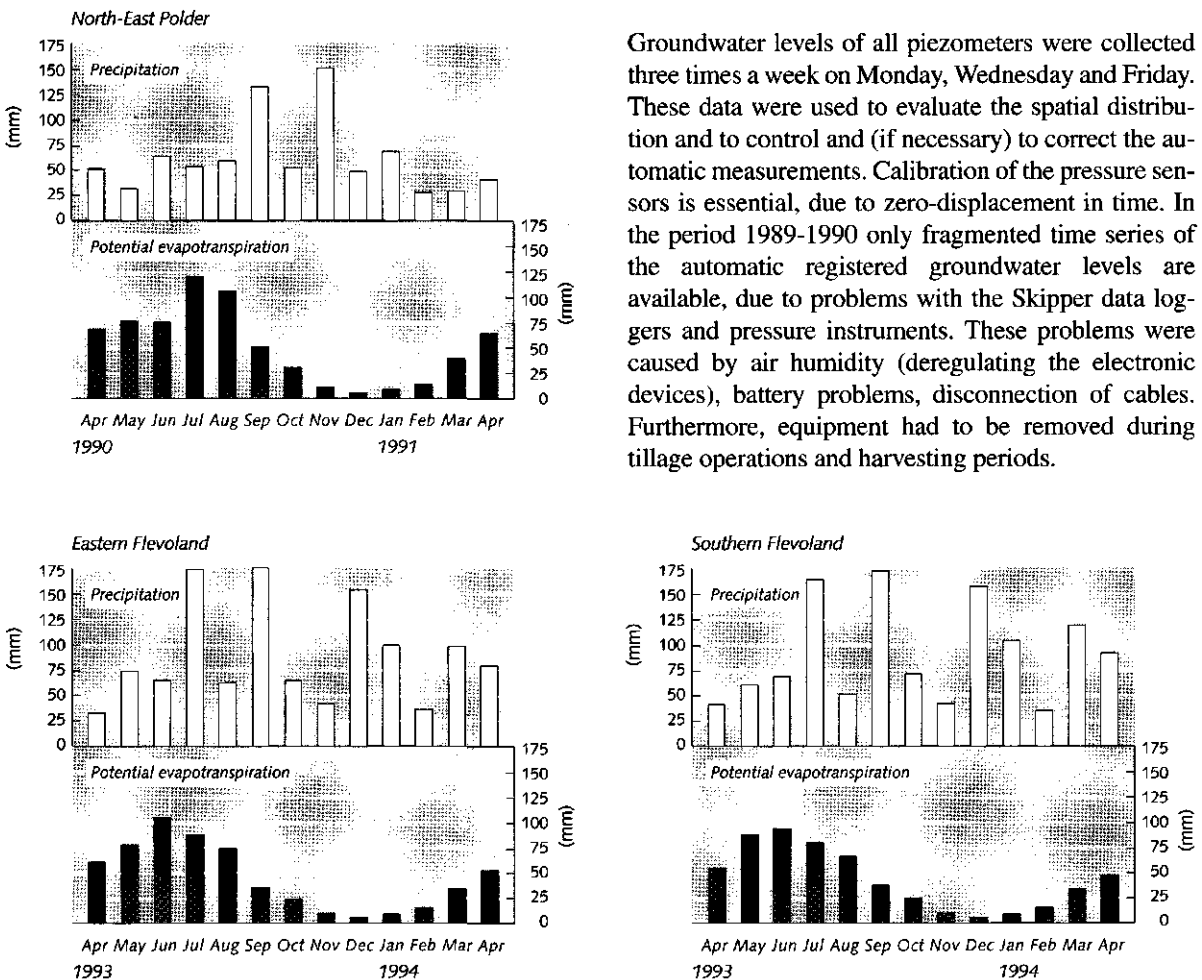


Figure 3.21. Example of the precipitation and the potential evapotranspiration at the experimental fields in the *North-East Polder* (April 1990 - April 1991), *Eastern Flevoland* (April 1993 - April 1994) and *Southern Flevoland* (April 1993 - April 1994).

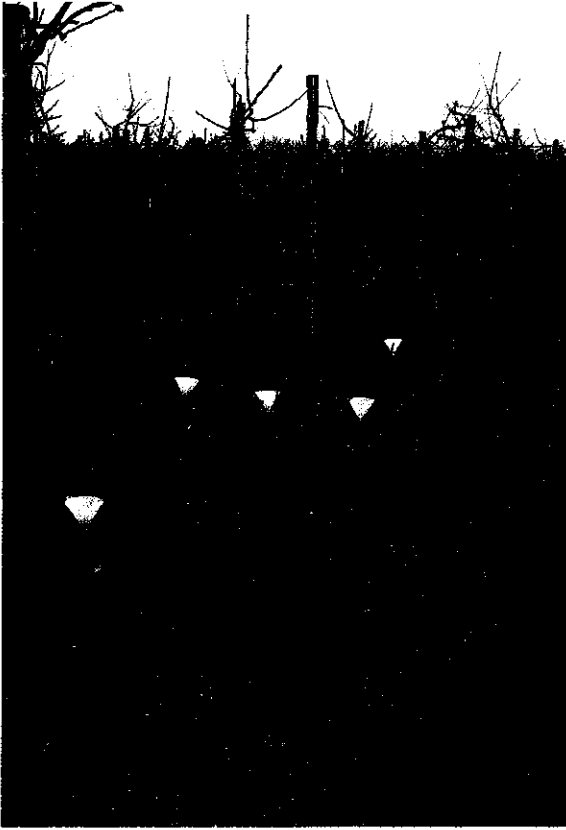


Photo 3.5. Measurements of interception and precipitation.

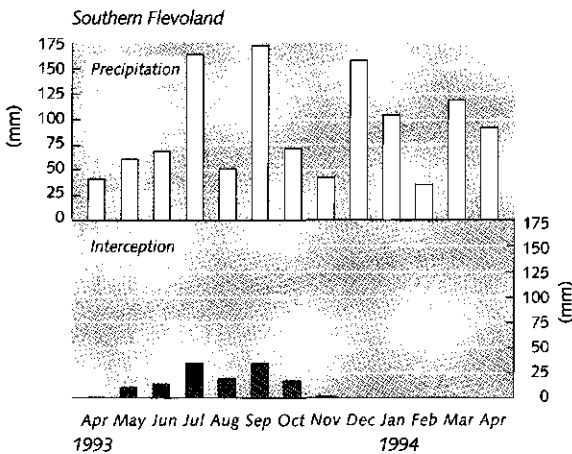


Figure 3.22. Interception of apple trees at the experimental field *Southern Flevoland* during the period April 1993 until April 1994.

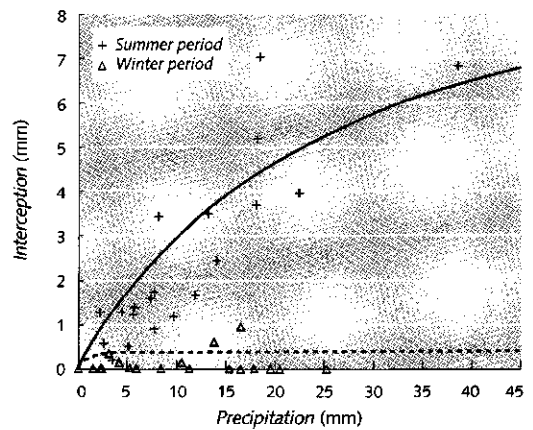
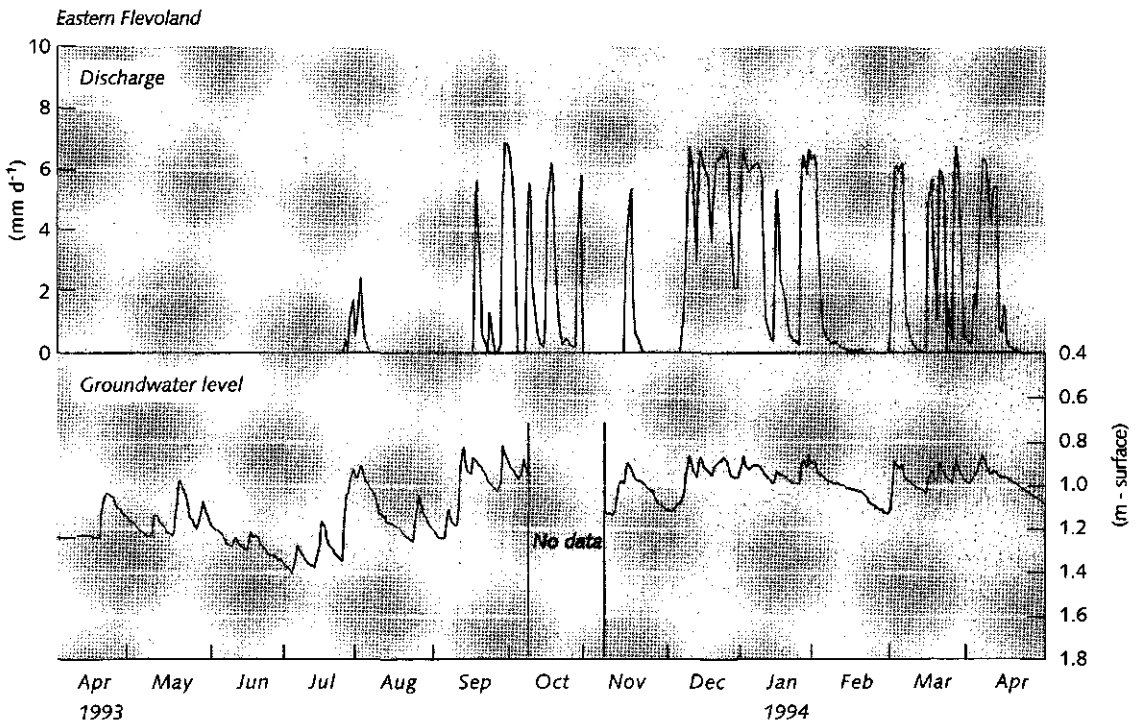
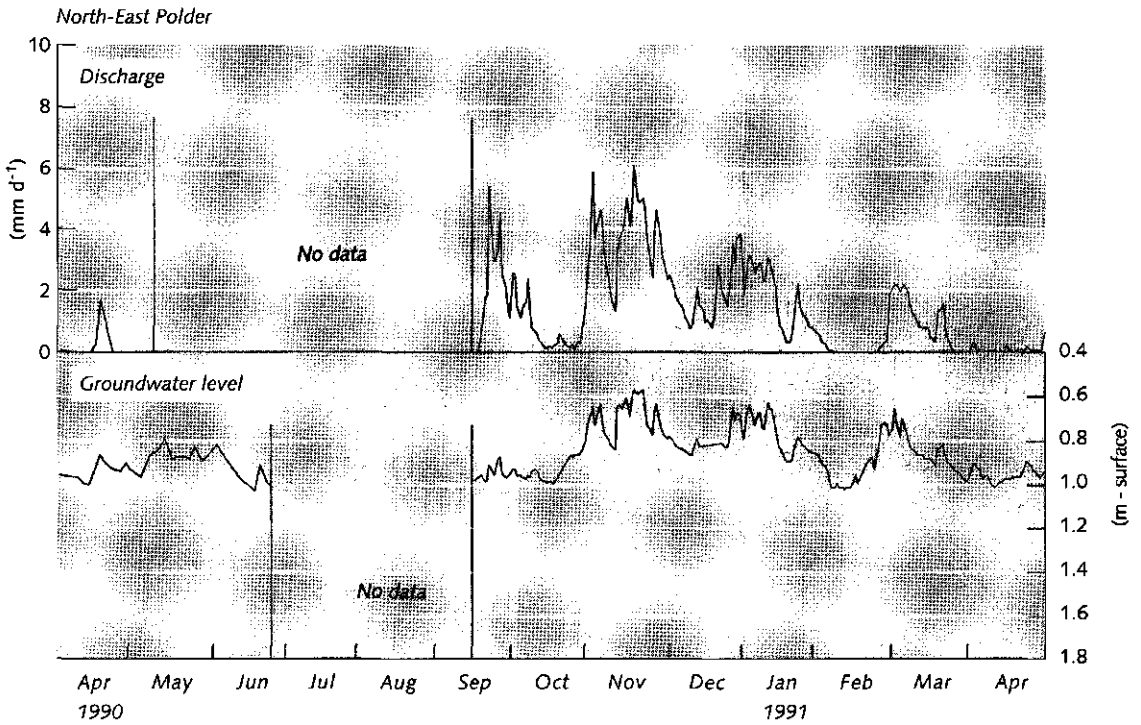


Figure 3.23. Relation between daily precipitation rate and daily interception rate for apple trees at the experimental field *Southern Flevoland*.



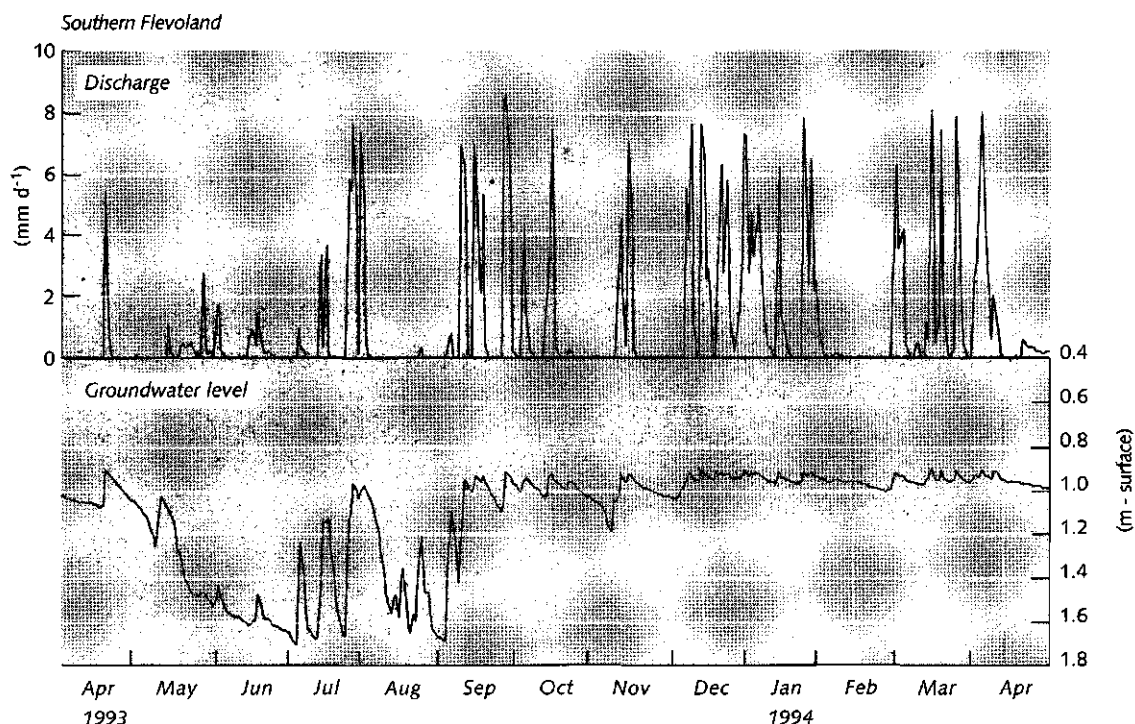


Figure 3.24. Examples of the drain discharges and groundwater levels at the experimental fields *North-East Polder* (plot II: April 1990 - April 1991), *Eastern Flevoland* (plot II: April 1993 - April 1994) and *Southern Flevoland* (April 1993 - April 1994).

Figure 3.24 presents some results of the observed drain discharges and groundwater levels at the experimental fields *North-East Polder*, *Eastern Flevoland* and *Southern Flevoland*. In principle, drain discharges were observed if the groundwater level rose above the level of the drain pipes. The only exception can be seen at the experimental field *Southern Flevoland* during the month May and June. During this period the water level in the ditch rose above the level of the drain pipes. Due to short-circuiting, water from the ditch ran through the side of the ditch into the drain pipes.

Figure 3.25 presents the relation between groundwater levels and drain discharges for the experimental fields in the *North-East Polder*, *Eastern Flevoland* and *Southern Flevoland*.

North-East Polder: The presented groundwater levels and drain discharges were measured during a relatively

dry winter period. In spite of the short drain distance of 4 m, groundwater levels were still dynamic and varied from 1.1 m to a maximum of 0.6 m below the soil surface. Due to upward seepage groundwater levels below 1.1 m below the soil surface never occurred. During wet periods groundwater levels up to 0.3 m below the soil surface were recorded. As the drain distance amounts to only 4 m, this indicates that the permeability of the subsoil is relatively low. The drainage resistance ($\Upsilon = \Delta h_m / q$) is calculated at approximately 110 days.

Eastern Flevoland: During the period April 1993 - April 1994 the groundwater level varied from 1.4 to 0.85 m below the soil surface. The groundwater level rose approximately 0.1 - 0.15 m above the level of the drain pipes. During wet periods the water level in the collector drain rose above the level of the drain pipes and the drain discharge decreased due to a smaller head

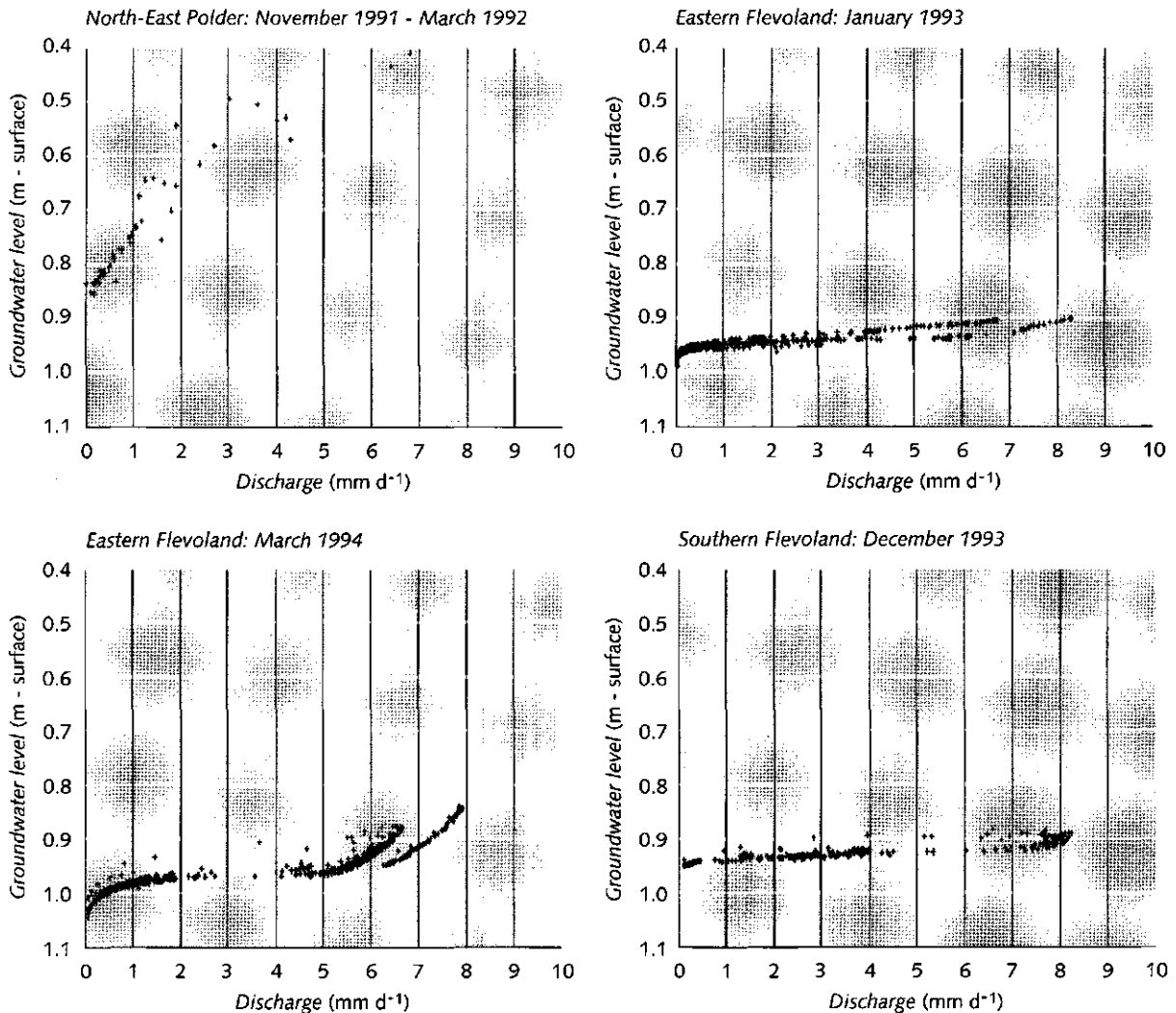


Figure 3.25. Relation between groundwater levels (m below soil surface) and drain discharges for the experimental field *North-East Polder* (plot II), *Eastern Flevoland* (plot I - January 1993 and plot II - March 1994) and *Southern Flevoland*.

difference. During the summer period the groundwater level sunk to a level of 1.40 m below the soil surface. Due to upward seepage deeper groundwater levels were not recorded.

For the relationship between the groundwater level and drain discharge, figures are presented separately for plot I and plot II. At plot I the groundwater level hardly rises, as the discharge increases. Since drain distances

amount to 48 m, this indicates that the permeability of the subsoil is very high. At plot II, the groundwater level starts to rise again at high drain discharges. This was generated by rising water levels in the collector drain, which prevented the draining of groundwater. The drainage resistance is calculated at approximately 5 days.

Southern Flevoland: During the period April 1993 -

April 1994 the groundwater level varied from 1.65 to 0.90 m below the soil surface. The groundwater level never rose more than 0.1 m above the level of the drain pipes. During the winter period the water level in the collector drain never rose above the level of the drain pipes. During the summer period the groundwater level sunk into the unripened subsoil to 1.70 m below the soil surface. At this depth groundwater levels were very variable within a few meters. Measurements on the hydraulic head in the Pleistocene subsoil indicated that no upward seepage occurred. Again, the groundwater levels hardly rose, as the drain discharge increased. This indicates that the permeability of the subsoil is very high. The drainage resistance is calculated at approximately 5 days.

3.2.7 Soil moisture content

In the first part of the project (North-East Polder; 1989-1991) soil samples to determine the soil moisture content were taken manually at four different depths (0-0.20, 0.20-0.40, 0.40-0.60 and 0.60-0.80 m below the soil surface). The soil samples were collected at certain time intervals. Because of the spatial variability of the moisture content, each soil sample is a mixture of 20 different borings. The borings were usually placed in a square grid with a mutual distance between the borings from one to two meters. The number of borings were increased to 30 per site in very dry soils and in heterogeneous soils (De Jong et al., 1961).

In addition to soil samples to determine the soil moisture content, 10 tensiometers were installed at four different depths (0.2, 0.4, 0.6 and 0.8 m below the soil surface: Jett Fill Tensiometer; Soil Moisture Equipment Organisation, Great Britain). These tensiometers measure the soil moisture pressure head by means of a manometer. In combination with soil moisture retention curves the water content of the soil can be calculated. The calculated soil moisture content obtained from tensiometer measurements appeared to be highly unreliable. The tensiometer method does not account for hysteresis effects, it is only suitable for $|h|$ -values below 1000 cm and no correction is made for air pressure gradients. Furthermore, tensiometers are filled with water and cannot be used during frost periods. During periods with intensive precipitation relative errors of more than 50% occurred, due to compression

of soil pore air, causing higher soil moisture pressure heads.

In the second part of the project (experimental plots at Eastern Flevoland and Southern Flevoland) measurements on the soil moisture content were taken semi-automatically working by means of time domain reflectometry (TDR) (Trime-system; IMKO, Micromul-technik, Germany). TDR is a relatively new method for measuring the volumetric water content of a porous medium. It is based on the principle of the travel time of electromagnetic waves in the soil, which is dependent on the dielectric constant (Topp et al., 1980; Rawlins and Rhoades, 1984; Dalton et al., 1984). Before applying this method, a calibration curve for clay soils was validated for the heavy clay soils of Eastern and Southern Flevoland. Each experimental field contained two clusters of probes. Within a cluster, 5-10 probes were installed at different depths (0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9, 1.1 and 1.3 m).

The TDR method is less time consuming than the manual collection of soil samples, which makes it possible to measure more frequently. The manual collection of soil samples incorporates the spatial variability of the soil moisture content, while the TDR probes, like the tensiometers, were only installed in two different clusters at a distance of at least 50 m. However, corresponding measurements showed only relatively small differences.

North-East Polder: At the experimental field North-East Polder, data on soil moisture content were collected using soil samples and tensiometers. Results of the measurements show that variety in the soil moisture content is small and the changes in water storage between winter period and growing season roughly amounted to 75 mm (figure 3.26). The small fluctuations of the water storage are the result of the soil characteristics and the applied irrigation water during the growing season.

Eastern Flevoland: Data on soil moisture content were collected three times a week. During the growing season the TDR probes were installed both in the potato ridges and in the furrows. Generally the soil moisture content in the ridges was lower and rose less during

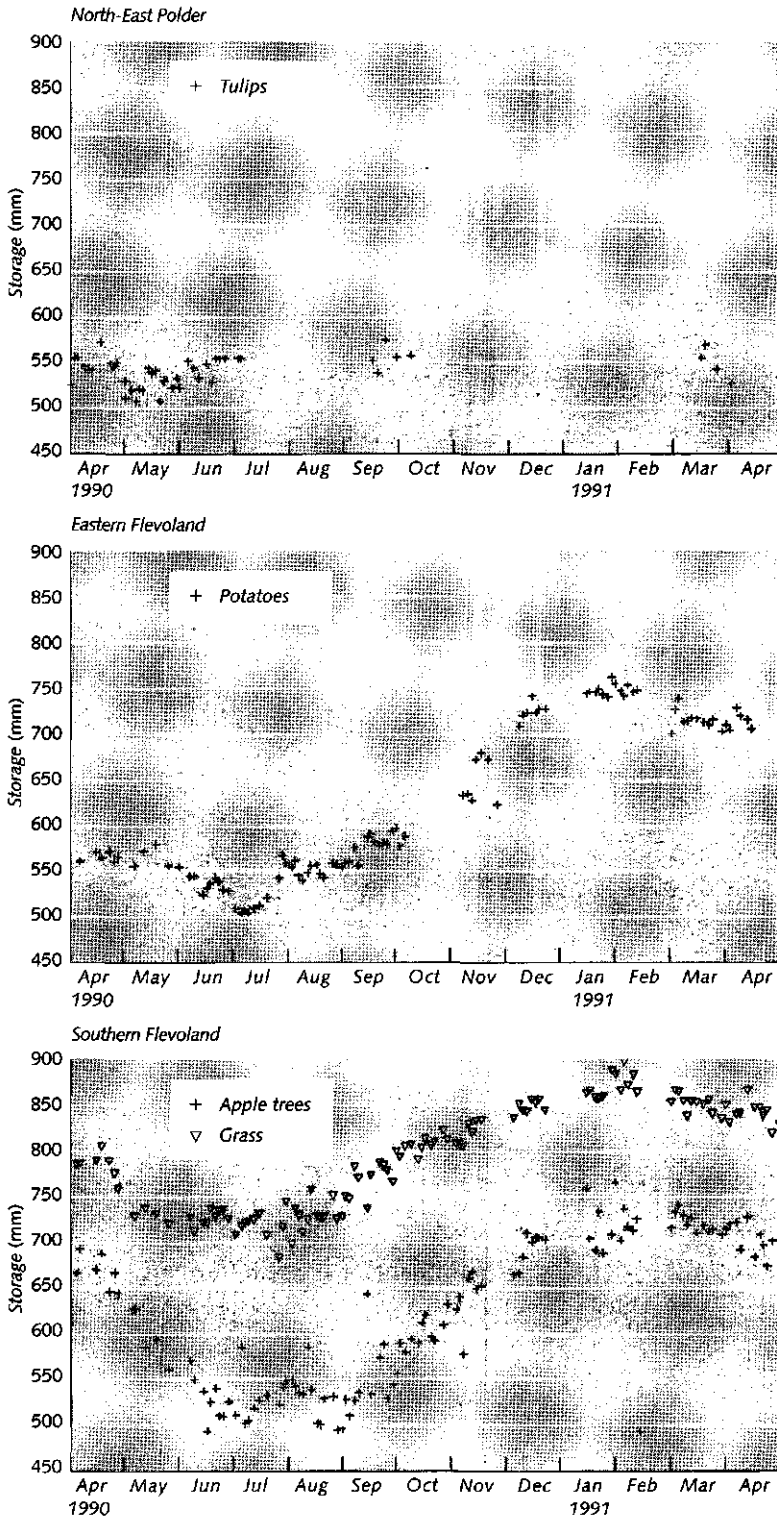


Figure 3.26. Soil moisture storage from the soil surface to a depth of 1.2 m at the experimental fields in the *North-East Polder* (April 1990 - April 1991), *Eastern Flevoland* (April 1993 - April 1994) and *Southern Flevoland* (April 1993 - April 1994).

wet periods. In figure 3.26 the soil moisture content is presented as a mean value of the probes installed at the same depth and collected at the same point of time. Results of the measurements show that the band in which the soil moisture storage (from the soil surface to a maximum of 1.2 m below the soil surface) moves, varies from 500 mm during the growing season up to 760 mm during the winter period. During the growing season, the greater part of the soil moisture is extracted from the plough layer. The soil moisture content is at field capacity during the winter period.

Southern Flevoland: During the field experiments, data on soil moisture content were collected three times a week. At the experimental field in Southern Flevoland rows of apple trees are alternated by grass strips (width approximately 2 m). The difference between the soil moisture storage (from the soil surface to a maximum of 1.2 m below the soil surface) beneath the grass strip and the strip where the apple trees are planted amounts to roughly 150 mm (figure 3.26). This is caused by the soil ripening process, which converts the soil from waterlogged materials into a more compact aerated and permeable material (see also subsection 2.3.2. and 3.1.1.3). The ripening process is induced by drainage and evapotranspiration. As the actual evapotranspiration rate is higher at the strip where the apple trees are planted, the soil ripening process proceeded additionally faster. Figure 3.26 shows that saturated ripened soil contains less water than saturated unripened soil. The difference amounts to 150 mm. The band in which the soil moisture storage moves is smaller for unripened soil (200 mm) than for the ripened soil (260 mm). It is remarkable to notice that differences in the course of the soil ripening process occur within a few meters. The variation in the soil moisture content of the ripened soil at the experimental plot in Southern Flevoland is comparable to the soil of the experimental field in Eastern Flevoland.

3.2.8 Drain discharges

Drainage water was collected using a 230 liter tank, which was partially sunken into the bottom of the collector drain. The number of drain outlets, which were connected with the tank by plastic tubes, is dependent on the drain spacing (North-East Polder, drain spacing 4 m, 9 connected drain outlets; Eastern Flevoland,

drain spacing 48 m, 3 connected drain outlets; Southern Flevoland, drain spacing 24 m, 5 connected drain outlets).

Samples were collected on a discharge proportional base (figure 3.27). Whenever the water level in the tank reaches the floating contact H, the tank was separated from the plastic tube by a valve. After a water sample was pumped automatically in from the tank into an automatic water sampler (PB-Mos, Edmund Bühler GMBH, BDR), the remaining water was drained off into the ditch and the valve was opened again when the water level reached floating contact L.

In this way water samples were taken every 0.4 mm of drain discharge. The complete system was controlled with a Campbell recorder (Campbell 21x, micro logger, Campbell Scientific Inc. USA) with 40 Kbyte memory, which in addition registered the volume of the drain discharges. Data were transported with a Husky Hunter micro computer, which could also be used as additional memory for the micro logger to load new programs in the micro logger (Groen and Dekkers, 1991).

In 1989 and 1990 various problems occurred with the discharge proportional sampling process. Due to these problems, only fragmented time series of the automatic registered drain discharges are available in this period. The problems were related to failure of mains voltage, the freezing of the valve in the winter period, a strike of lightning, a too small pumping capacity and a broken collector pipe. In 1991 the system was improved, protected against frost and lightning and the pumping capacity increased. At the experimental fields in Southern and Eastern Flevoland hardly any malfunctioning of the discharge proportional sampling process occurred.

For all experimental fields drain discharges mainly occur during the winter season. Examples of the monthly precipitation and monthly drain discharge are presented in figure 3.28. Variation in the differences between monthly precipitation and monthly drain discharge are caused by potential evapotranspiration, soil characteristics, drain distances and type of crop.

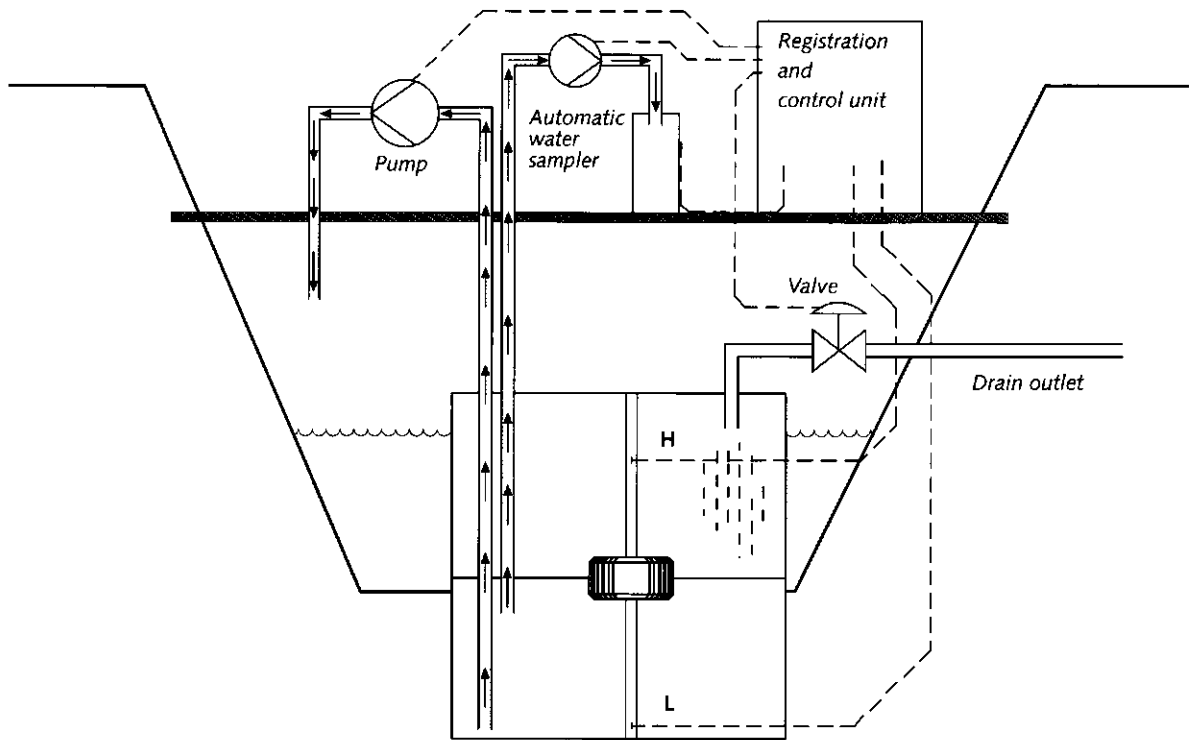


Figure 3.27. Outline of the drain discharge proportional sampling process.

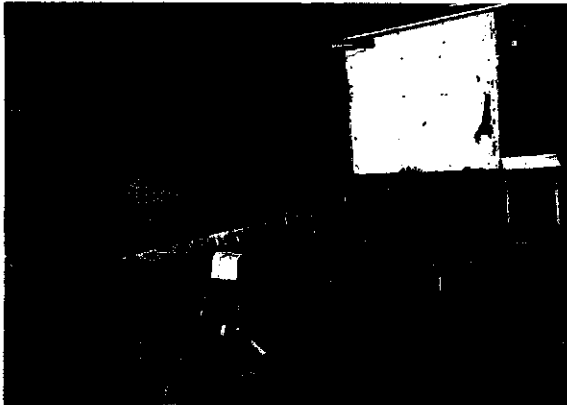


Photo 3.6. General impression of the drain discharge proportional sampler.

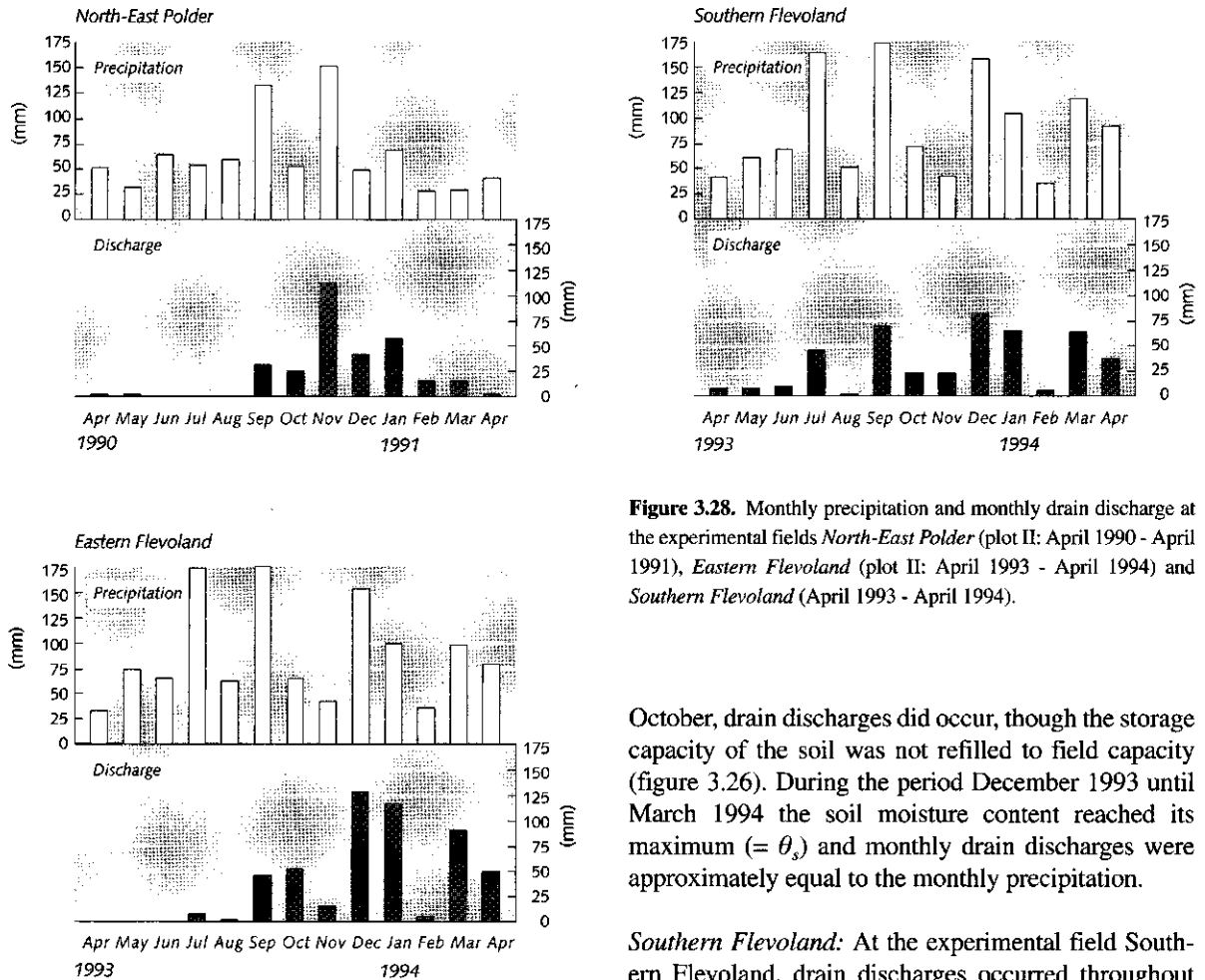


Figure 3.28. Monthly precipitation and monthly drain discharge at the experimental fields *North-East Polder* (plot II: April 1990 - April 1991), *Eastern Flevoland* (plot II: April 1993 - April 1994) and *Southern Flevoland* (April 1993 - April 1994).

October, drain discharges did occur, though the storage capacity of the soil was not refilled to field capacity (figure 3.26). During the period December 1993 until March 1994 the soil moisture content reached its maximum ($= \theta_s$) and monthly drain discharges were approximately equal to the monthly precipitation.

Southern Flevoland: At the experimental field Southern Flevoland, drain discharges occurred throughout the year, though the soil moisture content did not reach its maximum ($= \theta_s$) during the summer period. During the winter period (November 1993 until March 1994) monthly drain discharges were significantly lower than the monthly precipitation. This was probably induced by a combination of the high saturated permeability of the subsoil, which gave high drain discharges at short time intervals, and the capacity of the pump, which was inadequate for such situations. As the saturated permeability of the cracked subsoil is exceptionally high ($300\text{--}500 \text{ m d}^{-1}$), part of the drainage water flowed to drain pipes which were not connected to the discharge proportional sampler or flowed directly to the ditch. However, it was calculated that this was only a small part of the total lateral drainage flux (Brongers and Groen, 1995).

North-East Polder: At the experimental field North-East Polder, drain discharges during the months of December, January and February were almost equal to the precipitation rate as the potential evapotranspiration rate amounts to only a few millimeters per month (figure 3.28). The change in water storage during a dry and wet period amounts to only 75 mm (figure 3.26). Consequently, drain discharges often occurs during wet summer periods. On the other hand sprinkler irrigation is applied frequently during dry periods to provide the vegetation with sufficient water.

Eastern Flevoland: At the experimental field Eastern Flevoland, drain discharges during the summer period are exceptional. During the months of September and

3.2.9 Concentrations of solutes and pesticides in drainage water

3.2.9.1 *Procedures for collection, extraction and analyses of water samples*

Water samples to establish the amount of solutes and pesticides in drainage water were collected by the automatic water sampler (PB-Mos, Edmund Bühler GMBH). The discharge proportional sampling process has already been discussed in subsection 3.2.8. As variations in concentrations of solutes and pesticides in the drain pipes are the rule rather than the exception, a number of drain outlets were connected to the discharge proportional sampler in order to obtain a statistically reliable average concentration.

Samples from the automatic water sampler were collected three times a week on Monday, Wednesday and Friday. Thus, the residence time of the samples at the automatic water sampler was never more than two days. Especially in periods with high temperatures, the residence time should be kept as short as possible, due to transformation and volatilization. Fortunately, most of the precipitation surplus drained away during the winter period. Laboratory tests with the volatile pesticide 1,3-dichloropropene showed that if the samples stayed in the automatic water sampler for two days, roughly 10% of 1,3-dichloropropene transformed or evaporated. Losses due to volatilization will be smaller for metamitron, aldicarb and simazine as a result of their characteristics.

Drainwater samples collected at the experimental field North-East Polder were analyzed for (Z) and (E) 1,3-dichloropropene, metamitron and bromide. Samples collected at the experimental field Eastern Flevoland were analyzed for aldicarb and bromide. Samples collected at the experimental field Southern Flevoland were analyzed for simazine and bromide. After collection, the samples were taken to the laboratory. The period between the collection of the samples and laboratory analysis was less than one week. During this period the samples were stored in a dark room at 5 °C.

Bromide was analyzed according to the principle of spectrophotometry, based on the method of analysis as

described by Fishman and Skougstad (1963). The detection limit of this method for bromide amounted to $100 \mu\text{g l}^{-1}$, which is no objection as the detection limit is far below the background concentration.

The method of analysis for metamitron for the drain water samples is the same as the method of analysis used for the standard solutions in the sorption experiments as described in subsection 3.1.2.1. It was assumed that the analytic recovery amounted to 95%. Results were corrected for recovery. Detection limit for the water samples amounted to $0.1 \mu\text{g l}^{-1}$.

The concentration of 1,3-dichloropropene in the water samples was measured with a HP 5880A gas-chromatograph, using the Purge and Trap method as described in subsection 3.1.2.2. Analytic recovery amounted to 70%. Results were corrected for recovery. Detection limit for both the (Z) and (E) isomer amounted to $0.05 \mu\text{g l}^{-1}$.

The method of analysis for the concentration of aldicarb, aldicarb sulphoxide and aldicarb sulphone in the water samples is the same as the method of analysis used for the standard solutions in the sorption experiments as described in subsection 3.1.2.3. Analytic recovery amounted to approximately $90\% \pm 5\%$ for aldicarb, aldicarb sulphoxide and aldicarb sulphone. Results were corrected for recovery. Detection limit for aldicarb, aldicarb sulphoxide and aldicarb sulphone in the water samples amounted to $0.1 \mu\text{g l}^{-1}$.

The method of analysis for the concentration of simazine in the water samples is similar to the method of analysis used for the standard solutions in the sorption experiments as described in subsection 3.1.2.4. It was assumed that the recovery amounted to 90%. Results were corrected for recovery. Detection limit for the water samples amounted to $0.1 \mu\text{g l}^{-1}$.

3.2.9.2 *Results for the experimental field North-East Polder*

Concentrations of solutes and pesticides in drain pipes vary both in time and space. An example of the variation in the concentration of solutes and pesticides is presented in figure 3.29. (Z) 1,3-dichloropropene was measured at the drain pipes of three adjacent drains. In

this case the concentration between the adjacent drain pipes varied with one order of magnitude. At the experimental fields Eastern and Southern Flevoland similar deviations were observed both for pesticide and bromide concentrations. Therefore, a number of drain outlets were connected to the discharge proportional sampler.

Bromide 1990 (figure 3.30: 23 February 1990): At the start of the experiment the bromide concentrations amounted to 0.2 mg l^{-1} , which is equal to the background concentration. Seventy days after applications, concentration levels of bromide started to rise a maximum level of 4 mg l^{-1} . The load of bromide leaving the drain pipes amounted to 193 g ha^{-1} (0.6 % of the quantity applied). This was the result of a low cumulative drain discharge over the sampling period, which amounted to 30 mm only.

Bromide 1991/1992 (figure 3.30: 14 March 1991):

During the first 200 days of the experiment the bromide concentrations were very capricious and varied from 0.2 to 11 mg l^{-1} . After 200 days concentration levels of bromide varied from approximately 3 to 6 mg l^{-1} . The cumulative drain discharge over the sampling period amounted to 416 mm. The load of bromide leaving the drain pipes was 16.4 kg ha^{-1} (58% of the amount applied; the results were corrected for background concentrations).

Concentration levels of 1,3-dichloropropene in the drain pipes of the experimental field North-East Polder are only presented for the (Z) isomer. Concentration dissimilarity between the Z and E isomer hardly occurred for concentrations below $200 \mu\text{g l}^{-1}$ (figure 3.31). For values of the concentration of both (Z) and (E) 1,3-dichloropropene above $200 \mu\text{g l}^{-1}$ the concentration of (E) 1,3-dichloropropene was slightly higher than for the (Z) isomer. However, differences never amounted to more than 5%. Thus, both the concentra-

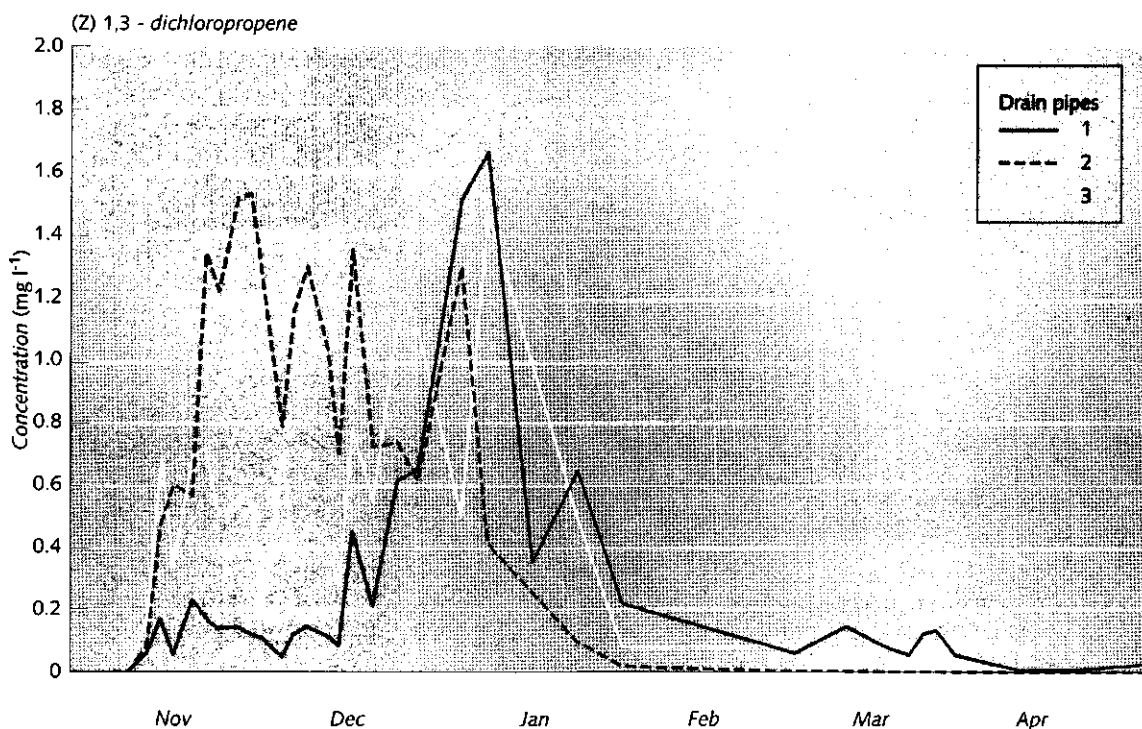


Figure 3.29. Variation of the concentration of (Z) 1,3-dichloropropene at the drain outlets of three adjacent drain pipes at the experimental field North-East Polder (plot III).

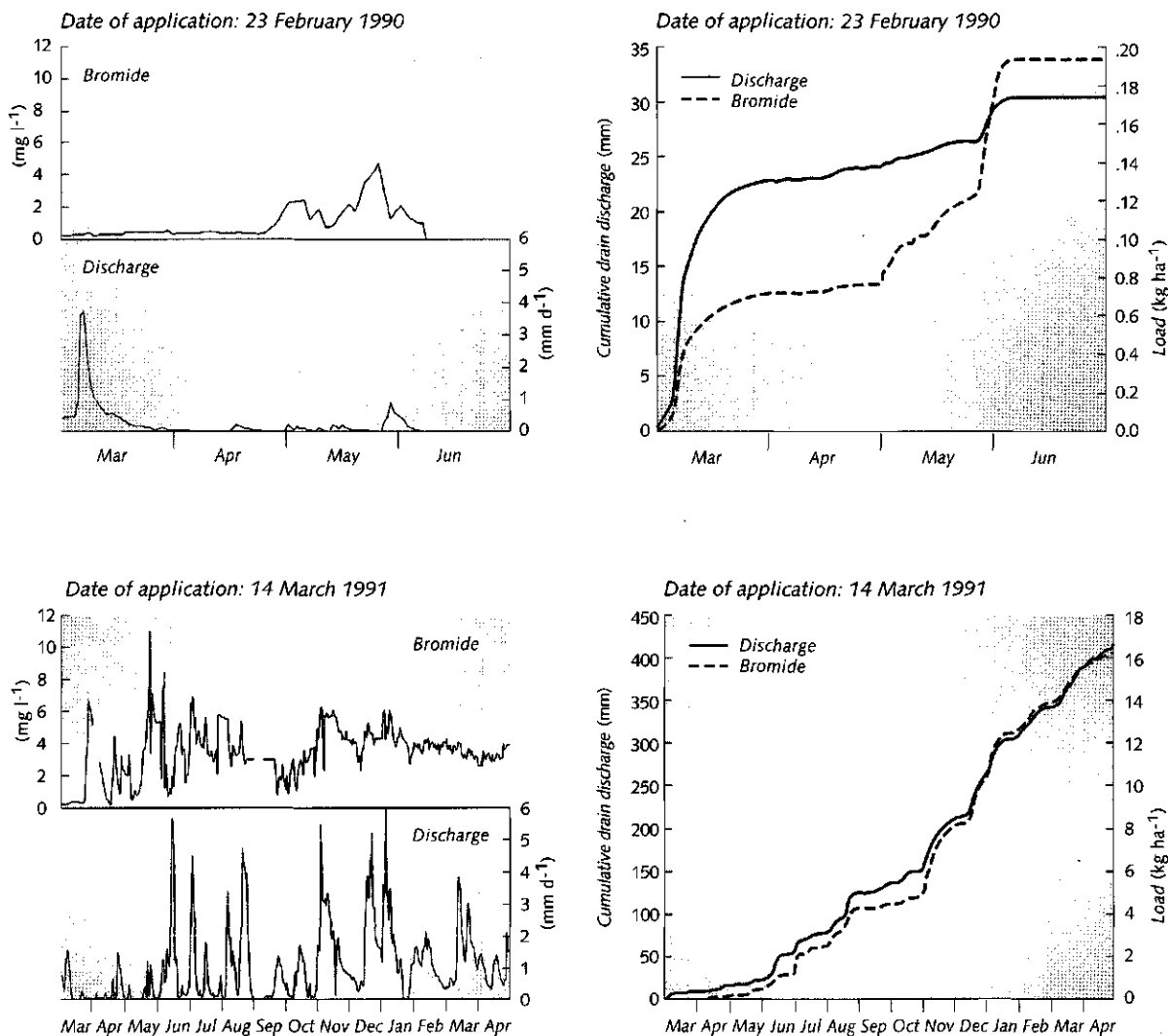


Figure 3.30.

LEFT: Concentration of bromide in the drain pipes in relation to the drain discharge at plot I (23 February 1990) and plot II (14 March 1991) of the experimental field North-East Polder.

RIGHT: Cumulative drain discharge and leaching of bromide for the same plots.

tion 1,3-dichloropropene in the drain pipes and the load leaching through the drain pipes can be obtained by multiplying the concentration of (Z) 1,3-dichloropropene by a factor 2.

It is remarkable that differences in concentrations of the two isomers are so small: their air-water distribu-

tion is significantly different (the Henry coefficient of the Z isomer is about 50% higher than that of the E isomer; Leistra, 1972). This is an indication that the differences in losses due to volatilisation have had a limited effect on the leaching of both isomers.

(Z) 1,3-dichloropropene plot I (figure 3.32: 6 Septem-

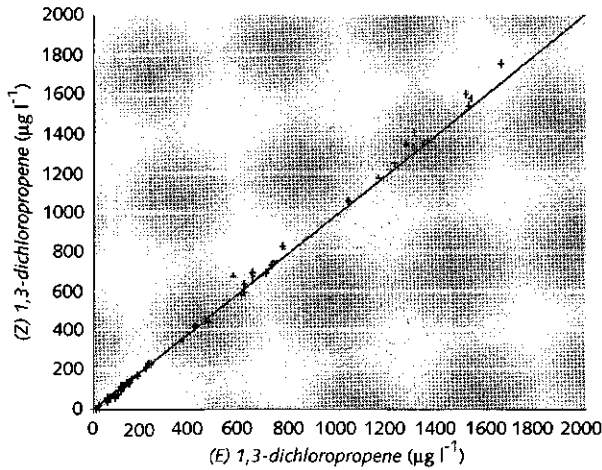


Figure 3.31. Relationship between the concentration of (E) and (Z) 1,3-dichloropropene in water samples from the experimental field North-East Polder.

ber 1989): In 1989 the concentration (Z) 1,3-dichloropropene in the drain pipes rose to a level $0.3 \mu\text{g l}^{-1}$ 20 days after application. In September and October concentrations between 0.1 and $0.3 \mu\text{g l}^{-1}$ were assessed. The total load of (Z) 1,3-dichloropropene leaving the drain pipes during the period 6 September 1989 until 31 December 1989 amounted to 0.02 g ha^{-1} , which is less than 0.001% of the quantity applied.

(Z) 1,3-dichloropropene plot II (figure 3.32: 13 September 1990): In 1990 the concentration of (Z) 1,3-dichloropropene in the drain pipes was measured from the second day until 100 days after application. Concentrations for the Z isomers varied from 0.0 up to $1.0 \mu\text{g l}^{-1}$. During the period 13 September 1990 until 31 December 1990 the total load of (Z) 1,3-dichloropropene leaving the drain pipes amounted to 0.33 g ha^{-1} which is roughly 0.004% of the quantity applied.

(Z) 1,3-dichloropropene plot III (figure 3.32: 7 November 1990): The concentration of (Z) 1,3-dichloropropene in the drain pipes rose to a level of $1200 \mu\text{g l}^{-1}$ approximately 60 days after application. This is 2500 times the concentration levels measured at the previous experimental fields. The total load of (Z) 1,3-dichloropropene leaving the drain pipes during the period 7 November 1990 until 30 April 1991 amounted to 1.1 kg ha^{-1} which is approximately 1.3% of the quantity applied.

Metamitron 1990 (figure 3.33: 23 February 1990): In 1990 the concentration of metamitron in two samples descending from the drain pipes directly after application of metamitron amounted to 4.5 and $8 \mu\text{g l}^{-1}$. Probably these concentrations are an artefact, caused by contamination of glass in the laboratory. Only two days later the concentration in the drain pipes fell back to the original level of less than $0.1 \mu\text{g l}^{-1}$. During two

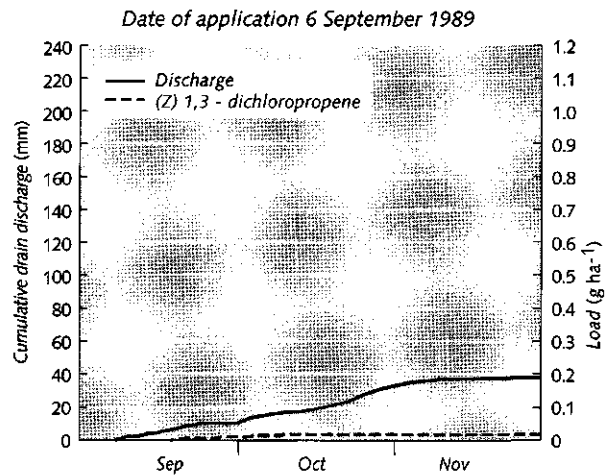
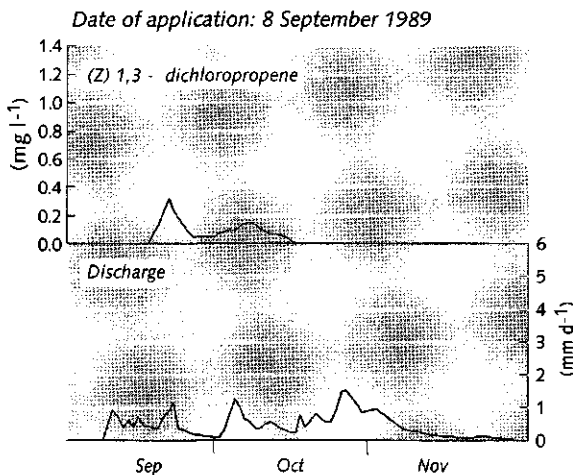


Figure 3.32. Continued on next page.

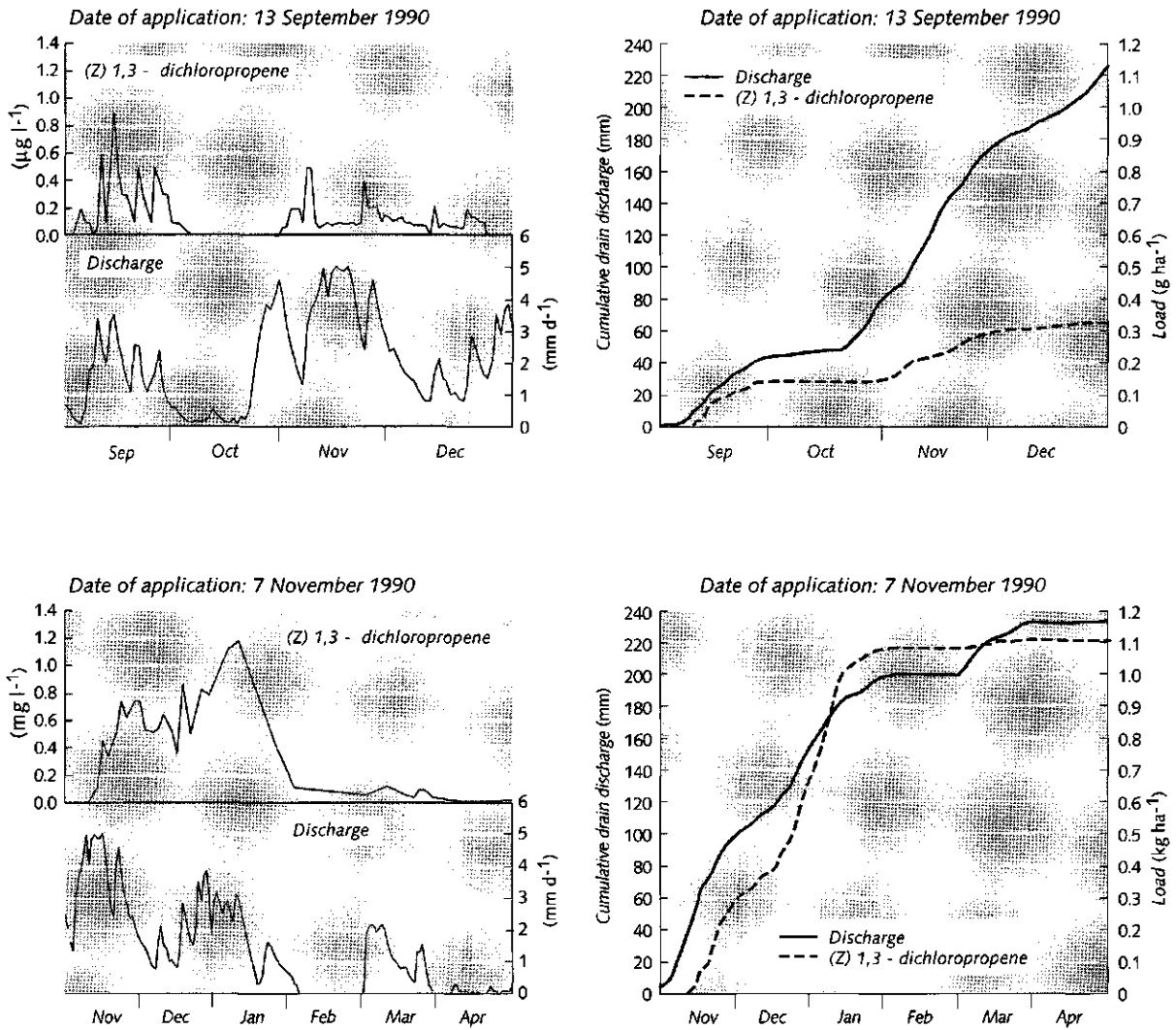


Figure 3.32.

LEFT: Concentration of (Z) 1,3-dichloropropene in the drain pipes in relation to the drain discharge at three plots (Date of application: 6 September 1989; 13 September 1990; 7 November 1990) at the experimental field *North-East Polder*.

RIGHT: Cumulative drain discharge and leaching of (Z) 1,3-dichloropropene at the same plots.

For 6 September 1989 and 13 September 1990 the concentration and load are presented in $\mu\text{g l}^{-1}$ and g ha^{-1} respectively; for 7 November the concentration and load are presented in mg l^{-1} and kg ha^{-1} respectively.

short periods, approximately 60 and 105 days after application, the concentration level of metamitron in the drain pipes rose to $0.5 \mu\text{g l}^{-1}$. The load of metamitron leaving the drain pipes was 110 mg ha^{-1} (0.005 % of the amount applied). However, the cumulative drain discharge over the sampling period amounted to only 30 mm.

Metamitron 1991/1992 (figure 3.33: 14 March 1991): In 1991 the concentration of metamitron in the drain pipes rose slightly to a level of $0.1 \mu\text{g l}^{-1}$ directly after application of metamitron. During two short periods, approximately 140 and 200 days after application, the concentration rose to $0.5 \mu\text{g l}^{-1}$ and $0.2 \mu\text{g l}^{-1}$ respectively. The cumulative drain discharge over the sam-

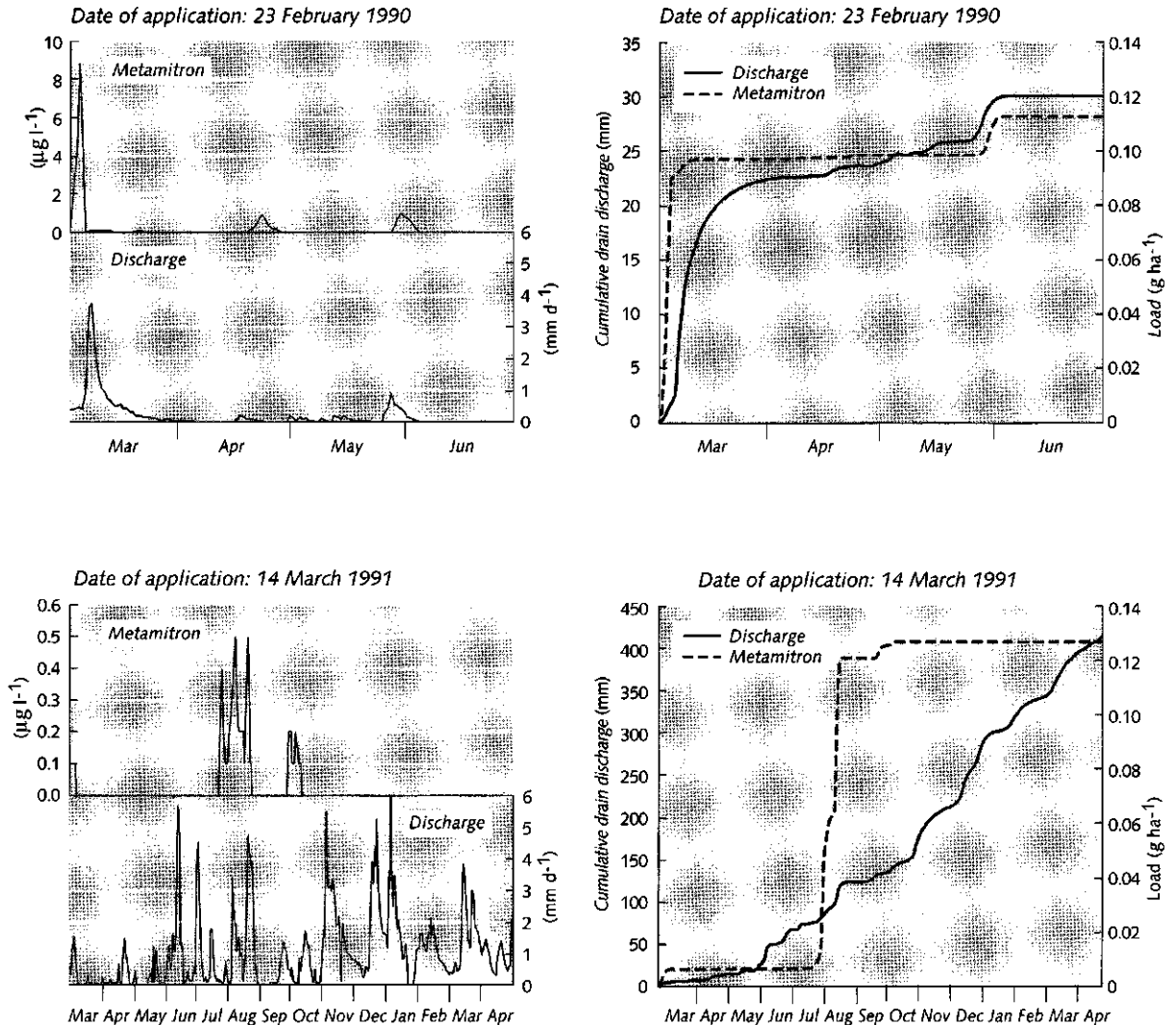


Figure 3.33.

LEFT: Concentration of metamitron in the drain pipes in relation to the drain discharge at plot I (23 February 1990) and plot II (14 March 1991) of the experimental field North-East Polder.

RIGHT: Cumulative drain discharge and leaching of metamitron for the same plots.

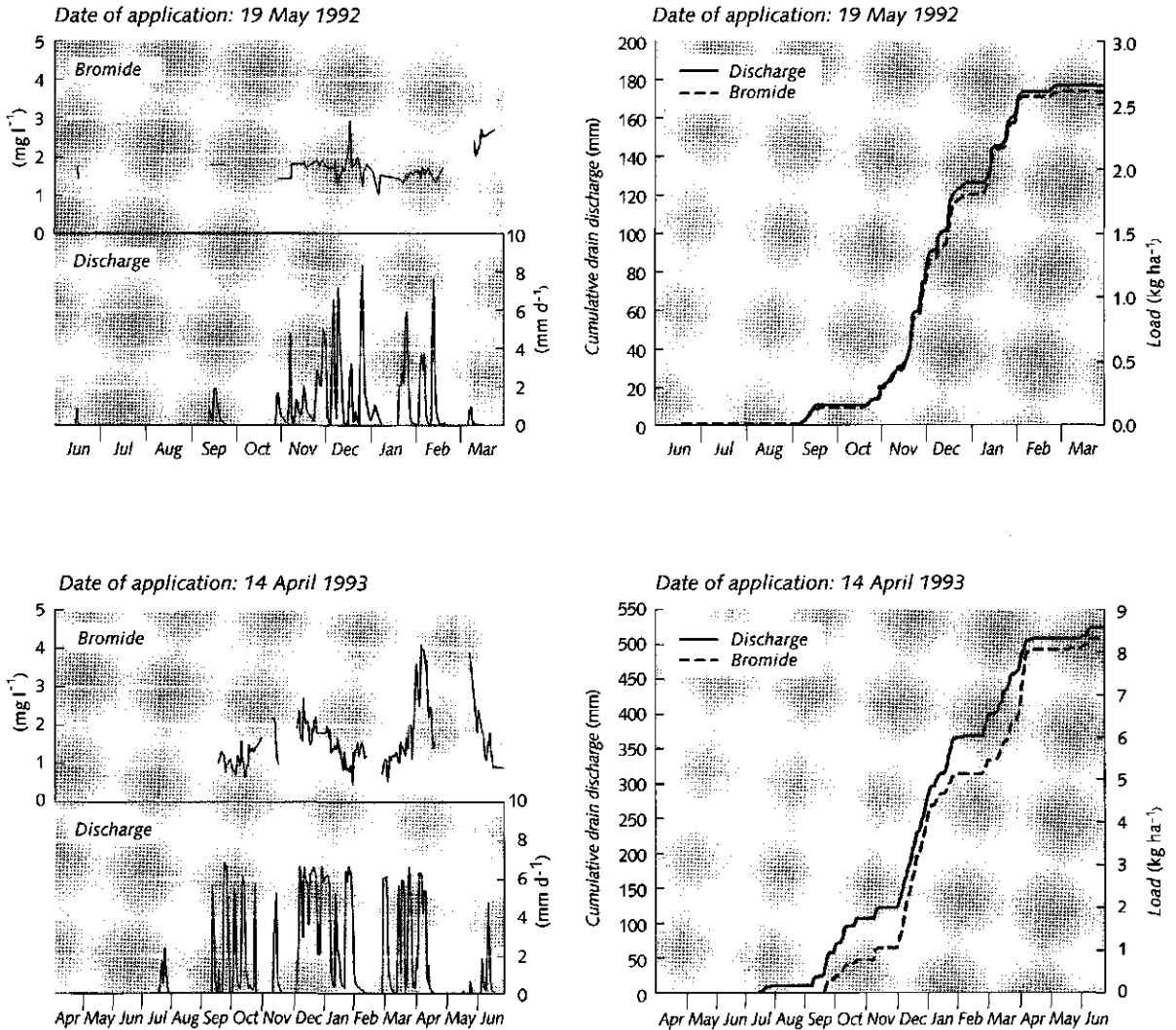


Figure 3.34.

LEFT: Concentration of bromide in the drain pipes in relation to the drain discharge at plot I (19 May 1992) and plot II (14 April 1993) of the experimental field *Eastern Flevoland*.

RIGHT: Cumulative drain discharge and leaching of bromide for the same plots.

pling period amounted to 416 mm. The load of metamitron leaving the drain pipes was 126 mg ha⁻¹ (0.016 % of the amount applied).

3.2.9.3 Results for the experimental field *Eastern Flevoland*

Bromide 1992/1993 (figure 3.34: 19 May 1992): In

1992 the concentration of bromide in the drain pipes varied from 0.9 to 3 mg l⁻¹. The background concentration, which was measured for one month previous to the application of bromide, amounted to 0.85 ± 0.07 mg l⁻¹. The cumulative drain discharge over the sampling period amounted to 172 mm. During the period 19 May 1992 until 30 March 1993 the load of bromide

leaving the drain pipes was 2.7 kg ha^{-1} (15% of the amount applied; the results were corrected for background concentrations).

Bromide 1993/1994 (figure 3.34: 14 April 1993): In 1993 the concentration of bromide in the drain pipes varied from 0.9 to 4 mg l^{-1} . The background concentration, which was measured for two months previous to the application of bromide, amounted to $0.93 \pm 0.15 \text{ mg l}^{-1}$. The cumulative drain discharge over the sampling period amounted to 523 mm . During the period 14 March 1993 until 1 July 1994 the load of bromide leaving the drain pipes was 8.3 kg ha^{-1} (29% of the amount applied; the results were corrected for background concentrations).

Aldicarb-sulphoxide/sulphone 1992/1993 (plot I): In 1992 the concentrations of aldicarb-sulphoxide and aldicarb-sulphone in the drainage water were measured until 320 days after application. The cumulative drain discharge over the sampling period amounted to 172 mm . During this period no traces of aldicarb-sulphoxide and aldicarb-sulphone were demonstrated.

Aldicarb-sulphoxide/sulphone 1993/1994 (figure 3.35: 30 March 1993): In the period 14 March 1993 until 1 July 1994, the concentrations of aldicarb-sulphoxide and aldicarb-sulphone in the drainage water were measured until 450 days after application. The cumulative drain discharge over the sampling period amounted to 523 mm . The concentration of aldicarb-sulphoxide in the drainage water grew with every new discharge wave up to a concentration of $4 \mu\text{g l}^{-1}$. Traces of aldicarb-sulphone were demonstrated during the complete sampling period. The maximum concentration amounted to $1 \mu\text{g l}^{-1}$.

3.2.9.4 Results for the experimental field Southern Flevoland

Bromide 1992/1993 (figure 3.36: 9 June 1992): In 1992 the concentration of bromide in the drain pipes varied from 1.4 to 4.5 mg l^{-1} . The background concentration, which was measured for one month previous to the application of bromide, amounted to $1.6 \pm 0.2 \text{ mg l}^{-1}$. During the period 9 June 1992 until 21 April 1993 the cumulative drain discharge over the sampling period amounted to 200 mm . The load of bromide leaving the drain pipes was 6.1 kg ha^{-1} (17% of the amount

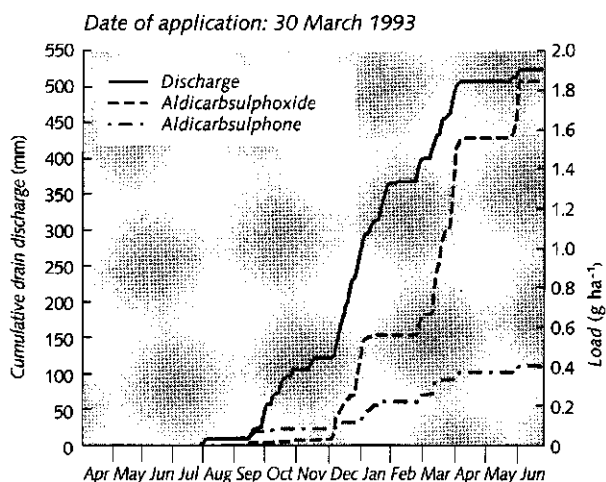
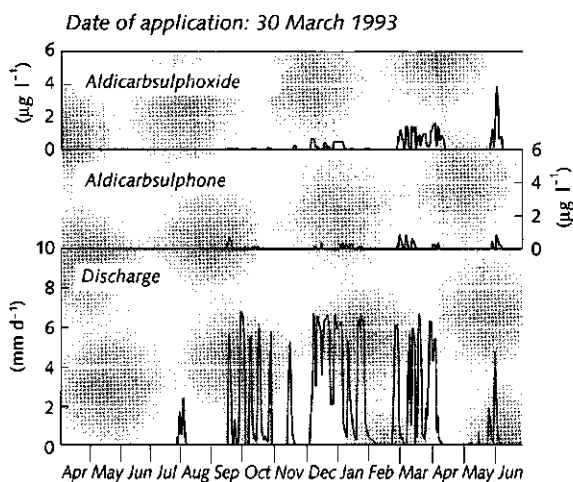


Figure 3.35.

LEFT: Concentration of aldicarb-sulphoxide and aldicarb-sulphone in the drain pipes in relation to the drain discharge in 1993/1994 at plot II of the experimental field Eastern Flevoland.

RIGHT: Cumulative drain discharge and leaching of aldicarb-sulphoxide and aldicarb-sulphone for plot II.

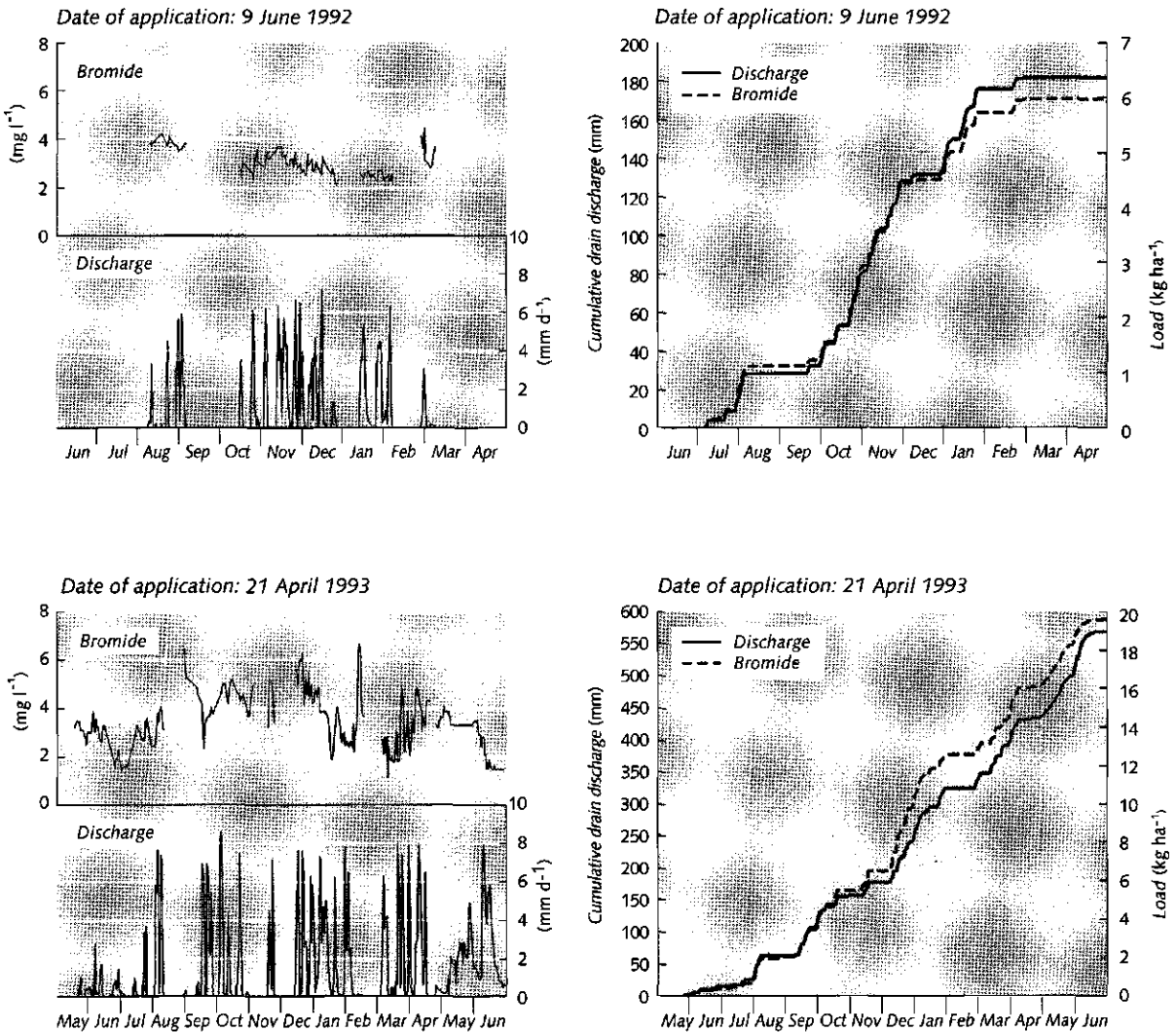


Figure 3.36.

LEFT: Concentration of bromide in the drain pipes in relation to the drain discharge at the experimental field Southern Flevoland.
RIGHT: Cumulative drain discharge and leaching of bromide.

applied; the results were corrected for background concentrations).

Bromide 1993/1994 (figure 3.36: 21 April 1992): In 1993 the concentration of bromide in the drain pipes varied from 1.2 to 7 mg l^{-1} . The background concentration, which was measured for two months previous to

the application of bromide, amounted to $1.5 \pm 0.3 \text{ mg l}^{-1}$. During the period 21 April 1993 until 1 July 1994 the cumulative drain discharge over the sampling period amounted to 570 mm. The load of bromide leaving the drain pipes was 19.6 kg ha^{-1} (33% of the amount applied; the results were corrected for background concentrations).

Simazine 1992/1993 (figure 3.37: 11 April and 9 June 1992): The concentration of simazine in the drain pipes went upwards instantly after application. Simazine remained traceable until approximately 200 days after application. The maximum concentration in the drainage water amounted to $7.0 \mu\text{g l}^{-1}$. During the period 11 April 1992 until 21 April 1993 the load of

simazine leaving the drain pipes was 1.5 g ha^{-1} (0.2% of the amount applied).

Simazine 1993/1994 (figure 3.37: 21 April 1993): Again, the concentration of simazine in the drain pipes went upwards instantly after application and simazine remained traceable until approximately 200 days after

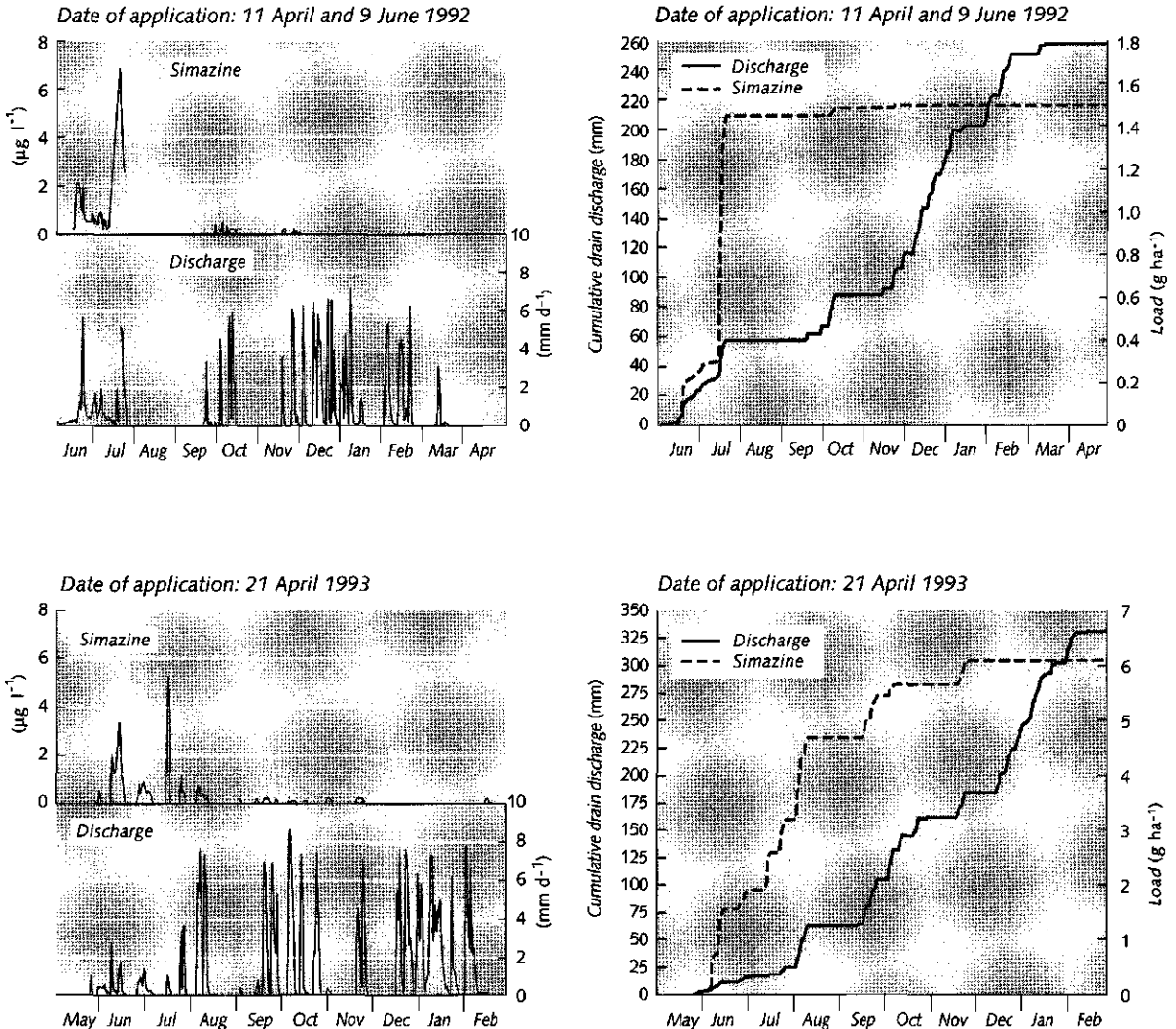
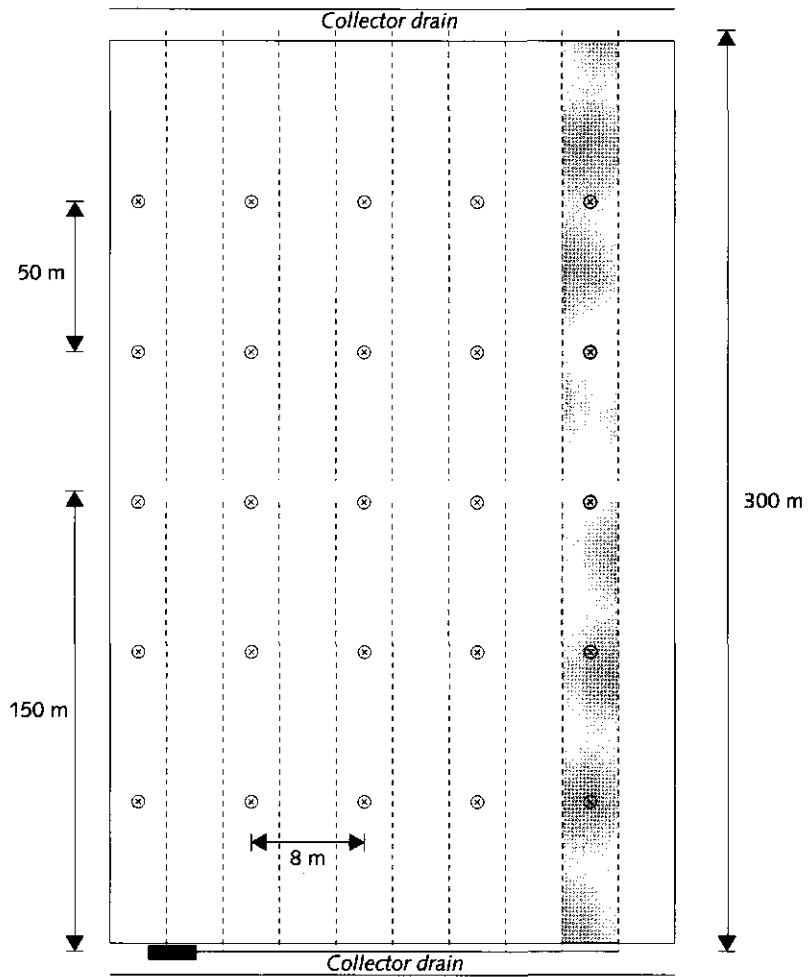


Figure 3.37.

LEFT: Concentration of simazine in the drain pipes in relation to the drain discharge for 1992 (11 April and 9 June 1992) and 1993 (21 April 1993) at the experimental field *Southern Flevoland*.

RIGHT: Cumulative drain discharge and leaching of bromide.



Experimental plot

- Drain pipes
- ⊗ Sampling point
- Discharge proportional sampler
- ▨ Section

Figure 3.38. Soil sampling process at the experimental field *North-East Polder*.

application. The maximum concentration in the drainage water amounted to $5 \mu\text{g l}^{-1}$. The load of simazine leaving the drain pipes was 0.6 g ha^{-1} (0.02% of the amount applied).

3.2.10 Concentration profiles of solutes and pesticides

3.2.10.1 Procedure for the collection, extraction and analysis of soil samples

Concentration profiles of solutes and pesticides were collected to deduce the movement of solutes and pesticides in the soil profile, to examine the transformation of pesticides in the field and to calculate mass balances for solutes and pesticides. To collect data on the concentration profiles at a particular sampling time, the various plots of the experimental fields (subsection 3.2.1) were divided into five different sections. Each section consisted of five different subsections. From each subsection four soil samples were taken every 0.20 m up to the depth of the drain pipes. The different samples of the same depth, section and time were mixed and transported to the laboratory. This procedure resulted into twenty mixed soil samples for each chemical at each sampling time (figure 3.38).

The concentration of the applied solute (e.g. pesticide) in a soil sample taken from the upper or lower part of a bore hole may differ over a factor 1000. To obtain reliable data, the collection of soil samples has to be performed extremely accurately. Even the smallest mixing of soil from the top layer with the lower soil layers influences the result. For each soil layer a distinctive Piston sampler (diameter 0.02 m) was used. To prevent soil from the upper soil layers falling into the bore hole, an Edelman auger (diameter 0.10 m) was used to widen the gap, before taking a sample of the underlying soil layer.

Generally, soil samples were only collected for the areas where the pesticide was applied. E.g. during the first year of the experiment at the experimental field Eastern Flevoland, aldicarb was only applied in the ridges. So, soil samples were only collected at the ridges. During the second year of the experiment aldicarb was applied before the planting of the potatoes as a full field application. During this year soil samples

were collected both at the furrows and ridges. Each section consisted of six different subsections; three subsection were located at the furrows and three at the ridges. From each subsection different soil samples were taken every 0.2 m up to the depth of the drain pipes. The different samples of the same depth, section and time were mixed and transported to the laboratory. At the experimental field Southern Flevoland, simazine was only applied at the strip where the apple trees are planted. Thus, soil samples were only collected at these strips.

Before application of a solute or pesticide, a soil sampling was undertaken to establish the initial content. After application the sampling intensity depended on:

- *Rate of transformation.* If a pesticide transforms rapidly, soil sampling should be intensified. At the experimental fields soil samples were generally collected 1, 3, 7, 14, 30, 60 and 120 days after application;
- *Humus content and sorption capacity.* Normally pesticides with a high sorption capacity will move slowly downwards into the soil profile. A high humus content will retard the movement of pesticides even more. In such a situation, the frequency of soil sampling was reduced;
- *Precipitation surplus.* For non-sorbing and non-degrading materials like bromide and chloride, convective transport, which proceeds during the winter season, is the most important process. Therefore sampling was intensified during irrigation and the winter season.

Mixed soil samples collected at the experimental field North-East Polder were analyzed for (Z) and (E) - 1,3 dichloropropene, metamitron and bromide. Soil samples collected at the experimental field Eastern Flevoland were analyzed for aldicarb and bromide. Samples collected at the experimental field Southern Flevoland were analyzed for simazine and bromide. After soil sampling, the mixed samples were taken directly to the laboratory. The period between soil sampling and laboratory analysis was generally less than one week. During this period the samples were always stored in a dark room at 5°C .

To determine the bromide content in the soil samples, a

known amount of soil (roughly 10 g) was taken from the sample, put in a glass jar and shaken with 100 ml water for 1 hour (175 motions per minute). Afterwards the sample was filtrated (0.2 mm membrane) and the bromide content in the extract was analyzed according to the principle of spectrophotometry, based on the

method of analysis as described by Fishman and Skougstad (1963). The detection limit of this method for bromide amounted to 0.1 mg kg^{-1} . Recovery of this method was assumed to be 100%. In order to determine the soil moisture content, another part of the soil samples was dried in a oven at 105°C . The results of

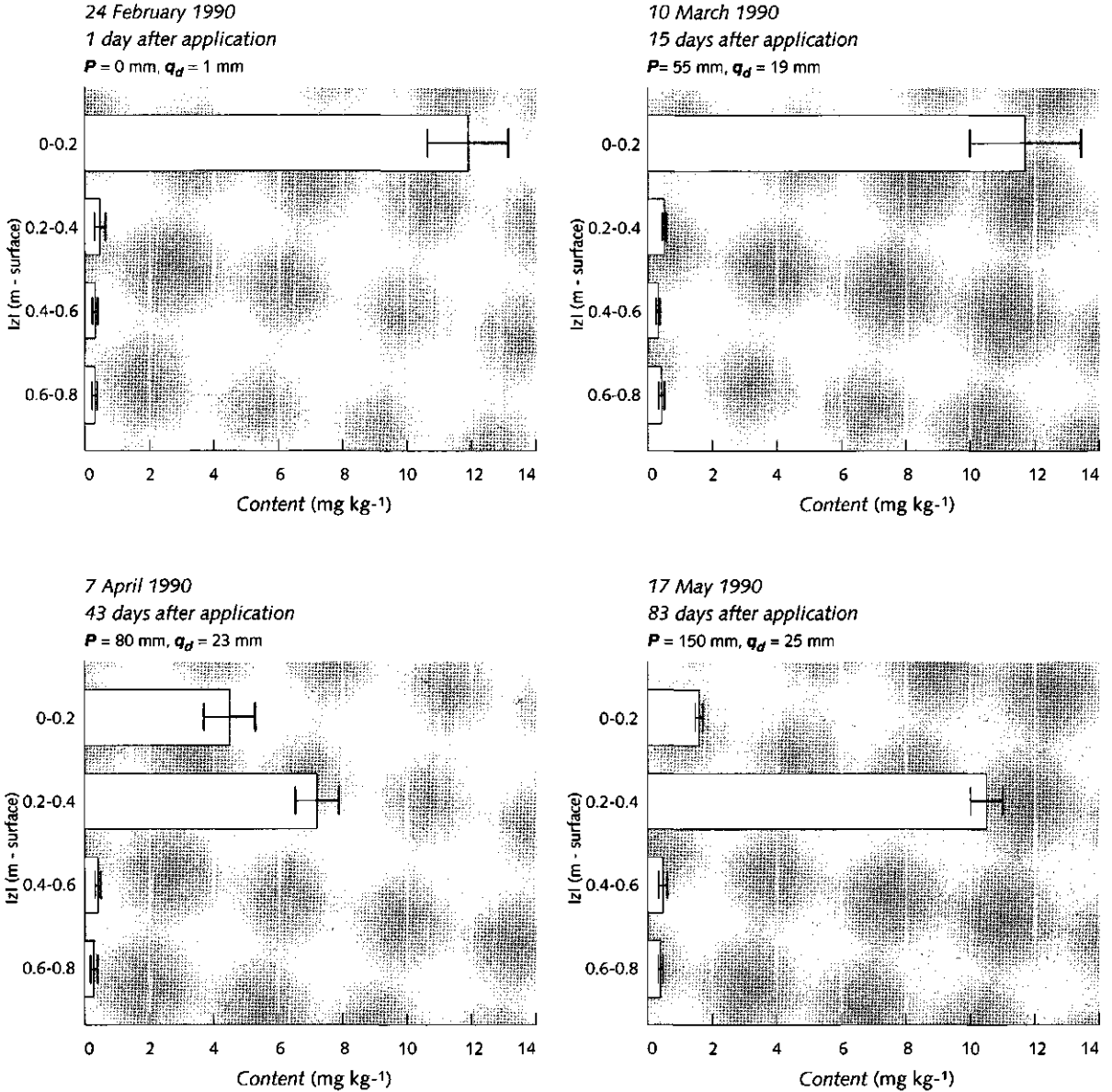


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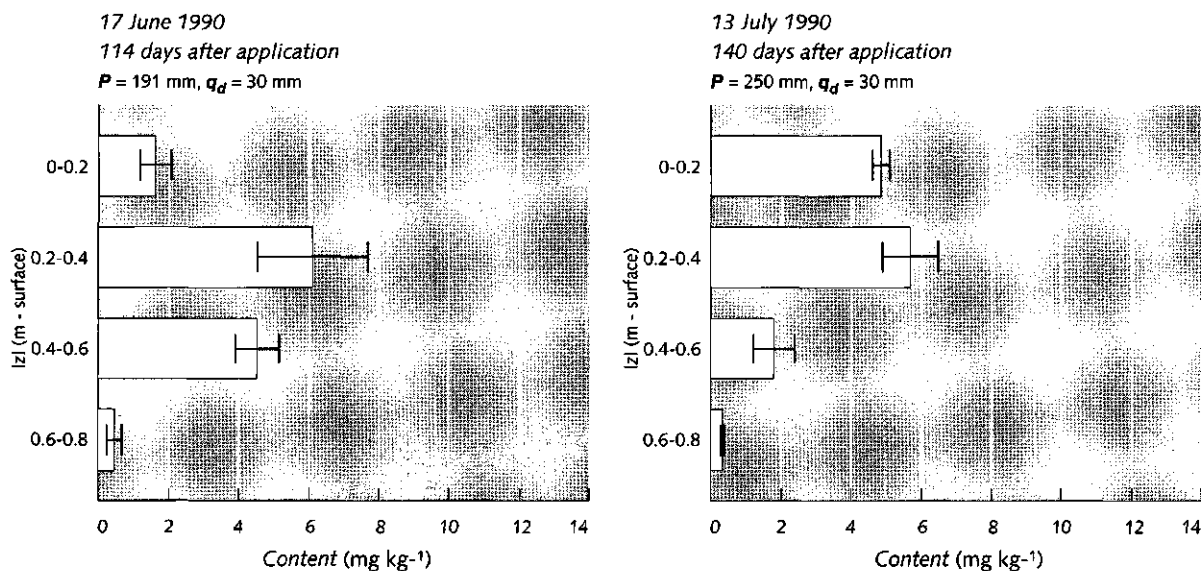


Figure 3.39. Concentration profiles of bromide through the soil profile in 1990 at plot I of the experimental field *North-East Polder* including standard deviation (P = cumulative precipitation; q_d = cumulative drain discharge rate).

the content of bromide in the soil samples are presented in mg bromide / kg dry soil. For the soils in the IJsselmeerpolders the background content of bromide in the soil is higher than the detection limit.

The extraction and chemical analysis for metamitron in soil samples is identical to the method of analysis used for the flasks in the transformation experiments as described in subsection 3.1.2.1. Detection limit for the soil samples amounted to 0.03 mg kg^{-1} . Analytic recovery amounted to $65 \pm 7\%$. Results were corrected for recovery.

The extraction and chemical analysis to determine the content of 1,3-dichloropropene in the soil samples is identical to the method of analysis used for the glass jars in the transformation experiments as described in subsection 3.1.2.2. Detection limit for both the (Z) and (E) isomer amounted to 0.01 mg kg^{-1} . Analytic recovery amounted to $70 \pm 5\%$. Results were corrected for recovery.

The extraction and chemical analysis of aldicarb sulphoxide and aldicarb sulphone in the soil samples is identical to the method of analysis used for the glass

jars in the transformation experiments as described in subsection 3.1.2.3. Detection limit for the soil samples amounted to 0.1 mg kg^{-1} . Analytic recovery of aldicarb sulphoxide and aldicarb sulphone amounted to $65 \pm 7\%$ and $80 \pm 5\%$ respectively. Results were corrected for recovery.

The method of analysis for the content of simazine in the soil samples is identical to the method of analysis used for the flasks in the transformation experiments as described in subsection 3.1.2.4. Detection limit for the soil samples amounted to 0.01 mg kg^{-1} . Analytic recovery amounted to $75 \pm 5\%$. Results were corrected for recovery.

3.2.10.2 Results for the experimental field *North-East Polder*

Bromide 1990 (plot I): The applied amount of bromide was equal to 33.0 kg ha^{-1} . The content of bromide in the soil was sampled at 6 different dates (table 3.16 and figure 3.39). On 13 July 1990, 140 days after application the bromide had moved deeper into the soil profile. However, only 200 g ha^{-1} (which is 0.6% of the dose applied) left the soil profile through the drain pipes. Nearly all the bromide applied was still present in the soil.

Table 3.16. Total amount of bromide and metamitron from the soil surface to 0.8 m below the soil surface at plot I of the experimental field *North-East Polder* (N.D. = not detected).

Date	Days after application	Solute / Pesticide			
		Bromide		Metamitron	
		Total amount (kg ha ⁻¹)	% of dose	Total amount (kg ha ⁻¹)	% of dose
07-02-1990	Initial	4.1 ± 0.9		N.D.	N.D.
24-02-1990	1	38.5 ± 4.2	104 ± 11	2.11 ± 0.68	95 ± 32
10-03-1990	15	40.2 ± 8.0	108 ± 22	1.04 ± 0.20	50 ± 10
07-04-1990	43	36.2 ± 4.4	98 ± 12	0.45 ± 0.03	21 ± 2
17-05-1990	83	37.2 ± 2.2	100 ± 6		
17-06-1990	114	36.9 ± 8.5	100 ± 23		
13-07-1990	140	37.1 ± 5.0	100 ± 13		

Table 3.17. Total amount of bromide and metamitron from 0 to 0.8 m below the soil surface at plot II of the experimental field *North-East Polder* (N.D. = not detected).

Date	Days after application	Solute / Pesticide			
		Bromide		Metamitron	
		Total amount (kg ha ⁻¹)	% of dose	Total amount (kg ha ⁻¹)	% of dose
21-02-1991	Initial	3.8 ± 0.4		N.D.	N.D.
15-03-1991	1	30.2 ± 4.2	100 ± 16	0.70 ± 0.18	88 ± 23
22-03-1991	8	30.6 ± 8.0	101 ± 30	0.61 ± 0.15	76 ± 19
26-04-1991	43	32.2 ± 4.4	106 ± 17		
17-05-1991	64	32.3 ± 2.2	107 ± 8	0.10 ± 0.02	13 ± 3
06-08-1991	145	28.9 ± 8.5	95 ± 32		
02-11-1991	233	27.5 ± 5.0	91 ± 19		
05-12-1991	266	26.4 ± 4.9	87 ± 19		
11-01-1992	303	15.9 ± 9.1	52 ± 34		
06-02-1992	329	18.3 ± 2.1	60 ± 8		
06-03-1992	358	19.0 ± 1.8	62 ± 7		
07-04-1992	390	15.1 ± 3.1	50 ± 12		
07-05-1992	420	14.6 ± 3.2	48 ± 11		

Movement of bromide through the soil profile in 1990 is presented in figure 3.39. It shows that 43 days after application bromide has moved deeper into the soil profile. In the period from 43 to 83 days after application (April/May) the drain discharge rate is only 2 mm; the bromide moves deeper into the plough layer, but concentration levels in the deeper soil layers did not rise. This situation changes in the period 83-114 days after application (May/June). In this period an addi-

tional 60 mm water to the normal precipitation was applied by sprinkler irrigation, resulting in a drain discharge of 30 mm and a downward movement of bromide. In the period 114-140 days after application (June/July) the tulips were harvested, which caused a thorough mixing of the bromide in the plough layer. Besides, the bromide moved upward again, due to capillary rise.

Bromide 1991/1992 (plot II): In 1991 and 1992 the movement of bromide through the soil and leaching of bromide through the drain pipes were recorded during a period of 420 days after application. Results of the concentration levels in the drain pipes have already been presented in subsection 3.2.8. Results of the soil sampling at 13 different dates are presented in table 3.17.

Figure 3.40 shows the movement of bromide through the soil. It is obvious that the movement and leaching of bromide is directly related to the precipitation excess and mainly takes place during the winter period. In the spring and summer of 1991 the drain discharge was higher than in 1990. As a consequence the bromide moved deeper into the soil profile. During the

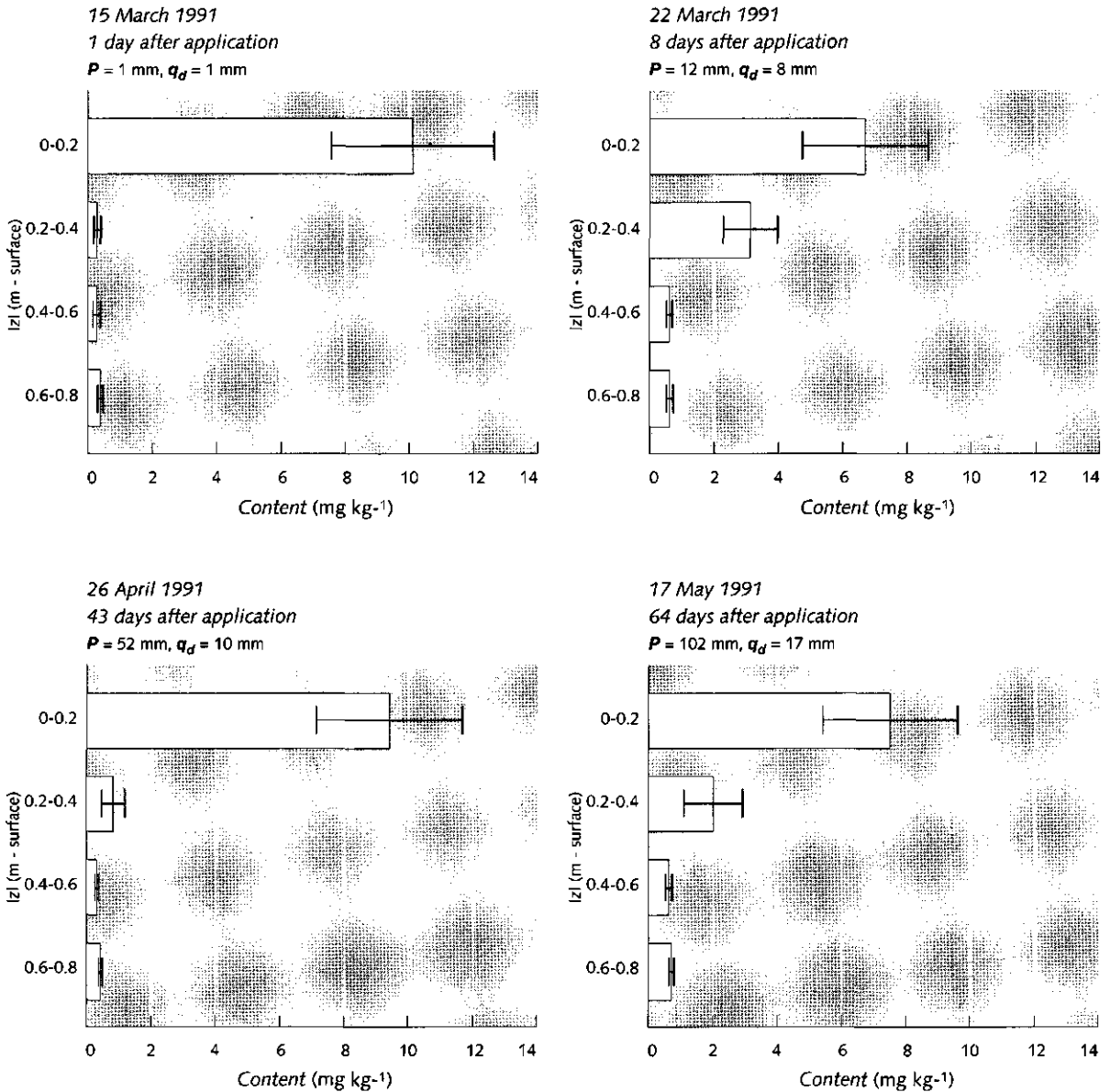


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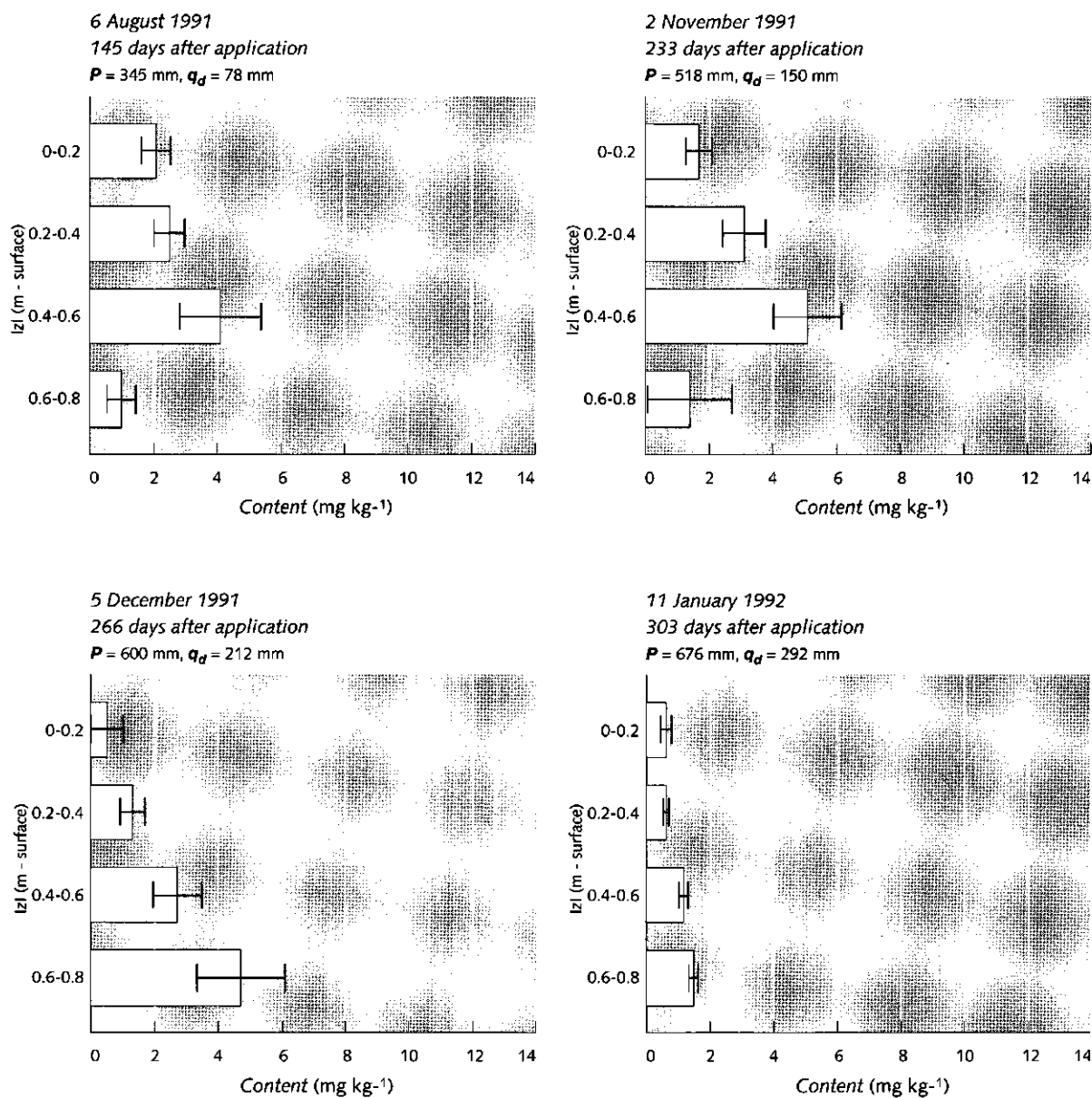


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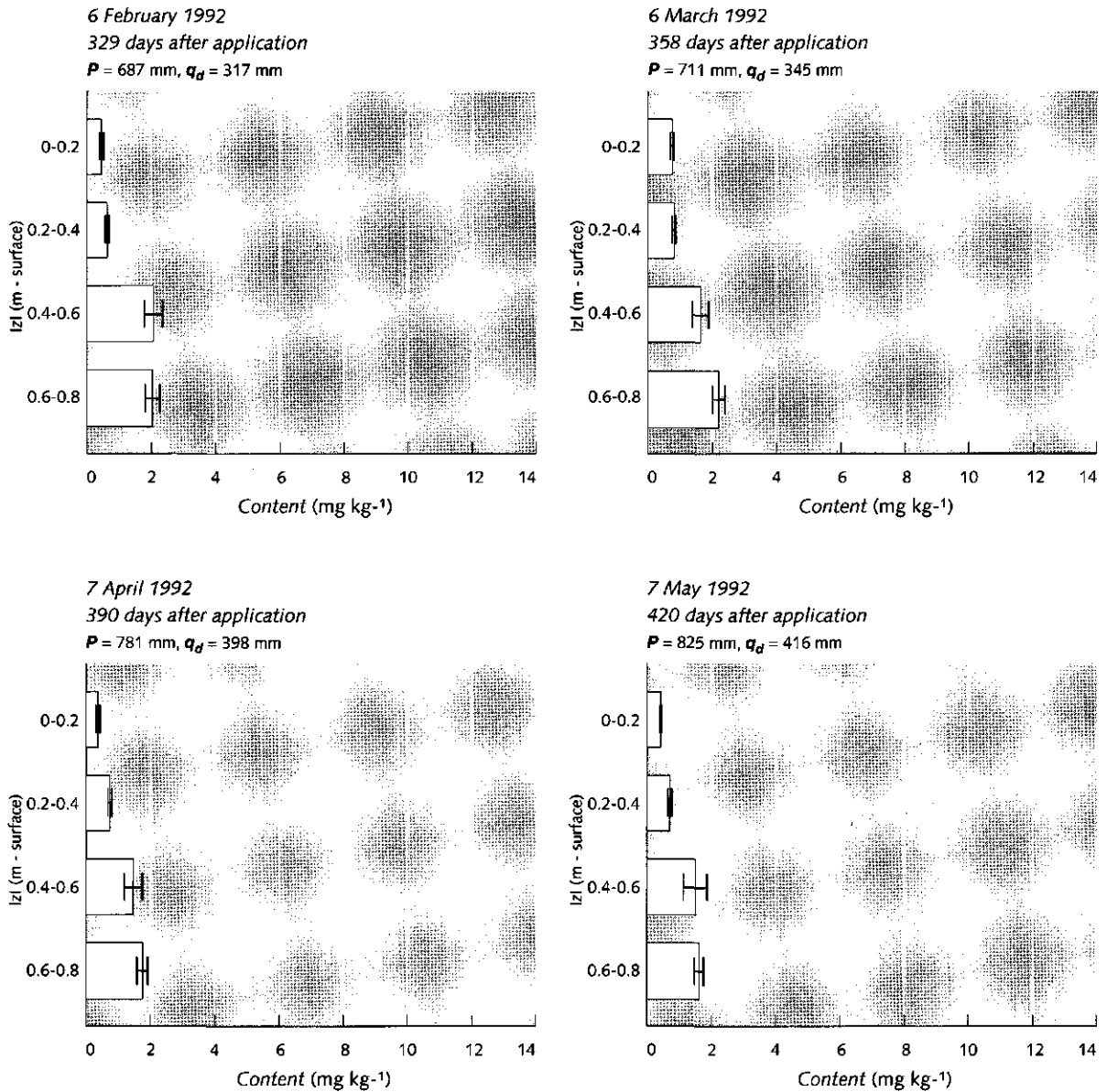


Figure 3.40. Concentration profiles of bromide in 1991/1992 at plot II of the experimental field *North-East Polder* including standard deviation (P = cumulative precipitation; q_d = cumulative drain discharge rate).

Table 3.18. Total amount of bromide compared with the cumulative precipitation, drain discharge and leached quantity of bromide at plot II of the experimental field *North-East Polder*.

Date	Days after application	Cumulative precipitation (mm)	Cumulative drain discharge (mm)	Bromide leached (kg ha ⁻¹)	Total amount of bromide in soil (kg ha ⁻¹)
21-02-1991	Initial				3.8 ± 0.4
15-03-1991	1	1	1	0.0	30.2 ± 4.2
22-03-1991	8	12	8	0.0	30.6 ± 8.0
26-04-1991	43	52	10	0.1	32.2 ± 4.4
17-05-1991	64	102	17	0.2	32.3 ± 3.2
06-08-1991	145	345	78	2.5	28.9 ± 8.5
02-11-1991	233	518	150	4.8	27.5 ± 5.0
05-12-1991	266	600	212	8.1	26.4 ± 4.9
11-01-1992	303	676	292	11.9	15.9 ± 9.1
06-02-1992	329	688	318	12.8	18.3 ± 2.1
06-03-1992	358	711	345	14.0	19.0 ± 1.8
07-04-1992	390	782	398	15.8	15.1 ± 3.1
07-05-1992	420	825	416	16.4	14.6 ± 3.2

Table 3.19. Total amount of (Z) 1,3-dichloropropene (Z-DCP) and the amount leached through the drain pipes in 1989 (plot I), 1990 (plot II) and 1990 (plot III) at the experimental field *North-East Polder*.

Date	Days after application	Cumulative precipitation (mm)	Cumulative drain discharge (mm)	Z-DCP leached (g ha ⁻¹)	Total amount of Z-DCP in soil (kg ha ⁻¹)
Plot I					
4-9-1989	Initial				0.1 ± 0.0
7-9-1989	1	0.0	0.0	0.00	66.1 ± 12.0
21-9-1989	15	44.3	4.7	0.00	0.4 ± 0.1
26-10-1989	50	111.5	21.4	0.02	0.1 ± 0.0
01-12-1989	86	142.4	40.3	0.02	
Plot II					
4-9-1990	Initial				0.1 ± 0.0
14-9-1990	1	0.0	0.0	0.00	93.7 ± 32.5
17-9-1990	4	6.2	1.7	0.02	84.5 ± 21.9
21-9-1990	8	39.0	11.2	0.03	33.8 ± 18.6
27-9-1990	14	61.0	26.1	0.15	2.9 ± 1.8
05-10-1990	22	81.8	40.3	0.22	1.5 ± 0.4
26-10-1990	43	88.9	47.8	0.23	1.1 ± 0.2
31-12-1990	109	317.8	228.9	0.33	
Plot III					
08-11-1990	1	0.6	4.5	0.01	
14-11-1990	7	34.6	22.7	0.03	
10-12-1990	33	119.8	104.6	324.3	
31-03-1991	123	251.6	230.9	1105	

winter period of 1991-1992 (November until March) approximately 60% of the amount applied leached through the drain pipes and 40% of the amount applied was still present in the deeper soil layers.

In table 3.18 both the quantity of bromide leached (kg ha^{-1}) and the content of bromide in the soil are presented. The initial content of bromide in the soil ($3.8 \pm 0.4 \text{ kg ha}^{-1}$) increased with the applied quantity (26.5 kg ha^{-1}) should correspond to the leached quantity in addition to the actual soil content. Results show that this is correct within the limits of the standard deviation.

(Z) 1,3-Dichloropropene 1989 (plot I): On 6 September 1989, DD95 was injected at plot I. Plot I was last treated with 1,3-dichloropropene in 1986. The initial content amounted to 0.1 kg ha^{-1} . These small amounts may originate from soil-bound residue that was released by distillation. Literature data indicated that the half-life time of 1,3-dichloropropene varied from 10 up to 30 days (e.g. Smelt, 1989). Therefore, the content of 1,3-dichloropropene in the soil profile was determined 1, 15 and 50 days after application (table 3.19).

After 15 days only 0.4 kg ha^{-1} was still present in the soil profile, which is only 0.5% of the dosage. After 50 days the soil content was comparable to the initial soil content. Only 0.02 g ha^{-1} leached through the drain pipes (less than 0.001% of the dose applied). The soil temperature during this period varied from 14 - 17 °C. One day after application the total amount of (Z) 1,3-dichloropropene in the soil was equal to 66.1 kg ha^{-1} . This is approximately 80% of the initial amount applied, which was equal to 81.6 kg ha^{-1} ($170 \text{ kg ha}^{-1} \cdot$

48%). At each sampling spot the total amounts of the (E) and (Z) 1,3-dichloropropene differed never more than 5%.

(Z) 1,3-Dichloropropene 1990 (plot II): On 13 September 1990, DD95 was injected at plot II. Plot II was last treated with 1,3-dichloropropene in 1987. As the results of the soil sampling in 1989 indicated that the rate of transformation was distinctly higher than expected, the soil sampling intervals were shortened substantially. The content of (Z) 1,3-dichloropropene in the soil profile was determined 1, 4, 8, 14, 22 and 43 days after application (table 3.19 and 3.20). One day after application the total amount of (Z) 1,3-dichloropropene in the soil was equal to 93.7 kg ha^{-1} . This is approximately ($93.7 / 81.6 =$) 115% of the initial amount applied. Again, differences between the (E) and (Z)-isomer were small.

After 4 days an accelerated transformation of (Z) 1,3-dichloropropene is observed. Only 0.33 g ha^{-1} leached through the drain pipes (0.004% of the dose applied). Table 3.20 presents the soil content for (Z) 1,3-dichloropropene 1, 4, 8, 14, 22 and 43 days after fumigant injection. The highest concentrations in the soil were measured 1 day (top layer), 4 days (second layer: 0.2 - 0.4 m below the soil surface), 14 days (third layer: 0.4 - 0.6 m below the soil surface) and 8 days (fourth layer: 0.6 - 0.8 m below the soil surface) after injection of (Z) 1,3-dichloropropene. Soil temperatures varied from 12 - 16 °C. The average soil temperature in the plough layer during this period was roughly 14 °C.

Both at plot I and plot II the observed total amount of (Z) 1,3-dichloropropene in the soil one day after appli-

Table 3.20. Content of (Z) 1,3 dichloropropene in the soil (in mg kg^{-1} dry soil) 1, 4, 8, 14, 22 and 43 days after fumigant injection (13-9-1990) at plot II of the experimental field *North-East Polder*.

Soil depth (m)	Days after application					
	1	4	8	14	22	43
0.0 - 0.2	21.74 ± 6.08	17.70 ± 5.06	3.28 ± 1.74	0.78 ± 0.43	0.20 ± 0.05	0.15 ± 0.02
0.2 - 0.4	10.35 ± 5.30	11.08 ± 2.43	7.98 ± 4.44	0.22 ± 0.15	0.25 ± 0.05	0.17 ± 0.02
0.4 - 0.6	0.011 ± 0.004	0.009 ± 0.003	0.046 ± 0.006	0.052 ± 0.023	0.022 ± 0.021	0.010 ± 0.008
0.6 - 0.8	0.004 ± 0.002	0.023 ± 0.019	0.031 ± 0.024	0.027 ± 0.025	0.001 ± 0.001	0.001 ± 0.000

cation deviated from the initial injected amount. These deviations (and the high standard deviations) are presumably caused by the number of soil samples for each soil layer (5) and the small surface area (3.14 cm^2) of the bore hole.

(Z) 1,3-Dichloropropene 1990 (plot III): On 7 November, DD95 was injected at plot III. Plot III was last treated with 1,3-dichloropropene in 1987. No soil samples were collected at plot III (table 3.19).

Metamitron 1990 (plot I): Results of the total amount of metamitron in the soil 1, 15 and 43 days after application are presented in table 3.16. The calculated average total amount showed high standard deviations. Metamitron was only detectable in the plough layer. In the deeper soil layers no traces were indicated. The detection limit for the soil samples amounted to 0.03 mg kg^{-1} . After 43 days only 21% of the applied dose of metamitron was detected and therefore no further soil sampling was acquired. As less than 0.005% of the dosage applied leached through the drain pipes, it may be concluded that metamitron was nearly completely transformed.

Metamitron 1991/1992 (plot II): Results of the total content of metamitron in the soil 1, 7 and 63 days after application are presented in table 3.17. Metamitron was only detected in the plough layer. In the deeper soil layers no traces were demonstrated. The detection limit for the soil samples amounted to 0.03 mg kg^{-1} . After 63 days only 13% of the dosage applied was observed and therefore no further soil sampling was required.

3.2.10.3 Results of the experimental field Eastern Flevoland

Bromide 1992/1993 (plot I): In 1992 roughly 7.7 kg ha^{-1} bromide was applied to the first experimental plot. The initial bromide content in the soil (to a depth of 1.2 m) amounted to $5.8 \pm 1.1 \text{ kg ha}^{-1}$. The movement of bromide through the soil and leaching of bromide through the drain pipes were recorded during a period of 294 days after application. One day after application of bromide, the total amount was $22.8 \pm 6.8 \text{ kg ha}^{-1}$. This is not in agreement with the initial content increased by the applied amount of bromide, which ap-

proximates $(7.7 + 5.8 =) 13.5 \text{ kg ha}^{-1}$. Moreover, increasing amounts of bromide were not only observed in the upper layer, but through all layers of the soil profile. After 1.5 mm drain discharge, the applied amount of bromide was not observed in the soil profile. However, it did not leach through the drain pipes. After approximately 1 year, only 15% of the amount applied could be traced in the drain pipes.

Bromide 1993/1994 (plot II): Due to the disappointing results in the previous year, the amount of bromide applied to the experimental field was increased to 11.7 kg ha^{-1} . The movement of bromide through the soil and leaching of bromide through the drain pipes were recorded during a period of 441 days after application. Unfortunately results were comparable to the previous year. Again, increasing amounts of bromide were not only observed in the upper layer, but through all layers of the soil profile after 23 mm of precipitation. Only 28% of the amount applied could be traced in the drain pipes. For both experimental plots the movement of bromide in the soil and the content of bromide in the successive soil layers do not seem reliable. Presumably, the extraction method and chemical analysis are highly unreliable in these clay soils. Due to the poor results of the soil sampling, the figures will not be used for the calibration of the model.

Aldicarb 1992/1993 (plot I): Soil sampling of aldicarb-sulphone and aldicarb-sulphoxide was undertaken 1, 3 and 28 days after application. No traces of aldicarb-sulphone and aldicarb-sulphoxide were retrieved in the soil profile. Results were below the detection limit, which amounted to 0.1 mg kg^{-1} . This detection limit corresponds to roughly 0.4 kg ha^{-1} . As the quantity applied amounts to only 0.5 kg ha^{-1} , it seems acceptable that no traces of aldicarb-sulphone and aldicarb-sulphoxide were demonstrated in the soil profile.

Aldicarb 1993/1994 (plot II): Soil sampling of aldicarb-sulphone and aldicarb-sulphoxide was undertaken 3 and 13 days after application. After three days the concentration of aldicarb-sulphone and aldicarb-sulphoxide in the upper soil layer (0 - 0.20 m) amounted to $0.11 \pm 0.05 \text{ mg kg}^{-1}$ and $0.75 \pm 0.15 \text{ mg kg}^{-1}$ respectively. This agrees with roughly 75% of the amount of aldicarb applied (3 kg ha^{-1}). No traces of

aldicarb-sulphone and aldicarb-sulphoxide were retrieved in the upper part of the soil (0-20 cm) after 13 days. Below 0.20 the concentration of aldicarb-sulphone and aldicarb-sulphoxide were below the detection limit. The limit amounted to 0.1 mg kg^{-1} .

3.2.10.4 Results of the experimental field Southern Flevoland

Bromide 1992/1993: On 9 June 1992 bromide was applied at the experimental field Southern Flevoland (16.8 kg ha^{-1}). The initial content of bromide (from the soil surface to 1.2 m below the soil surface) amounted

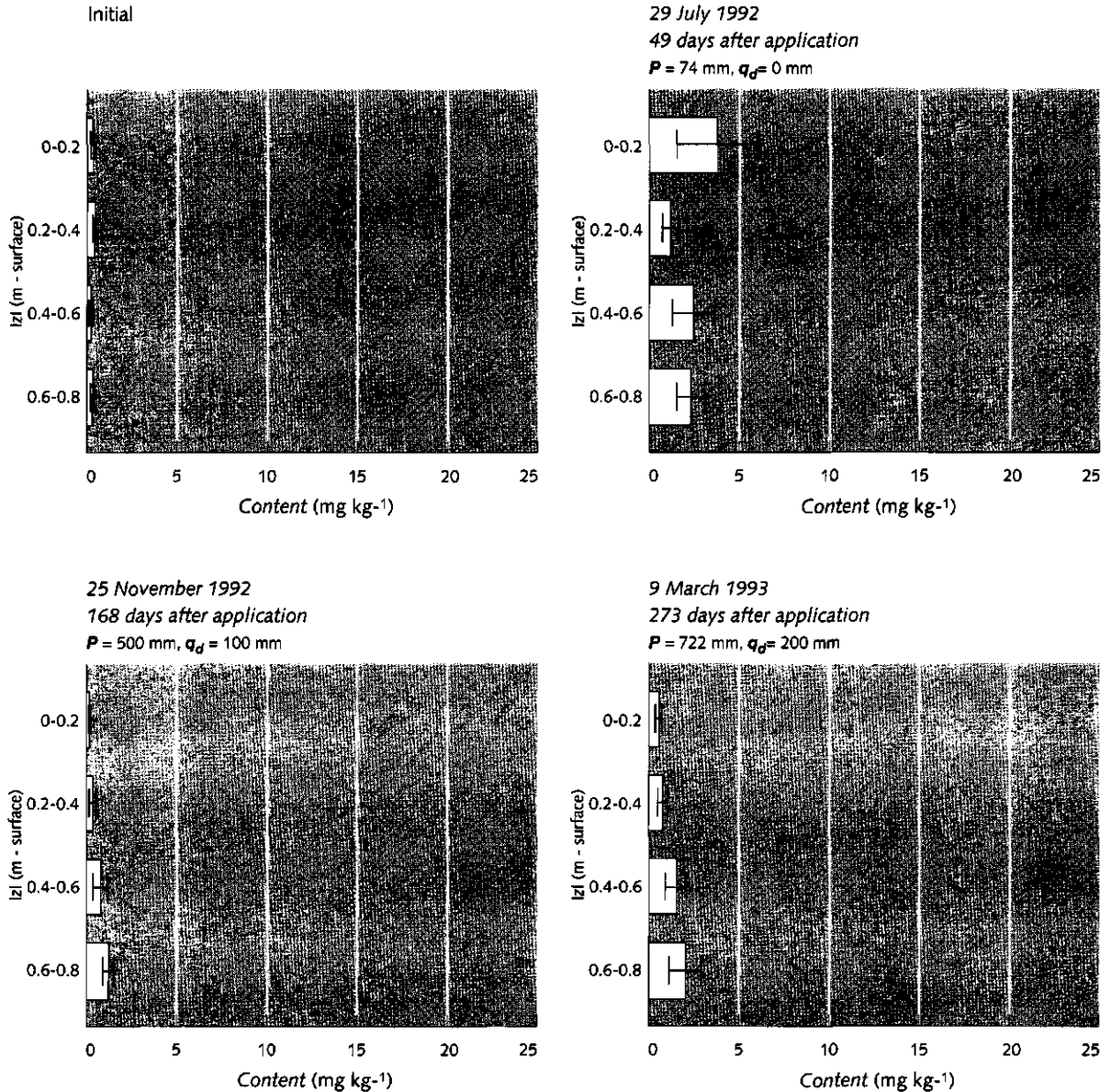


Figure 3.41. Concentration profiles of bromide in 1992/1993 at the experimental field *Southern Flevoland* including standard deviation (P = cumulative precipitation; q_d = cumulative drain discharge rate).

to $1.7 \pm 0.6 \text{ kg ha}^{-1}$. Forty-nine days after application the applied amount of bromide could be detected, mainly in the upper soil layer (figure 3.41). As no drain discharge was observed, the leached quantity of bromide was equal to 0 g ha^{-1} . 168 days after application the soil content (to a depth of 1.2 m below the soil surface) amounted to only $3.9 \pm 1.6 \text{ kg ha}^{-1}$. As only 3.25 kg ha^{-1} left the experimental field through the drain pipes, the deficiency could be calculated at roughly 11.4 kg ha^{-1} ($16.8 + 1.7 - 3.9 - 3.25 \text{ kg ha}^{-1}$).

It is possible that part of this deficiency can be explained by the root uptake of bromide by the apple trees. After 273 days approximately 16% of the bromide applied left the experimental field through the drain pipes. These figures were adjusted for the background concentrations.

Bromide 1993/1994: About a year after the first application, bromide was applied at the same plot. The amount of bromide applied to the experimental field was doubled to 33.6 kg ha^{-1} . The movement of bromide through the soil and leaching of bromide through the drain pipes were recorded during a period of 435 days after application. Results of the soil sampling on six different dates are presented in table 3.21. Figure 3.42 shows the movement of bromide through the soil. Both figure 3.42 and table 3.21 show that it is obvious

that the movement and leaching of bromide are directly related to the precipitation surplus and mainly take place during the winter period. During the winter period of 1993-1994 (November until March) approximately 40% of the amount applied leached through the drain pipes and 30% of the amount applied was still present in the deeper soil layers. The deficiency (approximately $30\% \approx 10 \text{ kg ha}^{-1}$) can be explained by the root uptake of bromide by the apple trees.

Simazine 1992/1993/1994: During the period July 1992 until July 1994 the soil sampling process was executed 8 times. With the exception of 20-04-1993, simazine was found during each of these occasions, but only detected in the upper part of the soil profile (0 - 0.2 m below the soil surface). During the summer period the average concentrations in the upper part of the soil amounted to approximately 0.05 mg kg^{-1} dry matter. However, in the early spring (before application of simazine) the average concentrations in the upper part of the soil amounted to 0.02 mg kg^{-1} dry matter. Table 3.22 indicates that only roughly 10% of the amount applied (table 3.14) could be detected in the upper part of the soil. Combination of figure 3.37 and table 3.22 shows that leaching of simazine mainly takes place during the summer and autumn, when concentrations of simazine in the upper soil layer are higher than during the early spring.

Table 3.21. Total amount of bromide in the soil profile compared with the cumulative precipitation, drain discharge and leached quantity of bromide at the experimental field *Southern Flevoland*.

Date	Days after application	Cumulative precipitation (mm)	Cumulative drain discharge (mm)	Bromide leached (kg ha^{-1})	Total amount of bromide (kg ha^{-1})
initial					1.7 ± 0.6
29-07-1992	49	74	0	0.00	15.0 ± 6.8
25-11-1992	168	500	100	3.25	3.9 ± 1.6
09-03-1993	273	722	200	5.98	7.7 ± 2.9
27-04-1993	7	2	0	0.00	34.0 ± 5.2
11-06-1993	52	88	11	0.32	33.8 ± 10.8
22-07-1993	93	203	26	0.69	32.8 ± 7.4
13-10-1994	176	583	150	5.28	26.2 ± 15.7
03-03-1994	317	950	347	13.13	8.8 ± 7.4
29-06-1994	435	1280	570	19.63	10.2 ± 5.1

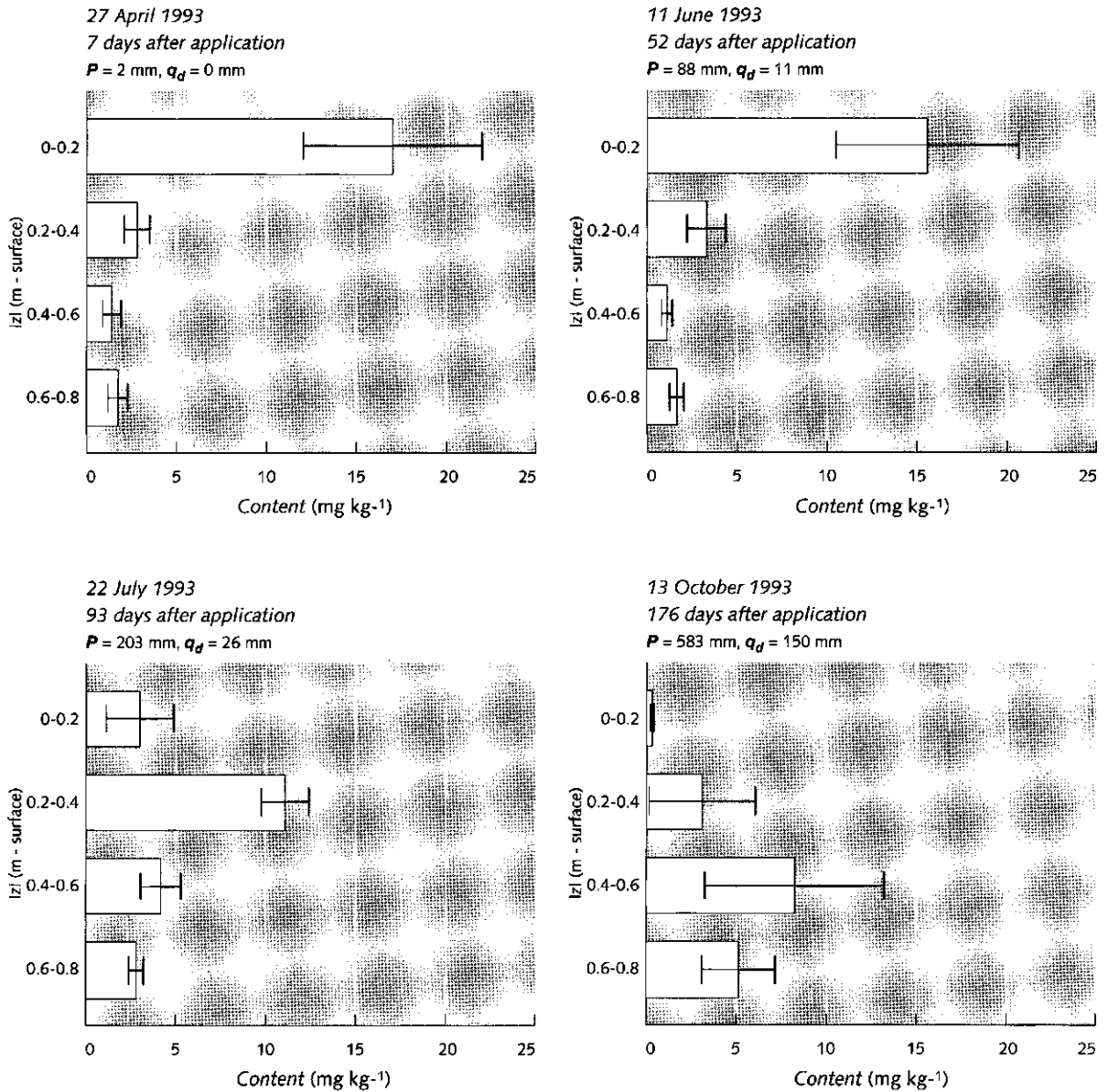


Figure 3.42. Continued on next page.

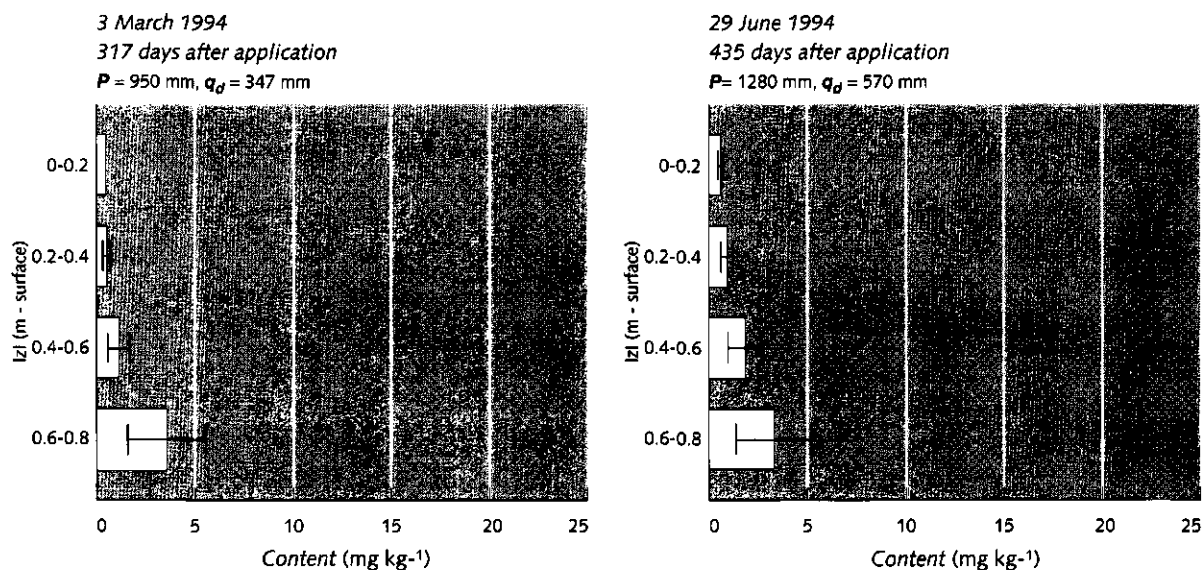


Figure 3.42. Concentration profiles of bromide in 1993/1994 at the experimental field *Southern Flevoland* including standard deviation (P = cumulative precipitation; q_d = cumulative drain discharge rate).

Table 3.22. Total amount of simazine in the soil (0 - 1.2 m) and the amount of simazine leached through the drain pipes at the experimental field *Southern Flevoland* (N.D. = not detected).

Day of application (amount applied)	Day of soil sampling	Total amount of simazine (g ha ⁻¹)	Cumulative amount of simazine leached (g ha ⁻¹)
04-04-1992 (0.25 kg ha ⁻¹) 09-06-1992 (0.50 kg ha ⁻¹)			(From 4 - 4 - 1992)
	29-07-1992	58 ± 18	1.45
	25-11-1992	61 ± 19	1.50
	09-03-1993	12 ± 9	1.50
	02-04-1993	24 ± 16	1.50
21-04-1993 (0.75 kg ha ⁻¹)			(From 21 - 4 - 1993)
	20-04-1993	N.D.	0.00
	11-06-1993	60 ± 22	0.16
	22-07-1993	48 ± 5	0.32
	13-10-1993	19 ± 7	0.56

3.2.11 Preferential flow

Preferential flow paths in the soil can cause an accelerated movement of solutes (and pesticides) in the unsaturated-saturated soil system. Rapid transport of solutes (and pesticides) can be caused by flow through

cracks in structured soils, unstable wetting fronts and funnel flow. If preferential flow paths are present in the soil, models for solute transport in the soil, based on the Richards' equation and the convection-dispersion equation, supplemented with sorption and transforma-

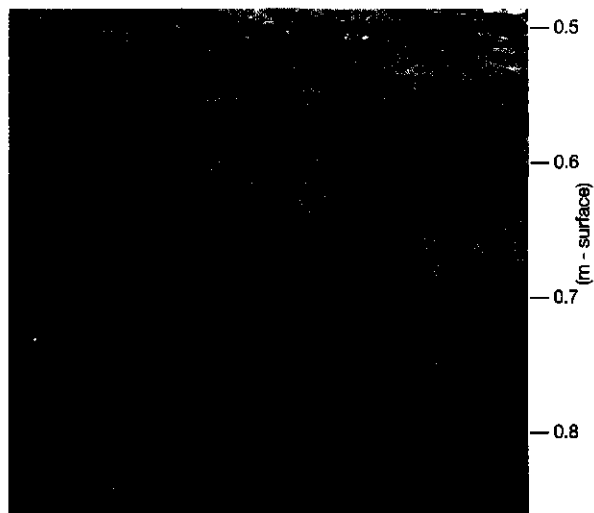


Photo 3.7. Top view (left) and side view (right) of the soil profile at the experimental field North-East Polder. The soil is aerated along the former root channels of reed. These channels are possibly responsible for preferential flow.

tion characteristics for pesticide transport (chapter 2), are unable to predict this fast transport. Then preferential flow should be included in the model. For the North-East Polder and Eastern Flevoland, field experiments were executed to demonstrate preferential flow paths. Several techniques to visualize preferential flow have been introduced (e.g. Bouma et al., 1981, Bouma et al., 1982, Bowman, 1984, Van Ommen et al., 1988). The method applied depends among other factors on the colour of the soil and sorbing capacity of the soil. For soils with a high organic matter content, adsorbing materials, like most dyes, are less suitable as tracers.

North-East Polder: The soil of the experimental field in the North-East Polder can be classified as a non-structured soil. In these soils preferential paths through the soil matrix may occur at any depth depending upon the depth of soil horizons. In order to visualize preferential flow, the ion iodide (I^-) was used as a tracer. Iodide has the same non-sorbed properties as the often used soil water tracers chloride (Cl^-) and bromide (Br^-). However, iodide cannot be used in mass balance studies, as it oxidizes under aerobic field conditions. After application of the iodide-solution, horizontal cross-sections of the soil were obtained by removing slices of the soil. At each depth the soil was powdered

with dry starch and treated with bleaching liquid. After oxidation of the iodide, it was visualized by starch, forming a coloured dark blue complex.

At the experimental field in the North-East Polder an iodide-solution was applied at three different plots of 1 m^2 . After roughly 50 mm, 100 mm and 150 mm of precipitation surplus, the soil profile of these plots was horizontally excavated and the applied starch visualized. As the precipitation surplus increased the iodide-solution slowly moved downwards, but at all three plots no preferential flow paths could be visualized.

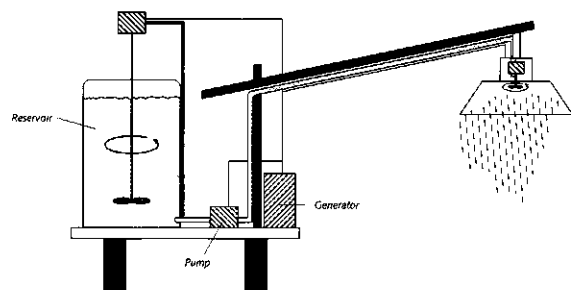
However, preferential flow was recognized at the experimental field in the North-East Polder. Accelerated leaching of the inert ion bromide and pesticide metamitron were measured in the subsurface drainwater. The concentration level of bromide in the drain pipes, which was used as a tracer and applied in the early spring together with the pesticide metamitron, increased tremendously after only 10 mm of subsurface drain discharge. The preferential flow is presumably induced by the former root channels of reed, which was sown after the reclamation of the North-East Polder (photo 3.7). Underneath the plough layer the former root channels are still present and function as



Figure 3.43. Outline of the rainfall-simulator.

small drain pipes. The cross-section of the channels is approximately 0.2 to 1 cm. Due to the predominantly vertical direction of the channels, the horizontal permeability is not influenced by the former reed channels.

Eastern Flevoland: The soil of the experimental field in Eastern Flevoland can be classified as structured, heavy clay soil (e.g. subsection 2.3.2 and 3.1.1.2). Here, preferential stream paths through the soil matrix may occur at any depth, mainly depending upon the presence of cracks. Normally, these cracks occur below the plough layer, are irreversible and interconnected. If the storage capacity of the plough layer is exceeded, the water flows along the walls of the clay columns. The soil moisture content of the clay columns is hardly affected by this film flow and remains practically unchanged.



To simulate the process of leaching during a winter period, a rainfall simulator was used. The rainfall simulator was installed in November 1993, after the harvest of the potatoes. It imitates rain-showers; the intensity and the size of the drops can be varied (figure 3.43). The intensity of the applied irrigation water should not exceed the infiltration capacity of the soil. Formation of puddles should be prevented. The size of the plot irrigated by the rainfall simulator amounted to 2-3 m².

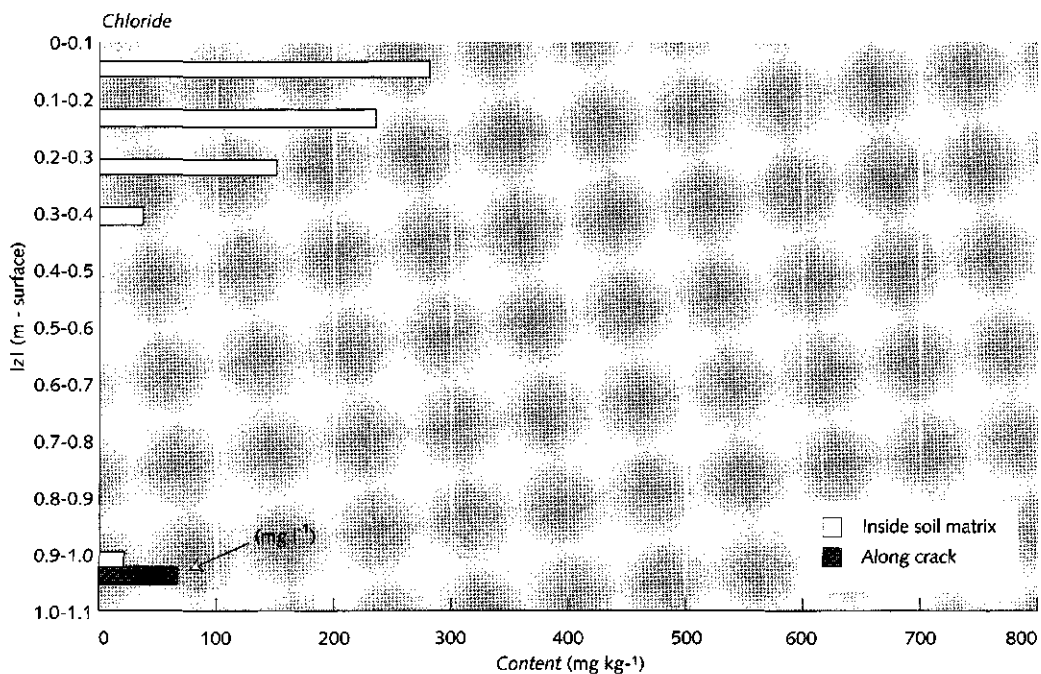
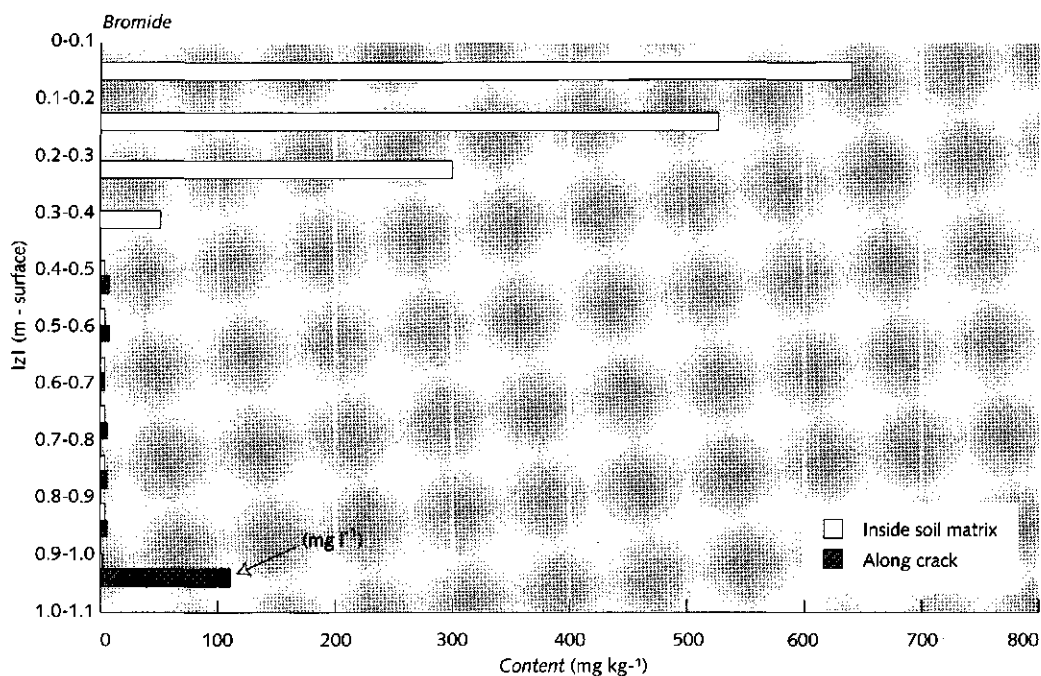


Figure 3.44. Content of bromide and chloride in the soil after application of 250 mm water containing 3 gr l⁻¹ bromide and 1.3 gr l⁻¹ chloride applied with the rainfall simulator at the experimental field *Eastern Flevoland*.

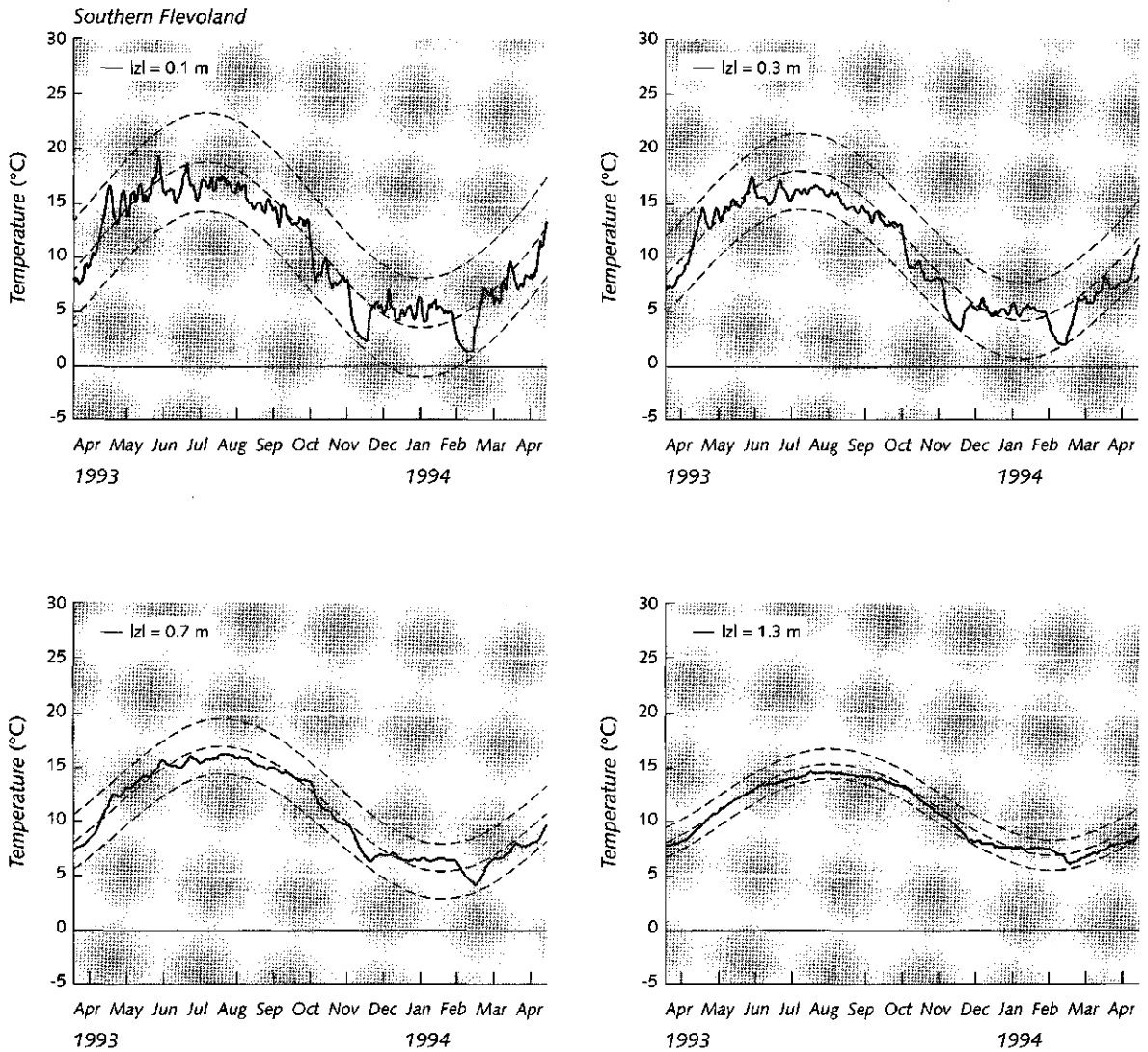


Figure 3.48c. Temperature of the soil at different depths at the experimental field. *Southern Flevoland* (April 1993 until April 1994). The dotted lines present $T(|z|, t) \pm T_{dev}$ (equations 2.56 and 3.1 with $T_{dev,max}$, T_m , T_a and d according to table 3.23; $\omega = 2\pi/365$, $t = 0$ at Julian day number 105 and $a_{dev} = 1 \text{ m}^{-1}$).

Chapter 4

Calibration of the extended model *SWACRO*

Calibration of the extended model *SWACRO*

The extended version of the model *SWACRO*, as presented in chapter 2, was calibrated using the results of the three field experiments situated on cracked clay and loamy sand in the IJsselmeerpolders. The calibration was performed in three steps:

Calibration of soil water fluxes. Daily input on precipitation rate (including irrigation), potential evapotranspiration rate, soil cover and water uptake by roots as a function of soil depth are needed for the calculation of soil water fluxes. If the soil characteristics, lower boundary conditions (e.g. seepage) and initial moisture content are known, the moisture content per soil layer, groundwater levels and drain discharge can be calculated. These values should correspond to the observed field data. During the calibration of soil water fluxes, the anisotropic factor and parameters for the lower boundary conditions were optimised. Calibrations of the soil water fluxes are presented in subsection 4.1.1 (North-East Polder), 4.2.1 (Eastern Flevoland) and 4.3.1 (Southern Flevoland).

Calibration of the concentration of conservative solutes in the drainage water and in the soil profile. If soil water fluxes can be calculated accurately and if the simulated values correspond to the observed values, an attempt can be made to simulate the solute fluxes of inert ions like bromide. Apart from the applied load, date of application, estimated dispersion length and (if necessary) parameters for preferential flow, no additional input is needed. The results of the simulation model are compared with concentration profiles of the solute sampled at certain time intervals and the concentration of the solute in the drainage water. If the simulated values do not correspond to the observed values, this could possibly be caused by preferential stream paths. For all experimental fields, field measurements were performed to locate these paths, if pre-

sent. During the calibration of bromide fluxes, the dispersion length and parameters for preferential flow (if necessary) were optimised. Results of the calibrations of the concentration of bromide in the drainage water and the concentration profiles of bromide are presented in subsection 4.1.2 (North-East Polder), 4.2.2 (Eastern Flevoland) and 4.3.2 (Southern Flevoland).

Calibration of the concentration of pesticides in the drainage water and transformation of pesticides. Finally an attempt has been made to simulate the pesticide movement in the soil. Due to sorption, which retards the movement of the pesticide and transformation, simulation of the transport of pesticides is even more complicated than simulation of the transport of conservative solutes. Transformation of the pesticide partly depends on the soil temperature and soil moisture content. To calculate the pesticide fluxes, pesticide transformation, concentration profiles and concentration in the drainage water, additional input is needed on daily values of soil temperatures at different depths, time of application of the pesticides, the amount applied and the sorption characteristics. Results of the calibrations of the concentration of pesticides in the drainage water and the transformation are presented in subsection 4.1.3 (North-East Polder), 4.2.3 (Eastern Flevoland) and 4.3.3 (Southern Flevoland).

4.1 North-East-Polder

4.1.1 Water flow

The collection of data at the experimental field in the North-East Polder has been presented in section 3.2. The data from the experimental field were either used as input for the model *SWACRO* or as observed values which were compared with calculated values.

Table 4.1. Set of the most important equations used for the description of water flow.

$$C(h) \frac{\delta h}{\delta t} = \frac{\delta}{\delta z} \left[K(h) \frac{\delta h}{\delta z} + 1 \right] - S \quad 2.4$$

$$C(h) = \frac{\delta \theta}{\delta h} \quad 2.5$$

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m} \quad 2.12$$

$$K(h) = K_s \frac{[(1 + |\alpha h|^n)^m - |\alpha h|^{n-1}]^2}{(1 + |\alpha h|^n)^m (\lambda + 2)} \quad 2.14$$

$$E_p = E_{sp} + E_{tp} \quad 2.16$$

$$E_p = f E_r \quad 2.18$$

$$E_{sp} = E_p \exp(-0.6 LAI) \quad 2.19$$

$$LAI = aS_c + bS_c^2 + cS_c^3 \quad 2.20$$

$$q_s = E_s - (P - E_i) \quad 2.21$$

$$\sum E_s = \sum E_{sp} \quad \text{for } \sum E_{sp} \leq \beta^2 \quad 2.22$$

$$\sum E_s = \beta \sqrt{\sum E_{sp}} \quad \text{for } \sum E_{sp} > \beta^2 \quad 2.22$$

$$E_i = a_i LAI \left(1 - \frac{1}{1 + \frac{P S_c}{a_i LAI}} \right) \quad 2.23$$

$$S(h) = \alpha(h) S_{\max} \quad 2.25$$

$$S_{\max} = \frac{E_{ge}}{|z_r|} \quad 2.26$$

$$q_b = \frac{h_{pl} - h_{phr}}{\gamma} \quad 2.28$$

$$q_d = \frac{8 K_b d_{eq} h_m + 4 K_r h_m^2}{L^2} \quad 2.29$$

For the calculation of water flow, the model *SWACRO* (Chapter 2) was used. The most important equations used for the description of water flow are summarized in table 4.1. To solve these equations the following input data are used:

Numerical method: To solve the tridiagonal system of equations, a stop criterium has to be defined according

to equation 2.11. The values for the relative tolerance and the absolute tolerance are presented in table 4.2.

Soil physical properties: The soil profile of the experimental field in the North-East Polder has been presented in subsection 3.1.1.1. The soil profile was subdivided in 6 compartments of 0.05 m (0-0.3 m) and 9 compartments of 0.1 m (0.3 - 1.2 m), with three different soil physical functions (figure 4.1). The soil physical functions are described by a soil moisture retention curve and the relationship between the hydraulic conductivity and the pressure head according to Genuchten (equation 2.12 and 2.14). The parameters for the soil water retention curve and the hydraulic conductivity curve, which were used for the model calculations, were determined in the laboratory and are presented in chapter 3 (table 3.2).

Upper boundary conditions: In order to calculate the soil water fluxes at the upper boundary, the daily pre-

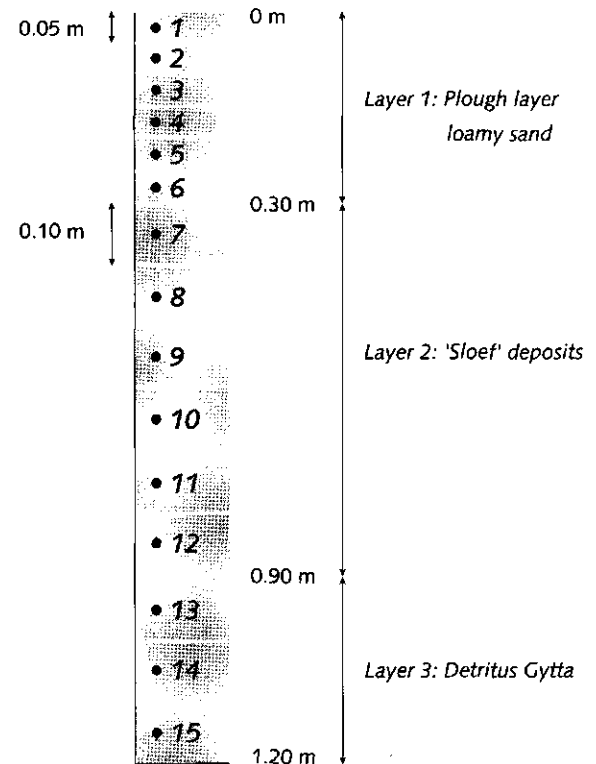


Figure 4.1. Schematisation of the soil profile.

Table 4.2. Input parameters to determine soil water fluxes for the experimental field *North-East Polder*.

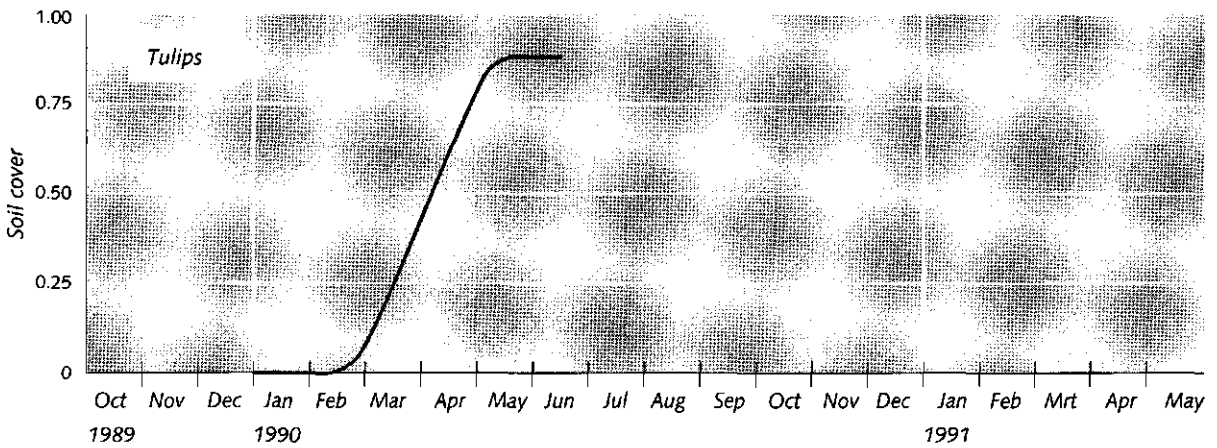
NUMERICAL METHOD			
Symbol	Parameter	Value	Equation
<i>reltol</i>	Relative tolerance	1.10^{-2}	2.11
<i>abstol</i>	Absolute tolerance	1 cm	2.11
UPPER BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
<i>P</i>	Precipitation	Daily values	
<i>E_r</i>	Reference evapotranspiration	Daily values	2.17
<i>f</i>	Crop factor	Decade values (table 4.3)	2.18
<i>a</i>	Regression coefficients for tulips	5.3	2.20
<i>b</i>		-11.5	
<i>c</i>		11.0	
<i>a</i>	Regression coefficients for grass	6.4	2.20
<i>b</i>		-17.7	
<i>c</i>		16.1	
<i>S_c</i>	Soil cover	Daily values (figure 4.2)	2.20
β	Parameter for actual soil evaporation	$1.7 \text{ mm}^{0.5}$	2.22
<i>a_i</i>	Parameter representing the specific property of the leaves	0.28	2.23
$ z_r $	Lower limit of the root zone	Daily values (figure 4.3)	2.26
$ h_1 $	Values of the soil water pressure head which determine	10 cm	2.25
$ h_2 $	the dimensionless sink term variable for water extraction	15 cm	
$ h_3 $	by roots, α for grass and tulips	400 cm	
$ h_4 $		600 cm	
$ h_5 $		16000 cm	
LATERAL BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
<i>L</i>	Drain spacing	4 m	2.29
$ z_{dr} $	Drain depth	0.85 m	
<i>u</i>	Wet perimeter	0.30 m	2.29

cipitation and daily reference evapotranspiration are presented as input files. The reference evapotranspiration according to Makkink is obtained from a nearby meteorological station in Lelystad. It is multiplied by a crop factor to obtain the potential evapotranspiration. The crop factors for grass and tulips are presented in table 4.2. During the winter period (October until February) and the periods during which there is no crop in the field, the potential evapotranspiration is assumed to be equal to the reference crop evapotranspiration. Thus, the factor *f* is equal to 1.

The partitioning of the potential evapotranspiration in potential soil evaporation and potential transpiration depends on the Leaf Area Index. The Leaf Area Index is a function of the soil cover according to equation 2.20. The values for the regression coefficients used in the model are presented in table 4.2.

The soil cover as function of time is presented in figure 4.2. The tulips were planted in October. In early spring the tulips started to grow and reached their full growth in May. At this time the soil cover amounted to ap-

Experimental plot I



Experimental plot II

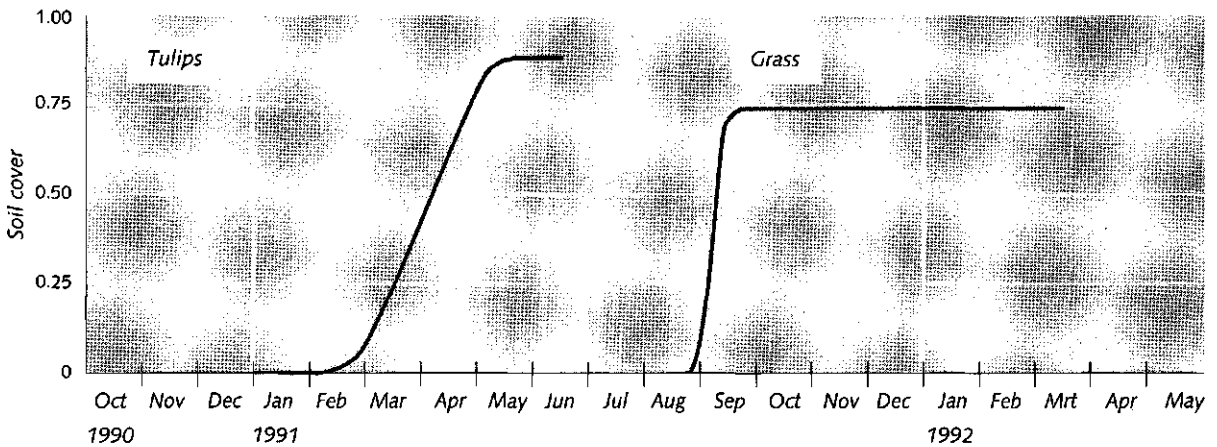


Figure 4.2. Soil cover of tulips and grass as function of time for the experimental field North-East Polder.

Table 4.3. Values for the dimensionless crop factor, f , for grass and tulips.

Month	March			April			May			June			July			August			September		
Decade	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Grass	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9
Tulips	-	-	-	0.9	0.9	1.0	1.0	1.1	1.1	1.1	0.9	0.6	-	-	-	-	-	-	-	-	-

proximately 0.8. In the beginning of June, the tulips started to wither. The tulips were harvested between the middle of June and the middle of July, depending on the weather. After harvesting the tulips, plot II was ploughed and grass was sown. After the winter period the experimental plots were ploughed again. No crop was present at plot III during the time of the field experiment.

The water uptake by the roots of the tulips is assumed to be homogenously distributed with depth, according to equation 2.26. At the experimental plot in the North-East Polder a number of observations were made on rooting depth. The lower limit of the root zone was examined at the experimental plot. Due to soil compaction at a depth of 0.3 m below soil surface, hardly any roots were observed below this depth. The maxi-

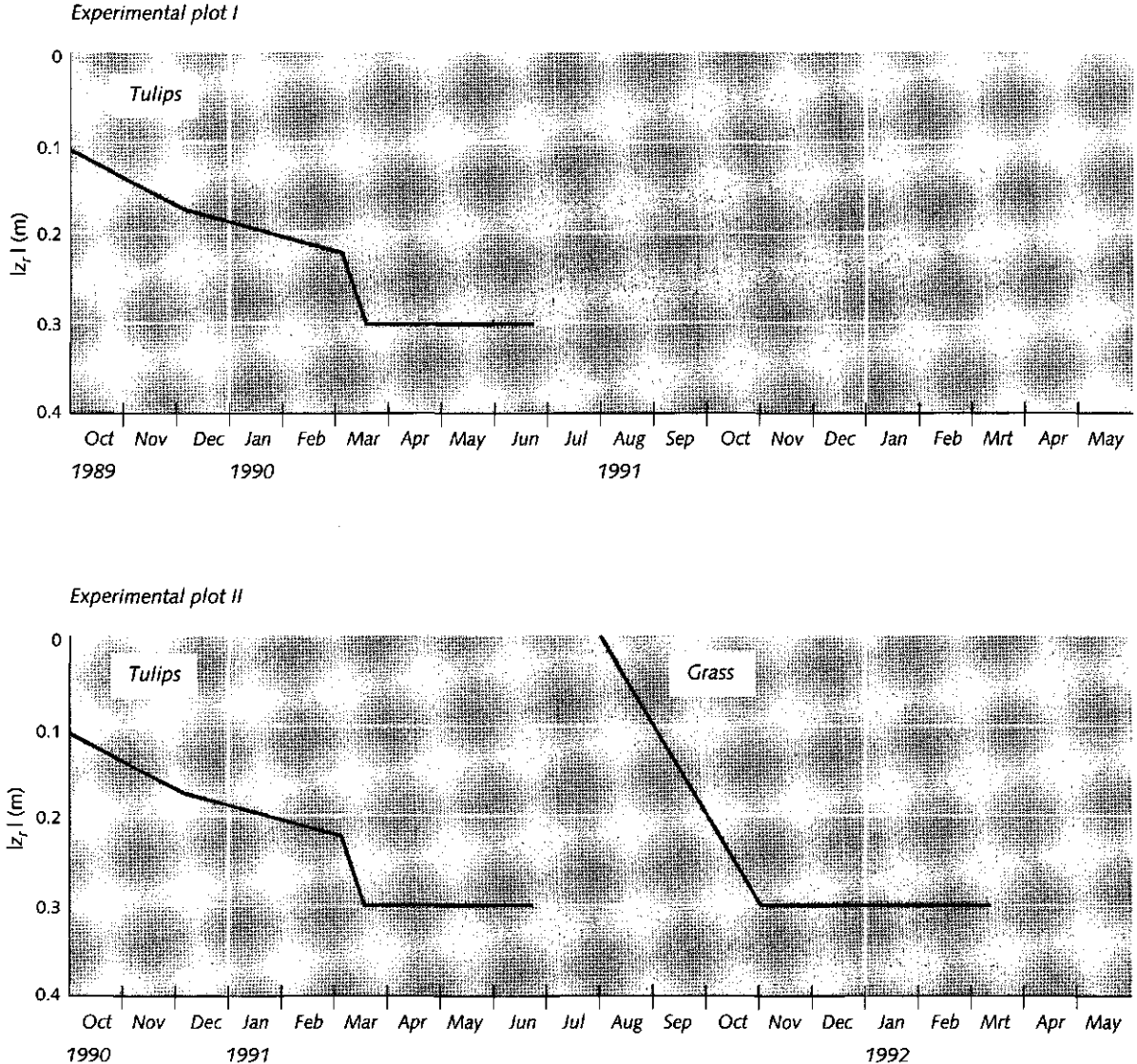


Figure 4.3. Maximum rooting depth L_r of tulips and grass as function of time for the experimental field North-East Polder

mum rooting depth as a function of time is presented in figure 4.3.

The function for the volumetric sink term depends on the pressure head. Under non-optimal conditions, i.e. either too dry or too wet, S_{max} is reduced by means of the pressure head (h) dependent α -function (equation 2.25; figure 2.4). For tulips and grass, the values of $|h_1|$, $|h_2|$, $|h_3|$ and $|h_4|$ are presented in table 4.2.

The actual soil evaporation is described according to Boesten (equation 2.22). For the loamy clay soil of the experimental field in the North-East Polder, Boesten (1986) carried out an experiment to obtain the value of β . He reported an average β value of $1.7 \text{ mm}^{0.5}$; upper and lower limits (which were obtained by least-squares linear regression approximation) were found to be 2.0 and 1.4 (table 4.2). The evaporation losses by interception were calculated according to Braden (1985) and this is a function of the Leaf Area Index, the soil cover, the precipitation and a parameter representing the specific properties of the leaves (a_i) (equation 2.23). For grass and tulips the parameter a_i is unknown, but generally a value of 0.28 is assumed (Braden, 1985). Minor changes in the water balance could be observed if this parameter was changed within a range from 0.1 up to 0.5.

Lower boundary conditions: At the experimental field North-East Polder, the magnitude of the flux at the lower boundary is dependent on the drainage resistance of the subsoil and the equilibrium value of the hydraulic head in the first aquifer. The lower boundary conditions were described in subsection 2.1.5 and solved according to equation 2.28. The model was calibrated for the hydraulic head in the Pleistocene subsoil and the drainage resistance.

Lateral boundary conditions: For the saturated zone both horizontal and vertical groundwater flow is taken into account. Values for the drain spacing, drain depth, wet perimeter are summarized in table 4.2. The drainage flux was calculated according to the Hooghoudt equation (equation 2.29). The anisotropic factor (horizontal saturated conductivity divided by the vertical saturated conductivity) is unknown. In spite of the relatively short distance between the drain pipes, the

groundwater elevation between the drain pipes may be as high as 0.4 m. The anisotropic factor was determined during calibration.

Optimization criteria: For the calibration of the model, the observed groundwater levels and the observed drain discharges were used. As data on the observed soil moisture content were limited and relatively unreliable, the model was not calibrated for the soil moisture content. The registration of the groundwater levels between the drain pipes was carried out with a frequency of one reading per hour (subsection 3.2.6). The daily groundwater levels were taken as an average of the hourly measurements. The drain discharge was measured at intervals by using the discharge proportional sampler (subsection 3.2.8). The daily drain discharge was obtained by adding the water volumes during a day.

The unknown parameters are the equilibrium value of the hydraulic head in the Pleistocene sand (h_{pi} ; equation 2.28), the drainage resistance of the subsoil (γ ; equation 2.28) and the anisotropic factor ($= K_h K_v^{-1}$). The vertical saturated permeability (K_v) is equal to the weighted average of the saturated permeability of the layers above the drain pipes (K_s ; table 3.2) and horizontal saturated permeability (K_h) is equal to K_T (equation 2.29). These parameters were optimized, using measured groundwater levels and drain discharges.

In order to obtain the best fit between the observed and calculated groundwater levels and drain discharge, the unknown parameters were optimized by minimizing the objective function Root-Mean-Square for groundwater levels (RMS_{gwl}) which is given by the equation:

$$RMS_{gwl} = \sqrt{\frac{1}{n} \sum_{i=1}^n (gwl_{obs,i} - gwl_{mod,i})^2} \quad 4.1$$

where:

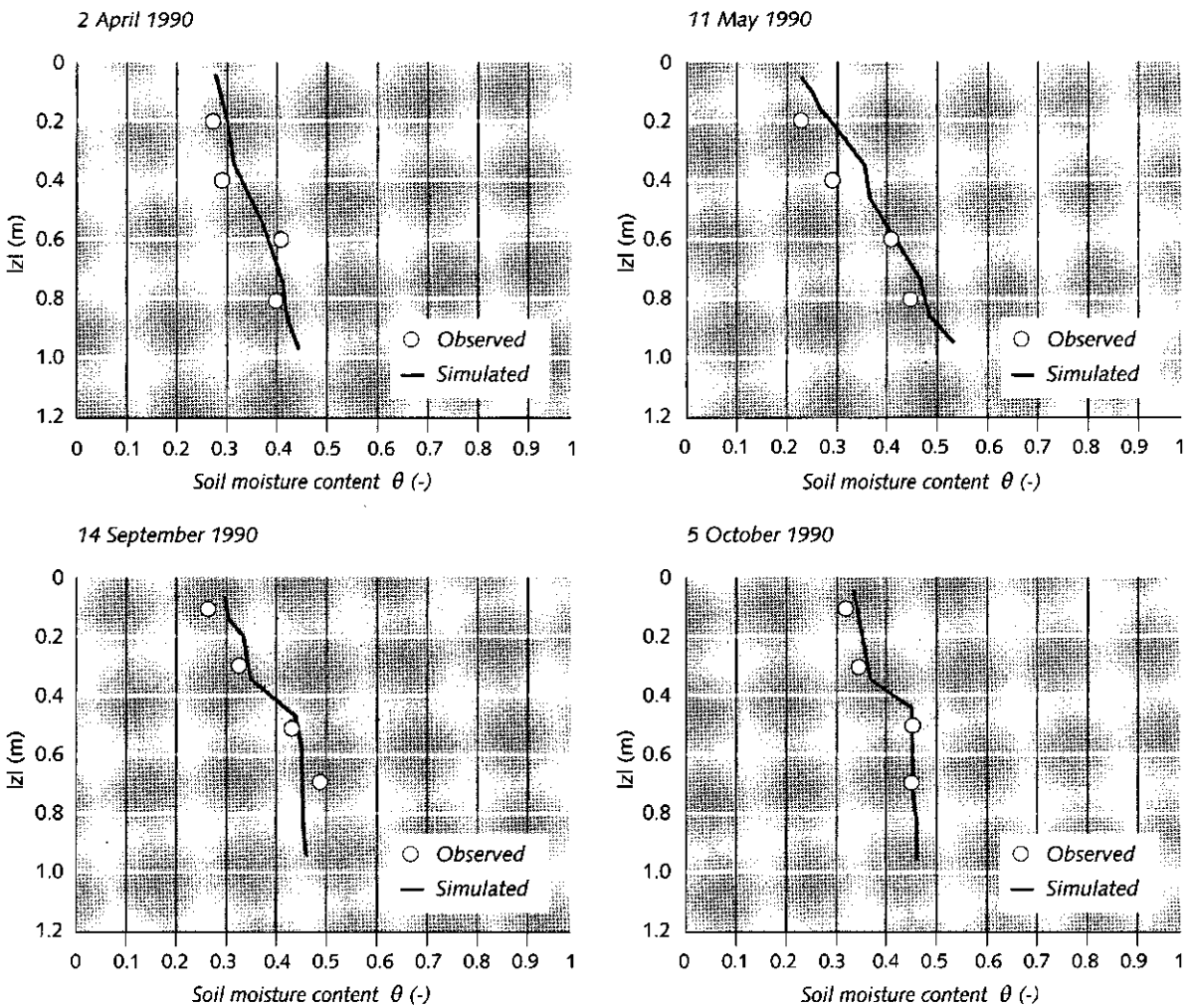
$gwl_{obs,i}$ = observed groundwater level at day i (L)

$gwl_{mod,i}$ = calculated groundwater level at day i (L)

RMS was selected as an objective function both for groundwater levels and drain discharges. The closer RMS reaches the value 0, the better the fit between the observed and calculated values.

Table 4.4. Optimum values for the object function Root-Mean-Square.

Object function	Optimum values				
	Υ (days)	h_{pt} (m)	$K_h K_v^{-1}$ (-)	RMS_q (mm d ⁻¹)	RMS_{gwl} (cm)
RMS_q	75	-0.90	7	0.8	6.5
RMS_{gwl}	50	-0.90	3	0.6	5.4


Figure 4.4. Observed and simulated soil moisture content at some selected days for the experimental field North-East Polder.

The optimum values of the *RMS* for the groundwater levels and the drain discharges are presented in table 4.4. The results of the model *SWACRO* are extremely sensitive to the lower boundary conditions, especially with respect to the hydraulic head in the Pleistocene subsoil (h_{pl}). For instance, if $h_{pl} = -0.95$ m (with $\Upsilon = 75$ days and $K_h K_v^{-1} = 7$), RMS_q and RMS_{gwl} are equal to 0.9 mm d^{-1} and 9.6 cm respectively. In comparison with h_{pl} , a 10% modification of the drainage resistance of the subsoil (Υ) and anisotropic factor ($K_h K_v^{-1}$) has a small impact on the value of RMS_q and RMS_{gwl} ($< 0.05 \text{ mm d}^{-1}$ and 0.5 cm respectively).

As the optimum values of the *RMS* for the groundwater levels and the drain discharge disagree, either one of the optimization functions is selected. One of the criteria for determining which optimization function to use to fix the optimum value is the quality of the observed data. For the soil water fluxes the *RMS* for drain discharge was selected as objective function. If

$\Upsilon = 75$ days, $h_{eq} = -0.90$ m and $K_h K_v^{-1} = 7$, the value of the object functions RMS_{gwl} amounted to 6.5 cm .

Results: The results of the calibration of the water flow for $\Upsilon = 75$ days, $h_{pl} = -0.90$ m and $K_h K_v^{-1} = 7$ are shown in figure 4.4, 4.5, 4.6 and 4.7.

Figure 4.4 shows the observed and calculated soil moisture content from the soil surface down to a depth of 0.8 m for a number of selected data. In general, the observed soil moisture content tends to be lower than the calculated soil moisture content, particularly during the summer periods. However, the deviation is relatively small. The soil moisture content at a depth of 0.1 m varies from 0.2 during dry periods to 0.35 during wet periods. At a depth of 0.8 m , the soil moisture content is nearly constant at 0.45 .

The change in water storage (ΔW) for a given period of time (Δt) is calculated according to equation 2.1. If the

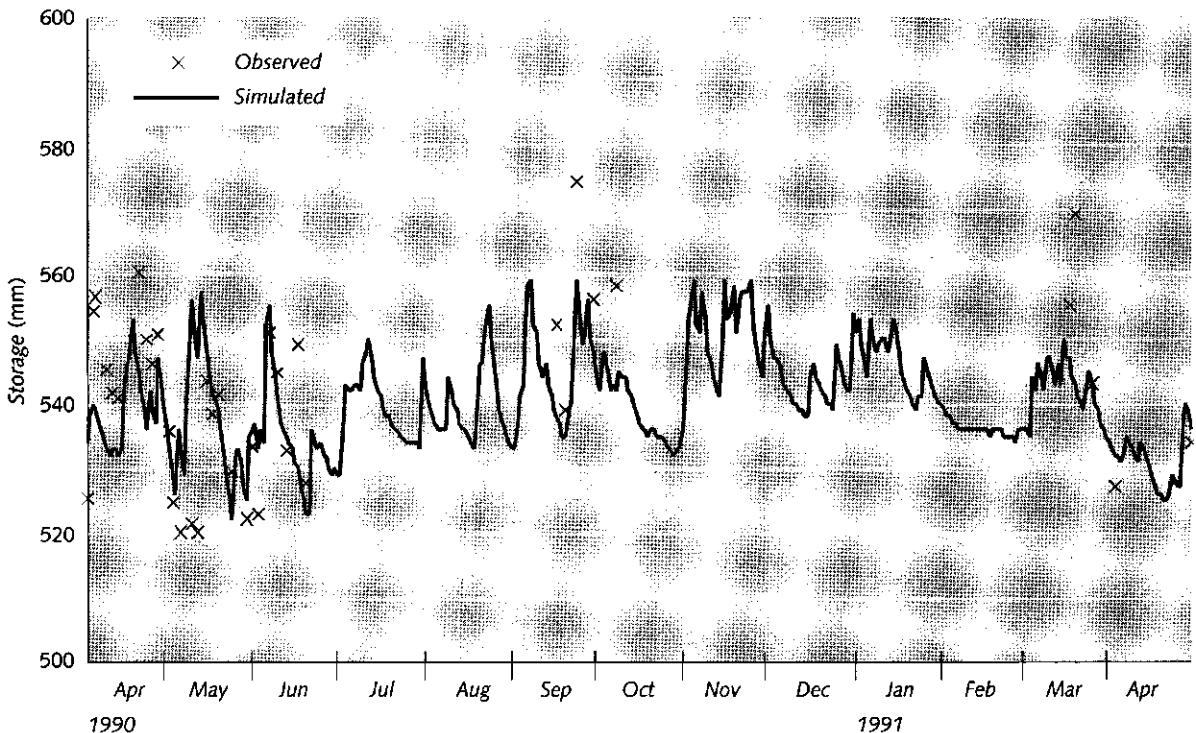


Figure 4.5. Observed and simulated soil water storage over a depth of 1.2 m for the experimental field *North-East Polder*.

soil moisture content at a particular time is known, the storage can be calculated according to:

$$W = \int_{z=-120}^{z=0} \theta(z) dz \quad 4.2$$

The observed and simulated storage over a soil depth of 1.2 m are presented in figure 4.5. The simulated soil water storage varies between 520 and 560 mm. The observed soil water storage varies between 520 and 580 mm.

Figure 4.6 shows the observed and simulated ground-water levels. In general, the observed and simulated groundwater levels show good agreement. The high groundwater levels at the end of June 1991 were caused by a heavy thunderstorm, with more than 40 mm of precipitation in two hours. The average observed groundwater level amounted to 0.819 m and deviates only slightly from the calculated average groundwater level which amounted to 0.830 m.

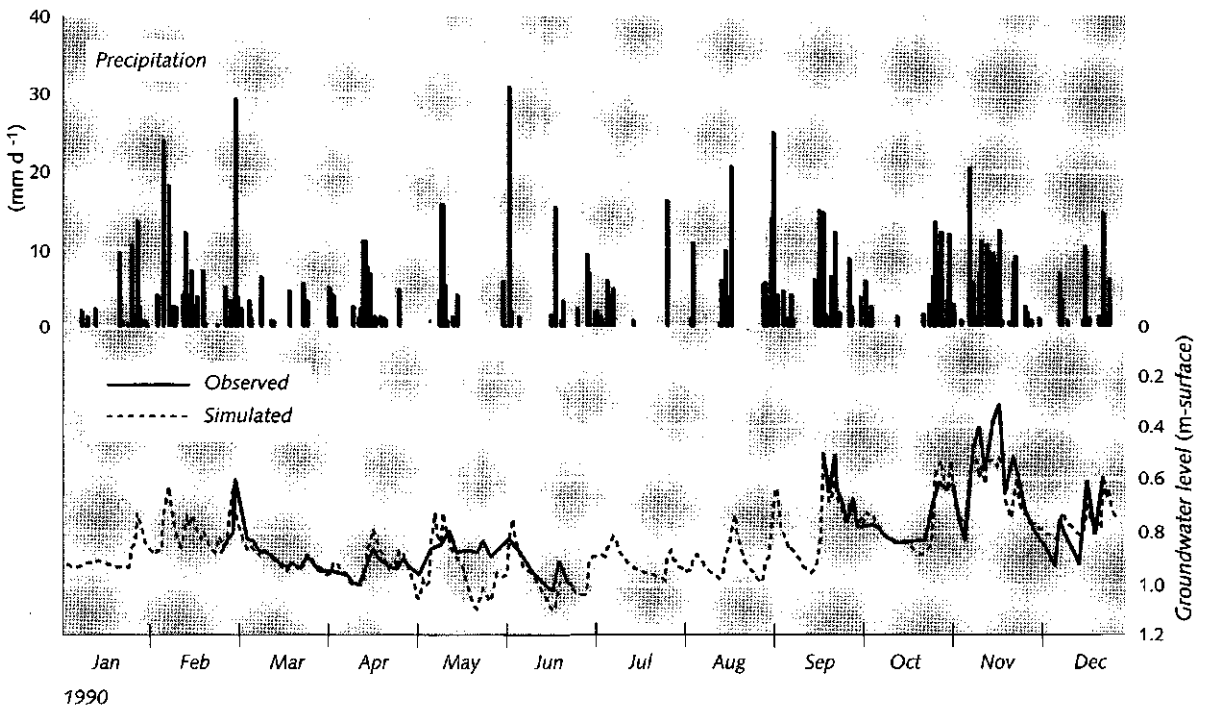
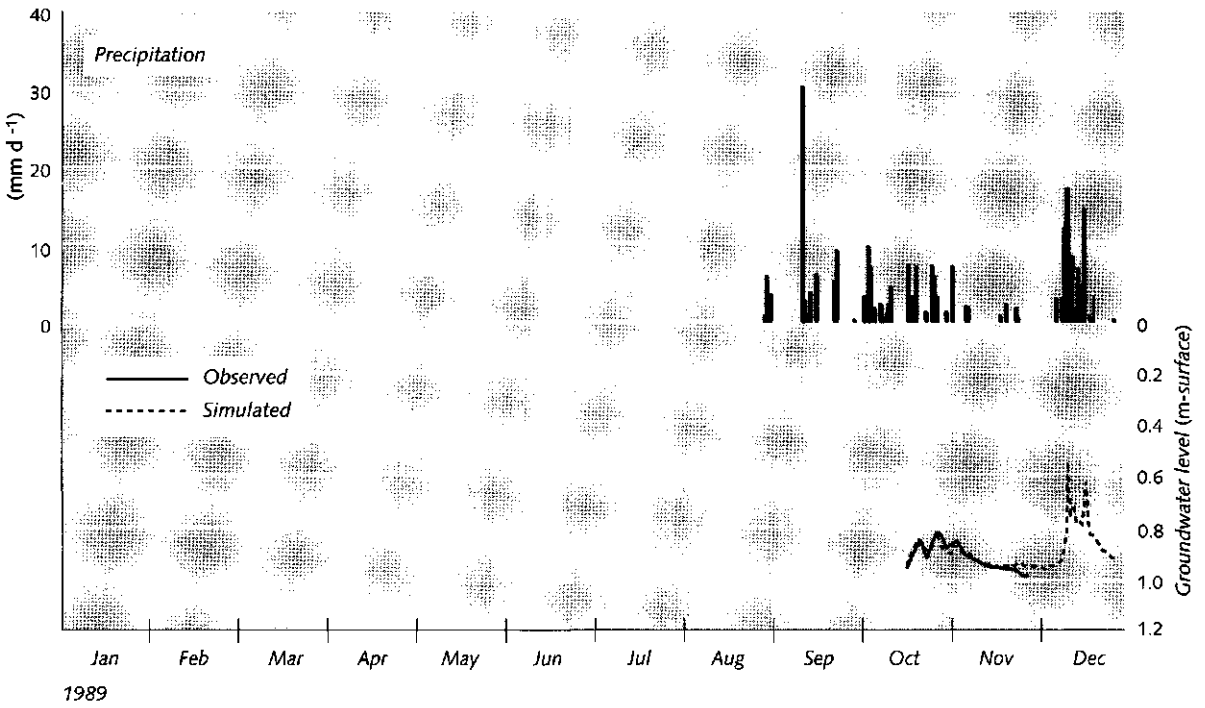
Figure 4.7 shows the observed and simulated drain discharge. The simulated drain discharge shows a good agreement with the observed drain discharge. The maximum observed drain discharge amounted to roughly 6 mm d⁻¹; the maximum simulated drain discharge amounted to 7 to 8 mm d⁻¹. The difference is caused by the limited capacity of the pump, which drained the water from the reservoir into the ditch. At high drain discharges, the drain water could not flow freely in the reservoir.

Generally, both the pattern of the discharge as well as the yearly cumulative drain discharge of the observed and simulated drain discharge show a good resemblance. However, in 1992 the observed drain discharge was higher than the calculated drain discharge. Table 4.5 shows the calculated soil water fluxes in 1989, 1990, 1991 and 1992. Each year has been calculated separately from 1 January until 31 December. The change in water storage for a year is negligible. The actual evapotranspiration amounted to 490 - 550 mm yr⁻¹.

Table 4.5. Simulated soil water fluxes at the experimental field *North-East Polder* in 1989, 1990, 1991 and 1992 (P = precipitation, I = irrigation, q_b = flux through the bottom of the soil profile (- = out), q_d = lateral drainage flux (- = out), E_i = interception, E_s = actual soil evaporation, E_t = actual transpiration).

Year	P (mm)	I (mm)	q_b (mm)	q_d (mm)	E_i (mm)	E_s (mm)	E_t (mm)
1989	680	62	-12	-215	43	243	229
1990	871	68	-53	-340	67	240	239
1991	635	229	-40	-331	58	211	224
1992	854	0	-20	-296	63	225	250

CALIBRATION OF THE EXTENDED MODEL SWACRO



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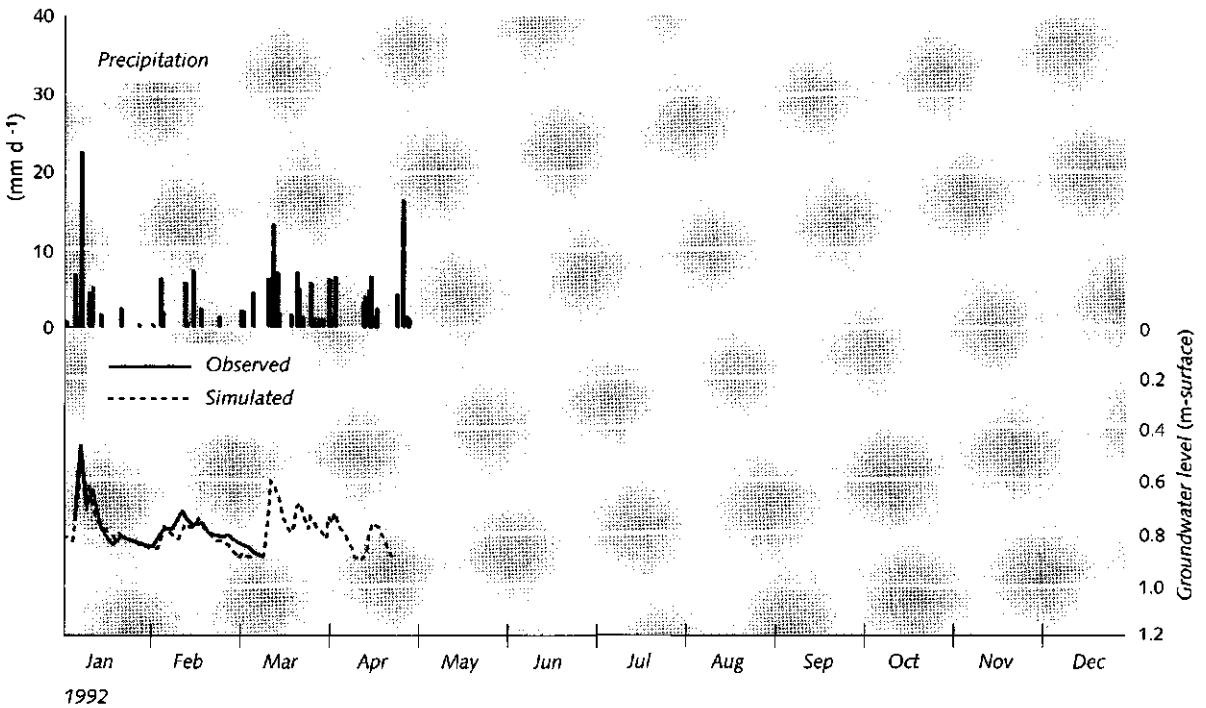
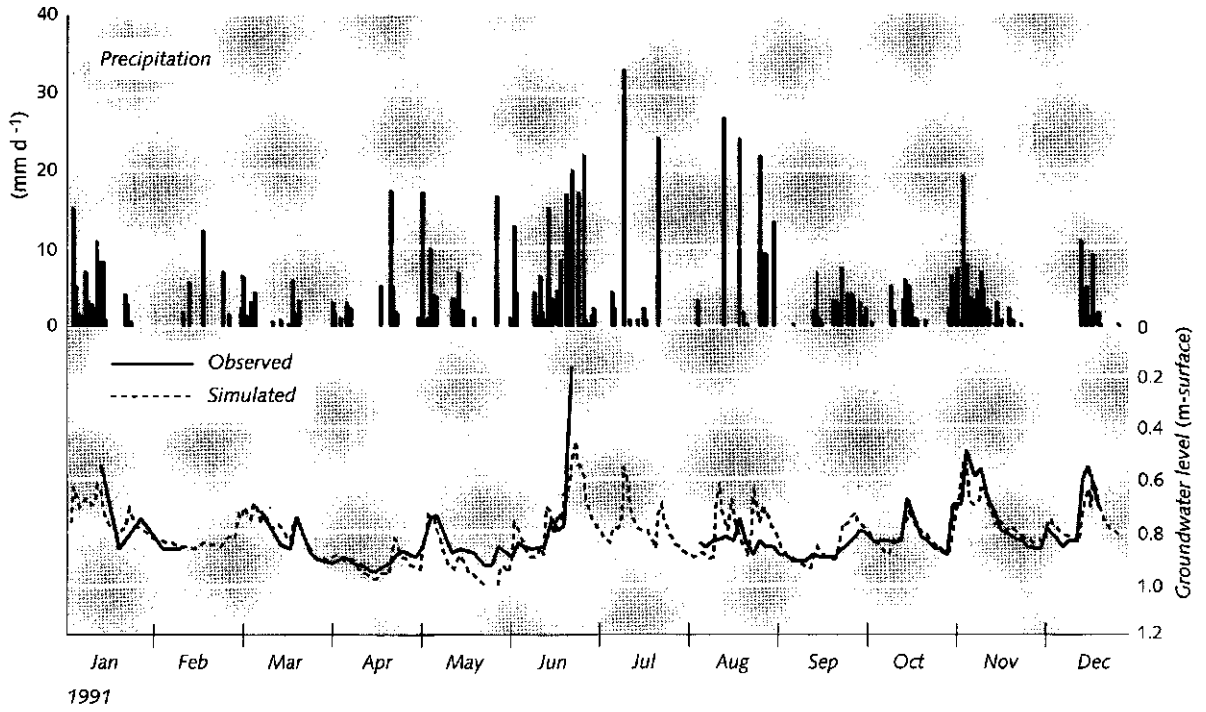
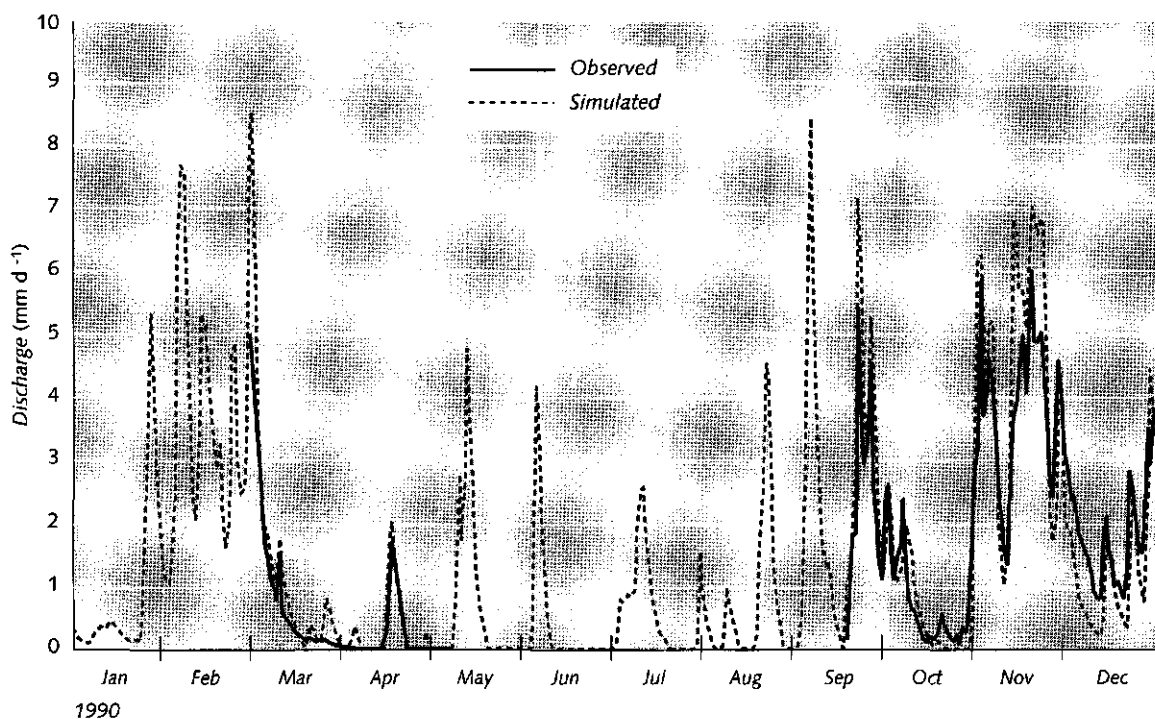
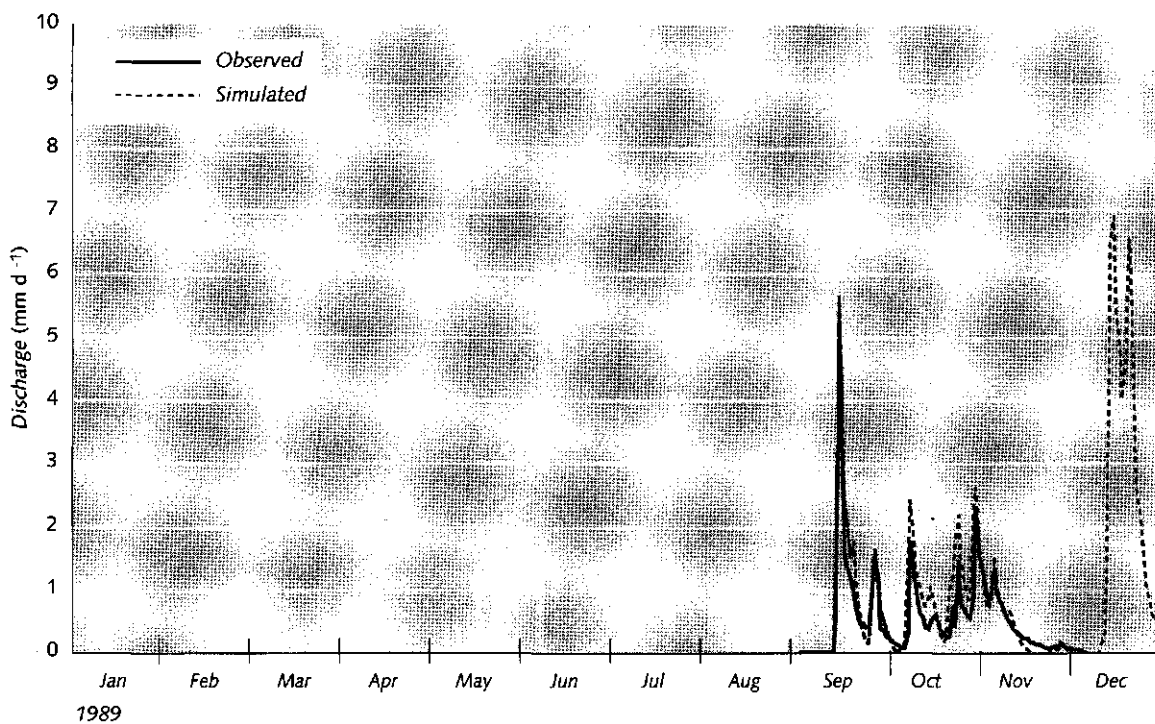


Figure 4.6. Observed and simulated groundwater levels at the experimental field North-East Polder.



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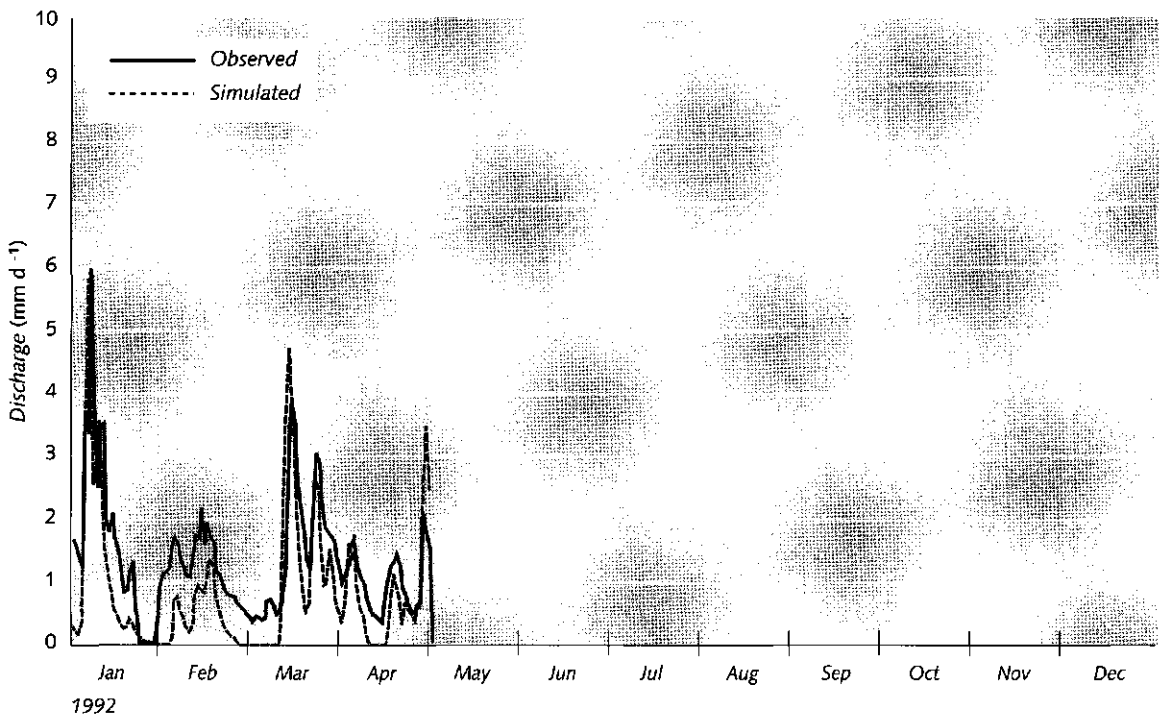
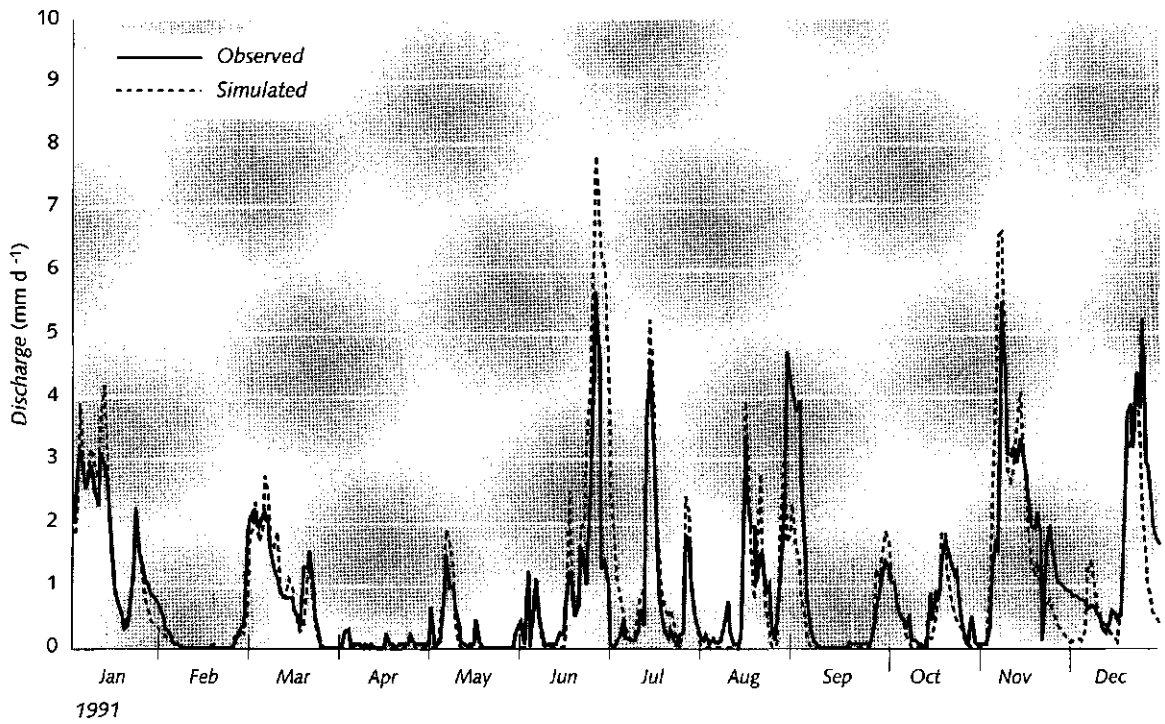


Figure 4.7. Observed and simulated drain discharges at the experimental field *North-East Polder*.

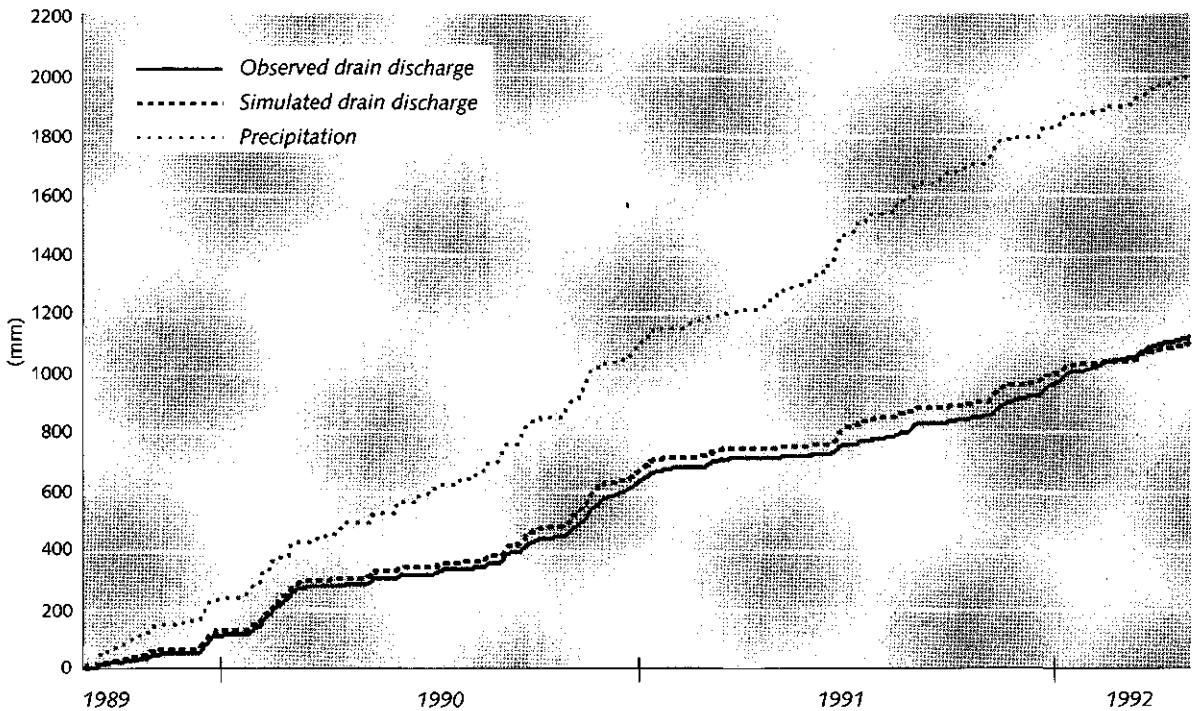


Figure 4.8. Observed and simulated cumulative drain discharge at the experimental field *North-East Polder*. Also shown is the cumulative precipitation.

4.1.2 Solute transport

As groundwater levels, moisture content and drain discharges could be simulated fairly accurately, an attempt was made to simulate the solute fluxes of the inert ion bromide. The soil water fluxes, as determined in the previous section, were applied to simulate bromide fluxes. The results of the simulation model were compared with concentration profiles of bromide sampled at particular time intervals and the concentration of bromide in the drainage water.

Model: As no cracks are visible at the loamy sand soil of the North-East Polder, flow of solutes is assumed to take place according to the convection-dispersion equation (equation 2.43). The dispersion coefficient is calculated according to equation 2.40. Preferential flow of solutes (if present) is assumed to take place according to the mobile/immobile concept as presented in subsection 2.3.1. (equations 2.63 - 2.65). Solute uptake by plant roots is calculated according to equation

2.60. The additional set of equations used for the transport of bromide are presented in table 4.6.

Input: For the calculation of bromide movement, input data on the applied load, the date of application, bromide uptake by plants, the estimated dispersion length and (if necessary) a concept for preferential flow, are needed. Data on the date of application, quantity applied and the period of the field measurements for bromide are presented in table 3.14.

The factor for uptake by plant roots (F) has to be estimated. Little is known about solute uptake of bromide by tulips and grass. However, due to the results of the mass balance for bromide during the second year of the experiment, which is presented in table 3.18, this value is assumed to be 0. Table 3.18 shows that the sum of the initial content of bromide in the soil and the applied quantity corresponds to the sum of the leached quantity and the actual soil content within the limits of standard deviation. If bromide uptake is taken into account, it

Table 4.6. Additional set of equations for water flow used for the simulation of the transport of bromide (See subsection 2.3.1. for mobile/immobile transport).

$J = qc_i - \theta(D_{dis} + D_{df}) \frac{\delta c_i}{\delta z} - D_{df,s} \frac{\delta c_g}{\delta z}$	2.43
$D_{dis} = L_{dis} v_e $	2.40
$R_u = F S c_i$	2.60
$R_d = q_d c_{i,n} \frac{dz_n}{dm^2} \frac{K_{s,n}}{K_{s,avg}}$	2.61

can have a significant impact on the mass balance for bromide.

Values of L_{dis} as presented in literature were compiled by Boesten (1986). The values were obtained from studies with non-sorbing conservative solutes such as chloride, bromide or tritiated water. Most values found for L_{dis} were smaller than 1 cm. However, these dispersion lengths were obtained from column studies with relative small column diameters and length. As the length and diameter of the columns increases, L_{dis} increases.

For field experiments, values for L_{dis} up to 20 cm were reported. For the plough layer at the experimental field North-East Polder, Boesten (1986) calculated the transport of bromide using $L_{dis} = 0.2$ cm as a lower limit and $L_{dis} = 3$ cm as an upper limit. As the value of L_{dis} was unknown and may vary considerably, L_{dis} was determined during calibration.

Preferential flow of bromide is calculated according to the mobile/immobile concept. Input data needed to calculate the movement of bromide in the soil are the mobile fraction, the water content in the immobile fraction and the exchange coefficient α . These parameters are difficult to define. Next to L_{dis} , the extent of the immobile fraction and exchange coefficient α were determined during calibration.

Optimalization criteria: For the transport of bromide through the soil the Root-Mean-Square ($RMS_{[Br]}$) was used as an optimalization criterium. $RMS_{[Br]}$ is formu-

lated in the same way as the Root-Mean-Square for groundwater levels (equation 4.1). The calculated concentration of bromide in the drain pipes was compared to the observed concentration of bromide.

Numerous model simulations were undertaken in order to acquire the best possible fit between observed and simulated data. Simulations were carried out for various combinations of α , the dispersion length (L_{dis} ; equation 2.40) and the ratio mobile/immobile. For the partitioning between the mobile/immobile part of the soil, values varied from 1.0 (mobile)/ 0.0 (immobile) up to 0.1 (mobile) / 0.9 (immobile). Values for the exchange coefficient α may vary between 0 and 1.

If the exchange coefficient α is set at 0, no exchange will take place between the mobile and immobile part of the soil. In this case, all bromide is assumed to be present in the mobile part of the soil. If the exchange coefficient increases, the difference between a soil with only mobile water and a soil which is partitioned between mobile and immobile fractions becomes smaller. The lowest value for the Root-Mean-Square ($RMS_{[Br]}$; calculated concentration of bromide in the drain pipes compared to the observed concentration) was obtained if the exchange coefficient α was set at 0.2 d⁻¹. The optimum value of the dispersion coefficient depends on the partitioning between the mobile and immobile fraction and L_{dis} varies from 3 cm to 17 cm.

Results: Figure 4.9 presents the optimum values of the dispersion length (L_{dis}) for each combination of values for the mobile/immobile concept, varying from 1.0 (mobile) / 0.0 (immobile) up to 0.1 (mobile) / 0.9 (immobile). The value of $RMS_{[Br]}$ hardly changes for various combinations of the dispersion length and the partitioning in mobile and immobile fractions. For 1990 (plot I: figure 3.19) and 1991/1992 (plot II) the value of $RMS_{[Br]}$ varied from 0.8 to 1.0 mg l⁻¹ and 1.9 to 2.0 mg l⁻¹ respectively.

Figure 4.9 shows that the optimum value for the dispersion length decreases with the increasing immobile fraction of the soil. For 1991/1992 the optimum value of the dispersion length is even more extreme than in 1990. This is mainly caused by the high concentration

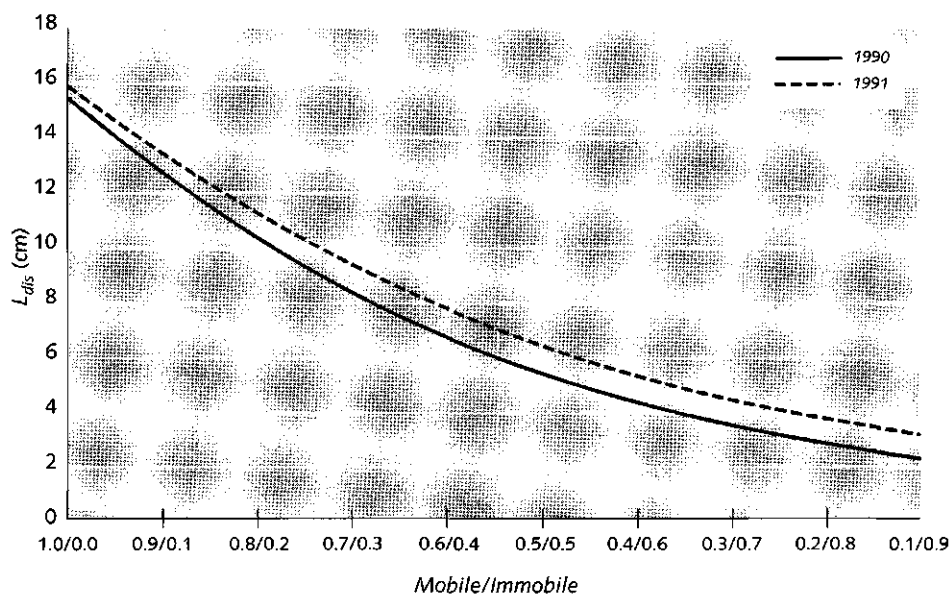


Figure 4.9. Relation between the optimum value of the dispersion length (L_{dis}) for various combinations of the mobile/immobile fraction in the soil at the experimental field *North-East Polder*. The exchange coefficient α was set at 0.2 d^{-1} .

of bromide in drain pipes between 40 and 150 days after application. Calibration of the model for bromide showed that the best fit was obtained if mobile and immobile phases were set at 0.5. For this distribution between the mobile and immobile phase, the dispersion length amounted to approximately 5 - 10 cm and the exchange coefficient α was equal to 0.2 d^{-1} . If the values for the mobile/immobile phases were set at 1.0 and 0.0 respectively, the optimum value for the dispersion coefficient amounts to 15 - 17 cm. The partitioning of the soil in a mobile and immobile phase conforms to a radius of aggregate containing a stagnant liquid phase. The radius was calculated according to Bolt (Bolt, 1979) and amounted to 3 cm.

Results 1990: The results of the concentration of bromide in the drain pipes in 1990 show a good agreement between the observed and simulated values. The dispersion length was kept constant at 5 cm. Model simulation showed that an increase of the immobile fraction accelerates the leaching of bromide if the exchange coefficient is kept at a constant value. Figure 4.11 shows that if the value of the exchange coefficient α is increased, the leaching of bromide is retarded. The

influence of the dispersion length on the leaching of bromide is presented in figure 4.13. It shows that an increase of the dispersion length gives an accelerated breakthrough of bromide. It may be concluded that an increase of the dispersion length gives almost the same effect as the mobile/immobile concept. The low concentration of bromide, which was measured in the drainage water between 100 and 115 days after application, can be explained by seepage, which caused dilution of the concentration of bromide in the drain pipes. This seepage was caused by high water tables in the submain drain. Unfortunately, the measurements were stopped after 140 days.

Figures 4.12 and 4.14 present the observed and calculated amount of bromide leaching through the drain pipes for both the mobile/immobile concept and the conventional convection-dispersion concept. The observed load of bromide, which leached through the drain pipes in 1990, was only 0.24 kg ha^{-1} . This is equal to approximately 1% of the amount applied. It corresponded fairly well with the calculated load of bromide leached. The best fit was achieved if $L_{dis} = 5 \text{ cm}$, mobile/immobile = 0.5/0.5 and $\alpha = 0.2 \text{ d}^{-1}$ for the

mobile/immobile concept and $L_{dis} = 16$ cm for the conventional convection-dispersion concept.

In figure 4.15 the calculated content of bromide in the soil at various depths is compared with the observed content of bromide for experimental field I (1990) ($L_{dis} = 16$ cm; mobile/immobile = 1.0/0.0). If $L_{dis} = 5$ cm, mobile/immobile = 0.5/0.5 and $\alpha = 0.2$ d⁻¹ minor changes in the calculated content of bromide in the soil could be observed. The greater part of the bromide was still present in the soil: 140 days after application the bromide moved to deeper soil layers. In the period 114 - 140 days after application (June/July) the tulips were harvested, which caused a thorough mixing of the bromide in the plough layer. For the simulations the mixing of bromide in the plough layer was anticipated. Besides, the bromide moved upwards again due to capillary rise.

Results 1991/1992: Results of experimental field II (1991/1992) show that the simulated values of the concentration of bromide in the drain pipes do not correspond to the observed values, especially between 40 and 150 days after application (figure 4.16). Surprisingly, this phenomenon was not observed in 1990. It can possibly be caused by preferential stream paths, such as root channels. The plough layer of the experimental field North-East Polder exists of homogeneous loamy sands. However, below the plough layer, in a fine layered loamy sand interlayered by sandy loam, former root channels of reed can be recognized. The

diameter of the former reed roots varies from 0.2 cm to 1 cm (figure 4.10): see also subsection 3.2.11 photo 3.7).

A fraction of the soil water flux flows through the channels directly to the drain pipes. Approximately 40 days after application, the bromide concentration at the lower part of the plough layer starts to rise. A fraction of the bromide will flow through the former reed channels to the drain pipes, causing high concentrations of bromide in the drain pipes. Approximately 170 days after application of bromide, concentrations at the lower part of the plough layer are equal to the concentration of bromide at the drain pipes. The major part of the bromide has been transported to the deeper soil layers. This process could not be described with a high dispersion length or the mobile/immobile concept.

Figure 4.16 shows the observed and simulated concentration of bromide in the drain pipes in 1991/1992 ($L_{dis} = 5$ cm). It shows that a decrease of the exchange coefficient α accelerates the leaching of bromide if the mobile fraction of the soil is kept at a constant value. The maximum concentration of bromide in the drain pipes will be higher if the mobile phase is set at 1 ($L_{dis} = 5$ cm). The influence of the dispersion length on the leaching of bromide is presented in figure 4.18. It shows that an increase of the dispersion length gives an accelerated breakthrough of bromide.

If $L_{dis} = 16$ cm and the mobile phase is set at 1, the cal-

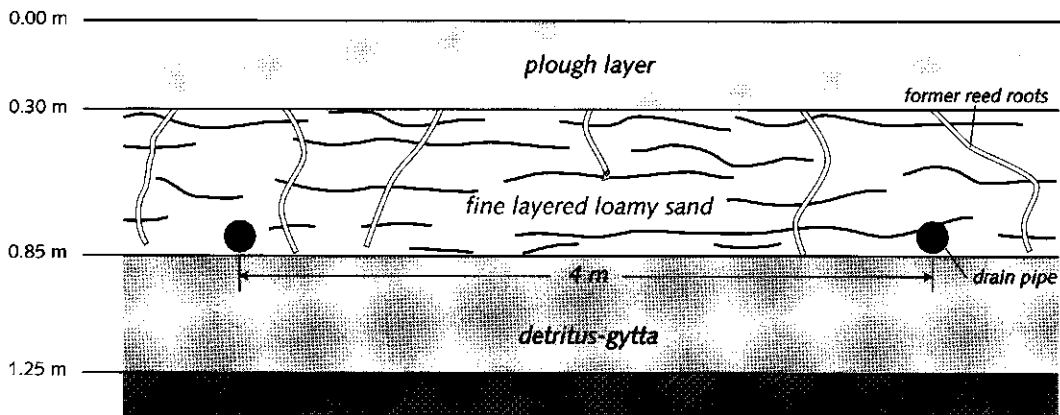


Figure 4.10. Schematic profile of the experimental field North-East Polder.

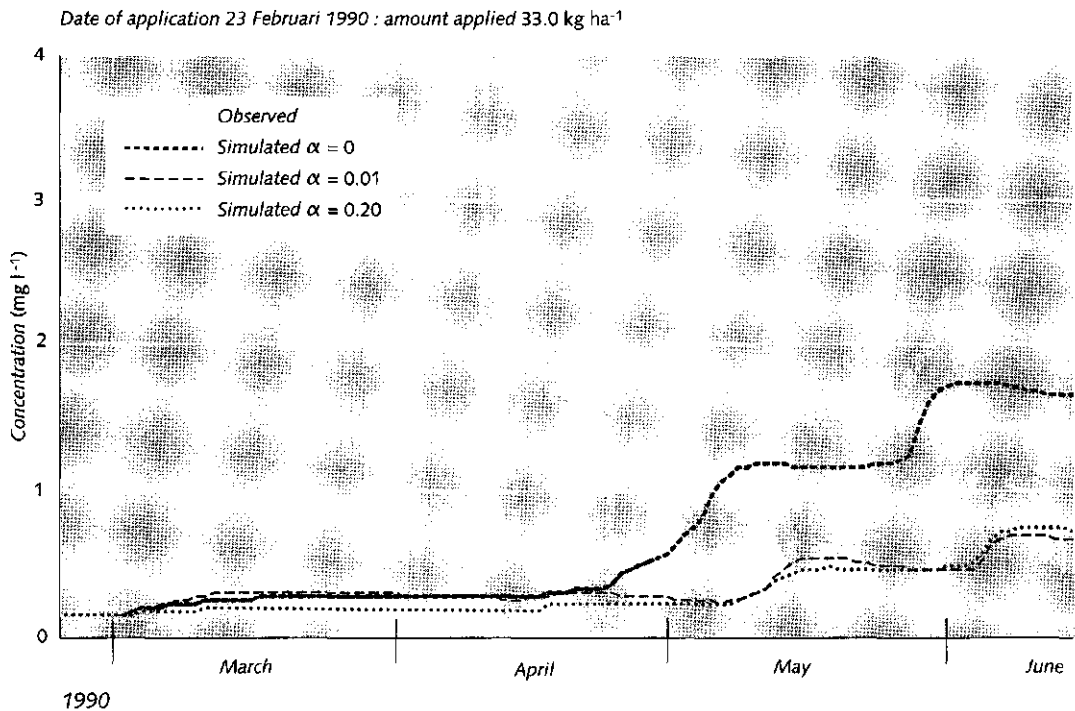


Figure 4.11. Observed and simulated concentration of bromide in the drain pipes for different values of the exchange coefficient (α) at the experimental field North-East Polder in 1990; $L_{dis} = 5$ cm, mobile/immobile = 0.5/0.5.

culated concentration of bromide is almost equal to the calculated concentration with mobile/immobile = 0.5/0.5, $\alpha = 0.2$ d⁻¹ and $L_{dis} = 10$ cm. As the conventional convection-dispersion equation (no immobile phase) is more simple than the convection-dispersion equation including mobile/immobile phases, the first is to be preferred to the latter.

Figures 4.17 and 4.19 present the observed and simulated amount of bromide leaching through the drain pipes for both the mobile/immobile concept and the conventional convection-dispersion concept. The observed amount of bromide, which leached through the drain pipes in 1991/1992, was 16.4 kg ha⁻¹. This is equal to approximately 58% of the amount applied. It corresponded fairly well with the calculated amount of bromide leached.

The content of bromide in the soil was measured at various soil depths and time intervals after application. In figure 4.20 (1991/1992) the calculated movement of bromide through the soil profile is compared with the observed movement of bromide ($L_{dis} = 16$ cm; mobile/immobile = 1.0/0.0). In 1990 the greater part of the bromide was still present in the soil: 140 days after application the bromide moved to deeper soil layers. In 1991 the behaviour of bromide in the soil was pursued for a period of 420 days. After 416 mm drain discharge, 58% of the bromide applied leached through the drain pipes. The remaining 41% could still be detected in the soil. However, the greater part of the bromide was present between 0.4 and 0.8 m below the soil surface. If $L_{dis} = 10$ cm, mobile/immobile = 0.5/0.5 and $\alpha = 0.2$ d⁻¹ minor changes in the calculated movement of bromide through the soil profile could be observed.

Date of application 23 February 1990 : amount applied 33.0 kg ha⁻¹

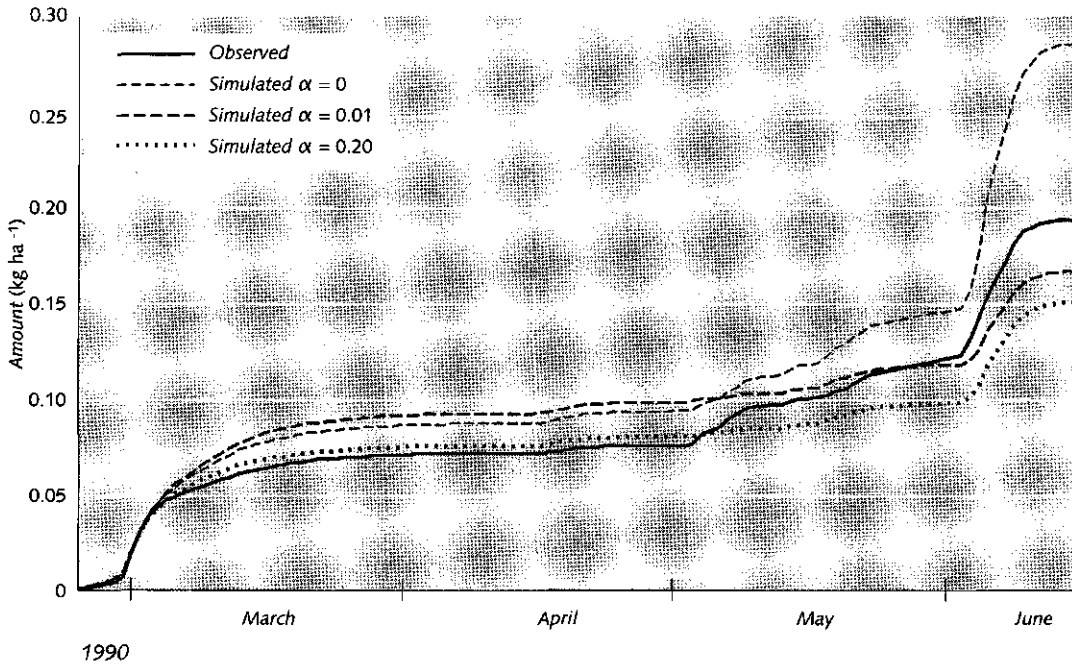


Figure 4.12. Observed and simulated amount of bromide leaching through the drain pipes for different values of the exchange coefficient (α) at the experimental field North-East Polder in 1990; $L_{dis} = 5$ cm, mobile/immobile = 0.5/0.5.

Conclusions: Both in 1990 and 1991/1992 the observed amount of bromide discharges through the drain pipes could be well simulated with the model SWACRO. Likewise, the observed movement of bromide through the soil profile calculated with the model SWACRO corresponded in general to the measured movement of bromide through the soil profile. However, the observed concentration of bromide in the drain pipes may diverge considerably from the simulated concentration (figures 4.11 and 4.16).

Results of experimental field II (1991/1992) show that the simulated values of the concentration of bromide in the drain pipes do not correspond to the observed values, especially between 40 and 150 days after application (figure 4.16). This could possibly be caused by preferential stream paths through root channels of former reed plants (figure 4.10). A fraction of the bromide will flow through the former reed channels to the drain pipes, causing high concentrations of bromide.

For the experimental field North-East Polder, partitioning of the soil water in mobile and immobile fractions produces minor changes in the concentration of bromide in the drain pipes. If the exchange coefficient α is taken as smaller than 0.2, differences between the two options (with and without immobile water) will increase. Generally, partitioning of the soil water in mobile and immobile fractions gives accelerated breakthrough of bromide, lower maximum concentrations and longer "tailing" effect. However, the same effect can be accomplished by increasing the dispersion length. This indicates that for the experimental field North-East Polder the mobile/immobile concept is exchangeable for a higher dispersion length. As the conventional convection-dispersion equation is more simple than the convection-dispersion equation including mobile/immobile phases, the first is preferred to the latter.

Date of application 23 Februari 1990: amount applied 33.0 kg ha⁻¹

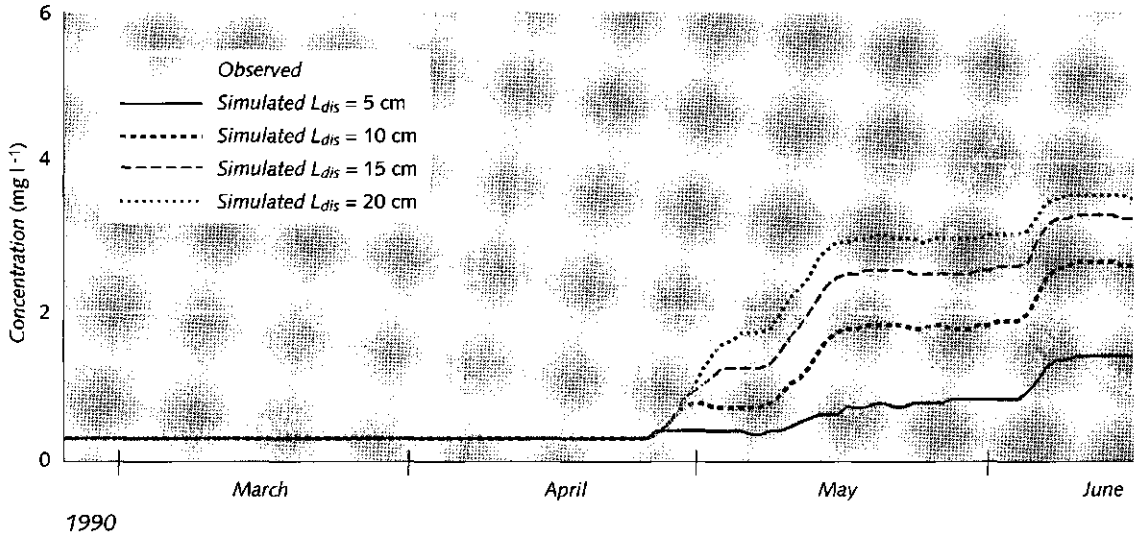


Figure 4.13. Observed and simulated concentration of bromide in the drain pipes for different values of the dispersion length (L_{dis}) at the experimental field North-East Polder in 1990; mobile/immobile = 1.0/0.0.

Date of application 23 February 1990: amount applied 33.0 kg ha⁻¹

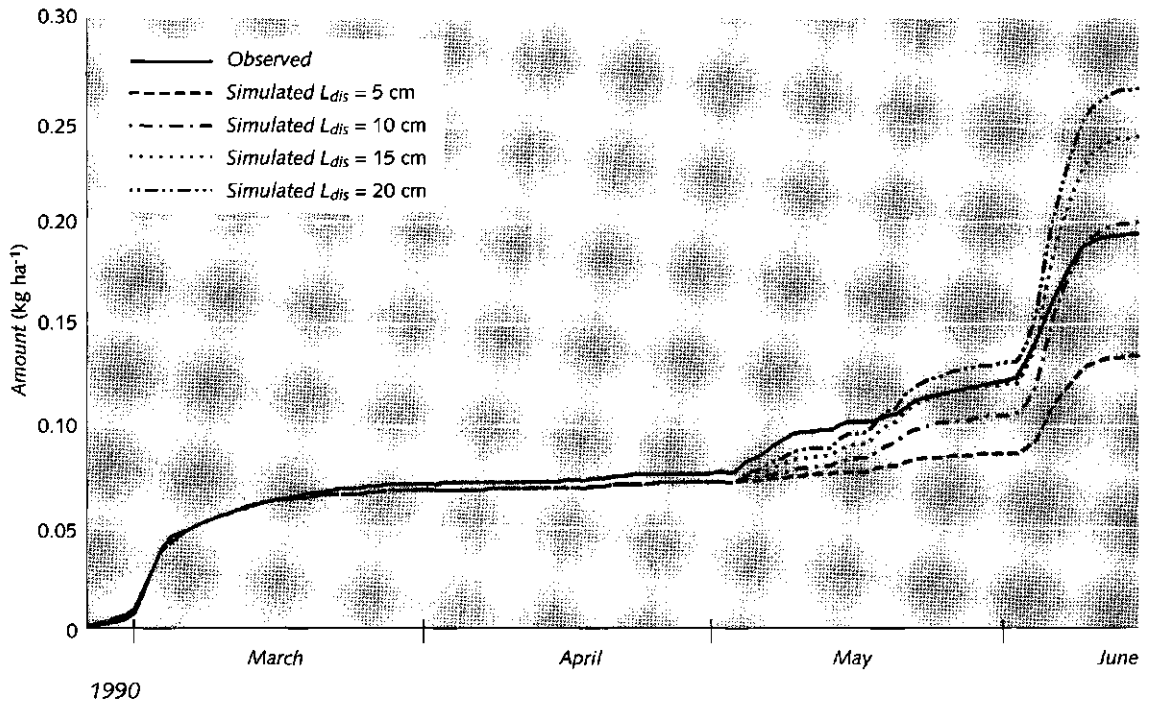


Figure 4.14. Observed and simulated amount of bromide leaching through the drain pipes for different values of the dispersion length (L_{dis}) at the experimental field North-East Polder in 1990; mobile/immobile = 1.0/0.0.

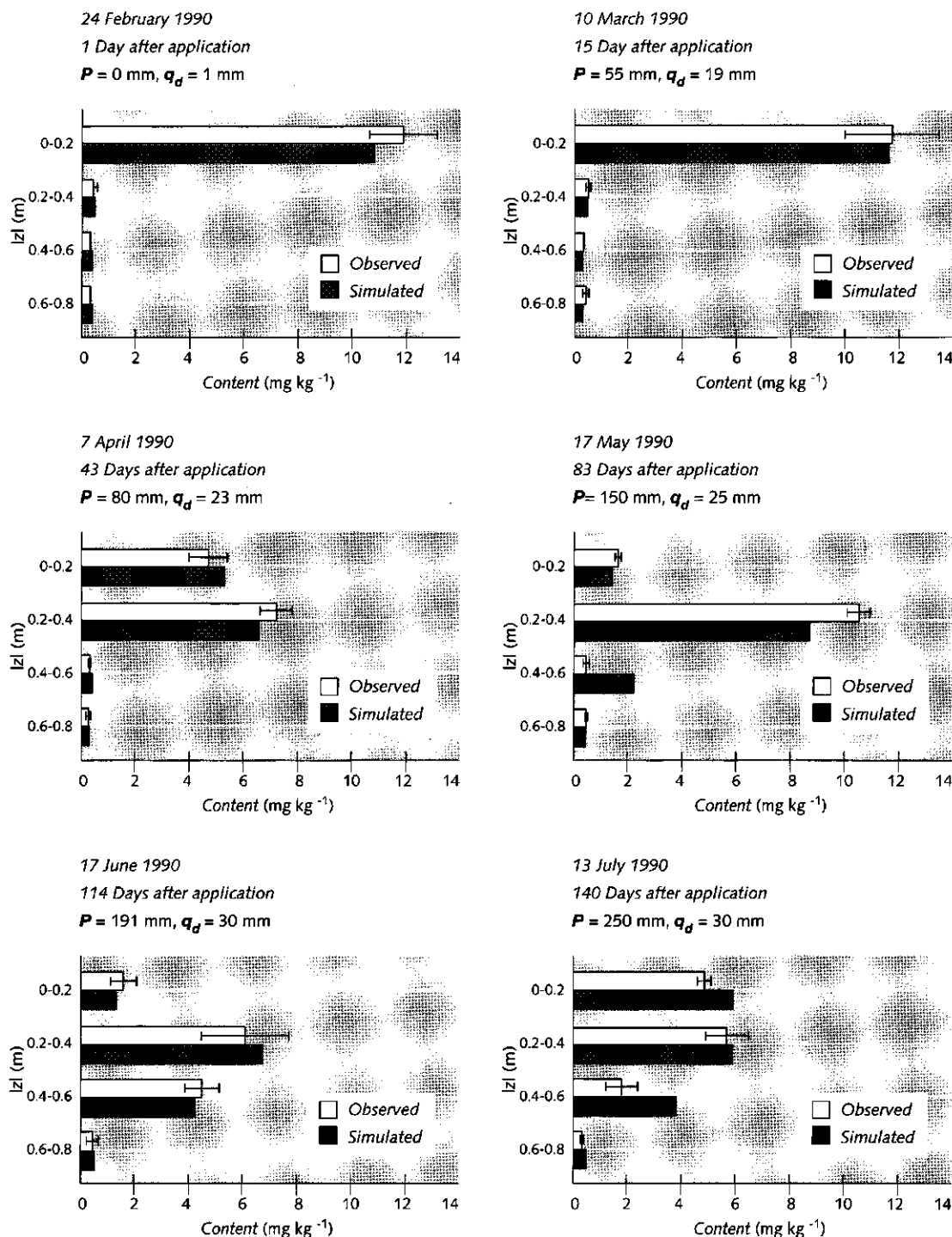


Figure 4.15. Observed and simulated movement (including the standard deviation) of bromide through the soil profile in 1990 at the experimental field North-East Polder (P = cumulative precipitation, q_d = cumulative drain discharge: $L_{dis} = 16$ cm; mobile/immobile = 1.0/0.0).

Date of application 14 March 1991: amount applied 26.5 kg ha⁻¹

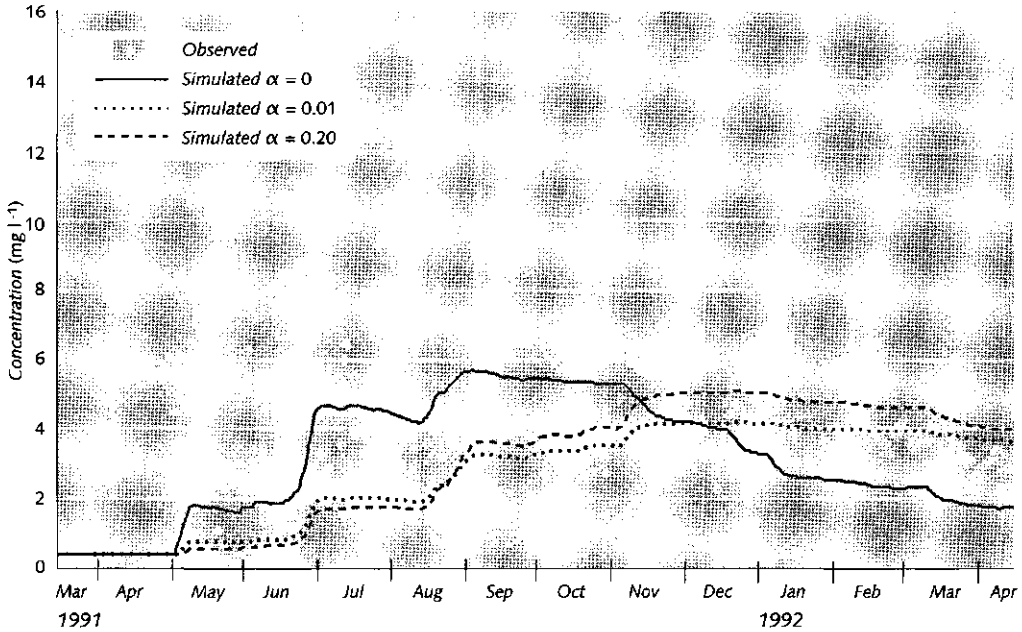


Figure 4.16. Observed and simulated concentration of bromide in the drain pipes at the experimental field *North-East Polder* in 1991/1992 with different values for the exchange coefficient α ; $L_{dis} = 10$ cm; mobile/immobile = 0.5/0.5.

Date of application 14 March 1991: amount applied 26.5 kg ha⁻¹

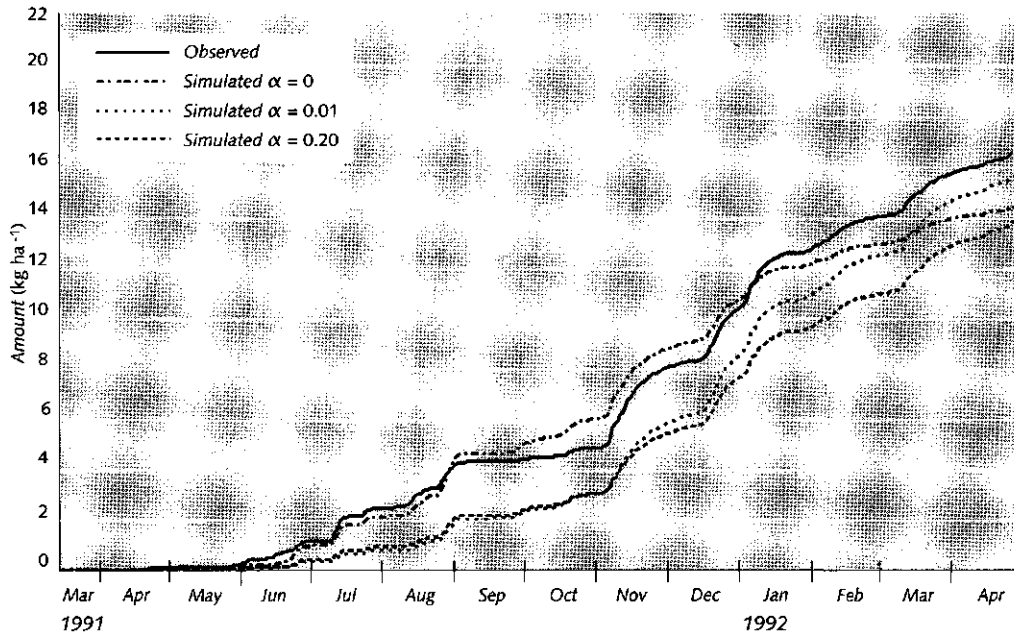


Figure 4.17. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field *North-East Polder* in 1991/1992 with different values for the exchange coefficient α ; $L_{dis} = 10$ cm; mobile/immobile = 0.5/0.5.

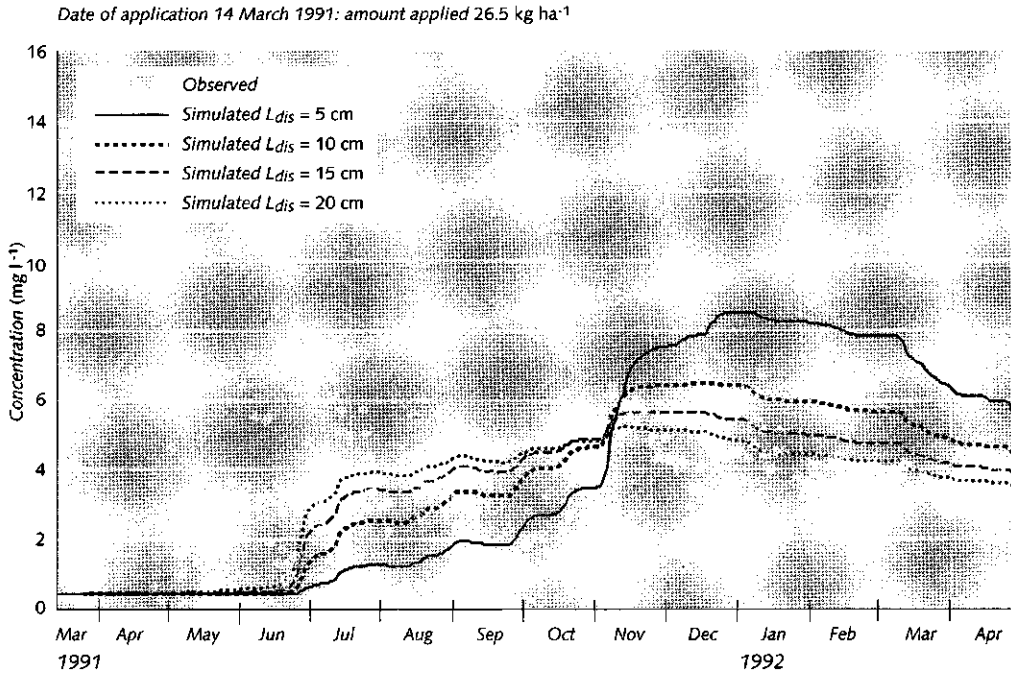


Figure 4.18. Observed and simulated concentration of bromide in the drain pipes at the experimental field *North-East Polder* in 1991/1992 for different values of the dispersion length (L_{dis}); mobile/immobile = 1.0/0.0.

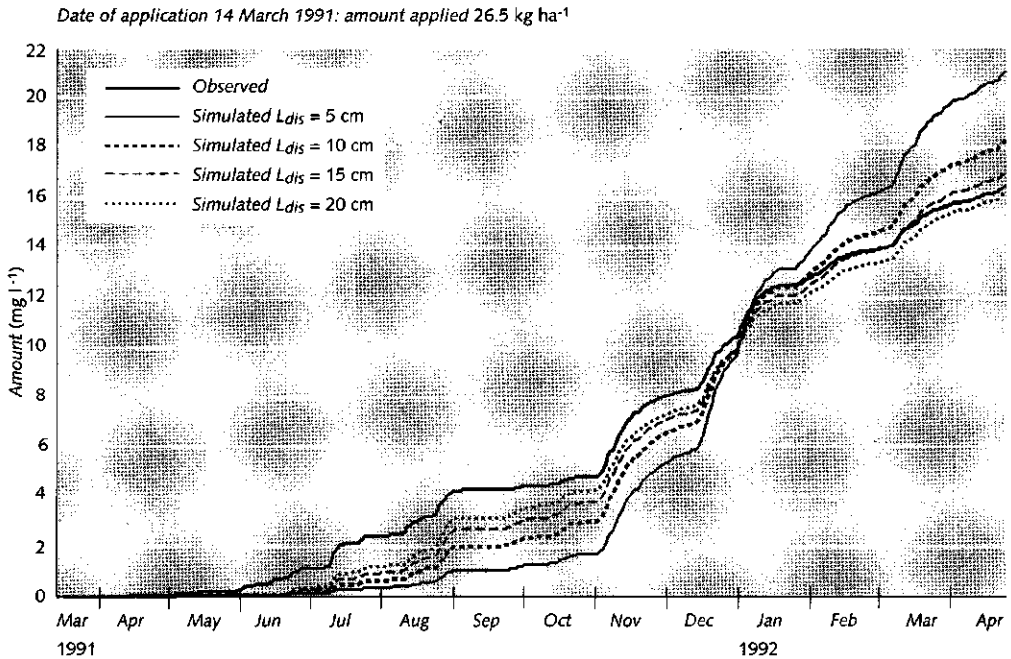
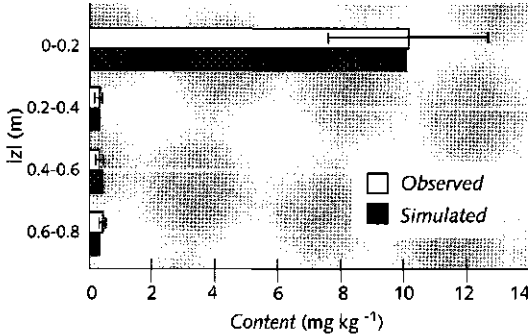


Figure 4.19. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field *North-East Polder* in 1991/1992 for different values of the dispersion length; mobile/immobile = 1.0/0.0.

15 March 1991

1 Day after application

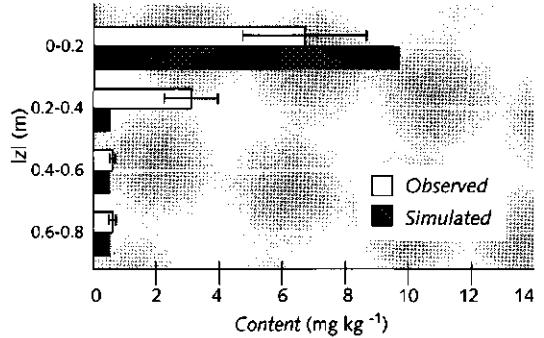
$P = 1 \text{ mm}$, $q_d = 1 \text{ mm}$



22 March 1991

8 Days after application

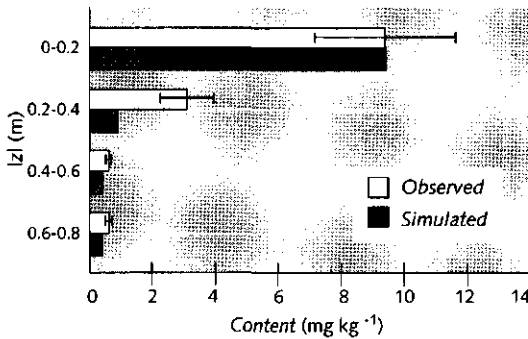
$P = 12 \text{ mm}$, $q_d = 8 \text{ mm}$



26 April 1991

43 Days after application

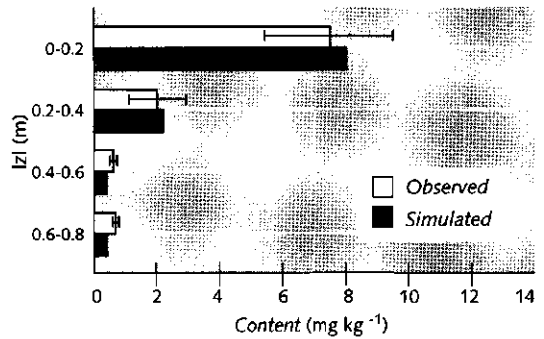
$P = 52 \text{ mm}$, $q_d = 10 \text{ mm}$



17 May 1991

64 Days after application

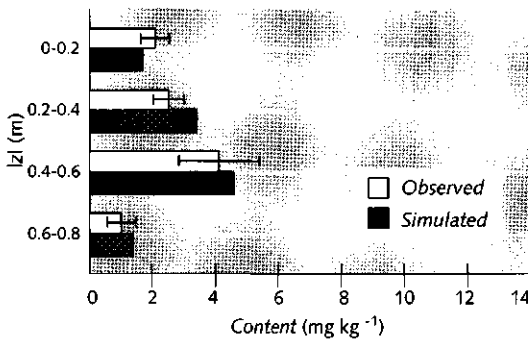
$P = 102 \text{ mm}$, $q_d = 17 \text{ mm}$



6 August 1991

145 Days after application

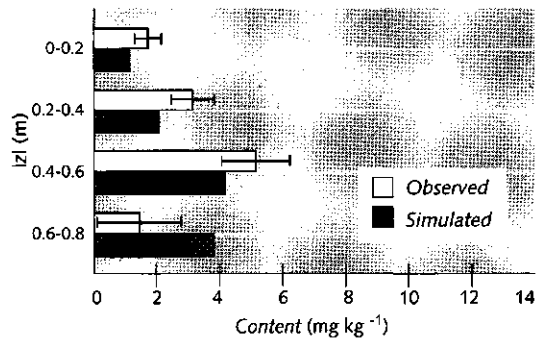
$P = 345 \text{ mm}$, $q_d = 78 \text{ mm}$



2 November 1991

233 Days after application

$P = 518 \text{ mm}$, $q_d = 150 \text{ mm}$

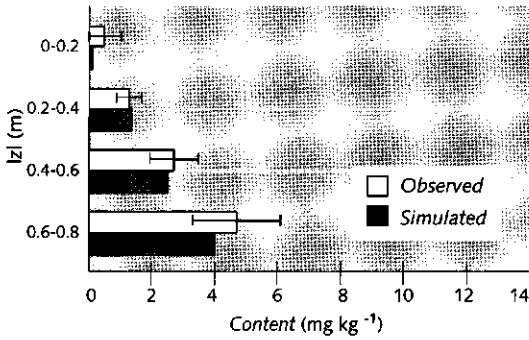


Continued on next page

5 December 1991

266 Days after application

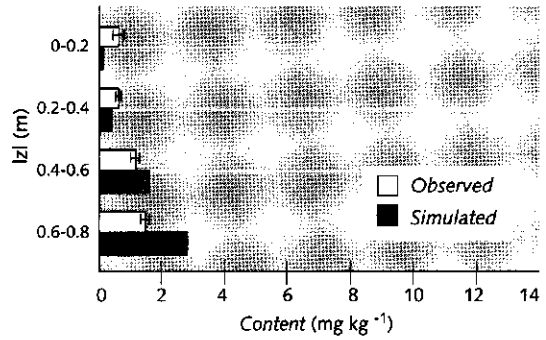
$P = 600$ mm, $q_d = 212$ mm



11 January 1992

303 Days after application

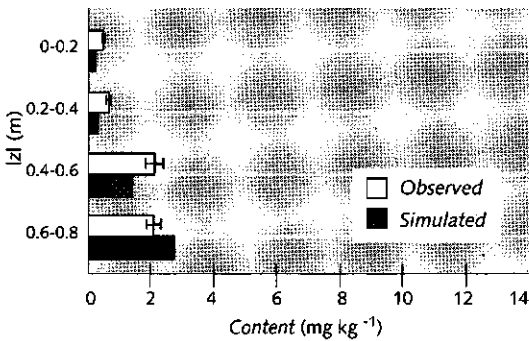
$P = 676$ mm, $q_d = 292$ mm



6 February 1992

329 Days after application

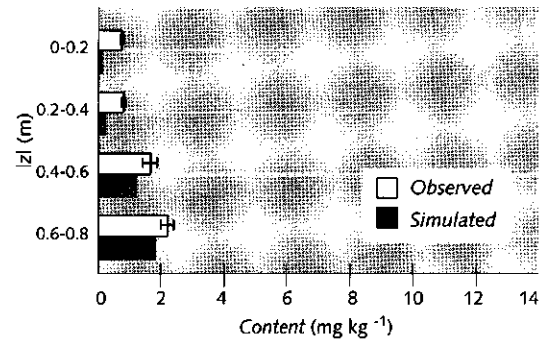
$P = 687$ mm, $q_d = 317$ mm



6 March 1992

358 Days after application

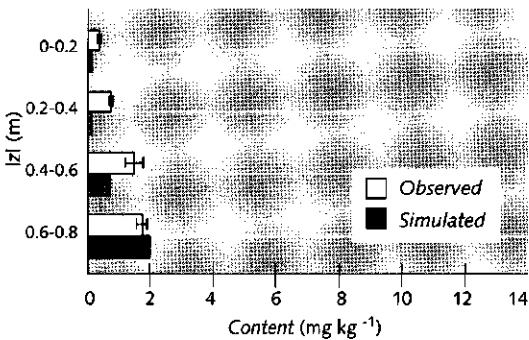
$P = 711$ mm, $q_d = 345$ mm



7 April 1992

390 Days after application

$P = 781$ mm, $q_d = 398$ mm



7 May 1992

420 Days after application

$P = 825$ mm, $q_d = 416$ mm

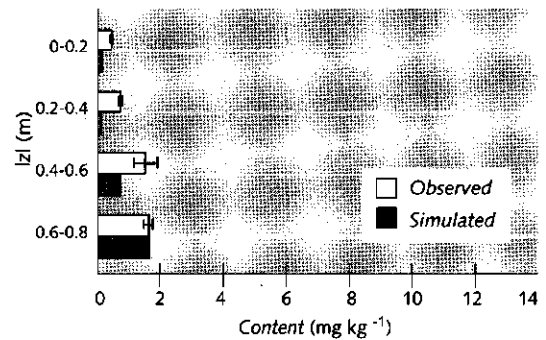


Figure 4.20. Observed and simulated movement (including the standard deviation) of bromide through the soil profile in 1991/1992 at the experimental field North-East Polder (P = cumulative precipitation, q_d = cumulative drain discharge) ($L_{dis} = 16$ cm; mobile/immobile = 1.0/0.0).

4.1.3 Pesticide transport

The next step in the calibration process is an attempt to simulate the behaviour of pesticides. Apart from the applied load and date of application, parameters that are related to transformation, pesticide uptake by plants, sorption and soil temperatures are needed. The results of the simulation model are compared with concentration profiles of pesticides sampled at particular time intervals and the concentration of the pesticide in the drainage water. At the experimental field North-East Polder, two pesticides were examined: metamitron and (Z) 1,3-dichloropropene.

4.1.3.1 Metamitron

Model: The flow of pesticides is partly described with the same equations as the flow of conservative solutes. The set of equations used to describe the transport of solutes are summarized in table 4.1 (water flow) and table 4.6 (solute flow). An additional set of equations is needed for the description of first-order transformation and sorption. The most important equations used to calculate transformation and sorption are summarized in table 4.7.

Input parameters: Data on time of application, quantity applied and period of the field measurements for metamitron were already presented in table 3.14. Input parameters to determine soil water fluxes are given in table 4.2. Optimization showed that the transport of bromide could be reasonably well described with the convection-dispersion equation, assuming a soil without an immobile phase (mobile = 1.0 / immobile = 0.0) and the dispersion length (L_{dis}) equal to 16 cm. The soil was subdivided in 15 compartments of 0.02 m (0 - 0.3 m) and 18 compartments of 5 cm (0.3 - 1.2 m).

The transformation of metamitron was analyzed in laboratory experiments, as described in subsection 3.1.2.1. The input parameters to determine the behaviour of metamitron in the soil are summarized in table 4.8. Transformation of metamitron is strongly influenced by soil temperatures.

Soil temperatures could be well described with equation 2.56. Some soil temperatures have been presented in subsection 3.2.12. The influence of the temperature on the rate of transformation is presented by equations

Table 4.7. Additional set of equations for water and solute flow used for the transport of metamitron.

$$R_i = k_i c^* \quad 2.45$$

$$k_i = f_T f_\theta f_z k_{i,ref} \quad 2.46$$

$$f_T = \exp[\gamma_a (T - T_{ref})] \quad 2.47$$

$$f_\theta = \left(\frac{\theta}{\theta_{ref}} \right)^{b_1} \quad 2.49$$

$$T(z, t) = T_m + T_a \exp\left(\frac{1}{d} z\right) \sin\left(\omega t - \frac{1}{d} z\right) \quad 2.56$$

$$X = K_F c_{i,ref} \left[\frac{c_i}{c_{i,ref}} \right]^{1/n} \quad 2.57$$

2.46 and 2.47. The coefficient (γ_a) was established at $0.15 \text{ } ^\circ\text{C}^{-1}$. The influence of the soil moisture content is given by equation 2.49. The parameters θ_{ref} and b_1 were set at 0.32 and 0.7 respectively. The influence of the soil depth on the rate of transformation is presented

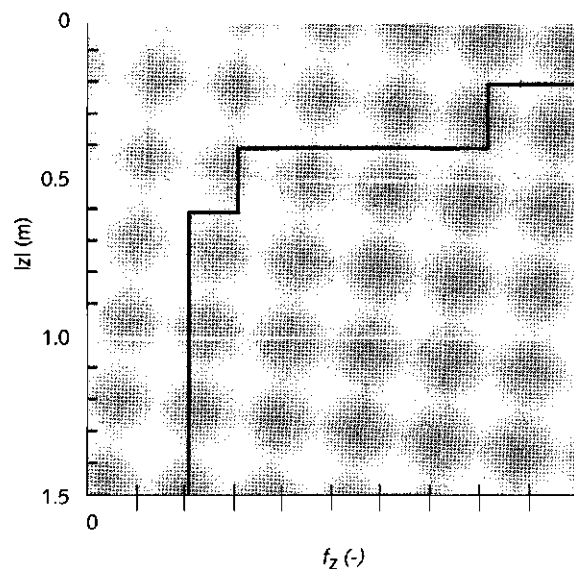


Figure 4.21. Reduction of the coefficient for the influence of soil depth on the rate of transformation (f_z) with depth.

Table 4.8. Input parameters to determine the leaching of metamitron

TRANSFORMATION AND UPTAKE			
Symbol	Parameter	Value	Equation
$k_{l,ref}$	Reference coefficient for first-order transformation rate	0.10 d ⁻¹	2.46
γ_a	Coefficient	0.15 °C ⁻¹	2.47
T_{ref}	Reference temperature	20 °C	2.47
θ_{ref}	Soil moisture content at a reference level	0.32	2.49
b_l	Parameter	0.7	2.49
f_z	Coefficient for the influence of soil depth on the rate of transformation	0.2 - 1.0 (figure 4.21)	2.46
F	Transpiration stream concentration factor	0.5	2.60
SORPTION			
Symbol	Parameter	Value	Equation
K_F	Freundlich coefficient	2.50 - 4.80 cm ³ g ⁻¹	2.57
(1/ n)	Freundlich exponent	0.74	2.57
$c_{l,ref}$	Reference concentration in the liquid phase	10 mg l ⁻¹	2.57
ρ	Dry soil bulk density	1465 kg m ⁻³	2.32
SOIL TEMPERATURE			
Symbol	Parameter	Value	Equation
T_m	Yearly average soil temperature	10.5 °C	2.56
T_a	Yearly amplitude of the soil temperature at the soil surface	8.9 °C	2.56
d	Damping depth	2.4 m	2.56

by a factor, f_z . This factor is equal to 1 in the plough layer and decreases with depth (figure 4.21).

Sorption is calculated according to equation 2.57. The Freundlich coefficient and exponent were obtained by laboratory experiments as presented in subsection 3.1.2.1. The value of the Freundlich coefficient was determined in laboratory experiments and varied between 2.50 and 4.80 cm³ g⁻¹. The Freundlich exponent amounted to 0.74 (table 3.9). Plant uptake is calculated according to equation 2.60. It was assumed that $F = 0.5$.

Results: Figure 4.22 gives the observed and simulated remaining amount of metamitron in the soil in 1990 and 1991. It shows a good resemblance between the observed and simulated values. In the early spring of 1990 soil temperatures were higher compared to the soil temperatures in the early spring of 1991. In spite of the fact that the date of application in 1990 was 20 days

earlier than the date of application in 1991, transformation in 1990 was more rapid.

In subsection 3.1.2.1 was noticed that the value of the parameter γ_a , derived from the laboratory experiments, is extremely high. Normally, the value of this parameter amounts to 0.08 °C⁻¹ (Boesten, 1986). The estimation of the parameter $k_{l,ref}$ for $\gamma_a = 0.08$ °C⁻¹ was based on results for the 0.05 - 0.15 m layer (figure 3.4), which resulted in $k_{l,ref} = 0.072$ d⁻¹. The concentration of metamitron in the drain pipes and the content of metamitron in the soil profile was calculated for $\gamma_a = 0.08$ °C⁻¹ and $k_{l,ref} = 0.072$ d⁻¹. Under these conditions, the concentration of metamitron in the drain pipes was below the detection limit. As metamitron was applied in the early spring, it was transformed faster under these circumstances.

Results of the observed and simulated concentration of metamitron in the drain pipes are presented in figure

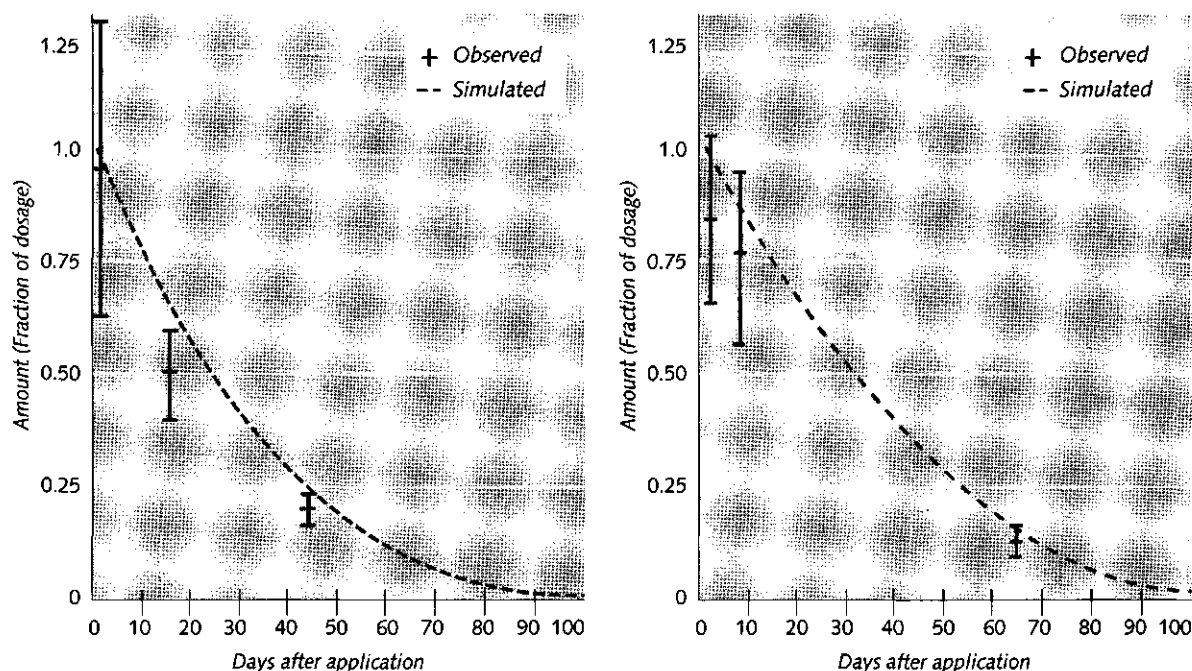


Figure 4.22. Observed (including the standard deviation) and simulated remaining amount of metamitron in the soil (as fraction of dose) in 1990 (Plot I: date of application 23 February) and 1991 (Plot II: date of application: 14 March) at the experimental field *North-East Polder*. The Freundlich parameters are according to table 3.9.

4.23. The concentration of metamitron in the drain pipes was simulated below the detection limit both for $\gamma_a = 0.08 \text{ }^{\circ}\text{C}^{-1} / k_{1,ref} = 0.072 \text{ d}^{-1}$ and $\gamma_a = 0.15 \text{ }^{\circ}\text{C}^{-1} / k_{1,ref} = 0.10 \text{ d}^{-1}$.

Optimization of the Freundlich coefficient: Figure 4.23 shows that the concentration of metamitron in the drain pipes is below the detection limit if the parameters obtained from the laboratory studies are used. In the optimization process only one value for the Freundlich parameters was distinguished for all soil layers. Results of the laboratory experiments showed that the upper and lower limit of the Freundlich coefficient and exponent for the various soil layers amounted to $2.50 - 4.80 \text{ cm}^3 \text{ g}^{-1}$ and $0.74 (-)$ respectively. Thus, it is assumed that the Freundlich exponent was equal to 0.74 and the value of the Freundlich coefficient varied from 2.50 to $4.80 \text{ cm}^3 \text{ g}^{-1}$.

Optimization criteria: For the different values of the

Freundlich coefficient, the Root-Mean-Square ($RMS_{[Me]}$) for metamitron was calculated. $RMS_{[Me]}$ is formulated analogous to the Root-Mean-Square for groundwater levels (equation 4.1). The simulated concentration of metamitron in the drain water was compared with the observed concentration of metamitron. As most values were below the detection limit, the best fit was often obtained if the simulated concentration of metamitron stayed below the detection limit. Besides the Root-Mean-Square as optimization criteria, the fact whether the model was able to predict the order of magnitude of the observed highest concentration level and the period of leaching was also taken into account.

Results: The optimum value of the Freundlich coefficient (K_F) is equal to 2.50 and $2.65 \text{ cm}^3 \text{ g}^{-1}$ for respectively the data sets of 1990 (Plot I) and 1991 (Plot II). These values agrees with the result of the laboratory experiments, in which the roughly same Freundlich coefficient and exponent were detected for the upper

part of the soil (0 - 0.40 m - soil surface). $RMS_{[Me]}$ amounted to $0.54 \mu\text{g l}^{-1}$ in 1990 and $0.15 \mu\text{g l}^{-1}$ in 1991. If the Freundlich coefficient (K_F) is more than $2.9 \text{ cm}^3 \text{ g}^{-1}$, the concentration of metamitron in the drain pipes was calculated below the detection limit.

Results of the calibration of the concentration metamitron are presented in figure 4.23. It shows a relatively good resemblance between the observed and simulated leaching of metamitron both for the period of leaching as well as the concentration level. In 1990, high concentrations of metamitron ($4.5 \mu\text{g l}^{-1}$ and $8.8 \mu\text{g l}^{-1}$) were measured directly after application. This could not be simulated, which explain the high value of $RMS_{[Me]}$ in 1990. Besides, in spite of the fact that bromide was applied at the same time, no high concentrations of bromide were measured directly after application. The most probable explanation is that the high concentrations of metamitron are caused by mistakes made in the laboratory.

Results for the simulated remaining amount of metamitron in the soil in 1990 and 1991 using the optimum value of the Freundlich coefficient (K_F) are corresponding to simulated remaining amount of metamitron in the soil as presented in figure 4.22.

Sensitivity analyses: Calibration showed that both the value of the Freundlich coefficient and the Freundlich exponent have a considerable impact on leaching and the concentration of metamitron in the drain pipes. The optimum value was reached if the Freundlich coefficient (K_F) is equal to $2.65 \text{ cm}^3 \text{ g}^{-1}$ and the Freundlich exponent ($1/n$) is equal to 0.74. If the Freundlich exponent was reduced to $1 \text{ cm}^3 \text{ g}^{-1}$ the concentrations of metamitron in the drain pipes increased by a factor 50 to 80. If the Freundlich coefficient was lowered to 0.60 (-), the concentrations of metamitron in the drain pipes increased by a factor 100 to 150.

Many model simulations were undertaken in order to test the sensitiveness for each combination of values for the mobile/immobile concept, varying from 1.0 (mobile)/ 0.0 (immobile) up to 0.1 (mobile) / 0.9 (immobile). For these calculations the dispersion length (L_{dis}) was set at 5 cm. The optimum value for the model-efficiency was obtained for the combination

mobile/immobile = 0.5/0.5. If the immobile fraction was set at 0.0 (only mobile water), the maximum concentration of metamitron in the drain pipes amounted to $0.0 \mu\text{g l}^{-1}$. If the immobile fraction was set at 0.9, the maximum concentration of metamitron in the drain pipes amounted to $3.4 \mu\text{g l}^{-1}$ in 1990 and $2.3 \mu\text{g l}^{-1}$ in 1991. If the exchange coefficient increases, the difference between a merely mobile soil and a soil which is divided between mobile and immobile fractions become smaller.

Results of sensitivity analyses show that the temperature has an enormous impact on the leaching of metamitron. If the average soil temperature was lowered by 5°C , the maximum concentration levels in the drain pipes increased by a factor 15 to 25.

The sensitivity of F (constant for selective uptake of metamitron by the root system) for leaching is relatively low, because sorption and temperature influences are dominant. Besides, uptake of water by tulips during the months of February, March and April is small.

Conclusions: Both in 1990 and 1991 the simulated concentration of metamitron in the drain pipes was below the detection limit if the Freundlich parameters obtained from the laboratory studies were used. However, the observed concentration of metamitron in the drain pipes could be reasonably well calculated with the model SWACRO, using the conventional convection-dispersion equation ($L_{dis} = 16 \text{ cm}$; mobile/immobile = 1.0/0.0) and the optimized Freundlich coefficient and exponent.

The optimum value of the Freundlich coefficient and exponent are approximately equal to the values which were detected in the plough layer during the laboratory experiments. However, according to the laboratory experiments the Freundlich coefficient increases with depth. Thus, it may be expected that leaching is retarded due to the stronger sorption. The fact that metamitron travels somewhat faster than may be expected on the basis of the laboratory study may be caused by the former reed roots in the subsoil (figure 4.10). Due to these former roots in the subsoil, metamitron reaches the sorption sites of the porous

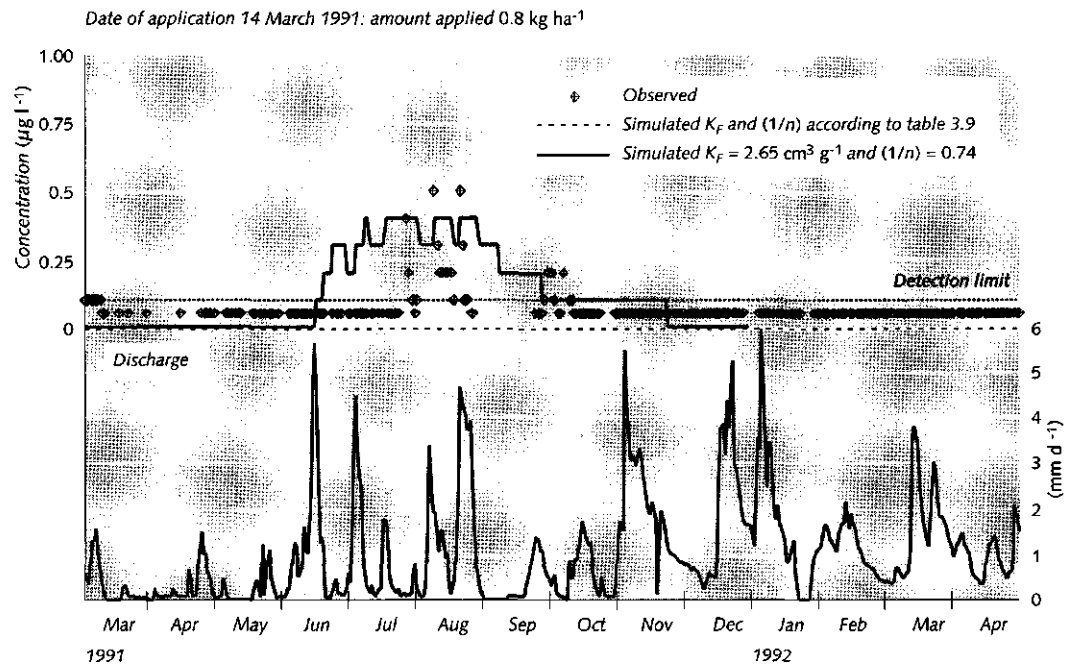
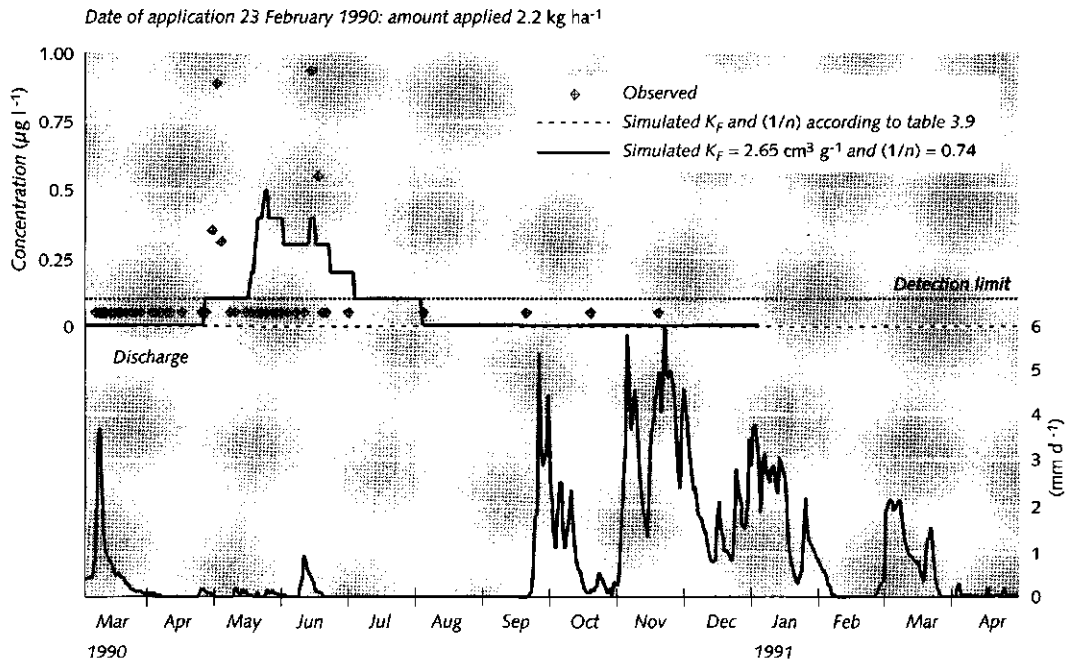


Figure 4.23. Observed and simulated concentration of metamitron in the drain pipes at the experimental field North-East Polder.

matrix in a less extent during its movement though the soil. Sorption is partly a diffusion controlled mechanism.

Sensitivity analyses showed that next to sorption, soil temperature has an enormous impact on the leaching of metamitron. At the experimental field North-East Polder, root uptake was of minor importance to the leaching of metamitron. The introduction of a mobile/immobile concept may increase the leaching of metamitron, dependent on the values taken for the mobile fraction, α and L_{dis} .

4.1.3.2 (Z) 1,3-Dichloropropene

The dosage of 1,3-dichloropropene applied at a depth of between 0.15 and 0.2 m, amounts to 170 kg ha⁻¹. It is a roughly equal mixture of the (E) and (Z)-isomer (subsection 3.2.2). Differences between the (E) and (Z)-isomer for sorption and transformation are small (subsection 3.1.2.2). As the difference between the observed concentration of the (Z) and (E)-isomer in the soil profile and drain pipes was very small (subsection 3.2.9 and 3.2.10), calculations will be limited to the (Z)-isomer.

Model: The flow of (Z) 1,3-dichloropropene is partly described with the same formula as the flow of metamitron. The set of equations used for transport of

solutes is summarized in table 4.1 (water flow), table 4.6 (solute flow) and table 4.7 (transformation and sorption). An additional set of equations is needed for the description of microbial transformation in the plough layer and volatilization. The most important equations, which have been used to calculate microbial transformation and volatilization, are summarized in table 4.9.

Input: Data on date of application, quantity applied and period of the field measurements for 1,3-dichloropropene have already been presented in table 3.14. Input parameters to determine soil water fluxes are given in table 4.2. Optimization showed that the transport of bromide could be reasonably well described with the convection-dispersion equation, assuming a soil without an immobile phase (mobile/immobile = 1.0/0.0) and the dispersion length (L_{dis}) equal to 16 cm.

The transformation of 1,3-dichloropropene was examined in laboratory experiments. These experiments showed that transformation in the top layer (0 - 0.4 m - surface) most likely took place along microbial pathways. The microbial development and microbial transformation are described by equation 2.52 and 2.53 respectively. The parameters needed to solve the equations were obtained using the statistical package BMPD. The microbial parameters α_m , β_m and γ_b cannot be estimated exactly, owing to the lack of explicit data about microbial activity after application of (Z) 1,3-dichloropropene.

Because of the short-term nature of the experiments, the microbial mortality parameters α and β were fixed to 0. The initial population size M_0 was set at 0.349 (10⁵ micro-organisms g⁻¹ dry weight) (Vink et al., 1994). The biological activity of micro-organisms strongly depends upon the soil temperature. The rate of a microbial reaction is presented in equation 2.54. The parameters needed to solve the equation were obtained from Vink et al. (1994). They are presented in table 4.10 and are equal for both the (Z) and (E)-isomer.

Below a depth of 0.4 m the transformation of 1,3-dichloropropene is described by first order reaction. The influence of the temperature on the rate of transformation is presented in equation 2.47. The coefficient γ_a

Table 4.9. Additional set of equations for water and solute flow used for the simulation of the transport of (Z) 1,3-dichloropropene in the soil.

$R_t = \frac{1}{\gamma_b} \frac{\mu_{max} c^*}{K_m + c^*} M$	2.52
$\frac{dM}{dt} = \frac{\mu_{max} c^*}{K_m + c^*} M - \alpha_m (1 + \beta_m M) M$	2.53
$\mu(T) = \mu_{max} \left(\frac{T_{max} - T}{T_{max} - T_{opt}} \right)^a e^{\frac{(T - T_{opt})}{T_{max} - T_{opt}}} \text{ for } T_{min} < T < T_{max}$	2.54
$\mu(T) = 0 \text{ for } T \leq T_{min} \wedge T \geq T_{max}$	2.54
$c_l = K_g c_g$	2.58
$K_g = b_2 \exp(-b_3 T)$	2.59

Table 4.10. Input parameters to determine the leaching of (Z) 1,3-dichloropropene

TRANSFORMATION IN THE TOP LAYER (0-40 CM)			
Symbol	Parameter	Value	Equation
α_m	Microbial mortality rate constant	0	2.53
β_m	Microbial mortality rate constant	0	2.53
γ_b	Gain factor for biomass production	0.56 d ⁻¹	2.52
K_M	Saturation constant of Monod's equation	0.64 mg kg ⁻¹	2.52/2.53
Q_{10}	Increase of decay by increase of temperature	3.22	2.55
T_{opt}	Optimum temperature for maximum microbial activity	15.6 °C	2.54
T_{max}	Lethal temperature for micro-organisms	40.0 °C	2.54
T_{min}	Minimum temperature for microbial activity	0 °C	2.54
TRANSFORMATION IN THE DEEPER SOIL LAYERS (40-80 CM)			
Symbol	Parameter	Value	Equation
$k_{1,ref}$	Reference coefficient for first-order transformation rate	0.51 d ⁻¹	2.46
γ_a	Coefficient	0.10 °C ⁻¹	2.47
T_{ref}	Reference soil temperature	20 °C	2.47
θ_{ref}	Soil moisture content at reference level	0.32	2.49
b_1	Parameter	1	2.49
f_z	Coefficient for the influence of the soil depth on the rate of transformation	1.0 - 0.9	2.46
DISTRIBUTION BETWEEN GAS AND LIQUID PHASE AND DIFFUSION IN THE GAS PHASE			
$D_{diff,air}$	Vapour diffusion coefficient in air	0.075 cm ² s ⁻¹	2.38
b_2	Parameter	70	2.59
b_3	Parameter	0.070 °C ⁻¹	2.59
τ_g	Tortuosity factor for diffusion in the gas phase	(figure 4.24)	2.38
SORPTION			
Symbol	Parameter	Value	Equation
K_F	Freundlich coefficient	1.0-2.0 cm ³ g ⁻¹ (table 3.12)	2.57
$(1/n)$	Freundlich exponent	0.65-0.90 (table 3.12)	2.57
$c_{l,ref}$	Reference concentration in the liquid phase	10 mg l ⁻¹	2.57
ρ	Dry soil bulk density	1465 kg m ⁻³	2.32

was established at 0.10 C⁻¹. The influence of the soil moisture content is given by equation 2.49. The parameters θ_{ref} and b_1 were set at 0.32 and 1. The influence of the soil depth on the rate of transformation is presented by a factor, f_z . This factor is equal to 1 for the soil layer at a depth of 0.4 - 0.6 m. Below this depth f_z is equal to 0.9 (subsection 3.1.2.2).

For most pesticides, the contribution of volatilization to the loss of the pesticide is negligible. However, for

1,3-dichloropropene volatilisation can be of significant importance. The relation between the concentration in the liquid phase and gas phase is described by equation 2.58. The ratio for partitioning the fumigant between the liquid and gas phase (K_g) is a function of the soil temperature (Leistra, 1972). K_g decreases when the soil temperature rises according to an exponential function (equation 2.59). The parameters b_2 and b_3 of this function are presented in table 4.10. The value of K_g is substantially higher for the (E)-isomer. This is connected

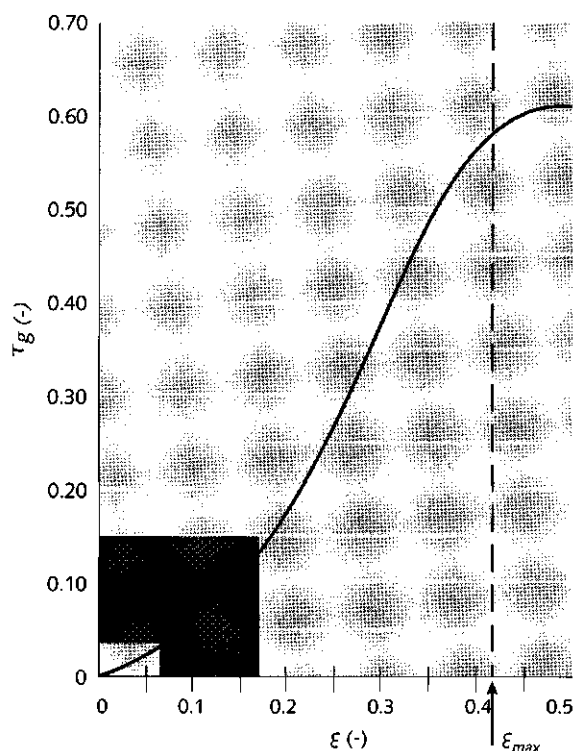


Figure 4.24. Relation between the volume fraction of the gas phase (ϵ) and the tortuosity factor (τ_g) for diffusion in the gas phase. For the experimental field *North-East Polder*, ϵ varies between 0.06 and 0.18 (data obtained from Leistra, 1972).

with a lower vapour pressure and a slightly greater solubility in water (Leistra, 1972).

Vapour diffusion in the gas phase is usually assumed to be the predominant process. The vapour diffusion coefficient of 1,3-dichloropropene in the soil is calculated according to equation 2.38. It depends on the gas-filled pore volume and the tortuosity factor. The vapour diffusion coefficient in air is presented in table 4.10. The tortuosity factor depends on the volume fraction of the gas phase as presented in figure 4.24.

Sorption of 1,3-dichloropropene was examined in laboratory experiments (subsection 3.1.2.2). Sorption is described with the Freundlich isotherm equation according to equation 2.57. The results are presented in table 3.12. The values of the Freundlich coefficient and

exponent measured in the laboratory experiments for (Z) 1,3-dichloropropene at a temperature of 10 °C were used as input.

Results: Figure 4.25 gives the observed and simulated content of (Z) 1,3-dichloropropene in the soil in 1989, 1, 15 and 50 days after application. The simulated content in the soil did not agree with the observed content of dichloropropene, particularly 1 and 15 days after application. Presumably, (Z) 1,3-dichloropropene was transformed faster than was calculated or the contribution of volatilization to the loss of dichloropropene was more extensive than simulated. Fifteen days after application no (Z) 1,3-dichloropropene could be detected in the soil profile.

Figure 4.26 shows the simulated and observed concentration of dichloropropene in the drain pipes in 1989. The concentration of (Z) 1,3-dichloropropene in the drain pipes was simulated below the detection limit. The results of the optimized Freundlich parameters will be discussed at the end of this subsection. The observed concentration level in the drain pipes never exceeded 0.5 $\mu\text{g l}^{-1}$.

Figure 4.27 gives the volatilisation of (Z) 1,3-dichloropropene into the air and shows that volatilisation strongly depends on precipitation. The maximum calculated source strength amounted to 5 $\text{mg m}^{-2} \text{d}^{-1}$.

Figure 4.28 gives the simulated fate of (Z) 1,3-dichloropropene in the soil in 1989. This figure shows that after two months more than 90% of (Z) 1,3-dichloropropene was transformed in the soil. The leached fraction is less than 0.1% and approximately 2% of the applied dose has volatilized into the air.

Figure 4.29 gives the observed and simulated concentration profiles of (Z) 1,3-dichloropropene in the soil in 1990, 1, 4, 8, 14, 22 and 43 days after application. It shows a fairly good agreement between the observed and simulated movement of (Z) 1,3-dichloropropene through the soil.

Figure 4.30 shows the simulated and observed concentration of dichloropropene in the drain pipes in 1990 (Plot II). The concentration of (Z) 1,3-dichloropropene

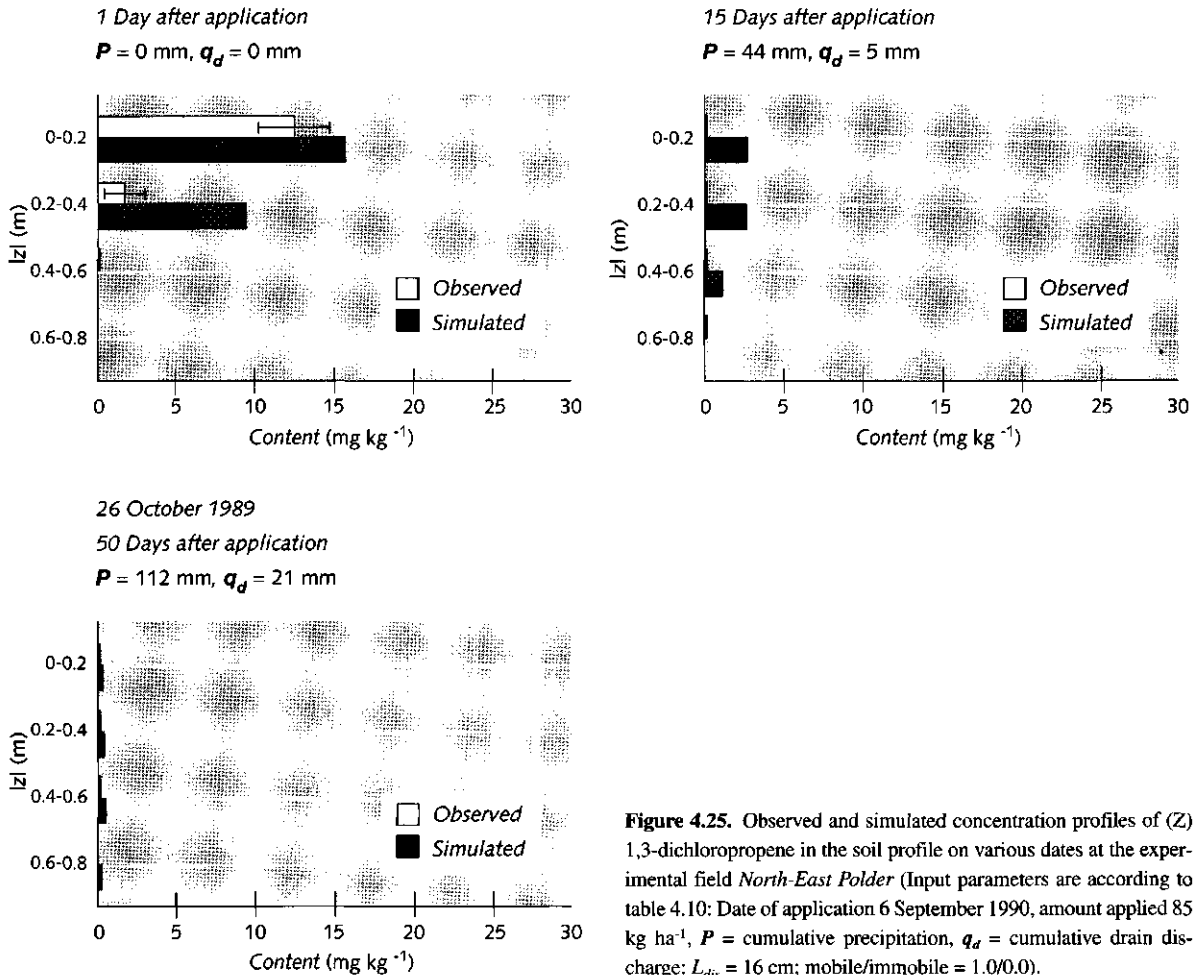


Figure 4.25. Observed and simulated concentration profiles of (Z) 1,3-dichloropropene in the soil profile on various dates at the experimental field North-East Polder (Input parameters are according to table 4.10: Date of application 6 September 1990, amount applied 85 kg ha⁻¹, P = cumulative precipitation, q_d = cumulative drain discharge: $L_{dis} = 16 \text{ cm}$; mobile/immobile = 1.0/0.0).

in the drain pipes was simulated below the detection limit. The results of the optimized Freundlich parameters will be discussed at the end of this subsection. The observed concentration level in the drain pipes never exceeded 0.5 $\mu\text{g l}^{-1}$. Approximately 20 days after application, traces of (Z) 1,3-dichloropropene could still be detected in the drain pipes. Due to the relatively wet autumn of 1990, the concentration in the drain pipes was slightly higher as compared to the previous year.

Figure 4.31 gives the volatilisation of (Z) 1,3-dichloropropene into the air in 1990 (Plot II). The maximum simulated source strength of (Z) 1,3-dichloropropene

was slightly less than the previous year and amounted to 4 mg m⁻² d⁻¹.

Figure 4.32 shows the simulated fate of (Z) 1,3-dichloropropene in the soil. In spite of the high precipitation surplus in the weeks after injection of 1,3-dichloropropene, the leached fraction is still smaller than 0.1 % of the dose applied. After 2 months more than 95% has been transformed in the soil. Due to the higher precipitation, the volatilisation was lower than the previous year and amounted to approximately 1% of the dose applied.

In the same year (1990), only 2 months later, 1,3-

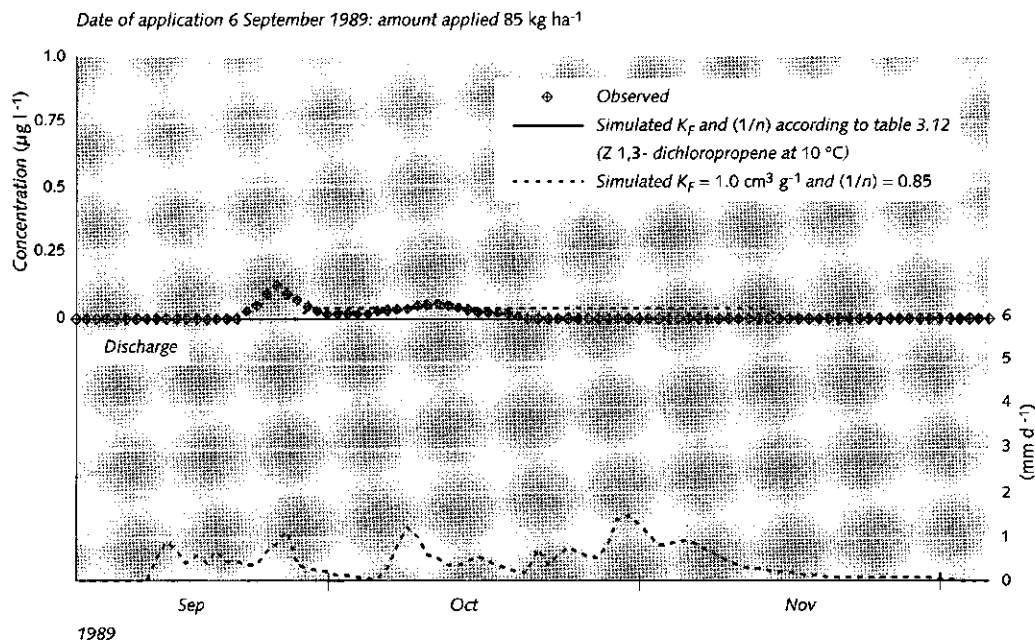


Figure 4.26. Observed and simulated concentration of (Z) 1,3-dichloropropene in the drain pipes at the experimental field *North-East Polder* with input parameters according to table 4.10 and for the optimized parameter set $K_F = 1.0 \text{ cm}^3$ and $(1/n) = 0.85$.

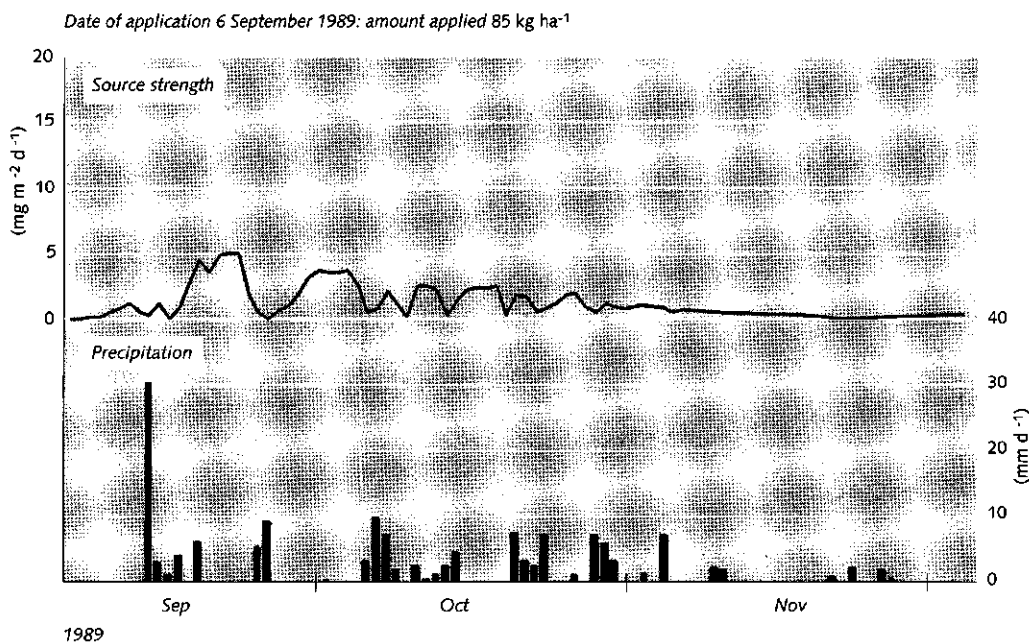


Figure 4.27. Simulated volatilisation of (Z) 1,3-dichloropropene in the air and precipitation at the experimental field *North-East Polder* (Input parameters are according to table 4.10).

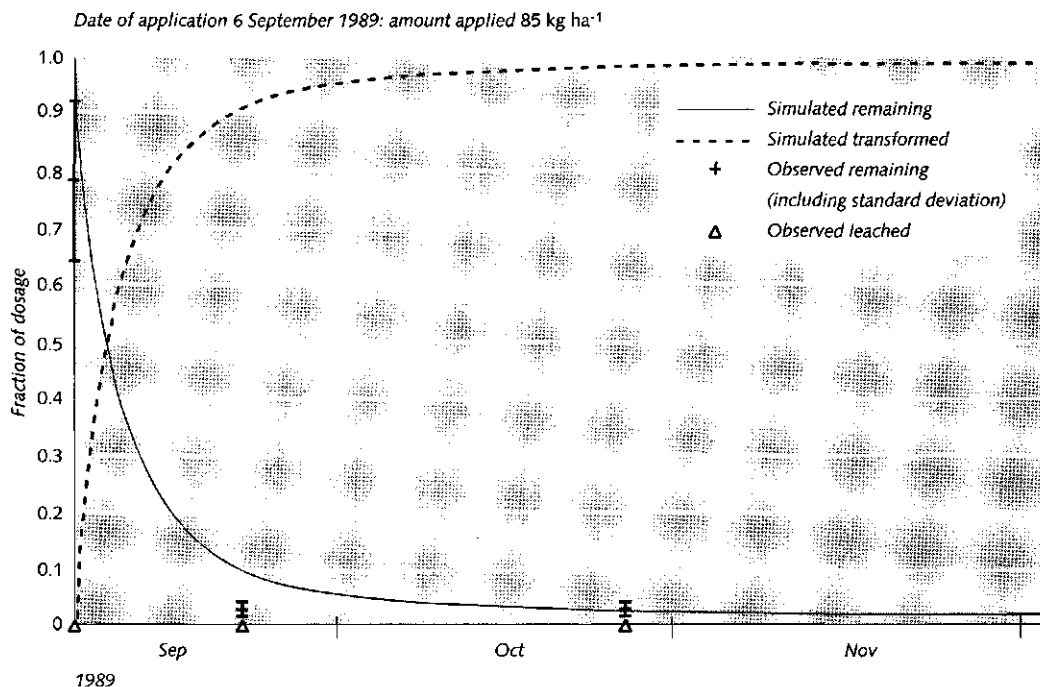


Figure 4.28. Observed and simulated fate of (Z) 1,3-dichloropropene in the soil at the experimental field *North-East Polder* in 1989 (Input parameters are according to table 4.10). Simulated volatilized ≈ 0.02 and simulated leached < 0.001 .

dichloropropene was injected at a different plot. Figure 4.33 shows that 33 days after application, (Z) 1,3-dichloropropene was simulated in the soil layer 0.6 - 0.8 m below soil surface. Unfortunately, no field research was undertaken to measure the concentration profiles in the soil.

The simulated and observed concentrations of 1,3-dichloropropene in the drain pipes are presented in figure 4.34. Due to the lower soil temperatures and increasing precipitation surplus, the concentration of (Z) 1,3-dichloropropene in the drain pipes increases over a factor 1000. The simulated concentration slightly underestimated the observed concentration. The results of the optimized Freundlich parameters will be discussed at the end of this subsection. The calculated concentration showed a longer tailing than was observed.

Figure 4.35 gives the volatilisation of (Z) 1,3-dichloropropene into the air in 1990 (Plot III: date of applica-

tion 7 November 1990). The maximum simulated source strength of (Z) 1,3-dichloropropene tripled compared to the previous applications and amounted to 15 mg m⁻² d⁻¹.

Figure 4.36 shows the simulated fate of (Z) 1,3-dichloropropene in the soil. Due to the high concentration of 1,3-dichloropropene in the drain pipes and high drain discharge during the winter period, the leached fraction amounted to approximately 3.5% of the dose applied. After 5 months, 90% of the dose applied has been transformed in the soil. Due to the higher concentrations of (Z) 1,3-dichloropropene in the soil during a longer period, volatilisation to the air amounted to approximately 6.5% of the dose applied. In spite of lower soil temperatures, the fraction volatilized to the air increased compared to the previous applications.

Optimization of the Freundlich coefficient and expo-

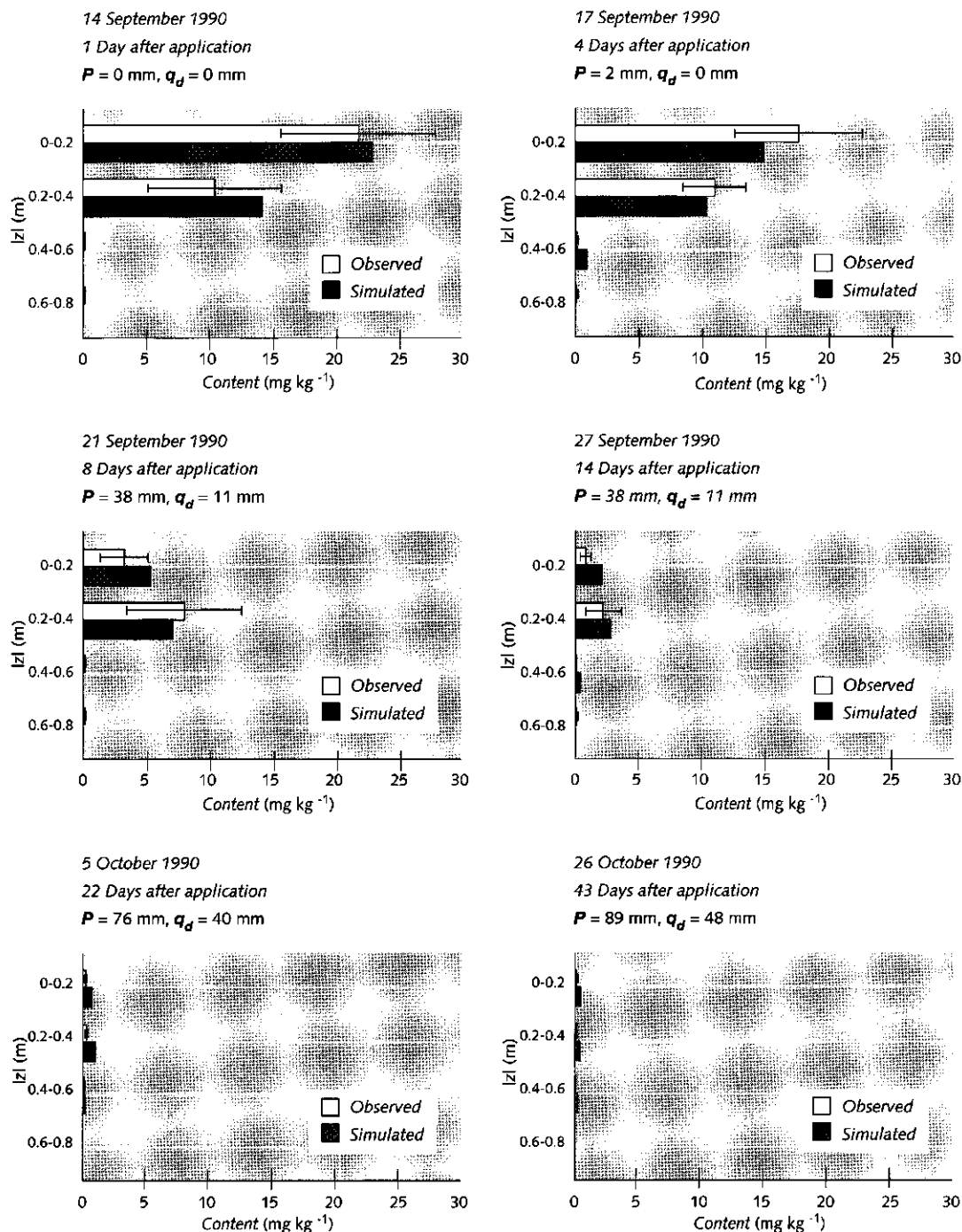


Figure 4.29. Observed and simulated concentration profiles of (Z) 1,3-dichloropropene in the soil profile on various dates at the experimental field North-East Polder (Input parameters according to table 4.10: Date of application 13 September 1990, amount applied 85 kg ha^{-1} , P = cumulative precipitation, q_d = cumulative drain discharge: $L_{ds} = 16 \text{ cm}$; mobile/immobile = 1.0/0.0).

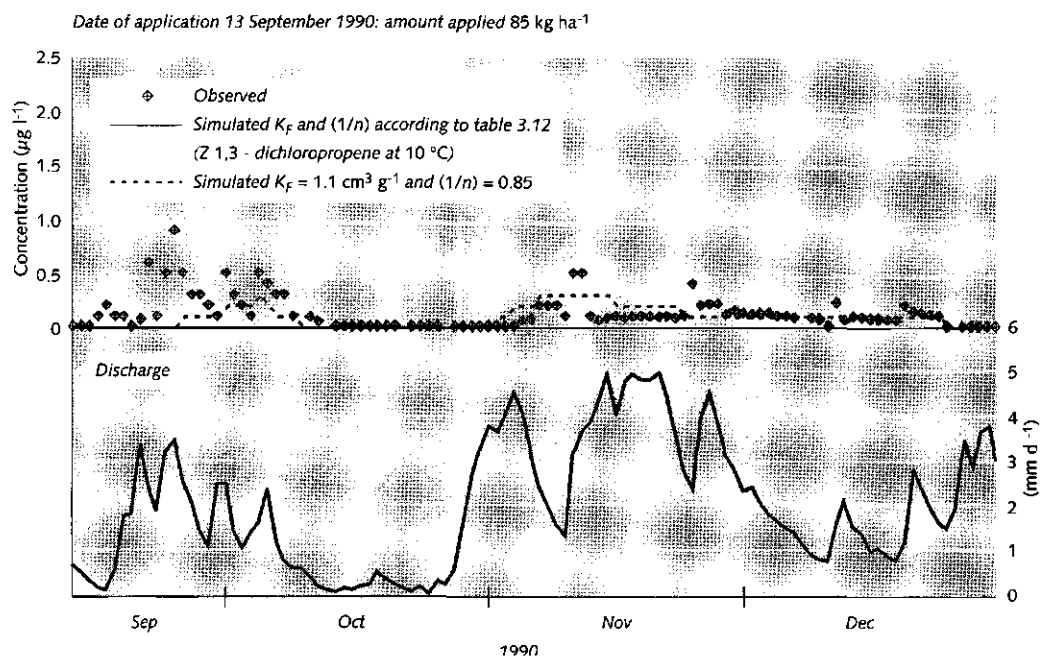


Figure 4.30. Observed and simulated concentration of (Z) 1,3-dichloropropene in the drain pipes at the experimental field *North-East Polder* with input parameters according to table 4.10 and for the optimized parameter set $K_F = 1.1 \text{ cm}^3$ and $(1/n) = 0.85$.

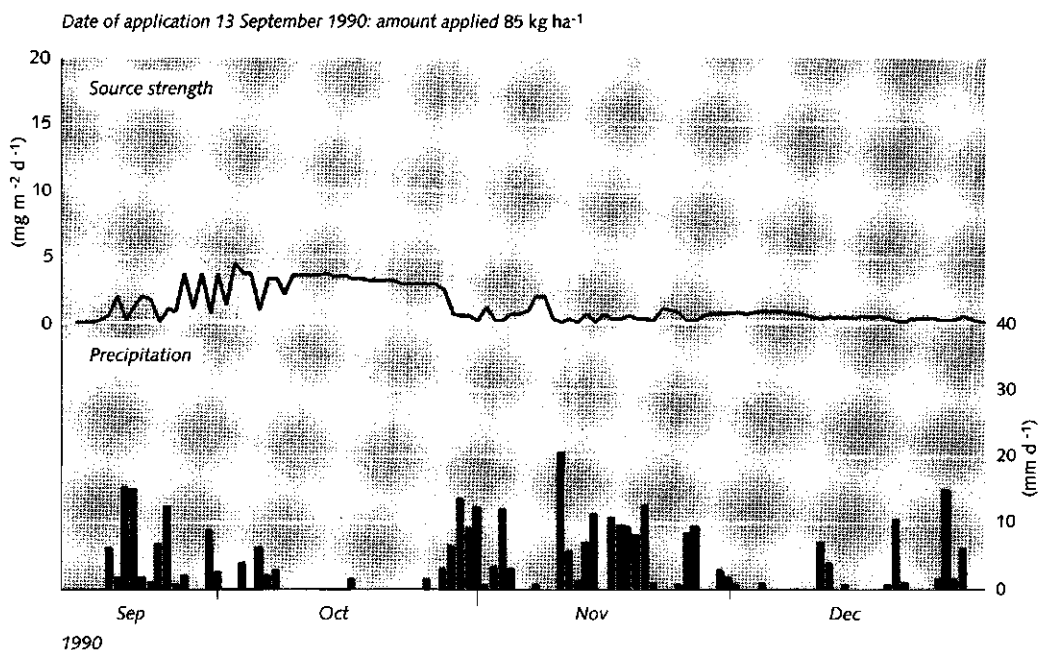


Figure 4.31. Simulated volatilisation of (Z) 1,3-dichloropropene in the air and precipitation at the experimental field *North-East Polder* (Input parameters according to table 4.10).

Date of application 13 September 1990: amount applied 85 kg ha⁻¹

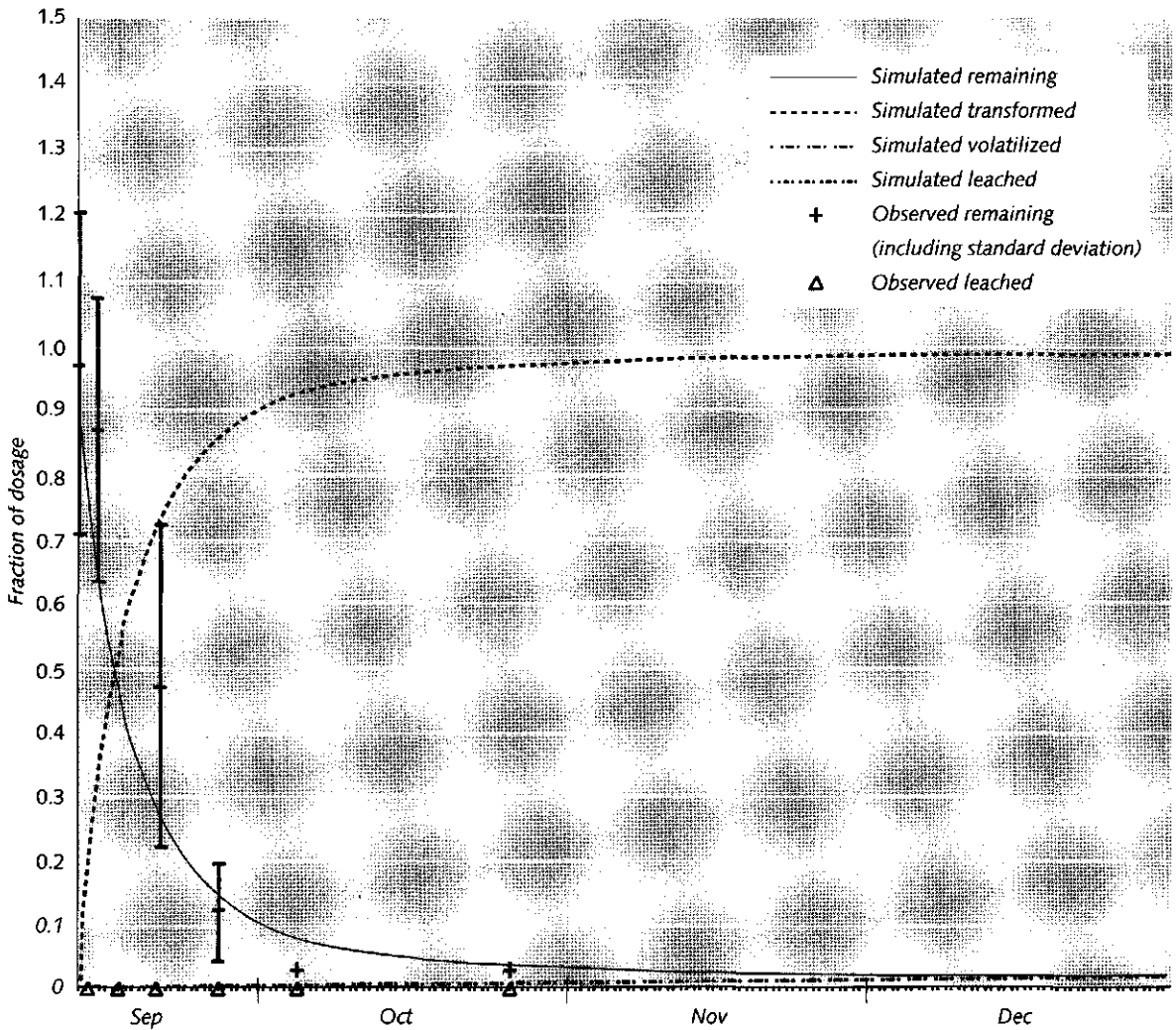


Figure 4.32. Observed and simulated fate of (Z) 1,3-dichloropropene in the soil and precipitation at the experimental field *North-East Polder* (Input parameters according to table 4.10).

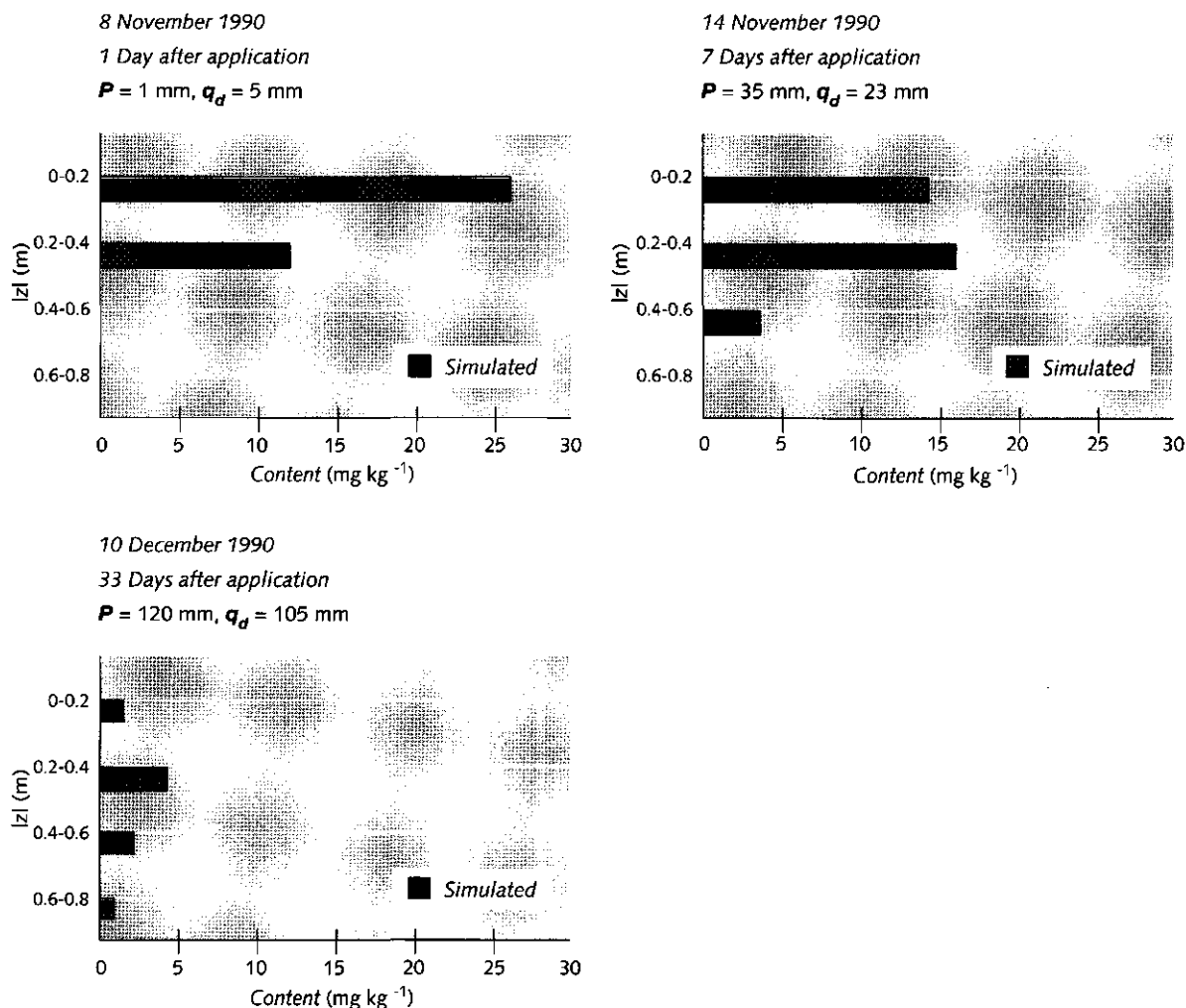


Figure 4.33. Observed and simulated concentration profiles of (Z) 1,3-dichloropropene in the soil profile on various dates at the experimental field North-East Polder (Day of application 7 November 1990, amount applied 85 kg ha^{-1} , P = cumulative precipitation, q_d = cumulative drain discharge: $L_{dis} = 16 \text{ cm}$; mobile/immobile = 1.0/0.0).

nent: Sorption of 1,3-dichloropropene was examined in laboratory experiments. The results of the experiments are presented in table 3.12 (subsection 3.1.2.2). It shows that the values of the sorption-isotherm vary with depth and soil temperature. As the model SWACRO does not differentiate various Freundlich coefficients and exponents for each soil temperature, these were determined during calibration. As a result of the laboratory experiments, the upper and lower

limit of the Freundlich coefficient and exponent amounted to $1.0 - 2.0 \text{ cm}^3 \text{ g}^{-1}$ and $0.65 - 0.90 (-)$ respectively. The concentration of (Z) 1,3-dichloropropene in the drain pipes was calculated for all combinations of K_F and $(1/n)$, starting from $K_F = 1.0 \text{ cm}^3 \text{ g}^{-1}$ and $(1/n) = 0.65$ up to $K_F = 2.0 \text{ cm}^3 \text{ g}^{-1}$ and $(1/n) = 0.90$.

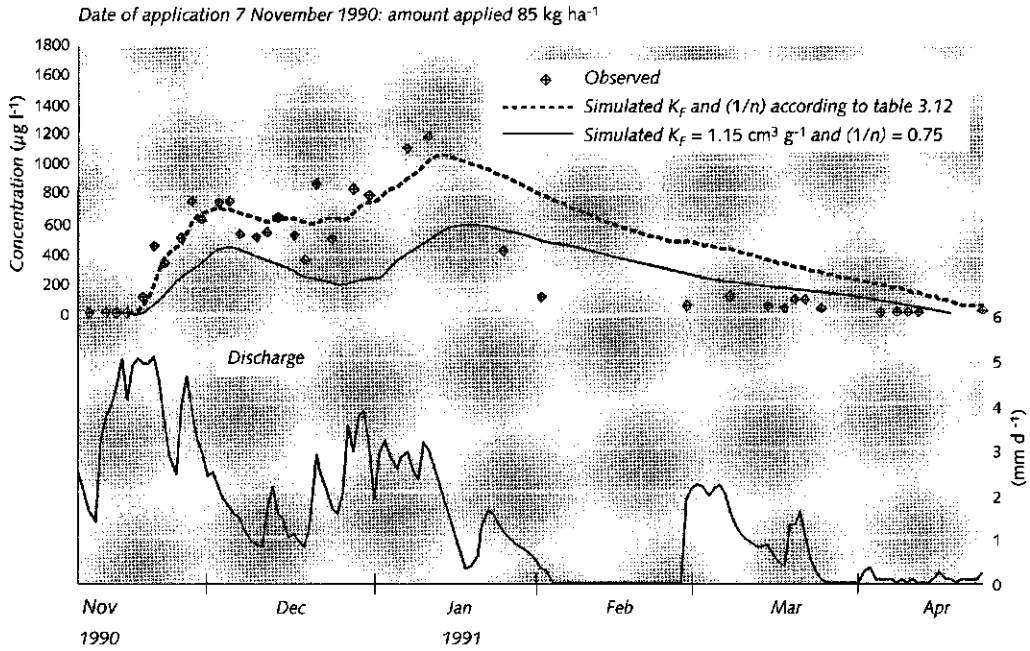


Figure 4.34. Observed and simulated concentration of 1,3-dichloropropene in the drain pipes at the experimental field *North-East Polder* with input parameters according to table 4.10 and for the optimized parameter set $K_F = 1.15 \text{ cm}^3$ and $(1/n) = 0.75$.

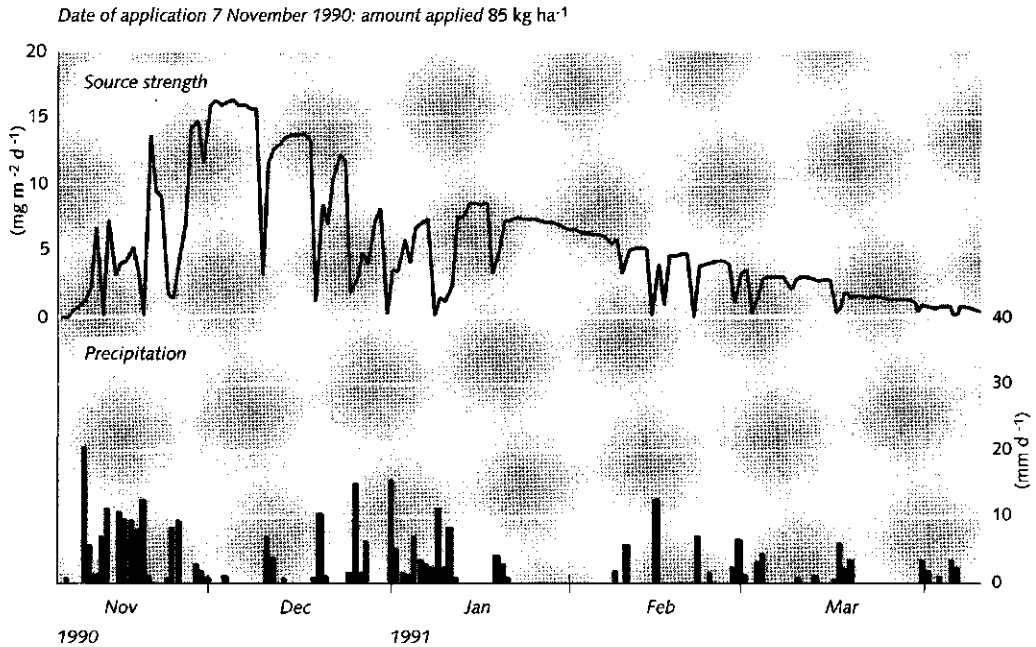


Figure 4.35. Simulated volatilisation of (Z) 1,3-dichloropropene in the air and precipitation at the experimental field *North-East Polder* (Input parameters according to table 4.10).

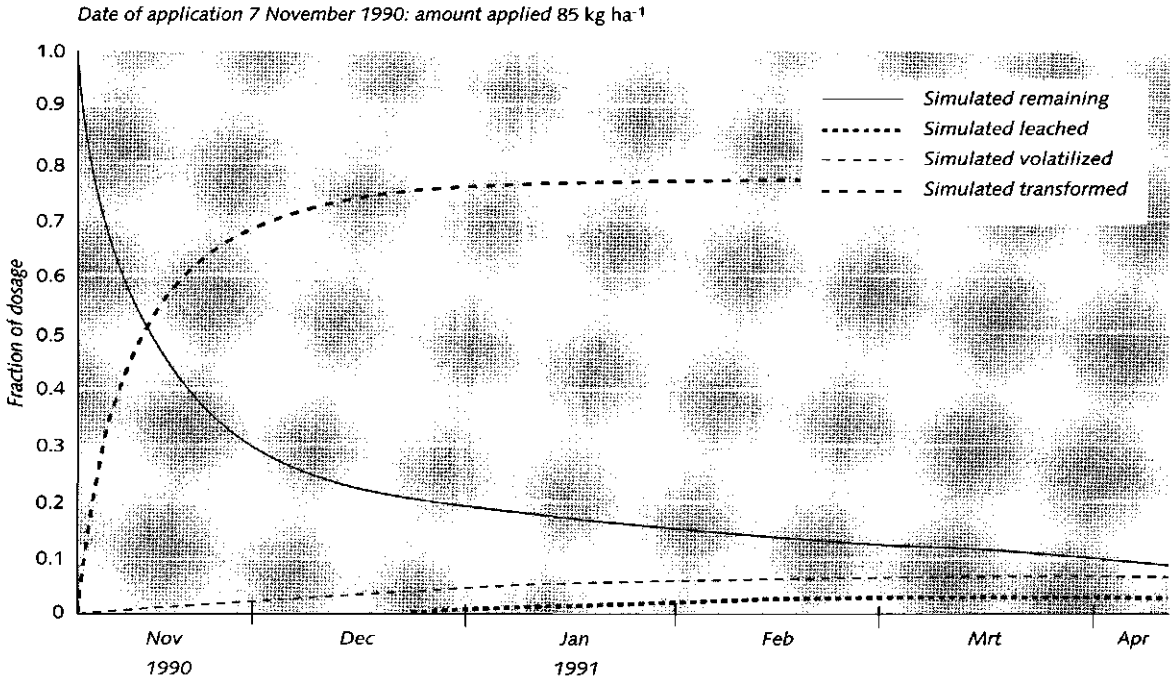


Figure 4.36. Simulated fate of (Z) 1,3-dichloropropene in the soil at the experimental field *North-East Polder* (Input parameters according to table 4.10).

Optimization criteria: For the transport of dichloropropene through the soil, the Root-Mean-Square (RMS_{IDCP}) was selected as the optimalization criterion. RMS_{IDCP} is formulated analogous to the Integral Square Error for groundwater levels (equation 4.1). Calibration of the model was undertaken by comparing the simulated concentration of (Z) 1,3-dichloropropene in the drain pipes with the observed concentration of (Z) 1,3-dichloropropene.

Results: Calibration showed that the value of the Freundlich exponent and Freundlich coefficient have a significant impact on leaching and the concentration of 1,3-dichloropropene in the drain pipes. The optimum value which was calculated for three data sets (time of application: September 1989, September 1990 and November 1990), is presented in table 4.11 (presented in bold print). The simulated concentration of (Z) 1,3-dichloropropene in the drain pipes are presented in figure 4.26 (September 1989), figure 4.30 (September 1990) and figure 4.34 (November 1990). The optimum

values for K_F and $(1/n)$ are within the range of results of the laboratory experiments.

The simulated concentration profiles of (Z) 1,3-dichloropropene in the soil profile, volatilisation of (Z) 1,3-dichloropropene in the air and fate of (Z) 1,3-dichloropropene in the soil have not been presented for the optimized Freundlich parameters, as the dissimilarity between the results of the optimized Freundlich parameters and the results of the Freundlich parameters obtained from the laboratory studies (table 3.12: (Z) 1,3-dichloropropene at 10 °C) are very small and can therefore be ignored.

Sensitivity analyses: If K_F and $(1/n)$ are set at 1.0 cm³ g⁻¹ and 0.65 and are compared to the optimum values, the maximum concentrations in the drain pipes are 2, 4 and 1.5 times as high for application in September 1989, September 1990 and November 1990 respectively. If the Freundlich coefficient was reduced to 0.5 cm³ g⁻¹ the concentrations of (Z) 1,3-dichloropropene

Table 4.11. Optimum value for the Freundlich coefficient (K_F) and Freundlich exponent ($1/n$) for three different experimental plots at the experimental field *North-East Polder* (Date of application: September 1989, September 1990 and November 1991). Optimum values for the various datasets are given in bold print.

K_F ($\text{cm}^3 \text{ g}^{-1}$)	$(1/n)$ (-)	$RMS_{(DCP)}$ ($\mu\text{g l}^{-1}$)		
		Plot I (September 1989)	Plot II (September 1990)	Plot III (November 1990)
1.0	0.85	0.08	0.18	275
1.1	0.85	0.09	0.15	244
1.15	0.75	0.11	0.21	218

in the drain pipes increased by a factor 1.5 to 10. If the Freundlich exponent was lowered by to 0.5, the concentrations in the drain pipes increased by a factor 3 (application in November) to 15 (application in September). If K_F and $(1/n)$ are set at $2.0 \text{ cm}^3 \text{ g}^{-1}$ and 0.95 and are compared to the optimum values, the maximum concentrations in the drain pipes are below the detection limit for application in September 1989 and September 1990. For application in November 1990, the maximum concentration drops by a factor 2.5.

The soil temperature has an enormous impact on the transformation and as a consequence on the leaching of (Z) 1,3-dichloropropene. This has already been demonstrated in the field experiments. The maximum concentration in the drain pipes amounted to more than 1 mg l^{-1} if (Z) 1,3-dichloropropene was injected in November. These concentrations increased by a factor 1.5 if soil temperatures were lowered by another 5°C .

Compared to the influence of the temperature and sorption, the influence of dividing the soil into immobile and mobile phases on the leaching of 1,3-dichloropropene was small. The concentration of 1,3-dichloropropene in the drain pipes only increased, if the exchange coefficient (α) was taken as smaller than 0.05. The introduction of a mobile/immobile concept may increase leaching, dependant of the values taken for the mobile fraction, L_{dis} and α .

Differences between the (E) and (Z)-isomer can be neglected as far as sorption and transformation are con-

cerned. However, the value of K_g (equation 2.58) is substantially higher for the (E)-isomer, indicating that the volatilisation of (E) 1,3-dichloropropene in the air will be smaller. Calculation of showed that the source strength of (E) 1,3-dichloropropene amounted approximately 2/3 of the size of the (Z)-isomer.

Conclusions: Both in 1990 and 1991 the observed concentration of (Z) 1,3-dichloropropene in the drain pipes could be reasonably well calculated with the model SWACRO, using the conventional convection-dispersion equation ($L_{dis} = 16 \text{ cm}$; mobile/immobile = 1.0/0.0) and the optimized Freundlich parameters. The optimum values for the K_F and $(1/n)$ are within the range of the results of the laboratory experiments. If the Freundlich parameters from the laboratory experiments were used, the simulated concentration of (Z) 1,3 dichloropropene in the drain pipes was lower than the observed concentration.

Both field experiments and sensitivity analyses showed that the soil temperature has an enormous impact on the leaching of (Z) 1,3-dichloropropene. Differences between the concentrations of (Z) 1,3-dichloropropene between application in September and November varied over a factor 1000. Due to relatively high soil moisture content, volatilisation to the air amounted never more than 10% of the dose applied. If (Z) 1,3-dichloropropene is applied in September, volatilisation to the air was approximately 1 - 2% of the dose applied.

4.2 Eastern Flevoland

4.2.1 Water flow

The collection of data at the experimental field in Eastern Flevoland is presented in chapter 3. The data from the experimental field were either used as input for the model *SWACRO* or as observed values which were compared with simulated values. The set of the most important equations used for the description of water flow is the same as for the experimental field North-East Polder and has been presented in table 4.1. In order to describe the flow of water in cracked clay soils, without leaving the concept of one-dimensional flow, imaginary drains were implemented at a depth of 0.35 m (figure 2.8). The concept of preferential flow through cracks in clay soil has been discussed in subsection 2.3.2. In order to show the effect of the implementation of imaginary drains, simulations were executed for two concepts: with and without imaginary drains. Except for the lateral boundary conditions input data are similar for both concepts. To solve the equations the following input data are used:

Numerical method: To solve the tridiagonal system of equations, a stop criterium was defined that applied for the experimental field Eastern Flevoland. The values for the relative tolerance and the absolute tolerance are presented in table 4.12.

Soil physical properties: The soil profile of the experimental field in Eastern Flevoland has been presented in subsection 3.1.1.2. The soil profile was subdivided in 8 compartments of 0.05 m (0 -0.40 m) and 14 compartments of 0.1 m (0.4 - 1.7 m), with five different soil physical functions (figure 4.37). The soil physical functions are described by a soil moisture retention curve and the hydraulic conductivity curve according to Van Genuchten (equations 2.12 and 2.14).

The parameters for the soil water retention curve and the (un)saturated conductivity curve, which were used for the model calculations, were determined in the laboratory and are presented in chapter 3 (table 3.4).

Upper boundary conditions: At the upper boundary, the daily precipitation and daily reference evapotranspiration are inputs. The reference evapotranspiration according to Makkink is obtained from a nearby mete-

orological station in Lelystad. It is multiplied by a crop factor (f) to obtain the potential evapotranspiration. The crop factors during the growing season for potatoes are presented in table 4.13. During the winter period (October until April), the potential evapotranspiration is assumed to be equal to reference crop evapotranspiration. Thus, the factor f is then equal to 1.

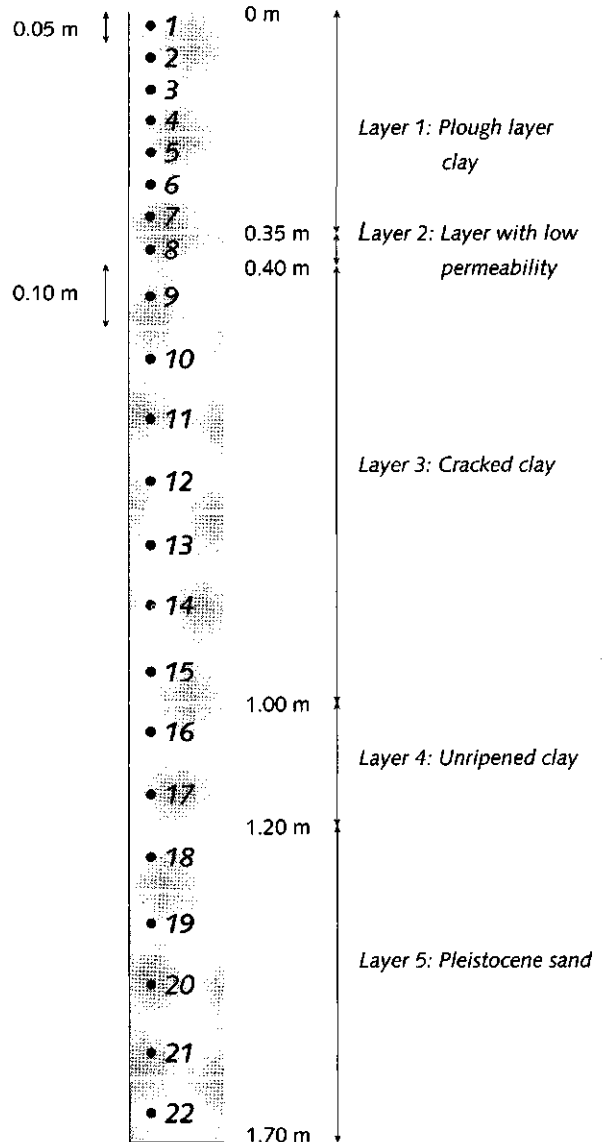


Figure 4.37. Schematisation of the soil profile.

Table 4.12. Input parameters to determine soil water fluxes for the experimental field *Eastern Flevoland*.

NUMERICAL METHOD			
Symbol	Parameter	Value	Equation
$reltol$	Relative tolerance	1.10^{-2}	2.11
$abstol$	Absolute tolerance	1 cm	2.11
UPPER BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
P	Precipitation	Daily values	
E_r	Reference evapotranspiration	Daily values	2.17
f	Crop factor	Decade values (table 4.13)	2.18
a	Regression coefficients for potatoes	2.6	2.20
b		1.5	
c		0.9	
S_c	Soil cover	Daily values (figure 4.38)	2.20
β	Parameter for actual soil evaporation	$2.0 \text{ mm}^{0.5}$	2.22
a_i	Parameter representing the crop dependant saturation value	0.68 mm d^{-1}	2.23
$ z_r $	Lower limit of the root zone	Daily values (figure 4.39)	2.27
$ h_1 $	Values of the soil water pressure head which determine	10 cm	2.25
$ h_2 $	the dimensionless sink term variable for water extraction	25 cm	
$ h_3 $	by roots, α	320 cm	
$ h_4 $		600 cm	
$ h_5 $		16000 cm	
$K_h K_v^{-1}$	anisotropic factor	5	
LATERAL BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
$ z_{dr} $	Drain depth (drainage level 1: imaginary drains)	0.35 m	
	Drain depth (drainage level 2)	0.95 m	
L	Drain spacing (drainage level 1: imaginary drains)	0.30 m	2.29
	Drain spacing (drainage level 2)	48 m	
u	Wet perimeter (drainage level 1: imaginary drains)	0.20 m	
	Wet perimeter (drainage level 2)	0.60 m	

The partitioning of the potential evapotranspiration in potential soil evaporation and potential transpiration depends on the Leaf Area Index (LAI). The Leaf Area Index is a function of the soil cover according to equation 2.19. The values for the regression coefficients, which are used in the model are presented in table 4.12, were obtained from Feddes et al. (1988).

The soil cover as function of time is presented in figure 4.38. The potatoes were planted in March. In April the

potatoes started to grow and reached their full growth in June. At this time the soil cover amounted to approximately 0.95. In September the potatoes started to wither. The potatoes were harvested in October. After harvesting, the plot was ploughed.

Under optimal soil water conditions, the maximum water extraction by the roots of the potatoes (S_{max}) is assumed to diminish with depth, according to a function of Prasad (1988). At the lower limit of the root

Table 4.13. Values for the dimensionless crop factor, f , for potatoes. During the winter period (second decade October until April) the crop factor is assumed to be 1.

Month	April			May			June			July			August			September			October		
Decade	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Potatoes	-	-	-	0.9	1.0	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.0	0.7	0.7	-	-

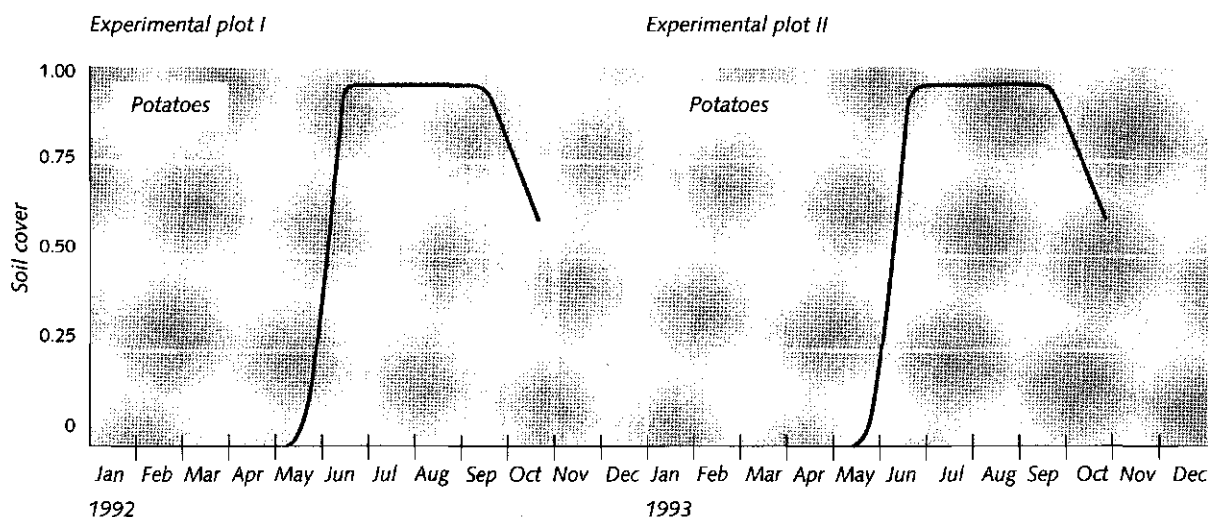


Figure 4.38. Soil cover of potatoes as function of time for the experimental field Eastern Flevoland.

zone, root extraction is taken to be zero. The maximum rooting depth as a function of time is presented in figure 4.39.

The function for the volumetric sink term depends on the soil water pressure head. Under non-optimal conditions, i.e. either too dry or too wet, S_{max} is reduced by means of the pressure head h dependent α -function (equation 2.25; figure 2.4). For potatoes the values of $|h_1|$, $|h_2|$, $|h_3|$ and $|h_4|$ are presented in table 4.13.

The actual soil evaporation is described according to Boesten (equation 2.22). The β values derived from field measurements reported in literature varied between 2 and 3 $\text{mm}^{0.5}$ (Boesten, 1986). From field data for clay soils obtained by Ritchie (1972) and Stroo-

snijder and Koné (1982) a β value of 2.0 $\text{mm}^{0.5}$ was derived. The same value was assumed for the clay soil of the experimental field in Eastern Flevoland. The evaporation losses by interception are calculated according to Braden (1985) and this is a function of the Leaf Area Index, the soil cover, the precipitation and a parameter representing the specific properties of the leaves (a_i ; equation 2.23). For potatoes the parameter a_i could be calculated by dividing the maximum interception rate (which amounts to 3.4 mm d^{-1} (Von Hoyningen-Huene, 1981) by the maximum LAI (which is equal to 5) yielding a value of 0.68 mm d^{-1} . Minor changes in the soil water balance could be observed if this parameter was changed within a range from 0.5 up to 0.8.

Lower boundary condition: The magnitude of the flux at the lower boundary depends on the drainage resistance of the subsoil and the hydraulic head in the Pleistocene sand according to a linear function. The lower boundary condition has been described in subsection 2.1.5 and was solved according to equation 2.28. The model was calibrated for the hydraulic head of the Pleistocene sand and the drainage resistance of the subsoil.

Lateral boundary condition: For the concept with imaginary drains, the flow of water is described according to figure 2.8. At a depth of 0.35 m imaginary drains were implemented, representing the cracks.

Due to the low permeability of layer 2 (0.35 - 0.40 m, i.e. just below the plough layer) perched water tables occur from time to time. If the precipitation surplus increases, only part of the soil water flux flows into the soil matrix of layer 3 (0.40 - 0.95 m). The extent of the

water flux into the soil matrix of layer 3 depends on the saturated conductivity of layer 2. The remaining water flows directly into the cracks. In the concept with imaginary drains, preferential flow through the cracks is described by imaginary drain pipes. Values for the drain spacing, drain depth, wet perimeter for the drainage levels at 0.35 and 0.95 m are summarized in table 4.12. The concept without imaginary drains has only one drainage level (level 2). The anisotropic factor (horizontal saturated conductivity divided by the vertical saturated conductivity) is the same for both concepts and is set at 5. The drainage flux is calculated according to the Hooghoudt equation (equation 2.29).

Calibration and optimization criteria: For the calibration of the model, the observed groundwater levels and the observed drain discharges were used. As data on the observed soil moisture content were relatively unreliable, the model was not calibrated for the soil moisture content. The registration of the groundwater levels

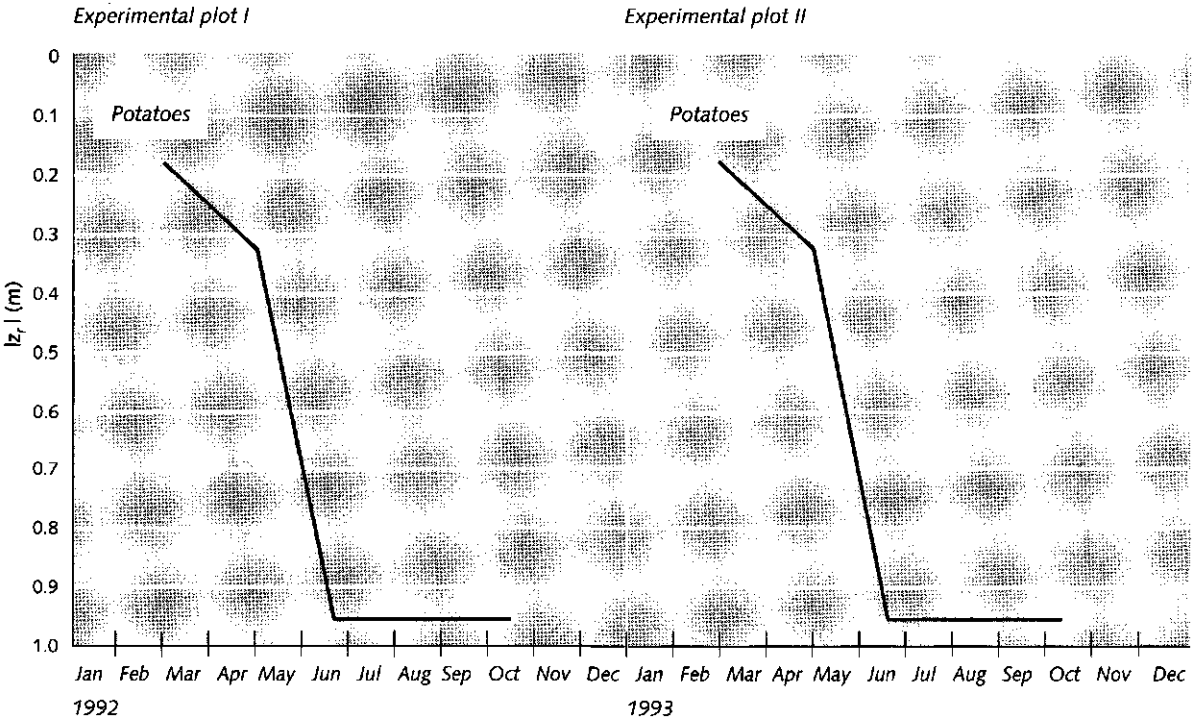


Figure 4.39. Rooting depth of potatoes as function of time for the experimental field *Eastern Flevoland*.

between the drain pipes were carried out with a frequency of one measurement per hour (subsection 3.2.6). The daily groundwater levels were taken as an arithmetic average of the measurements per hour. The drain discharge was measured at intervals by using the discharge proportional sampler (subsection 3.2.8). The daily drain discharge was obtained by adding the water volumes as measured during the day.

Unknown parameters were optimized using observed groundwater levels and drain discharges. The unknown parameters for both concepts are the equilibrium value of the hydraulic head in the Pleistocene sand (h_{pl} ; equation 2.28) and the drainage resistance of the subsoil (Υ ; equation 2.28). For the concept with imaginary drains, the parameter set was extended with the saturated permeability of layer 2 ($K_{sat,2}$). In order to obtain the best fit between the observed and simulated groundwater levels and drain discharges, these unknown parameters are optimized according to the objective function Root-Mean-Square as presented in equation 4.1.

Results: Results of the calibration procedure for both concepts are presented in table 4.14. For the concept with imaginary drains, the optimum value of h_{pl} and $K_{sat,2}$ are equal for RMS_q and RMS_{gwt} . However, the optimum value of Υ varied for RMS_q and RMS_{gwt} . As the groundwater level is more sensitive to variation of Υ

than the drain discharge, Υ is set at 155 days. The results of the calibration of the soil water flow for $\Upsilon = 155$ days, $h_{pl} = -1.1$ m and $K_{sat,2} = 0.005$ m day⁻¹ are shown in figures 4.40, 4.41, 4.42, 4.43, 4.44, 4.45 and 4.46. For the concept without imaginary drains, the optimum value of h_{pl} is equal for RMS_q and RMS_{gwt} , but varied for Υ . Table 4.14 shows that the drainage resistance of the subsoil hardly influences the value of RMS_q . As the groundwater level is more sensitive to variation of Υ than the drain discharge, Υ is set at 165 days. The results of the calibration of the soil water flow for $\Upsilon = 165$ days and $h_{pl} = -1.1$ m are shown in figures 4.40, 4.41, 4.43 and 4.46.

Figure 4.40 shows the observed and simulated soil moisture content from the soil surface down to a depth of 1.2 m for four selected periods (winter, spring, autumn and summer). Significant differences concerning moisture content between the concept with and without imaginary drains could be observed during the autumn. If the precipitation intensity is high and the moisture content of the plough layer exceeds field capacity, part of the precipitation surplus flows into the imaginary drains (e.g. cracks).

If no imaginary drains are present, the precipitation surplus will flow into the soil matrix of layer 2 and 3 respectively. The observed and simulated soil moisture

Table 4.14. Optimum values for various object functions.

Object function	Optimum values Concept with imaginary drains				
	Υ (d)	h_{pl} (m)	$K_{sat,2}$ (m d ⁻¹)	RMS_q (mm d ⁻¹)	RMS_{gwt} (cm)
RMS_q	95	-1.10	0.005	1.1	7.5
RMS_{gwt}	155	-1.10	0.005	1.2	6.9
	Optimum values concept without imaginary drains				
	Υ (d)	h_{pl} (m)		RMS_q (mm d ⁻¹)	RMS_{gwt} (cm)
RMS_q	115	-1.10		1.5	7.3
RMS_{gwt}	165	-1.10		1.6	7.0

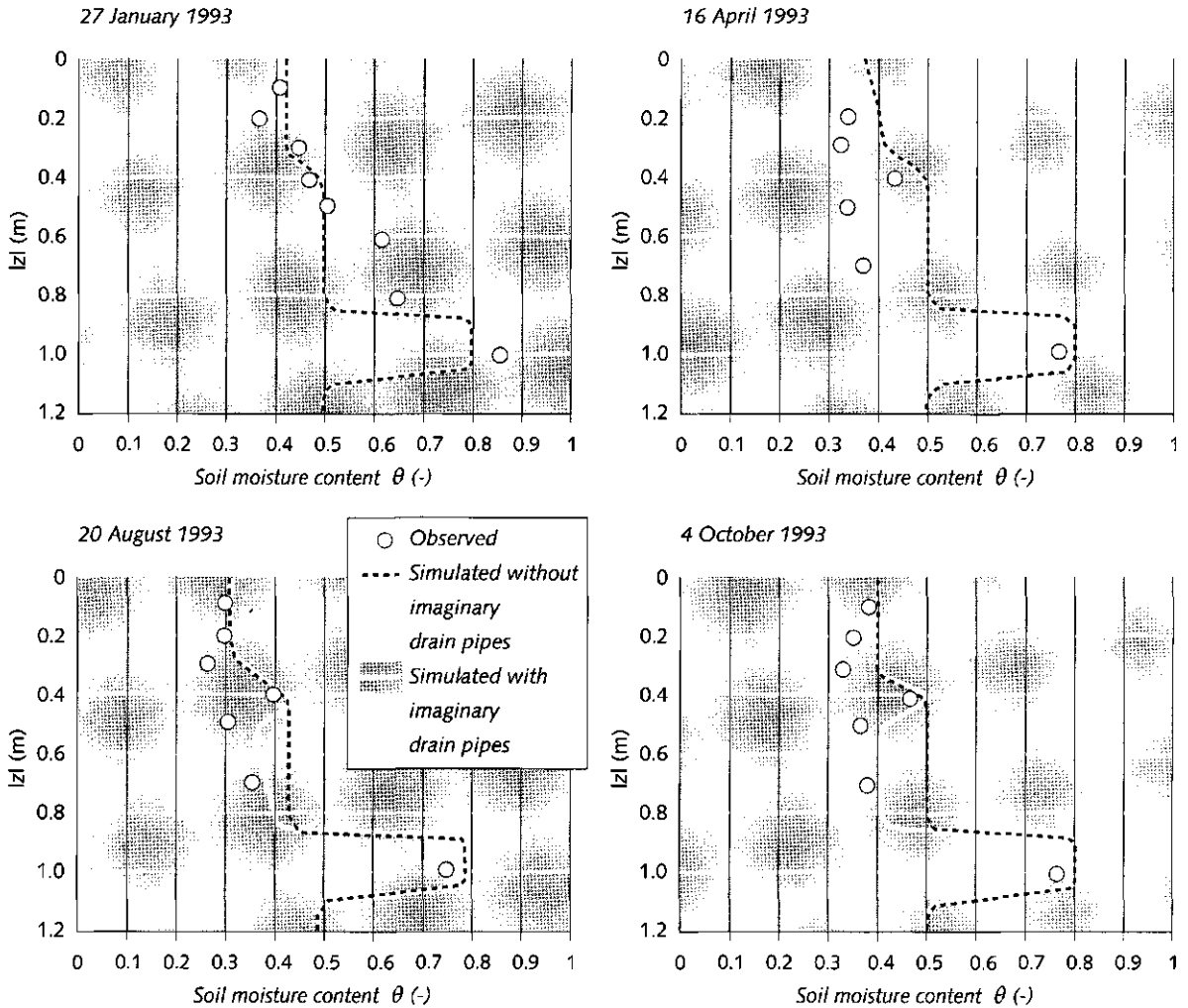


Figure 4.40. Observed and simulated soil moisture content at four selected days for the concept with and without imaginary drains at the experimental field *Eastern Flevoland*.

content in the plough layer varies from approximately 0.30 during dry periods to 0.45 during wet periods. At a depth of 0.8 m, the simulated soil moisture content is nearly constant at roughly 0.5. The moisture content of the unripened clay below the cracks is invariant and amounts to 0.80.

The change in water storage (ΔW) for a given period of time (Δt) is calculated according to equation 2.1. If the soil moisture content at a particular time is known, the

storage can be calculated according to equation 4.2. The observed and simulated storage over a depth of 1.2 m for both concepts (with and without imaginary drains) are presented in figure 4.41. The simulated water storage varies between 550 and 700 mm for both concepts. The observed water storage varies between 520 and 720 mm. Generally for both concepts the observed soil moisture content tends to be lower than the simulated soil moisture content, particularly during the summer periods and directly after implementation

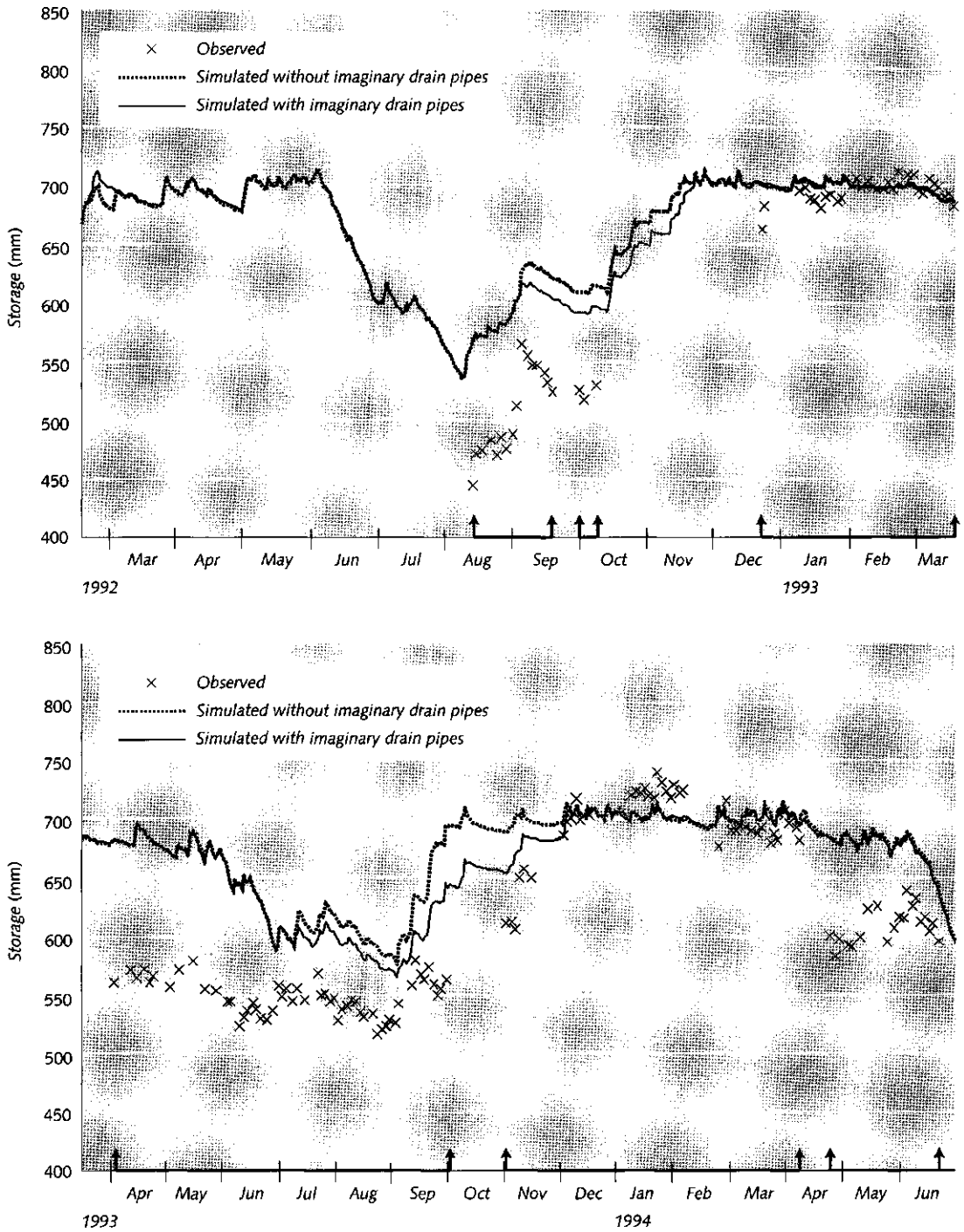


Figure 4.41. Observed and simulated soil water storage over a soil depth of 1.2 m (periods indicated in black at the bottom \approx periods where probes were implemented) from March 1992 until June 1994 for the experimental field *Eastern Flevoland*.

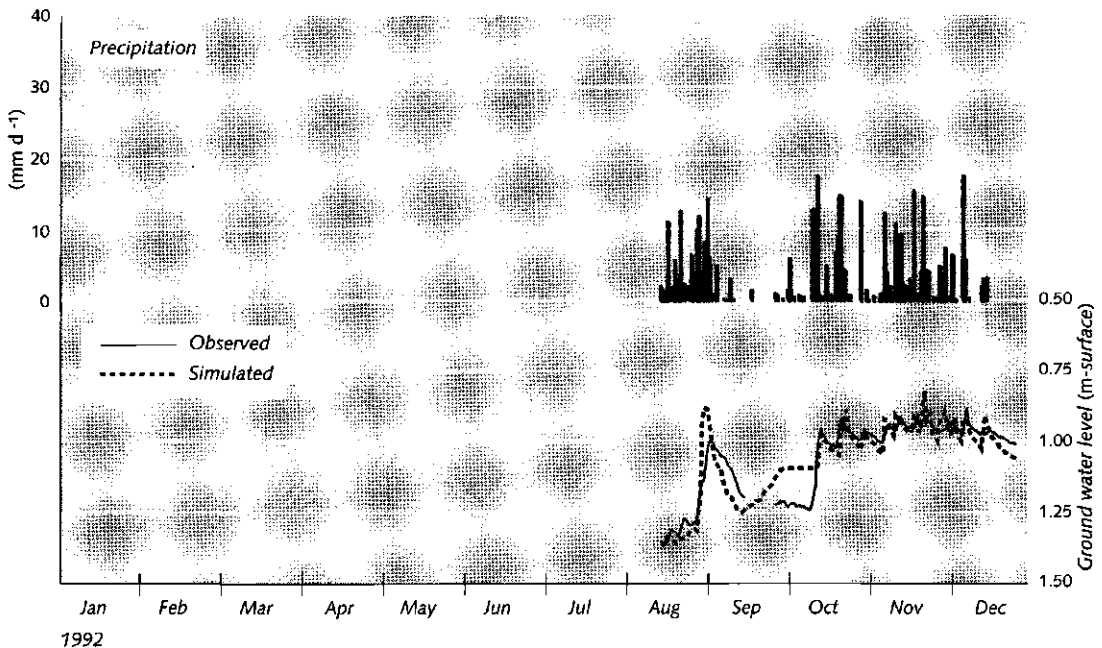
of the probes. The probes had to be removed twice a year because of planting and harvesting of the potatoes. Directly after re-implementation of the probes, the observed soil moisture content was much lower than simulated. It is likely that the discrepancy is caused by cracks which originate from the implementation. After rewetting, the observed moisture content corresponds to the simulated moisture content.

Differences in the simulated storage for the concept with and without imaginary drains can be observed during the autumn period, when the soil is rewetted again. Field measurements showed that it normally takes until December before the moisture content in the soil matrix of layer 3 reaches field capacity. This phenomenon could also be simulated if imaginary drains are implemented. Part of the precipitation surplus flows into the imaginary drains instead of contributing to the replenishment of the soil water storage.

Figure 4.42 shows the observed and simulated groundwater levels. The average observed groundwater level amounted to 1.07 m and deviates only slightly from the

simulated average groundwater level which amounted to 1.06 m. Differences between the groundwater levels calculated with and without imaginary drains appeared to be very small. For this reason only the simulated groundwater level for the concept with imaginary drains is presented.

Figure 4.43 shows the observed and simulated drain discharge with and without imaginary drains. Except during times of peak discharge, the simulated drain discharge with imaginary drains shows good agreement with the observed drain discharge. Drain discharges calculated without imaginary drains deviate strongly from the observed drain discharges during the summer and autumn period. If calculations are undertaken at only one drainage level at a depth of 0.95 m (without imaginary drains), the soil moisture content is replenished to field capacity before the drain pipes start to flow. This does not correspond to the observed situation, where drain pipes start to flow long before the soil moisture content of the basaltic structures (layer 3) reaches field capacity.



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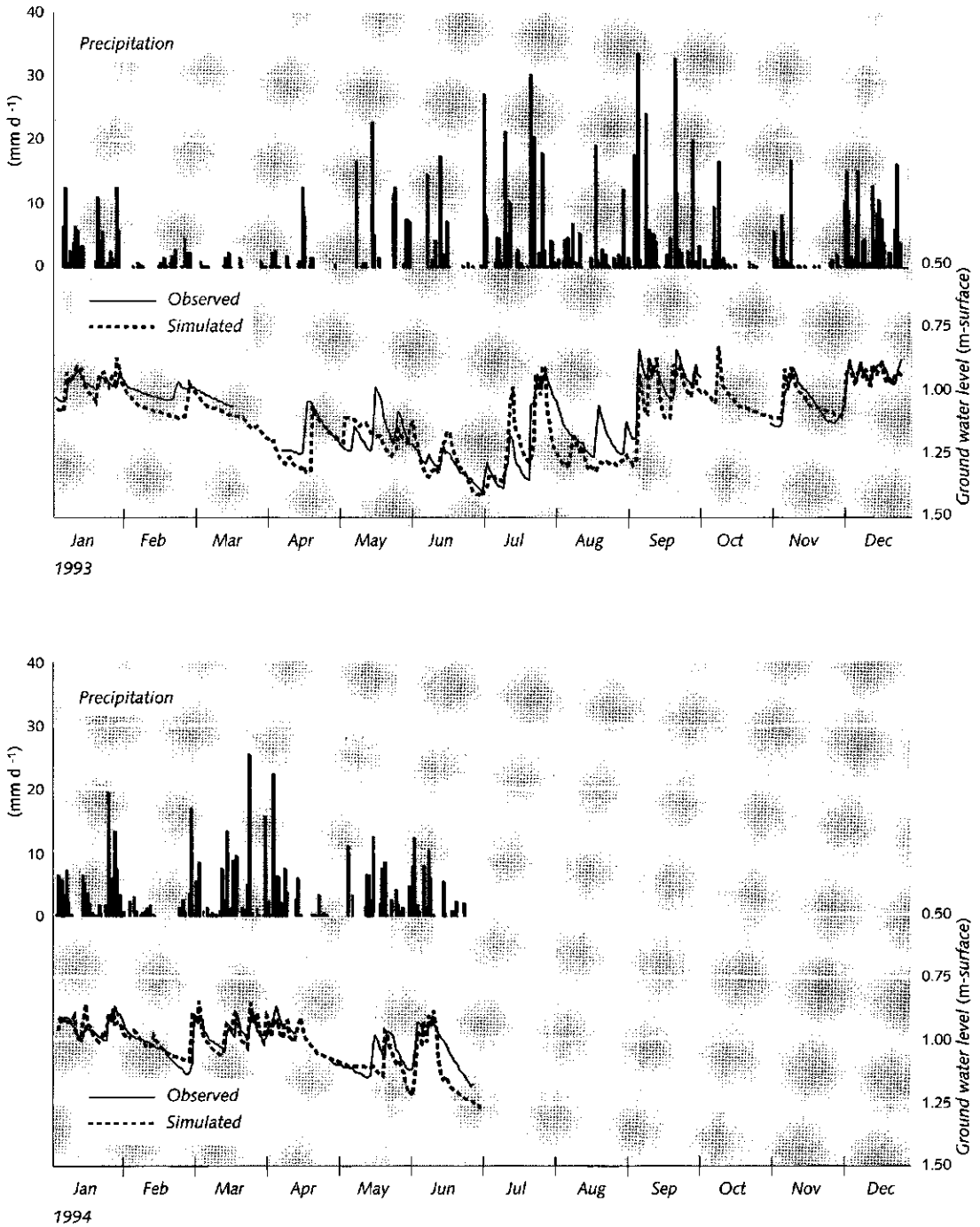
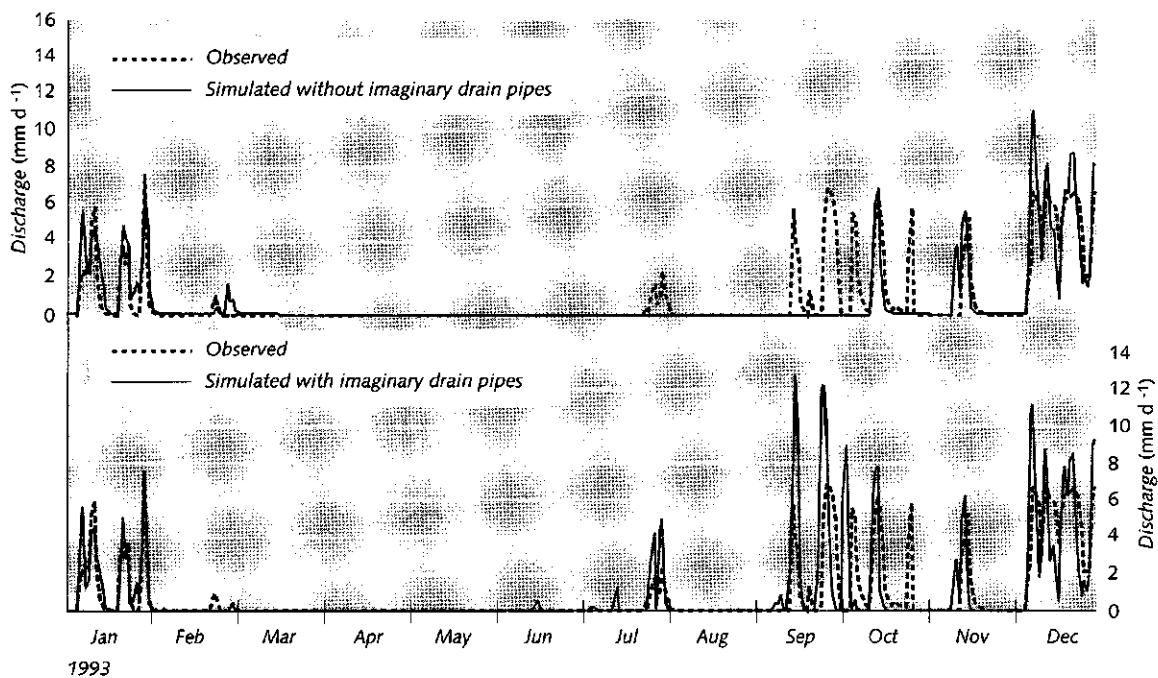
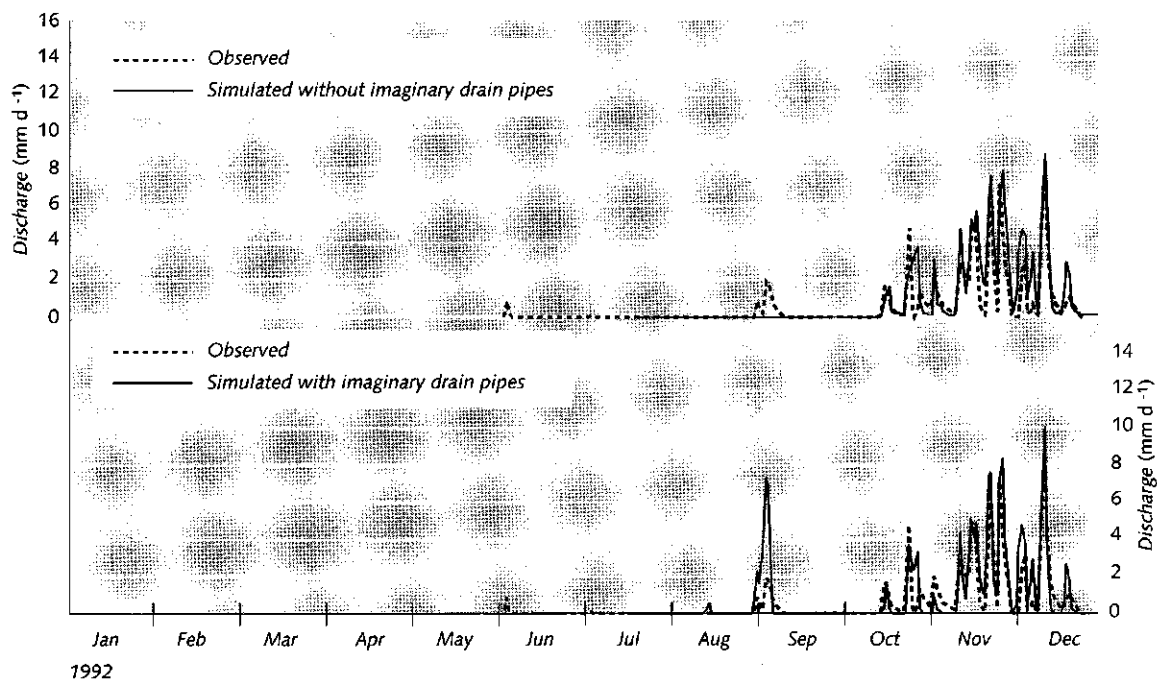


Figure 4.42. Observed and simulated groundwater levels (with imaginary drains) from March 1992 until June 1994 for the experimental field *Eastern Flevoland*.



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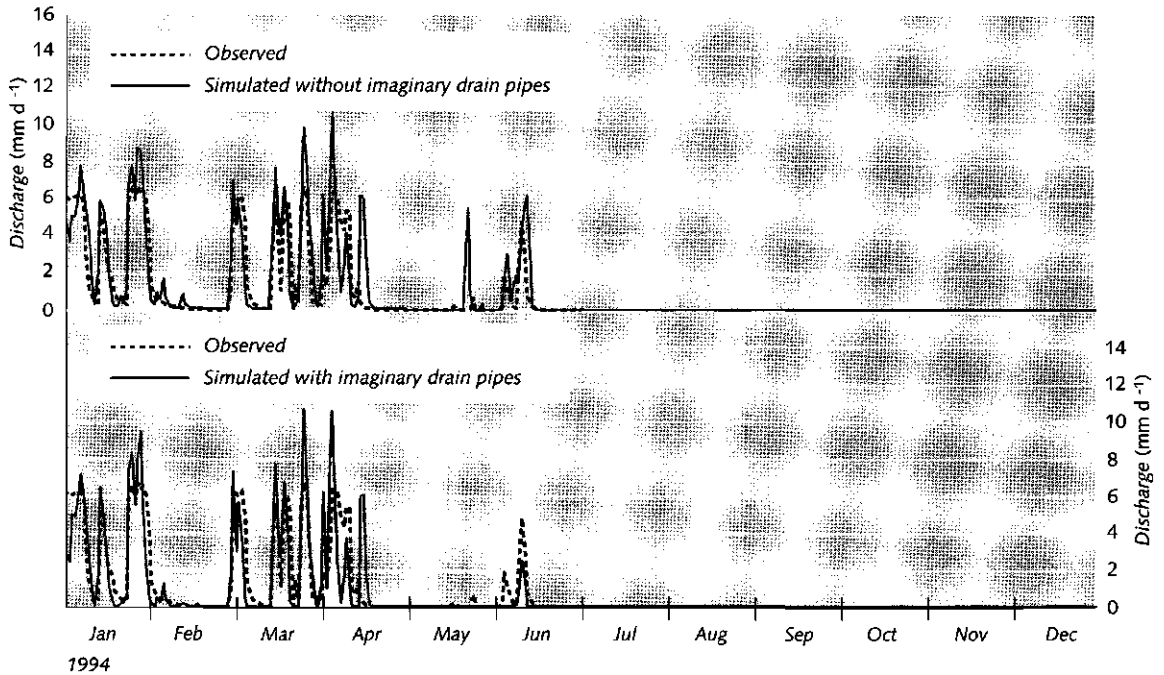


Figure 4.43. Observed and simulated drain discharge from March 1992 until June 1994 for the experimental field *Eastern Flevoland*. Notice the difference in the simulated drain discharge during the summer period for the concept with and without imaginary drains.

The maximum observed drain discharge amounted to roughly 7.5 mm d^{-1} ; the maximum calculated drain discharge amounted to roughly 12 mm d^{-1} . The difference is mainly caused by the limited capacity of the pump, which pumps the water from the reservoir into the collector drain. At high drain discharges, the drain water could not flow freely into the drain pipes. Moreover, at high discharges the water level in the collector drain rises above the level of the drain pipes. The drain water does not flow freely into the collector drain and the maximum drain discharge decreases. This was particularly the case at the second experimental plot (June 1993 until July 1994). However, the observed cumulative drain discharge conforms to the simulated cumulative drain discharge (both with and without the imaginary drains). This is presented in figure 4.46. With the implementation of imaginary drains, both the pattern of the simulated discharge as well as the yearly cumulative drain discharge show a good resemblance to the observed values.

With the implementation of imaginary drains, the total lateral soil water flux can be divided among two drainage levels (drainage level 1 - 0.35 m; drainage level 2 - 0.95 m). This is presented in figure 4.44. It shows that in the early autumn, the lateral soil water flux originates from drainage level 1. Figure 4.45 shows the cumulative drain discharge for both drainage levels. It shows that for this specific case roughly one third of the total drain discharge flows through the cracks. Table 4.15 shows the simulated soil water fluxes for the first and second experimental plot. Each year has been calculated separately from 1 March until March of the following year. The change in water storage can be ignored as the soil profile is still at field capacity at the end of February. The actual evapotranspiration amounted to 581 mm yr^{-1} for the first experimental plot and 501 mm yr^{-1} for the second experimental plot.

Sensitivity analyses: Changes in the soil moisture content are mainly determined by the actual evapotranspi-

Table 4.15. Calculated soil water fluxes in 1993 and 1994 for the concept with imaginary drains at the experimental field *Eastern Flevoland* (P = precipitation, I = irrigation, q_b = flux through the bottom of the soil profile (- = out), q_d = lateral drainage flux (- = out), E_i = interception, E_s = actual soil evaporation, E_t = actual transpiration).

Period	P (mm)	I (mm)	q_b (mm)	q_d (mm)	E_i (mm)	E_s (mm)	E_t (mm)
March '92 - March '93	946	0	- 48	- 317	71	190	320
March '93 - March '94	978	0	- 77	- 400	64	142	295

ration and net precipitation. However, for the concept with the imaginary drains, the moisture content of the third layer is strongly influenced by the saturated permeability of the second layer ($K_{sat,2}$), especially during the autumn (rewetting of the soil). The groundwater levels in the matrix are sensitive to the lower boundary conditions and strongly influenced by upward and downward seepage (defined by Υ and h_{pl}) for both concepts. Due to the extremely high saturated permeability of the third layer ($K_{sat,3} = 250 \text{ m d}^{-1}$), the con-

vexity between the drain pipes hardly exceeds 0.1 m. During periods of drain flow, groundwater levels vary between 0.85 and 0.95 m - soil surface.

The drain flow depends on the height of the groundwater table, the saturated permeability of the third layer $K_{sat,3}$ and the extent of downward seepage (defined by Υ and h_{pl}) for both concepts. For the concept with imaginary drains, drain flow is also influenced by $K_{sat,2}$. $K_{sat,2}$ determines the extent of the drainage flux

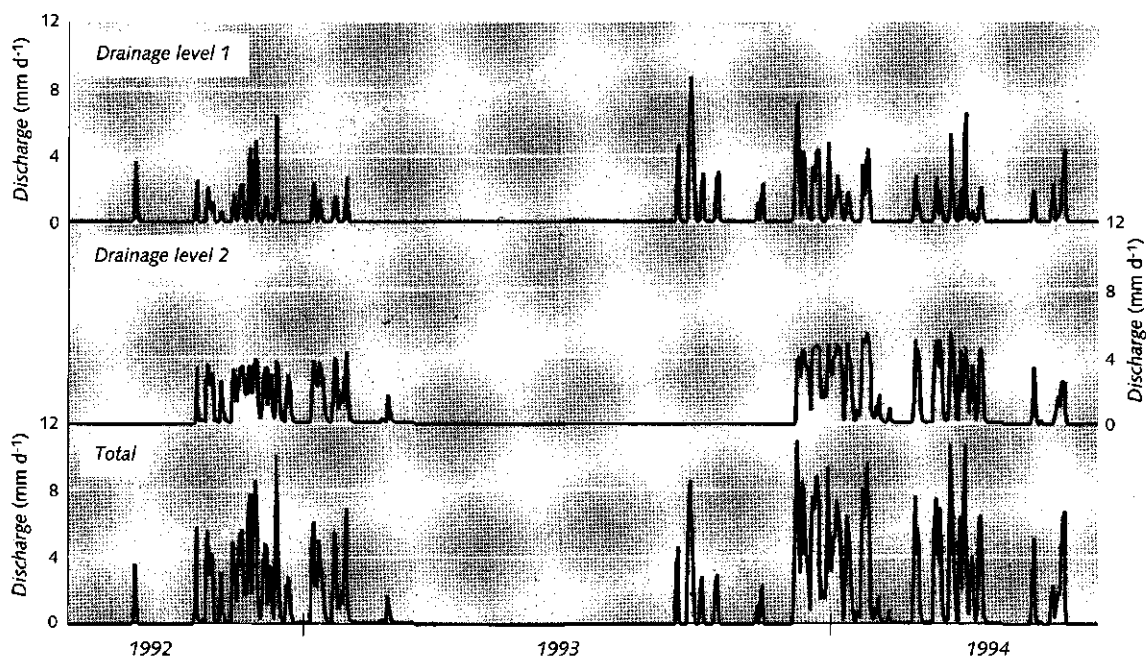


Figure 4.44. Partitioning of the total drain discharge over drainage level 1 (0.30 m) and drainage level 2 (0.95 m) for the concept with imaginary drains from March 1992 until June 1994 at the experimental field *Eastern Flevoland*.

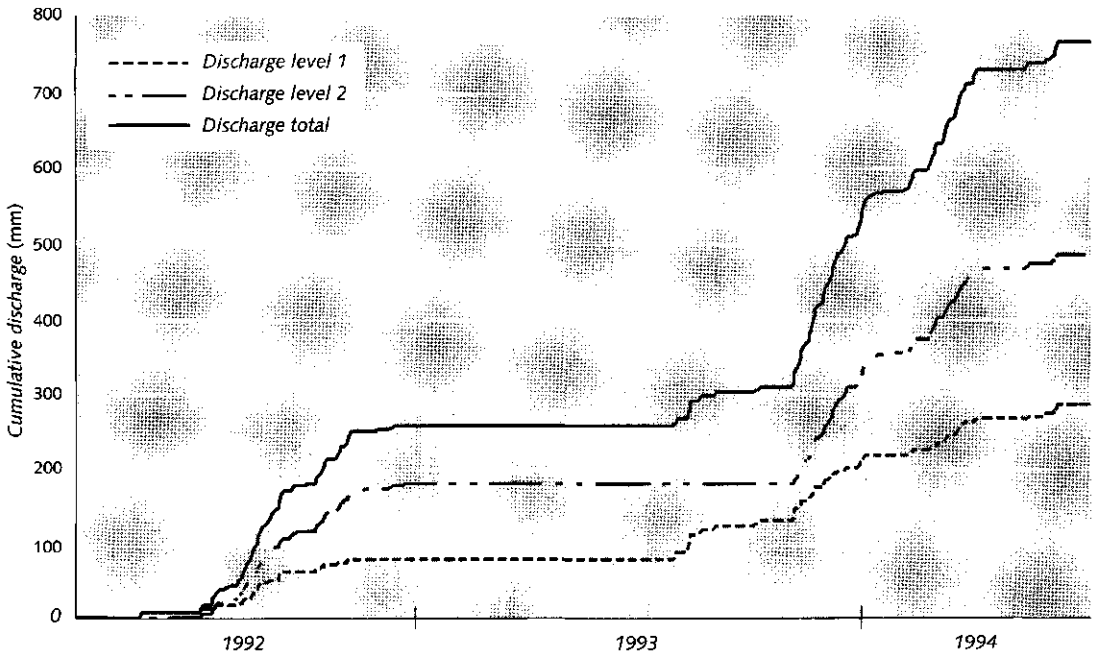


Figure 4.45. Partitioning of the simulated cumulative drain discharge over drainage level 1 (0.35 m) and drainage level 2 (0.95 m) for the concept with imaginary drains from March 1992 until June 1994 at the experimental field Eastern Flevoland.

of drainage level 1. If the value of $K_{sat,2}$ increases, the drainage flux decreases.

Soil water fluxes were simulated on a daily basis. For a few periods hourly values of precipitation were available. For these periods simulations were undertaken on a hourly basis and the results were compared with simulations carried out on a daily basis. Results showed that the optimum value of $K_{sat,2}$ will slightly increase ($K_{sat,2} = 0.006 - 0.008 \text{ m d}^{-1}$). The portion of the total drain discharge flowing through the cracks will increase for periods with high rainfall intensity (e.g. thunderstorms). During these periods the average percentage of drainage water flowing through the cracks (first drainage level) increased from approximately 35 to 60%. Differences between simulations undertaken on a daily and hourly basis slightly decreased for low rainfall intensities (e.g. drizzle), due to the higher value of $K_{sat,2}$.

Conclusions: In order to describe the flow of water in

cracked clay soils, without leaving the concept of one-dimensional flow, imaginary drains were implemented at a depth of 0.35 m. These imaginary drains represent the cracks, which are present just below the plough layer. In order to show the effect of the implementation of imaginary drains, simulations were undertaken for two concepts: with and without imaginary drains. Results of the simulations showed that the implementation of imaginary drains gave a better description of soil water flow in the cracked clay soils of Eastern Flevoland.

However, differences between the groundwater levels calculated with and without imaginary drains appeared to be very small. The groundwater levels are mainly influenced by the lower boundary conditions (upward and downward seepage). Drain discharges calculated without imaginary drains deviate strongly from the observed drain discharges during the summer and autumn period. If simulations are undertaken at only one drainage level at a depth of 0.95 m (concept without

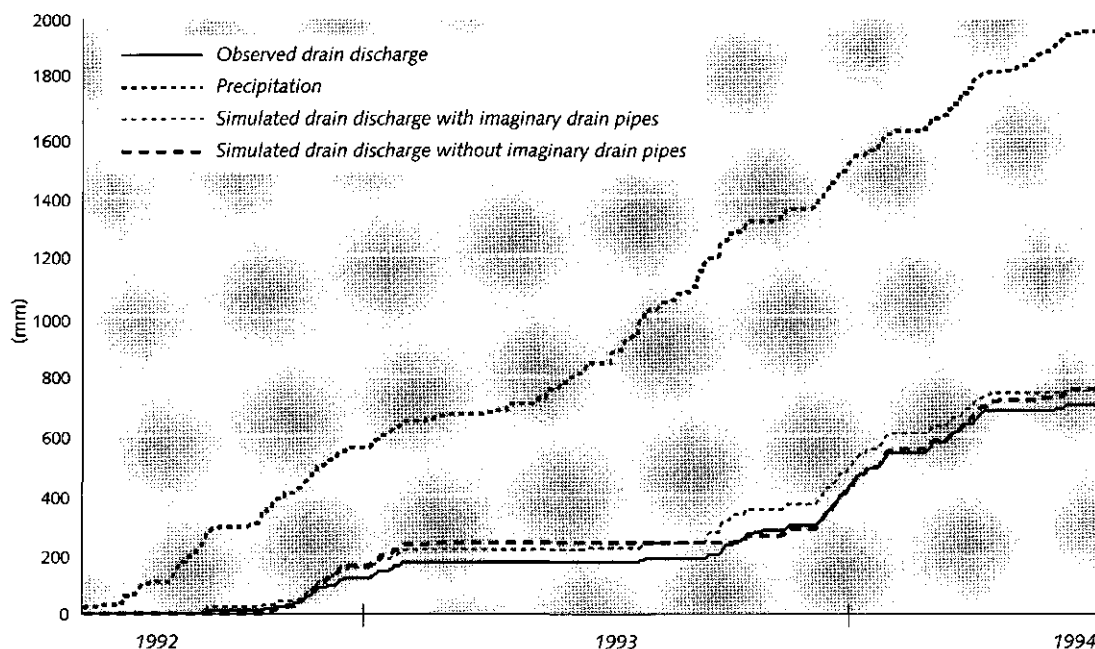


Figure 4.46. Observed and simulated total cumulative drain discharge and cumulative precipitation from March 1992 until June 1994 at the experimental field *Eastern Flevoland*.

imaginary drains), the soil moisture content is replenished to field capacity before the drain pipes start to flow (figure 4.40). This does not correspond to the observed situation, where drain pipes start to flow long before the soil moisture content of the basaltic structures (layer 3) reaches field capacity. However, if the observed cumulative drain discharge is compared with simulated cumulative drain discharge (for both concepts) over a longer period (two years), differences are small (figure 4.46). It should be noted that for the concept with imaginary drains, drain fluxes are originating from various drainage levels (figure 4.44 and 4.45). This may have a considerable impact on the leaching and the concentration level of solutes and pesticides in the drain pipes.

Soil water fluxes were simulated on a daily basis. If simulations are performed on an hourly basis, the fraction of the total drain discharge flowing through the cracks will increase. However, the increase is not proportional as the optimum value of $K_{sat,2}$ will also

increase. For periods with high rainfall intensity (e.g. thunderstorms), the average percentage of drainage water flowing through the cracks (first drainage level) increased from approximately 35 to 60%. Differences between simulations on a daily and hourly basis were neglectable for low rainfall intensities. For future simulations it is recommended to collect field data such as precipitation and drain discharges at an hourly basis, particularly when solute transport is involved. As stated before, *any change in the partitioning of drainage fluxes over the first and second drainage level, may strongly influence the concentration levels of solutes and pesticides in the drain pipes.*

4.2.2 Solute transport

As groundwater levels, moisture content and drain discharges could be simulated reasonably well, an attempt was made to simulate the solute fluxes of the inert ion bromide. The soil water fluxes for the concept with imaginary drains, as determined in the previous section, are used to simulate bromide fluxes. The results of the simulation model will not be compared with the concentration profiles of bromide sampled at particular time intervals as the results of the soil sampling were unreliable. This problem has already been discussed in subsection 3.2.9. For this reason the experiment with the rainfall simulator was introduced.

Model: At the clayey soil of Eastern Flevoland, flow of solutes is assumed to take place according to the convection-dispersion equation (equation 2.43). The dispersion coefficient is calculated according to equa-

tion 2.40. Solute uptake by plant roots is calculated according to equation 2.60. The additional set of equations used for the transport of bromide is the same as for the experimental field in the North-East Polder (Table 4.6).

Input: For the calculation of bromide flow, additional input is needed on the applied load, the date of application, bromide uptake by plants and the estimated dispersion length. Table 3.14 gives information on the date of bromide application, the quantity applied and the period of the field measurements for bromide.

As little is known about a possible solute uptake of bromide by the roots of potatoes (F : equation 2.60), which can have a significant impact on the mass balance for bromide, the model was calibrated for bromide uptake by roots. Reported values of the dispersion length (L_{dis})

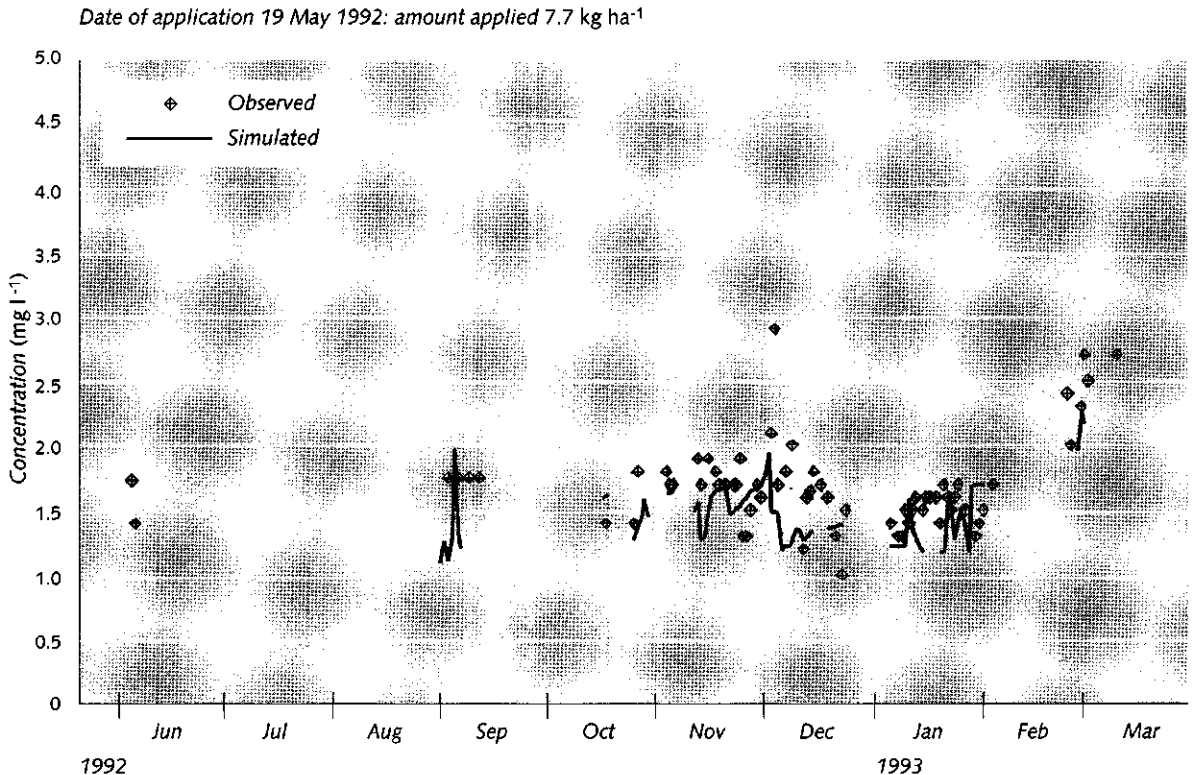


Figure 4.47. Observed and simulated concentration of bromide in the drain pipes at the experimental field Eastern Flevoland in 1992/1993 ($L_{dis} = 5 \text{ cm}$, $F = 0$).

in literature vary considerably from less than 1 cm up to more than 20 cm (section 4.1.2). As the value of L_{dis} was unknown and may vary considerably, L_{dis} was determined by calibration.

Optimization criteria: For the transport of bromide through the soil the Root-Mean-Square ($RMS_{[Br]}$) is used as an optimization criterium. $RMS_{[Br]}$ is formulated in the same way as the Root-Mean-Square for groundwater levels (equation 4.2). The simulated concentration of bromide is compared with the observed concentration of bromide in the drain pipes.

Parameters to optimize: Numerous model simulations were undertaken in order to acquire the best possible fit between observed and simulated data. Simulations were carried out for various combinations of the dispersion length (L_{dis} ; equation 2.40) and root uptake

(F ; equation 2.60). Calibration of the model for bromide showed that the best fit was obtained for $F = 0$ and $L_{dis} = 5$ cm. For the data set 1992/1993 and 1993/1994, $RMS_{[Br]}$ amounted to 0.88 mg l⁻¹ and 0.74 mg l⁻¹ respectively.

Results 1992/1993: The results of the concentration of bromide in the drain pipes in 1992/1993 shows a good agreement between the observed and simulated values (figure 4.47). The simulated concentration level of bromide in the drain pipes strongly depends on the distribution of the lateral soil water fluxes. In general, if the drain water originates from the upper soil layers, the concentrations are high during the first months after application. After the winter period concentration levels are high if the drain water originates from the lower soil layers (0.9-1.0 m below soil surface). As noticed in the previous section, the drain water origi-

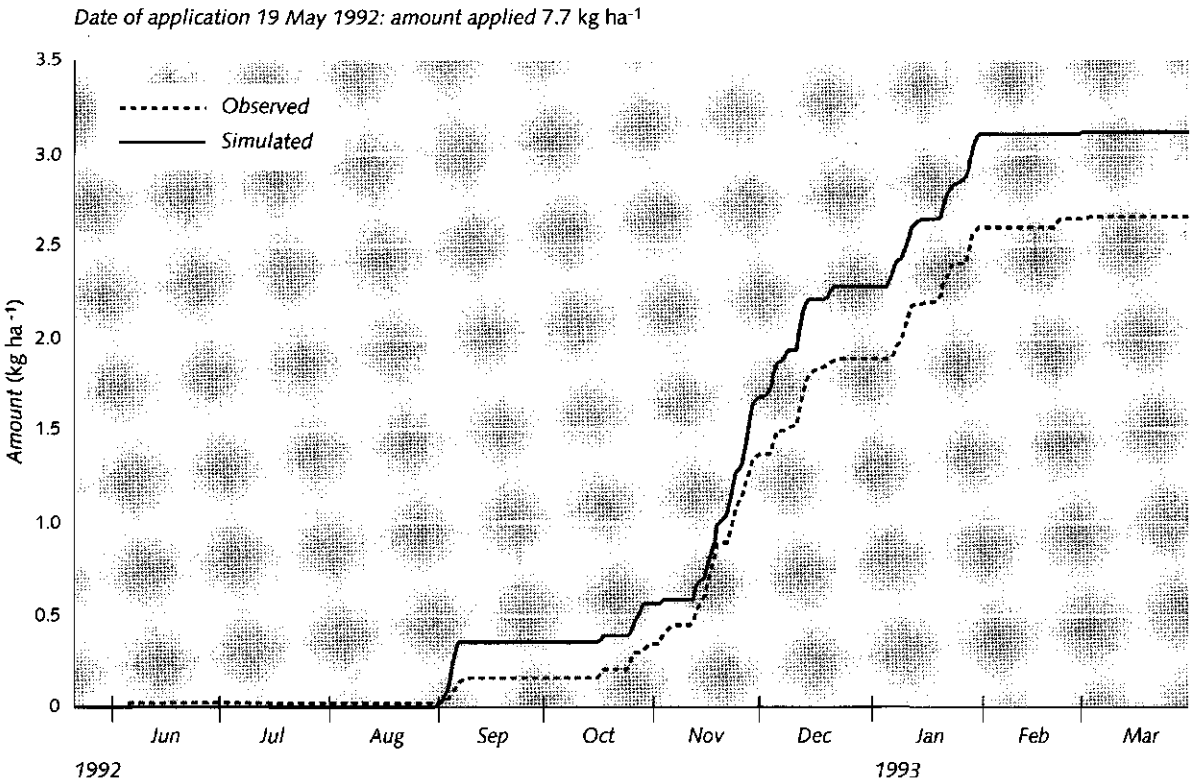


Figure 4.48. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field Eastern Flevoland in 1992/1993 ($L_{dis} = 5$ cm, $F = 0$).

Date of application 14 April 1993: amount applied 11.7 kg ha^{-1}

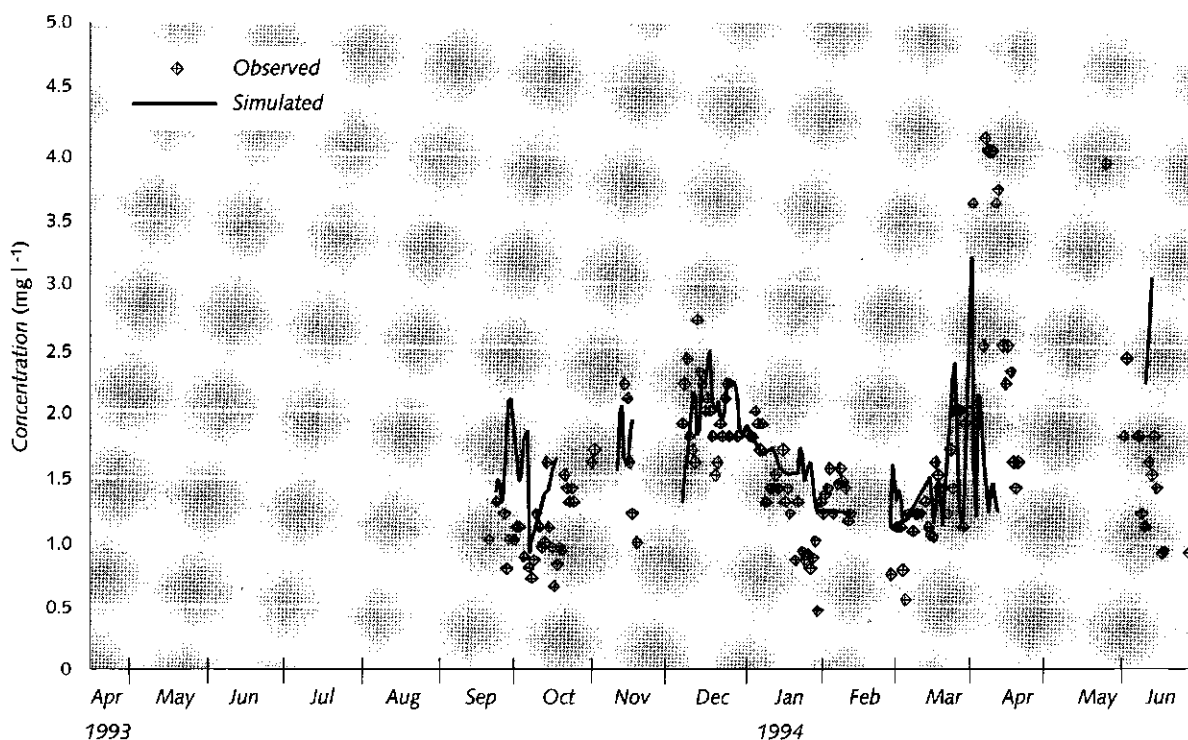


Figure 4.49. Observed and simulated concentration of bromide in the drain pipes at the experimental field *Eastern Flevoland* in 1993/1993 ($L_{dis} = 5 \text{ cm}$, $F = 0$).

nates from the upper soil layers if precipitation intensity is very high. It should be noted that the high background concentration of $0.7\text{--}0.9 \text{ mg l}^{-1}$ makes it more difficult to interpret the measurements.

Figure 4.48 presents the observed and simulated amount of bromide leaching through the soil into the drain pipes ($L_{dis} = 5 \text{ cm}$, $F = 0$). The observed amount of bromide in the drain pipes over the period 19-5-1992 until 30-3-1993, was 2.7 kg ha^{-1} . This is equal to approximately 15% of the load applied taking into account background concentrations (subsection 3.2.9.2). The simulated load of bromide, which leached through the drain pipes during the same period, was 3.1 kg ha^{-1} . The difference is mainly caused by the simulated drain discharges, which were higher than the observed drain discharges.

Results 1993/1994: At the second experimental field, the load of bromide was increased by a factor 1.5. Results of experimental field II (1993/1994) show that the simulated values of the concentration of bromide in the drain pipes correspond reasonably well to the observed values, especially between 40 and 150 days after application (figure 4.49). As at the previous experimental field, the concentration level of bromide in the drain pipes strongly depends on the distribution of the lateral soil water fluxes. Again, background concentrations of bromide made it difficult to interpret the measurements.

The observed load of bromide, which leached through the drain pipes during the period 14-4-1993 until 1-7-1994, was 8.3 kg ha^{-1} (figure 4.50). This is equal to approximately 29% of the amount applied, taking into account background concentrations. It corresponded

Date of application 14 April 1993: amount applied 11.7 kg ha^{-1}

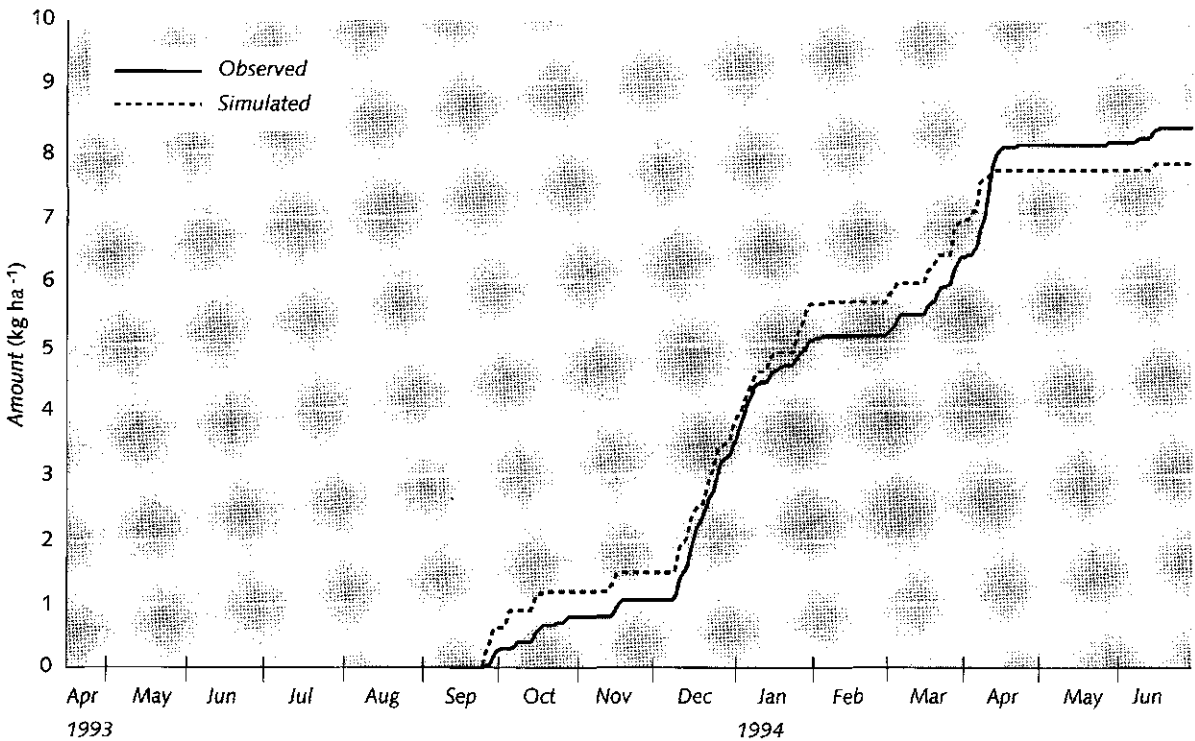


Figure 4.50. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field *Eastern Flevoland* in 1993/1993 ($L_{dis} = 5 \text{ cm}$, $F = 0$).

fairly well with the simulated load of bromide leached, which amounts to 7.9 kg ha^{-1} . The observed load of bromide leaving the drain pipes only differed considerably from the simulated load in the early spring.

Results experiment with rainfall simulator: The performance of the rainfall simulator has already been presented in subsection 3.2.11. In order to demonstrate the appearance of preferential flow, bromide is applied to the reservoir. The concentration of bromide in the reservoir amounted to 2.2 g l^{-1} , which is approximately a factor 1000 over the background concentration. In order to prevent ponding, rainfall intensity did not exceed 12 mm hr^{-1} . In two days 225 mm precipitation was applied to the plot (first day 145 mm; second day 80 mm). This corresponds to a load of 0.5 kg m^{-2} . At the end of the second day, the rainfall experiment was stopped and the plot was horizontally excavated by

removing slices of the soil. Samples were taken from the soil water in the cracks at a depth of 1.0 m, just below the groundwater table. The concentration bromide amounted to 110 mg l^{-1} . Due to the small size of the plot, groundwater levels did not rise above the levels of the drain pipes and no drain discharge could be observed.

Like the previous simulations, the dispersion length (L_{dis} ; equation 2.40) is set on 5 cm and root uptake (F ; equation 2.60) amounts to 0. As no crop was present during the experiment, parameters related to a crop are ignored. Remaining parameters used for the simulations have already been summarized in table 4.12. Due to the availability of data, calculations were carried out on an hourly basis and $K_{sat,2}$ was set at 0.007 m d^{-1} . Results of the observed and simulated content of bromide in the soil are presented in figure 4.51.

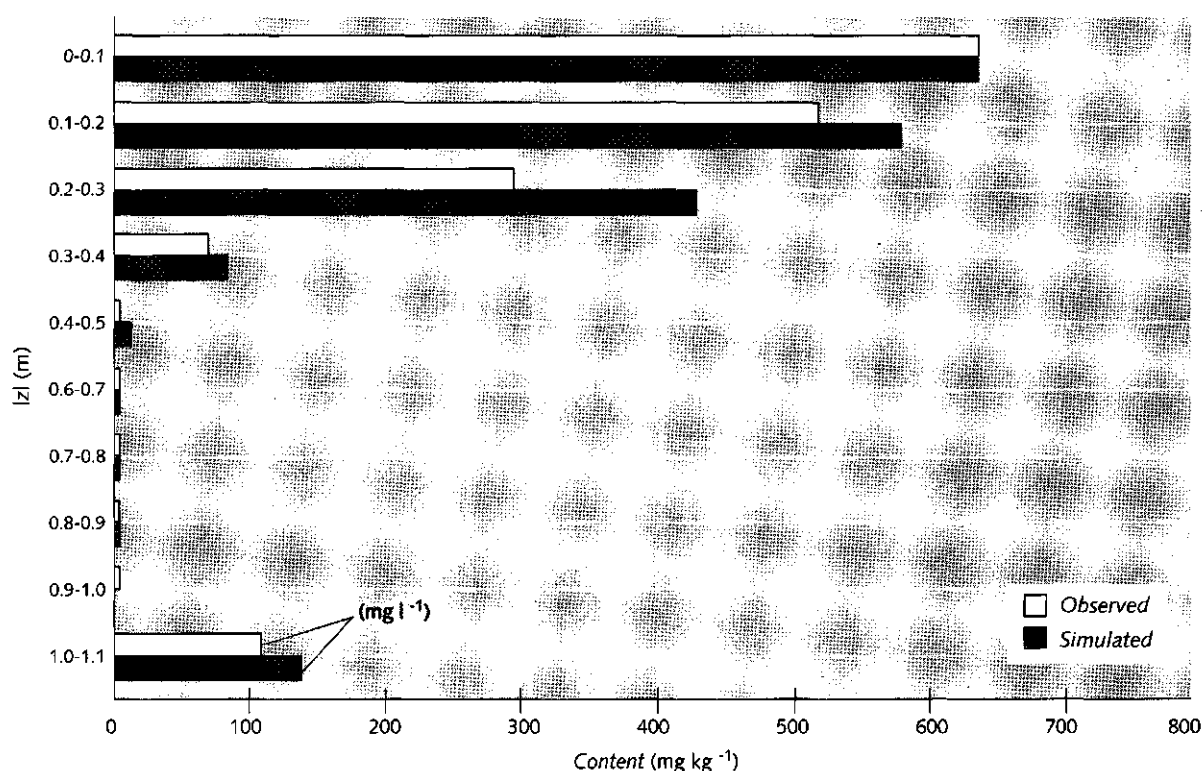


Figure 4.51. Observed and simulated movement of bromide through the soil profile at the experimental field *Eastern Flevoland* after 225 mm of irrigation water was applied with the rainfall simulator during a period of two days. The concentration of bromide in the irrigation water amounted to 2.2 g l^{-1} .

The simulated content of bromide in the soil hardly increased below a depth of 0.4 m. This corresponds to the observed values. Due to the very high rainfall intensity, it was calculated that 93% of the drainage flux flowed through the cracks (imaginary drains). At the end of the second day, the simulated concentration of bromide in the drain pipes amounted to 140 mg l^{-1} . This corresponded fairly well with the observed concentration of bromide in the cracks at a depth of 1.0 m (110 mg l^{-1}).

Sensitivity analyses: Calibration showed that the influence of the dispersion length on the concentration levels of bromide in the drain pipes is limited. This is mainly caused by the fact that the preferential flow of water through the cracks is of overriding importance.

Bromide uptake by roots decreases the concentration of bromide in the drain pipes. If $F = 1$ (maximum root uptake), the root uptake in 1992/1993 and 1993/1994 amounted to 2.7 kg ha^{-1} and 3.8 kg ha^{-1} respectively, which is 30-35% of the dosage.

Sensitivity analyses showed small differences between the simulation of solute fluxes undertaken on a daily and hourly basis. If simulations are carried out on an hourly basis, the contribution of the soil water flux originating from the upper soil layers to the drain flow will increase if rainfall intensity is very high. However, the optimum value for $K_{sat,2}$ increases from 0.005 m d^{-1} up to 0.007 m d^{-1} , if calculations are undertaken on an hourly instead of daily basis.

Conclusions: Both in 1992/1993 and 1993/1994 the

observed concentration of bromide in the drain pipes could be reasonably well calculated with model convection-dispersion equation if imaginary drains were implemented. Observed concentrations are a mixture of concentrations of bromide originating from the soil layers above the cracks and the soil layer below the cracks. If the drain water originates from the upper soil layers, the concentrations are high during the first months after application. After the winter period concentration levels are high if the drain water originates from the lower soil layers. The best fit is achieved if $L_{dis} = 5 \text{ cm}$ and $F = 0$.

The observed load of bromide, which leached through the drain pipes, corresponded fairly well with simulated load. Differences are caused by the deviation between simulated and observed drain discharges or deviation between simulated and observed concentrations in the early spring.

The experiment with the rainfall simulator showed that the major part of the soil water flux flows through the cracks (imaginary drains) if rainfall intensity is high. The observed movement of bromide through the soil profile corresponded to the simulated movement of bromide through the soil profile and observed concentrations of bromide in the cracks at a depth of 1.0 m corresponded to simulated concentrations of bromide in the drain pipes.

4.2.3 Pesticide transport

The next step in the calibration was an attempt to simulate the behaviour of pesticides in cracked clay soils. The soil water fluxes for the concept with imaginary drains were used to simulate bromide fluxes. Apart from the applied load and time of application, parameters that are related to transformation, pesticide uptake by plants, sorption and soil temperatures are needed. The results of the simulation model were compared with the concentration level in the drain pipes. At the experimental field Eastern Flevoland, the pesticide aldicarb and its metabolites aldicarb sulphoxide and aldicarb sulphone were examined. Laboratory experiments showed that less than 3% of the original amount of aldicarb was transformed into aldicarb sulphone. In order to simplify the complex transformation process of aldicarb, the content of aldicarb and aldicarb

sulphoxide were added up and the formation of aldicarb sulphone were neglected. Transformation of aldicarb/aldicarb sulphoxide is represented by first order transformation preceded by an initial phase (figure 3.14).

Model: The flow of pesticides is partly described with the same equations as the flow of solutes. Equations to describe the transport of water and solutes are summarized in table 4.1 (flow of water), table 4.6 (flow of solutes) and table 4.7 (flow of pesticides). Due to the complex transformation of aldicarb, the mathematical description was strongly simplified, so results of the simulations considered as indicative. The formulae for transformation were extended with an initial phase. Supplementary formulae to calculate the length of the initial phase are summarized in table 4.16.

Input parameters: Data on the time of application, quantity applied and period of field measurements for aldicarb were already been presented in table 3.14. Input parameters to determine soil water fluxes are given in table 4.12. This table is supplemented with parameters which were obtained from the optimization of water fluxes ($T = 155 \text{ days}$, $h_{pl} = -1.1 \text{ m}$, $K_{sat,2} = 0.005 \text{ m day}^{-1}$) and solute fluxes ($L_{dis} = 5 \text{ cm}$).

The transformation of aldicarb and its metabolites aldicarb sulphoxide and aldicarb sulphone were analyzed in laboratory experiments, as described in subsection 3.1.2.3. Results of these experiments showed that transformation of aldicarb and aldicarb sulphoxide in the plough layer is strongly influenced by soil temperatures. The length of the initial phase strongly

Table 4.16. Additional set of equations used for the transport of aldicarb/aldicarb sulphoxide.

$$\begin{aligned}
 R_i &= k_1 c^* & 2.45 \\
 k_1 &= 0 & \text{for } t \leq t_{apl} + t_{ini} \\
 t_{ini} &= f(T) \\
 k_1 &= f_T f_\theta f_z f_{k1,ref} & \text{for } t > t_{apl} + t_{ini} & 2.46
 \end{aligned}$$

Table 4.17. Input parameters to determine the leaching of aldicarb/aldicarb-sulphoxide.

TRANSFORMATION AND UPTAKE			
Symbol	Parameter	Value	Equation
$t_{\text{ini}, 10^\circ\text{C}}$	Time of initial phase at 10 °C	25 d	
$k_{1,\text{ref}}$	Reference coefficient for first-order transformation rate	0.30 d ⁻¹	2.44
γ_a	Coefficient	0.12 °C ⁻¹	2.47
T_{ref}	Reference soil temperature	20 °C	2.47
θ_{ref}	Soil moisture content at reference level	0.45	2.49
b_1	Parameter	1	2.49
f_z	Coefficient for the influence of the soil depth on the rate of transformation	1.0-0.5	2.46
F	Constant for selective uptake of the pesticide by the root system	0.5	2.60
SORPTION			
Symbol	Parameter	Value	Equation
K_F	Freundlich coefficient	0.41 cm ³ g ⁻¹	2.57
$(1/n)$	Freundlich exponent	1.0	2.57
$c_{1,\text{ref}}$	Reference concentration in the liquid phase	10 µg l ⁻¹	2.57
ρ	dry soil bulk density	1290 kg m ⁻³	2.32
SOIL TEMPERATURE			
Symbol	Parameter	Value	Equation
T_m	Average soil temperature over a year	11.2 °C	2.56
T_a	Amplitude of the soil temperature at the soil surface	7.7 °C	2.56
d	Damping depth	2.45 m	2.56

depends on soil temperatures. The average soil temperature in the month after application of aldicarb amounted to approximately 10 °C both in 1992/1993 and 1993/1994. The initial phase was determined during the laboratory experiments. For a soil temperature of 10 °C, the initial phase is calculated with the help of linear regression and amounts to 25 days.

After an initial phase of 25 days, $k_{1,\text{ref}}$ (at a reference temperature of 20 °C) amounts to 0.30 d⁻¹. The influence of the temperature on the rate of transformation is presented by equation 2.47. The coefficient γ_a was established at 0.12 C⁻¹. The influence of the soil moisture content is given by equation 2.49. The parameters θ_{ref} and b_1 were set at 0.45 and 1 respectively. The influence of the soil depth on the rate of transformation is presented by a factor, f_z . This factor is equal to 1 in the plough layer and normally decreases with depth. It is assumed that f_z is 0.5 beneath the plough layer. However, no data on the transformation of aldicarb and its

metabolites were available for the deeper soil layers.

Sorption is calculated according to equation 2.57. The Freundlich coefficient and exponent were obtained by laboratory experiments as presented in subsection 3.1.2.3. Experiments to determine K_F and $(1/n)$ were only undertaken for aldicarb and not for the metabolites. It is assumed that K_F and $(1/n)$ of aldicarb sulphoxide are identical to the values obtained for aldicarb. In the laboratory experiments it is assumed that an equilibrium of the partitioning between the solid and liquid phase is reached within hours, if samples are shaken intensively. However, this situation is not obtained in field experiments. If equilibrium is not achieved, it may accelerate the breakthrough of aldicarb/aldicarb sulphoxide in the drain pipes.

Plant uptake is calculated according to equation 2.60. It was assumed that $F = 0.5$. Sensitivity analyses for the concentration aldicarb/aldicarb sulphoxide have been

carried out for plant uptake. The parameters to determine the behaviour of aldicarb and its metabolites are summarized in table 4.17.

Results 1992/1993: In 1992 (14-04-1992) aldicarb was applied directly in the ridges when the potatoes were planted (figure 4.52). This method of application is relatively new and reduces the amount of aldicarb applied (subsection 3.2.3).

Computer simulations showed low concentrations of aldicarb/aldicarb sulphoxide in the drain pipes during the first discharge peaks in the autumn (figure 4.53). During this period the potatoes had not yet been harvested. It was calculated that after October the concentration of aldicarb/aldicarb sulphoxide was below the detection limit due to transformation. It was calculated that less than 2% of the amount applied was transported from the plough layer into the deeper layers. Field measurement with respect to the content of aldicarb/aldicarb sulphoxide in the soil transported into

the deeper soil layers were not performed. The observed concentration of aldicarb sulphoxide and aldicarb sulphone in the drain pipes were below the detection limit.

Figure 4.54 shows that if aldicarb is applied in April more than 95% of the dose will be transformed after the summer period. Soil sampling (1, 3 and 28 days after application) showed that no traces aldicarb/aldicarb sulphoxide were retrieved in the soil profile. Results were below the detection limit (subsection 3.2.10.3). This seems acceptable as the detection limit amounts to 0.4 kg ha^{-1} , which is equal to 0.8 as fraction of the dosage applied.

Results 1993/1994: Due to the fact that no traces of aldicarb, aldicarb sulphoxide and aldicarb sulphone could be traced in the drain pipes during the previous year, the method of application was changed to an older method, which is still used frequently. In 1993 (30-03-1993) the granules (30 kg ha^{-1} : 10% active ma-

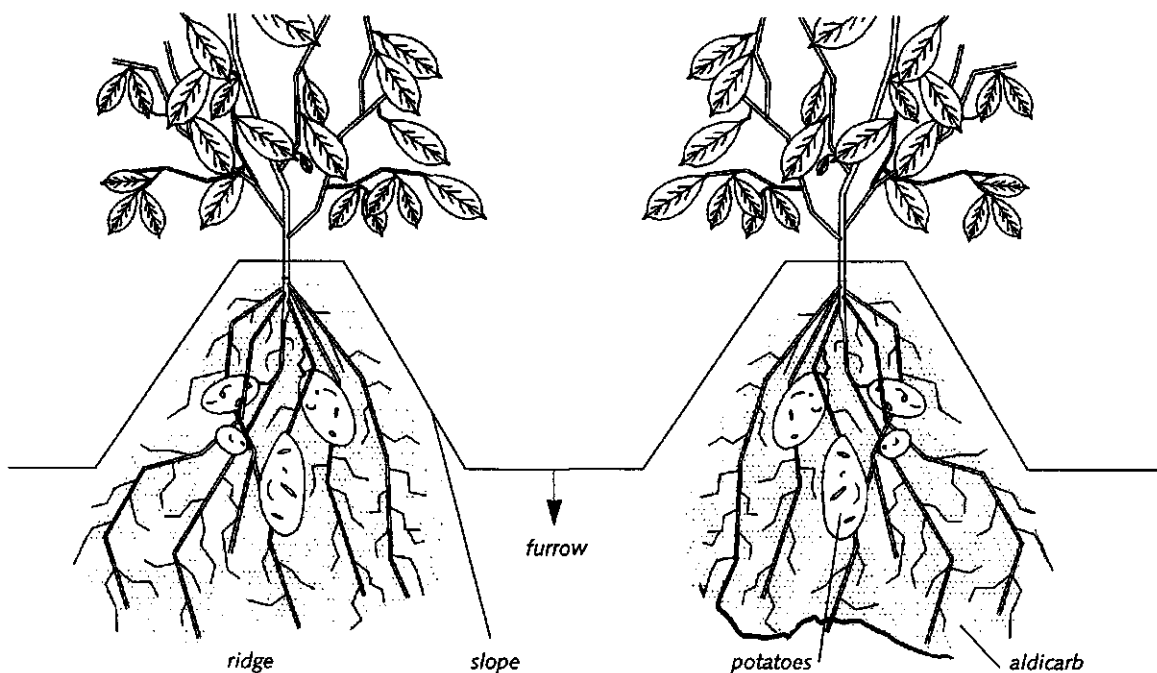


Figure 4.52. Distribution of aldicarb in the plough layer after application in March 1992 (In the dotted part high concentrations of aldicarb can be observed).

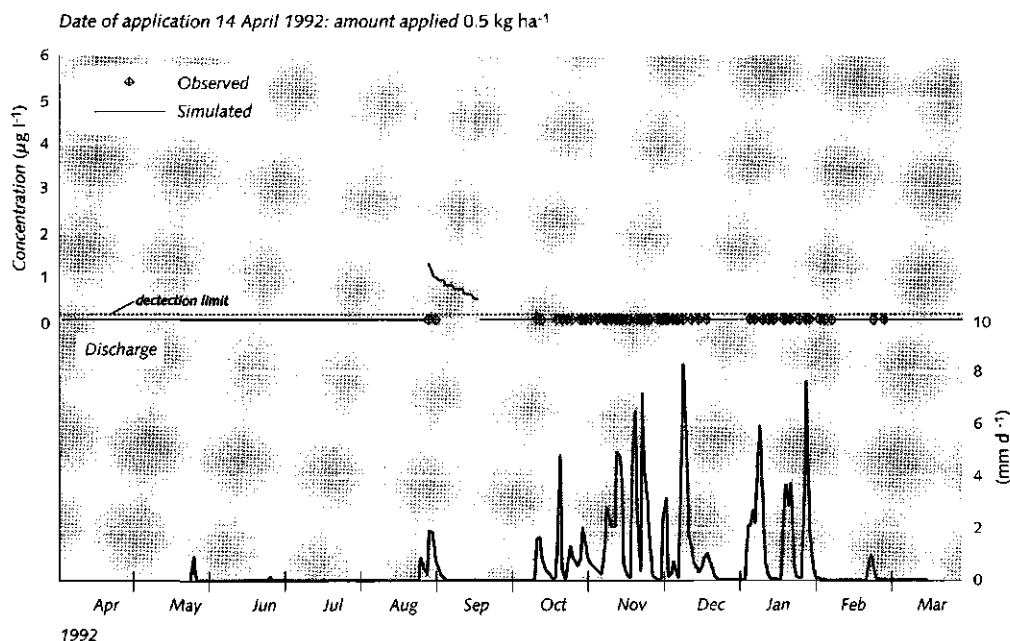


Figure 4.53. Observed and simulated concentration of aldicarb/aldicarb sulphoxide in the drain pipes at the experimental field *Eastern Flevoland* in 1992/1993 (parameters according table 4.17).

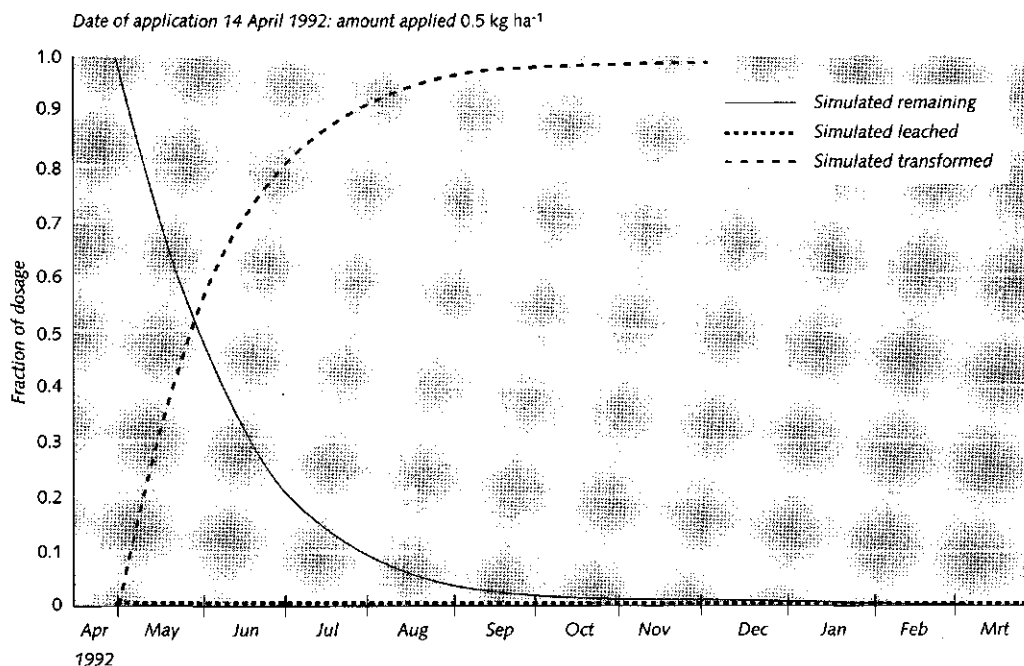


Figure 4.54. Simulated fate of aldicarb/aldicarb sulphoxide in the soil at the experimental field *Eastern Flevoland* in 1992/1993 (parameters according table 4.17).

Date of application 30 March 1993: amount applied 3.0 kg ha^{-1}

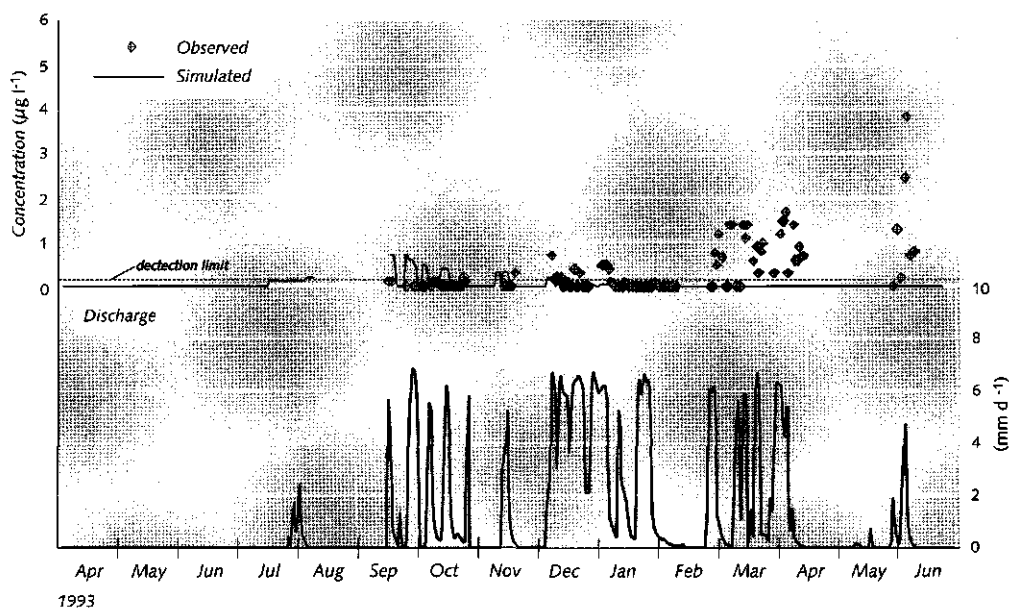


Figure 4.55. Observed and simulated concentration of aldicarb/aldicarb sulphoxide in the drain pipes at the experimental field *Eastern Flevoland* in 1993/1994 (parameters according table 4.17).

Date of application 30 March 1993: amount applied 3.0 kg ha^{-1}

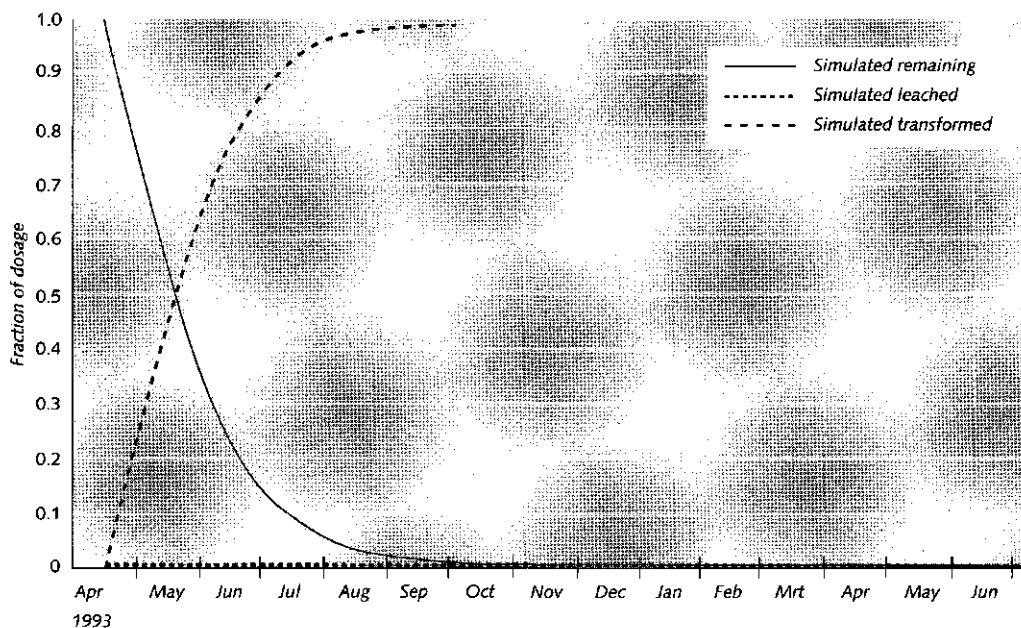


Figure 4.56. Simulated fate of aldicarb/aldicarb sulphoxide in the soil at the experimental field *Eastern Flevoland* in 1993/1994 (parameters according table 4.17).

terial) were spread on the land, mixed with soil by rotavation and incorporated to a depth of 0.15 m. Within two weeks after the treatment, potatoes were planted in ridges (0.75 m apart - approximately 0.2 m in height).

The leaching of aldicarb sulphoxide and aldicarb sulphone into the drain pipes was observed until June 1994 (up to 450 days after application). The cumulative drain discharge over the sampling period amounted to 535 mm, which was much higher than the previous year. The highest concentrations were observed in March and June 1994. The concentrations of aldicarb sulphoxide in the drainage water increased with every new discharge wave up to a concentration of $4 \mu\text{g l}^{-1}$. The observed concentration of aldicarb sulphone in the drain pipes varied from 0.1 up to $0.9 \mu\text{g l}^{-1}$ (subsection 3.2.9.3).

Computer simulations showed low concentrations of aldicarb/aldicarb sulphoxide in the drain pipes during the first discharge peaks in the autumn (figure 4.55). Due to more precipitation, the concentrations in the drain pipes were higher than the previous year. The concentration of aldicarb/aldicarb sulphoxide was below the detection limit due to transformation after November. It was calculated that approximately 5% of the amount applied was transported from the plough layer into the deeper layers. Figure 4.56 shows that if aldicarb is applied in March more than 95% of the dose will be transformed in August. Transformation of aldicarb/aldicarb sulphoxide was even faster than the previous year. Soil sampling was undertaken 3 and 13 days after application (subsection 3.2.10.3). After 3 days the observed content of aldicarb/aldicarb sulphoxide amounted to $75 \pm 20\%$ of the amount applied. After 13 days the observed content of aldicarb/aldicarb sulphoxide was below the detection limit (subsection 3.2.10.3). The detection limit amounts to 0.4 kg ha^{-1} , which is equal to 0.25 as fraction of the dosage applied.

Sensitivity analyses: Both the value of the Freundlich coefficient and the Freundlich exponent have a considerable impact on leaching and the concentration of aldicarb/aldicarb sulphoxide in the drain pipes. If the Freundlich coefficient was reduced to $0.25 \text{ cm}^3 \text{ g}^{-1}$ the concentrations of aldicarb/aldicarb sulphoxide in the

drain pipes increased by a factor 7 to 10. If the Freundlich coefficient is lowered to 0.7 (-), the concentrations of aldicarb/aldicarb sulphoxide in the drain pipes decreased by a factor 5 - 10.

Results of sensitivity analyses show that the temperature has an enormous impact on the leaching of aldicarb/aldicarb sulphoxide. If the average soil temperature was lowered by 5°C , the maximum concentration levels in the drain pipes increased by a factor 30 to 50.

The sensitivity of F (constant for selective uptake of aldicarb/aldicarb sulphoxide by the root system) for leaching is relatively low, because sorption and temperature influence are dominant. If $F = 0$, the concentration in the drain pipes increases by factor 1.5 to 5. Conversely, the concentration in the drain pipes decreases by factor 0.75 up to 0 if $F = 1$.

Conclusions: At the first experimental plot (1992/1993) the differences between simulated and observed values of the concentration of aldicarb/aldicarb sulphoxide are most likely caused by the fact that aldicarb is applied in the ridges. In the computer simulations the flow of water through the soil column is assumed to be uniform (figure 4.52). In reality infiltration of the precipitation will be far from uniform due to surface runoff (from the ridges into the furrows), interception (the leaves of the potatoes are not uniformly distributed) and root uptake (more root uptake in the furrows). The net downward flux of water through the furrows will be higher compared to the ridges. However, as the aldicarb was applied in the ridges, it moved downward more slowly.

Even more important than the application in the ridges, is the time of application in the early spring. After the application of aldicarb no drain discharge is observed for a period of roughly five months. During this period soil temperatures are high. This induces a rapid transformation of aldicarb/aldicarb sulphoxide and a limited net downward flux. The fact that no aldicarb sulphone could be traced in the drain pipes corresponds to the laboratory tests. The results of this study indicated that the major part of aldicarb was transformed into aldicarb sulphoxide, but only a very

small part of sulphoxide was transformed into sulphone.

At the second experimental plot (1993/1994) the simulated values did not correspond to the observed values. Contrary to results of the laboratory experiments, where aldicarb/aldicarb sulphoxide were transformed very rapidly into other compounds than aldicarb sulphone, with the results of the laboratory tests (e.g. half-life time, sorption) it is not possible to calculate concentrations of aldicarb sulphoxide in the drain pipes up to $4 \mu\text{g l}^{-1}$ more than a year after application.

A possible explanation for the differences between the observed and simulated values may be the transformation of aldicarb in the deeper layers (below the plough layer). The observed, accelerated transformation of aldicarb in the plough layer is most likely a microbial process. It corresponds to a very short half-life time with essentially no residues such as aldicarb-sulphone formed. Usually microorganisms are predominantly present in the upper part of the soil (e.g. plough layer). This may indicate that the transformation process in the deeper soil layers (e.g. below the plough layer) differs from the top soil. If transformation is not predominantly induced by microorganisms, it is most likely that the transformation rate will be much lower and metabolites such as aldicarb sulphoxide and aldicarb sulphone will be formed in a higher degree. It is recommended that the laboratory experiments for the transformation of aldicarb are not only performed for the plough layer but also for the subsoil. If it is assumed that $f_z = 0.05$ for the deeper soil layers, concentrations of aldicarb/aldicarb sulphoxide in the drain pipes are of the same order of magnitude as the observed values.

4.3 Southern Flevoland

4.3.1 Water flow

The collection of data at the experimental field in Southern Flevoland was presented in chapter 3. The set of the most important equations used for the description of water flow is the same as for the experimental field Eastern Flevoland including the concept for preferential flow with imaginary drains. As the results of

the simulations for the experimental field Eastern Flevoland showed that implementation of imaginary drains gives a better description of soil water flow in cracked clay soils, simulations are only undertaken for the concept with imaginary drains. At the experimental field Southern Flevoland the cracks start at a depth of approximately 0.35 m.

The actual flux through the soil surface (q_s) at the experimental field Southern Flevoland is strongly influenced by the spatial inhomogeneity of the net precipitation at the top of the soil, especially during the summer period. The inhomogeneity is caused by the fact that half of the surface of the orchard is covered by apple trees and the other half with grass. In addition the leaves of the apple trees strongly redistribute the precipitation. The actual flux through the soil beneath the apple trees may vary strongly within a few metres. In order to describe the spatial inhomogeneity of the precipitation at the top of the soil without leaving the concept of one-dimensional flow, the orchard is subdivided in a number of sections. Net precipitation and area will vary for each section. The equations needed to solve the flow of water in the unsaturated zone are equal to the equations used for the experimental field Eastern Flevoland.

Numerical method: To solve the tridiagonal system of equations, a stop criterium was defined that was applied for the experimental field Southern Flevoland. The values for the relative tolerance and the absolute tolerance are presented in table 4.18.

Soil physical properties: The soil profile of the experimental field Southern Flevoland has been presented in subsection 3.1.1.3. The soil profile was subdivided in four different soil layers containing 8 compartments of 0.05 m (0 - 0.40 m) and 14 compartments of 0.10 m (0.4 - 1.7 m) (figure 4.57). The soil physical functions of each layer are described by a soil moisture retention curve and the relationship between the hydraulic conductivity and the pressure head according to Van Genuchten (equations 2.12 and 2.14).

The parameters for the soil water retention curve and hydraulic conductivity curve, which were used for the model calculations, were determined in the laboratory

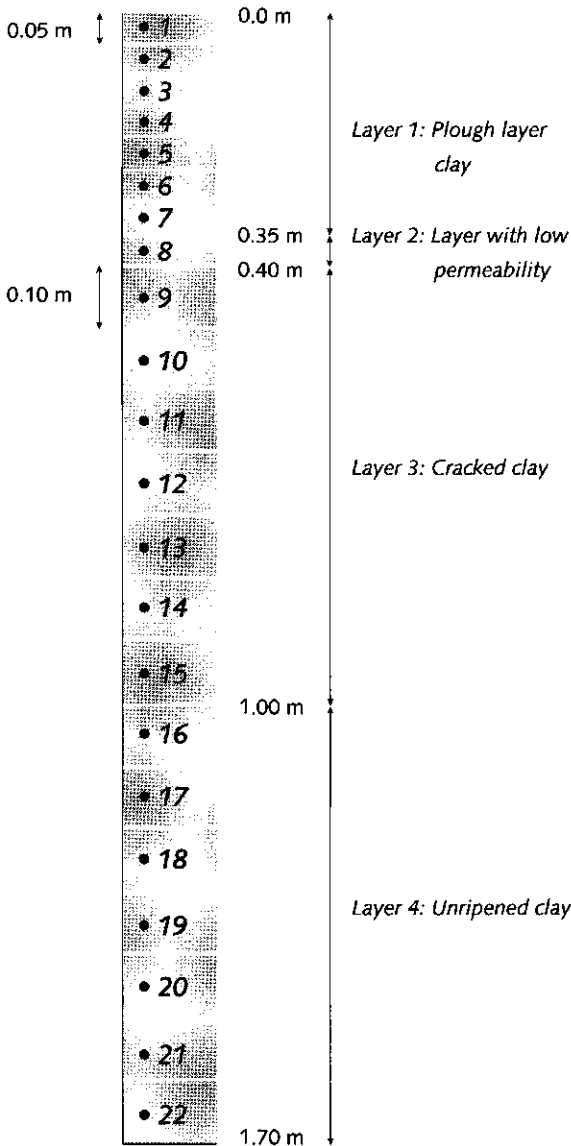


Figure 4.57. Schematisation of the soil profile at the experimental field Southern Flevoland.

and are presented in table 3.6. It should be noted that both the soil water retention curve and the (un)saturated conductivity curve are strongly influenced by the stage of ripening (Rijniersce, 1983). The stage of ripening depends on the withdrawal of water from the soil during successive growing seasons. As the grass

extracted less water from the soil than the apple trees, the physical soil ripening process under grass showed a smaller progress. Therefore a different depth of soil ripening should be used for the section "apple trees" and section "grass". For the section "grass" the unripened clay started at a depth of 0.8 m - soil surface.

Upper boundary conditions: In order to describe the spatial inhomogeneity of the precipitation and evapotranspiration without leaving the concept of one-dimensional flow, the orchard is subdivided in sections, as described in subsection 2.3.3. As half of the surface of the orchard is cropped by apple trees and the other half consists of grass, two sections are distinguished. Upper boundary conditions, such as interception and transpiration strongly deviate for both sections. Furthermore, the apple trees strongly redistribute the precipitation, which causes a strong spatial variability of the actual flux through the soil during the summer period (May until November). For this period the section "apple trees" is subdivided into four different sub-sections.

Section "grass": At the upper boundary, the daily precipitation and daily reference evapotranspiration are inputs. The reference evapotranspiration according to Makkink is obtained from a meteorological station at the experimental field. It is multiplied by a crop factor (f) to obtain the potential evapotranspiration. Crop factors for grass have already been presented in table 4.3. Input parameters, such as soil cover, regression coefficients for grass (a , b and c) and the parameters $|h_1|$, $|h_2|$, $|h_3|$, $|h_4|$ and $|h_5|$ are equal to the parameters taken for the experimental field North-East Polder. These parameters have already been presented in table 4.2. The lower limit of the root zone at the grass strip is equal to approximately 0.50 m and up to 80% of the roots can be found in the upper 0.2 m (Visser, 1983). Under optimal soil water conditions, the possible water extraction by the roots of grass (S_{max}) is assumed to diminish with depth, according to a function of Prasad (1988). The soil cover is assumed to be equal to 0.95 both for the summer and winter period. The actual soil evaporation is described according to Boesten (equation 2.22). The β value in this equation is assumed to be the same as for the experimental field Eastern Flevoland.

Table 4.18. Input parameters to determine soil water fluxes for the experimental field *Southern Flevoland*.

NUMERICAL METHOD			
Symbol	Parameter	Value	Equation
<i>reltol</i>	Relative tolerance	$1 \cdot 10^{-2}$	2.11
<i>abstol</i>	Absolute tolerance	1 cm	2.11
UPPER BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
<i>P</i>	Precipitation	Daily values	
<i>E_r</i>	Reference evapotranspiration	Daily values	2.17
<i>f</i>	Crop factor	Decade values (table 4.19)	2.18
<i>a</i>	Regression coefficients for apple trees	1.3	2.20
<i>b</i>		1.0	
<i>c</i>		0.6	
<i>S_c</i>	Soil cover	Daily values	2.20
β	Parameter for actual soil evaporation	2.0 mm ^{0.5}	2.22
<i>a_i</i>	Parameter representing the crop dependent saturation value	1.96	2.23
$ z_r $	Lower limit of the root zone	Daily values	2.27
$ h_1 $	Values of the soil water pressure head which determine	10 cm	2.25
$ h_2 $	the dimensionless sink term variable for water extraction	25 cm	
$ h_3 $	by roots, <i>a</i>	400 cm	
$ h_4 $		600 cm	
$ h_5 $		16000 cm	
<i>K_h K_v⁻¹</i>	anisotropic factor	5	
LATERAL BOUNDARY CONDITIONS			
Symbol	Parameter	Value	Equation
$ z_{dr} $	Drain depth (drainage level 1: imaginary drains)	0.35 m	
	Drain depth (drainage level 2)	1.00 m	
<i>L</i>	Drain spacing (drainage level 1: imaginary drains)	0.30 m	2.29
	Drain spacing (drainage level 2)	48 m	
<i>u</i>	Wet perimeter (drainage level 1: imaginary drains)	0.20 m	
	Wet perimeter (drainage level 2)	0.60 m	

Table 4.19. Values for the dimensionless crop factor, *f*, for apple trees (after Kodde and Kipp, 1990).

Month	April			May			June			July			August			September			October		
Decade	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Apple trees	-	-	-	0.9	1.0	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.0	1.0	0.9

Section "apple trees": To test the variability of throughfall under the trees, 23 similar gauges (140 mm diameter) were located under the trees at various distances from the stem and at different locations in the orchard. Two spiral stem flow gauges were used to measure the water flowing down the trunks of the trees. During the period of observation, which was more than one year, the gauges were emptied three times a week. Significant differences between the gauges could only be observed during the summer period. Figure 3.45 presents the cumulative throughfall for 23 rain gauges for the period from July until October 1993 and the period from January 1994 until April 1994. The measurements revealed the existence of dry and wet spots under tree crowns due to non-uniform area distribution of throughfall and the daily interception rate.

The evaporation losses by interception are calculated according to Braden (1985). Interception is a function of the Leaf Area Index, the soil cover, the precipitation and a parameter representing the specific properties of the leaves, a_i (equation 2.23). For apple trees the parameter a_i could be calculated by dividing the maximum interception rate (which amounts to 5.5 mm d⁻¹) by the maximum LAI (which amounts to 2.8) yielding a value of 1.96. Minor changes in the soil water balance could be observed if this parameter was changed within a range from 1.5 up to 2.5.

In order to simulate soil water fluxes the net precipitation ($P_n = P_{gr} - I$) is first calculated. Subsequently, the net precipitation is segmented into four sections of equal surface area. The actual flux through the soil surface per section is calculated according to equation 2.67. The total net precipitation is equal to the average precipitation per section according to equation 2.68. During the winter period both the variability of the throughfall and evaporation losses by interception can be ignored. Thus, net precipitation is the same for each section.

Apart from the segmentation of the net precipitation, other parameters which determine the upper boundary conditions are equal for all subsections. The crop factors during the growing season for apple trees are presented in table 4.19. During the winter period (October until April), the potential evapotranspiration is as-

sumed to be equal to reference crop evapotranspiration. Thus, the factor f is then equal to 1. Under optimal soil water conditions, the possible water extraction by the roots of the potatoes (S_{max}) is assumed to diminish with depth, according to a function of Prasad (1988). At the lower limit of the root zone root extraction is taken to be zero. The maximum rooting depth is equal to the depth of the highest groundwater tables and is assumed to be constant throughout the year.

Values of the soil water pressure head ($|h_1|$, $|h_2|$, $|h_3|$, $|h_4|$ and $|h_5|$), which describe the function of the dimensionless sink term variable for water extraction by roots of apple trees, α (equation 2.25), are presented in table 4.18. The soil cover is a function of time. After a flowering period in May, the leaves of the trees started to grow and reached their full growth in June. At this time the soil cover amounted to approximately 0.85. In October apples are harvested and in November the leaves started to wither. The β value, which determines the actual soil evaporation is assumed to be the same as for the experimental field Eastern Flevoland and amounts to 2 mm^{0.5}.

Lower boundary conditions: As the layer of unripened clay below the drain pipe is more than 2 m thick, the magnitude of the flux at the bottom boundary is equal to 0.

Lateral boundary conditions: For the concept with imaginary drains, the flow of water was described according to figure 2.8. At a depth of 0.35 m imaginary drains were implemented, representing the cracks. Due to the low permeability of layer 2 (0.35 - 0.40 m, i.e. just below the plough layer) perched water tables occur from time to time. If the precipitation surplus increases, only part of the soil water flux flows into the soil matrix of layer 3 (0.40 - 1.00 m). The extent of the water flux into the soil matrix of layer 3 depends on the saturated conductivity of layer 2. The remaining water flows directly into the cracks. Preferential flow through the cracks is described by imaginary drain pipes, identical to the experimental field Eastern Flevoland. Values for the drain spacing, drain depth, wet perimeter for the drainage levels at 0.35 and 1.00 m are summarized in table 4.18. The anisotropic factor ($K_h K_v^{-1}$) is the same for both concepts and is set at 5. The

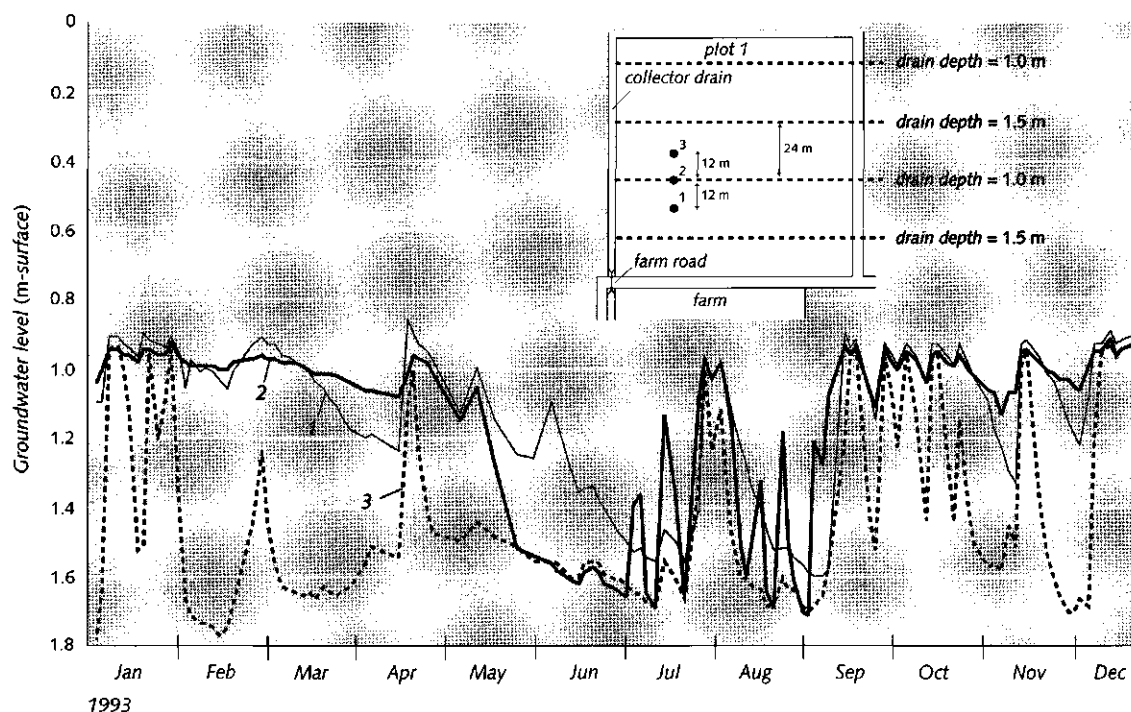


Figure 4.58. Observed groundwater levels at various locations at the strip under the apple trees at the experimental field Southern Flevoland.

drainage flux is calculated according to the Hooghoudt equation (equation 2.29).

Calibration and optimization criteria: For the calibration of the model, the observed drain discharges were used. The drain discharge was measured at intervals by using the discharge proportional sampler (subsection 3.2.8). As the spatial inhomogeneity of the observed groundwater tables was high (figure 4.58) the model was not calibrated for groundwater tables.

The distribution of the net precipitation at the section apple trees is calibrated using the observed drain discharge. The net precipitation is segmented into four subsections of equal surface area, represented by the parameters a_1 , a_2 , a_3 and a_4 (equation 2.67). Apart from the distribution of the net precipitation, the extent of the drainage flux is strongly influenced by the saturated permeability of layer 2 ($K_{sat,2}$). At the experimental field Eastern Flevoland $K_{sat,2}$ was considered as a parameter to be optimized. For the experimental field

Southern Flevoland $K_{sat,2}$ was set at 0.005 m d^{-1} , which is equal to the optimum value which was observed at the experimental field Eastern Flevoland. Drain discharges were calculated for five sections (4 * apple trees: 1 * grass). The simulated drain flow is taken as equal to the weighted average of the separate simulated drain flows of each section.

In order to obtain the best fit between the observed and simulated drain discharges, the unknown parameters which determine the distribution of the net precipitation are optimized according to the objective function Root-Mean-Square as explained in section 4.1.1. The simulated drain discharge is equal to the sum of the weighted average for each section.

Results: The parameters a_1 , a_2 , a_3 and a_4 were optimized for RMS_q , taking observed throughfall at dry, average and wet spots as a starting point. During the summer period the optimum values of a_1 , a_2 , a_3 and a_4 are equal to 0.3, 0.7, 1.2 and 1.8. During the winter pe-

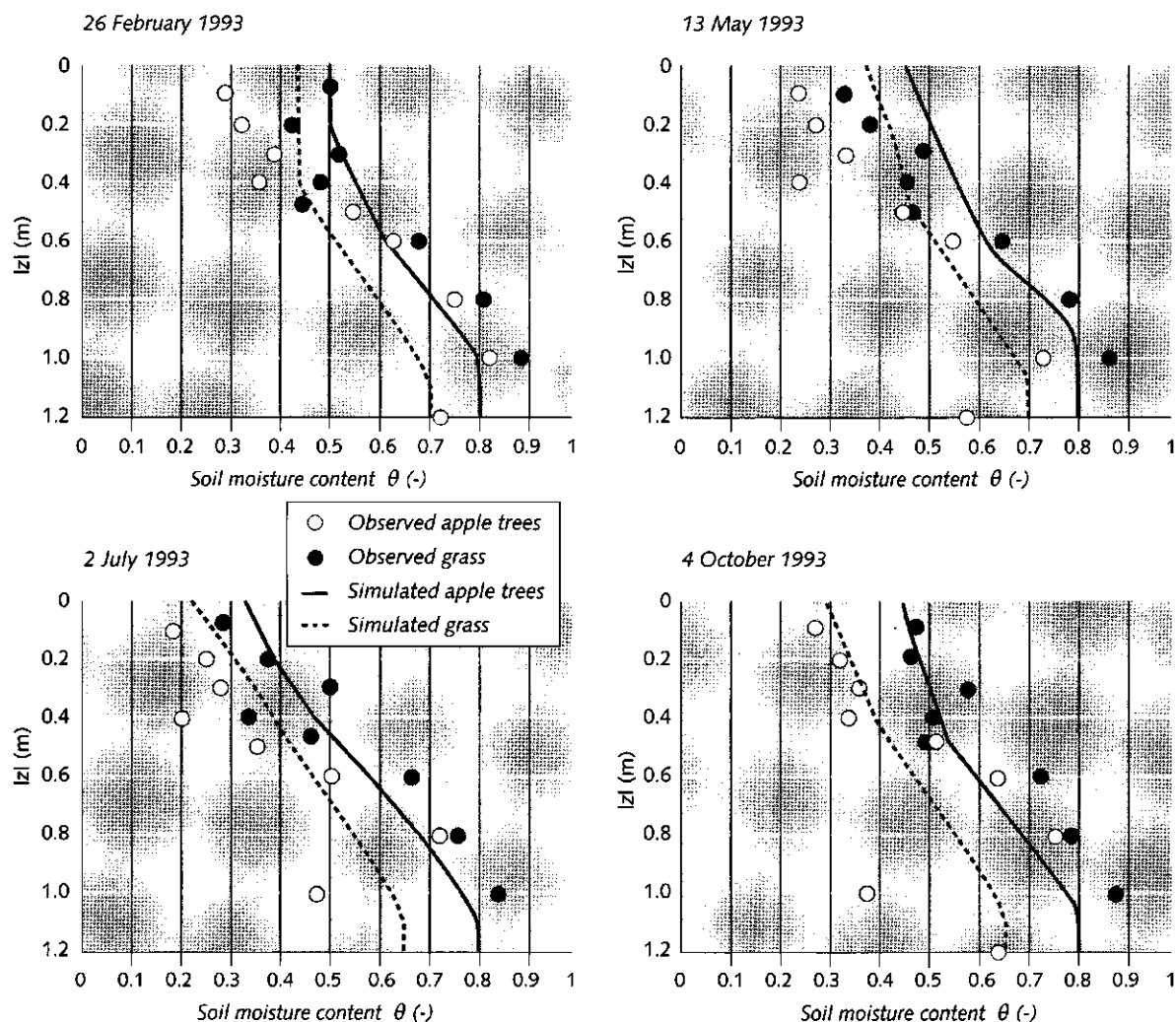


Figure 4.59. Observed and simulated soil moisture content at four selected days at the experimental field *Southern Flevoland*. Soil moisture content for the strip section "apple trees" was calculated with a uniformly distributed precipitation.

riod the values of a_1 , a_2 , a_3 and a_4 are equal to 1. The optimum value of RMS_q is calculated at 1.4 mm d^{-1} . The values of the parameters roughly agree with the observed values for throughfall, as presented in subsection 3.2.11 (figure 3.45). During the summer period the maximum observed throughfall is twice the net precipitation ($a_4 = 2.0$) and the minimum observed throughfall amounts to only 35% of the net precipitation ($a_1 = 0.35$). During the period July until October

1993 the observed interception was equal to 117 mm. During the winter period interception can be ignored. Differences between maximum and minimum observed throughfall are much smaller. This agrees with the assumption that the parameters a_1 , a_2 , a_3 and a_4 are equal to 1 during the winter period.

The results of the calibration of the soil water flow for the optimum values of a_1 , a_2 , a_3 and a_4 are shown in

Table 4.20. Simulated soil water fluxes in 1993 and 1994 for the section "grass" at the experimental field *Southern Flevoland* (P = precipitation, ΔB = change in storage (- = out), q_b = flux through the bottom of the soil profile (- = out), q_d = lateral drainage flux (- = out), E_i = interception, E_s = actual soil evaporation, E_t = actual transpiration).

Period	P (mm)	ΔB (mm)	q_b (mm)	q_d (mm)	E_i (mm)	E_s (mm)	E_t (mm)
Mar '92 - Dec '93	805	6	0	- 251	95	29	425
Jan '93 - Dec '93	925	-3	0	- 365	102	28	433
Jan '94 - May '94	480	-52	0	- 243	39	15	235

Table 4.21. Simulated soil water fluxes in 1993 and 1994 for the section "apple trees" at the experimental field *Southern Flevoland* (P = precipitation, ΔB = change in storage (- = out), q_b = flux through the bottom of the soil profile (- = out), q_d = lateral drainage flux (- = out), E_i = interception, E_s = actual soil evaporation, E_t = actual transpiration).

Period	P (mm)	ΔB (mm)	q_b (mm)	q_d (mm)	E_i (mm)	E_s (mm)	E_t (mm)
Mar '92 - Dec '93	805	5	0	- 212	115	137	336
Jan '93 - Dec '93	925	0	0	- 325	119	167	314
Jan '94 - May '94	480	-85	0	- 222	37	182	124

figures 4.59, 4.60, 4.61, 4.62 and 4.63. The simulated soil water fluxes for the section "grass" and the section "apple trees" are presented in respectively table 4.20 and table 4.21.

Figure 4.59 shows the observed and simulated soil moisture content from the soil surface down to a depth of 1.2 m for four selected dates (winter, spring, autumn and summer) for both the grass strip and below the apple trees. Significant differences concerning moisture content between the dry and wet spot below the apple trees could be seen during the summer period. If the precipitation intensity is high and the moisture content of the plough layer exceeds field capacity, part of the precipitation surplus flows into the imaginary drains (e.g. cracks). Due to the difference in the stage of soil ripening, the moisture content for the section "apple trees" and the section "grass" varied considerably at all soil depths. The moisture content of the unripened clay below the cracks is constant during the summer and winter period both for the section "grass" and the section "apple trees" and amounts to approximately 0.85.

The change in water storage (ΔW) for a given period

of time (Δt) is calculated according to equation 2.1. If the soil moisture content at a particular time is known, the storage can be calculated according to equation 4.2. The observed and simulated storage over a depth of 1.2 m are presented in figure 4.60. The observed and simulated water storage varies between 725 and 875 mm for the section "grass" and between 500 and 700 mm for the section "apple trees". During the summer period simulated groundwater levels varied considerably per section. This is caused by the spatial inhomogeneity of the net downward flux and the soil characteristics of unripened clay. Due to these characteristics, only small changes of the soil moisture content strongly influences groundwater levels. The differences in groundwater levels for the section "apple trees" are presented in figure 4.58. During the winter period differences in groundwater levels are small, as the spatial inhomogeneity of the net downward flux between the different subsections disappears. Due to the high variability in groundwater levels below the section "apple trees", groundwater levels were only simulated for the section "grass". Figure 4.61 shows the observed and simulated groundwater levels below the grass strip. The average observed groundwater level amounted to 1.16 m and deviates only slightly from the

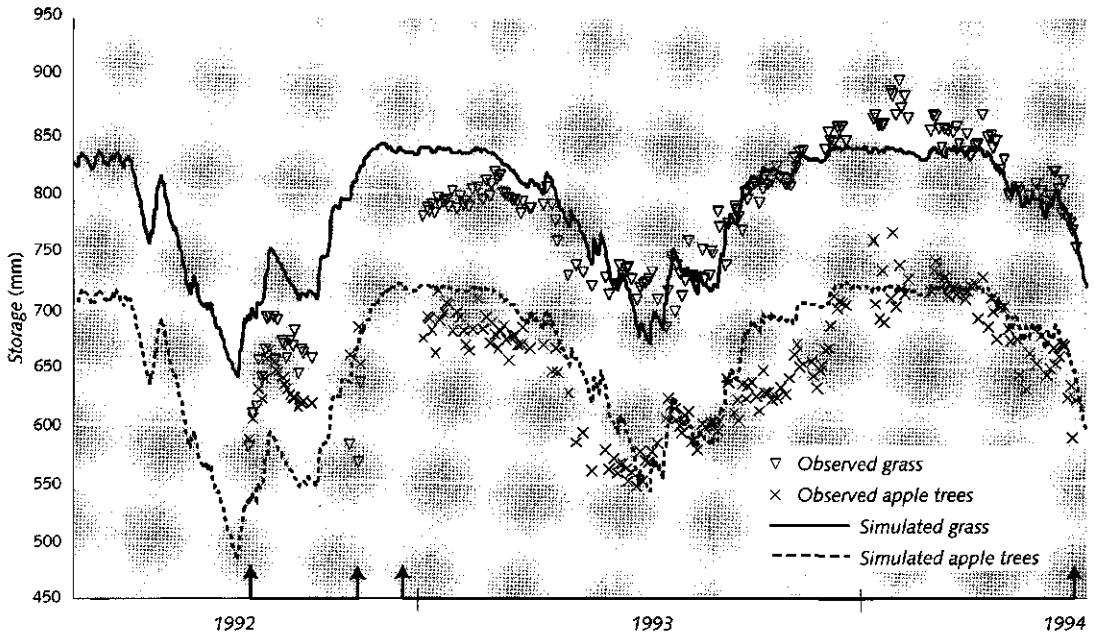
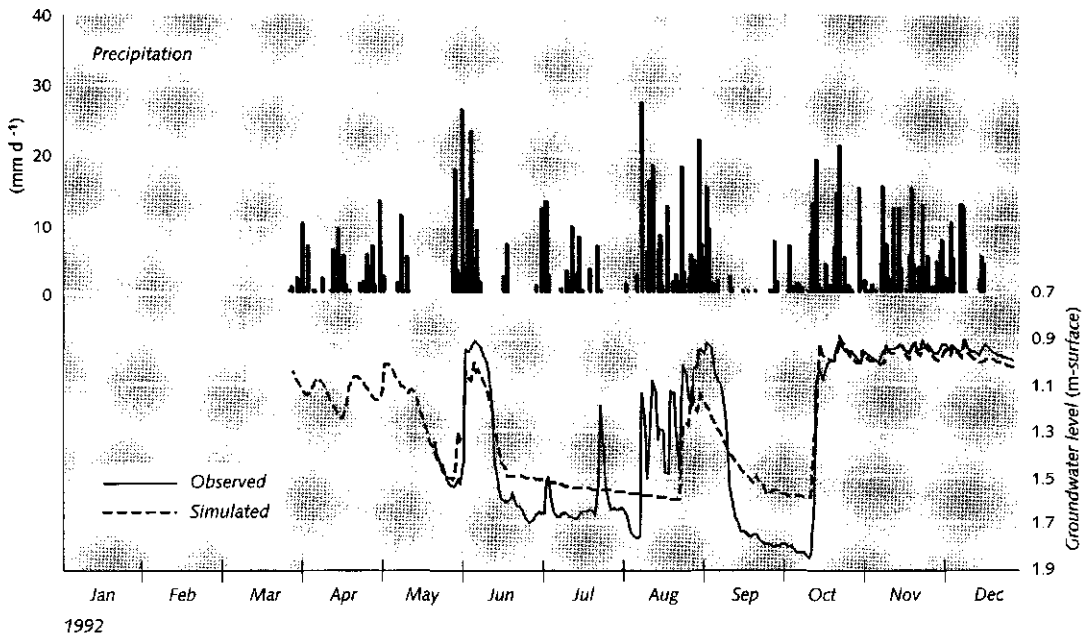


Figure 4.60. Observed (▽ and ×) and simulated (—) soil water storage over a depth of 1.2 m (periods indicated in black at the bottom = periods where probes were implemented) from March 1992 until June 1994 for the experimental field *Southern Flevoland*. Storage for the section “apple trees” was simulated with an uniformly distributed precipitation.



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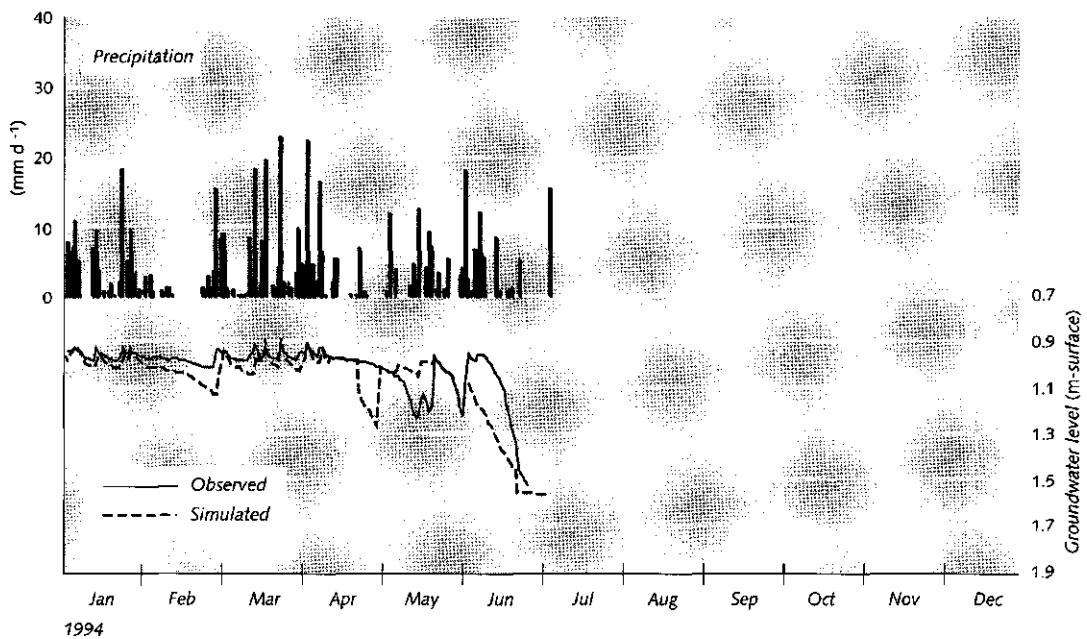
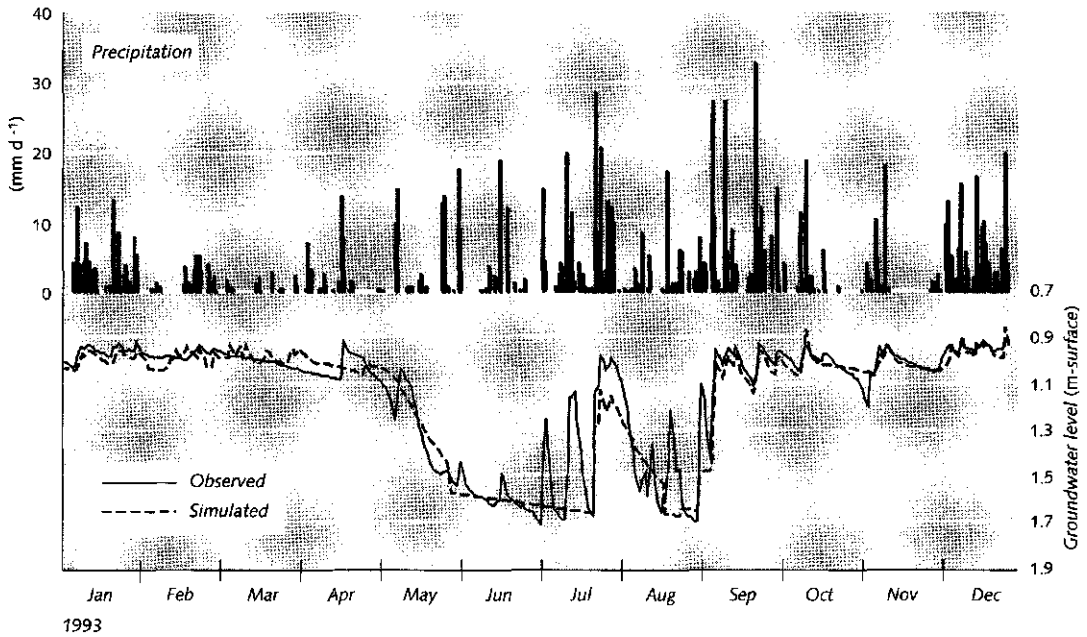
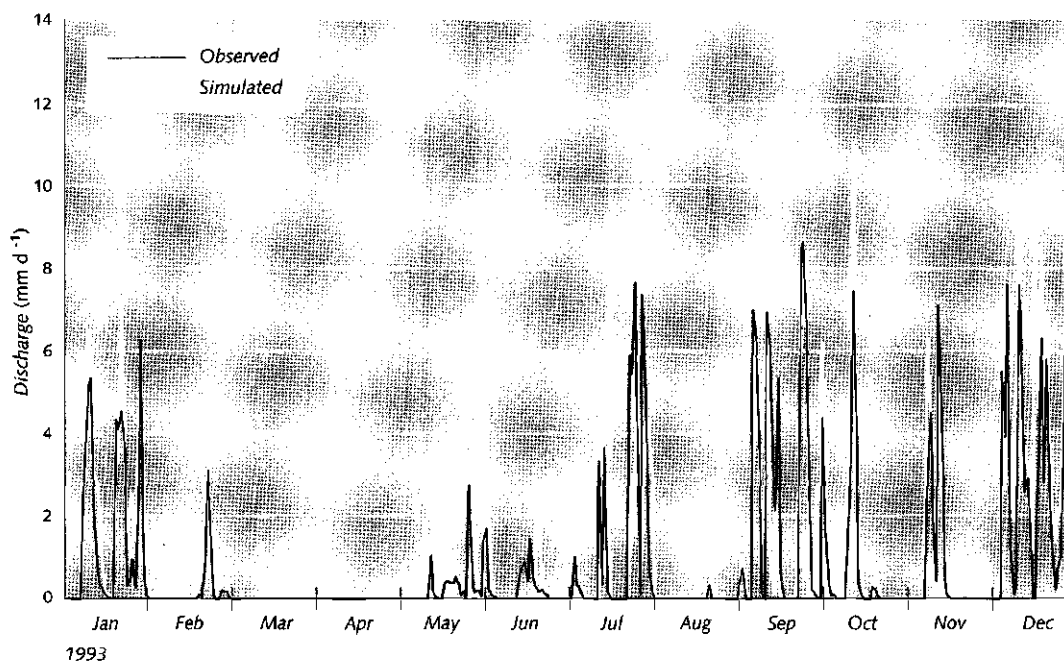
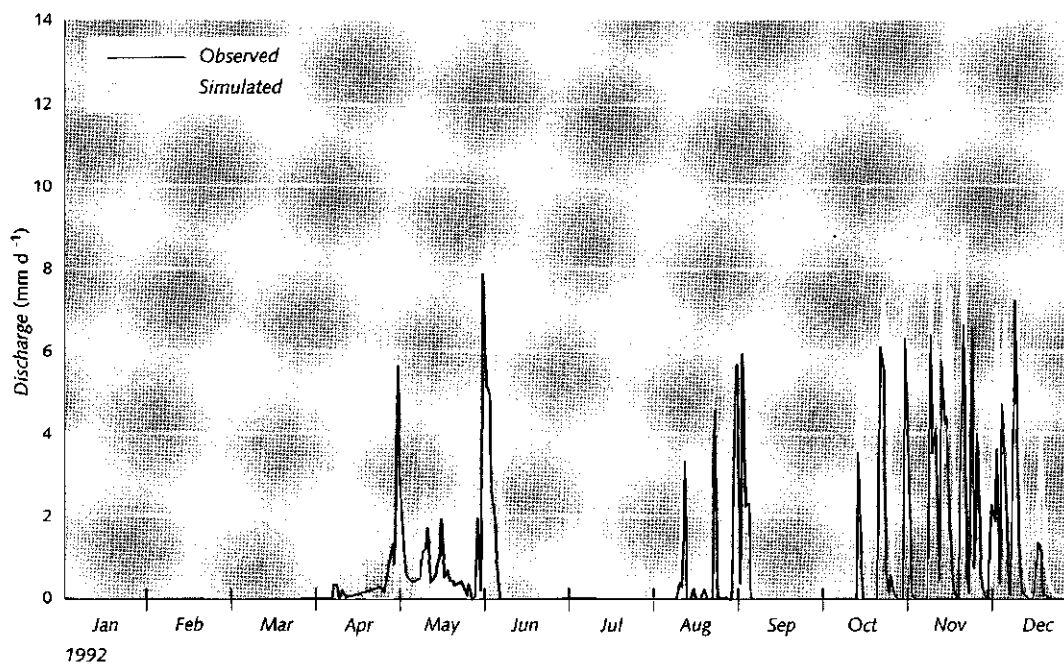


Figure 4.61. Observed and simulated groundwater levels for the section "grass" from March 1992 until June 1994 for the experimental field Southern Flevoland.



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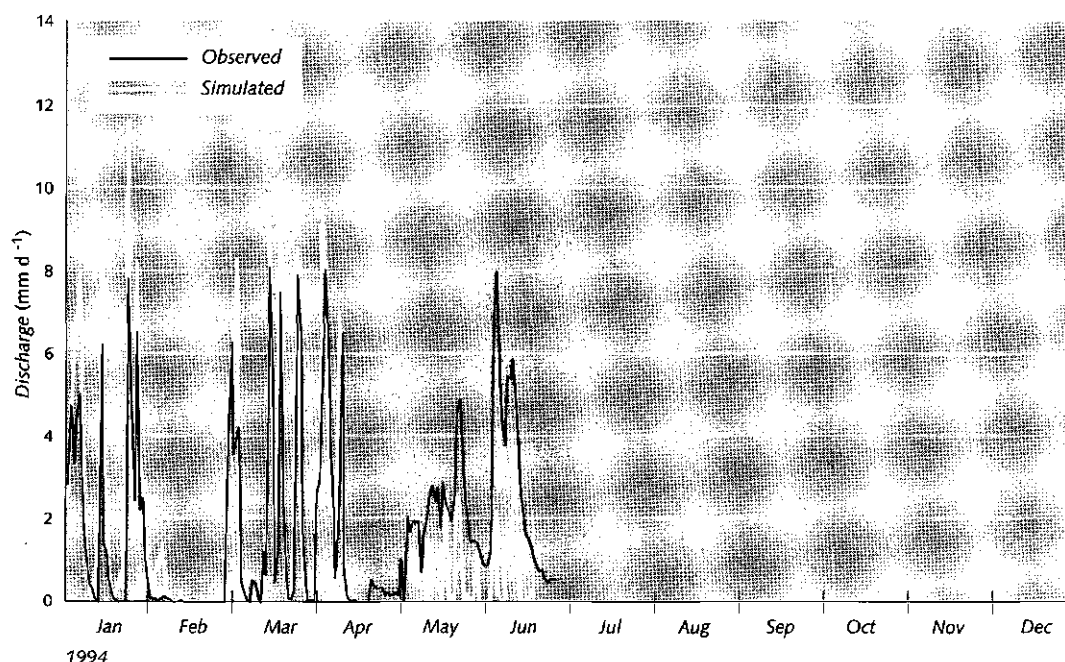


Figure 4.62. Observed and simulated drain discharge from March 1992 until June 1994 for the experimental field *Southern Flevoland*. Drain discharges were calculated for five sections (4 * apple trees: 1 * grass). Simulated drain flow is taken equal to the weighted average of the separate simulated drain flows of each section.

simulated average groundwater level which amounted to 1.18 m. RMS_{gwls} which was calculated according the parameters presented in table 4.18 and with $a_1 = 0.3$, $a_2 = 0.7$, $a_3 = 1.2$ and $a_4 = 1.8$, amounts to 0.104 m.

Figure 4.62 shows the observed and simulated drain discharges. Besides times of peak discharge, the simulated drain discharge shows good agreement with the observed drain discharge. The drain discharge peaks during the summer period are mainly caused by the wet spots (e.g. $a_4 = 1.8$). If the net precipitation was distributed uniformly, hardly any drain discharge was simulated during the summer period.

The maximum observed drain discharge amounted to roughly 8.0 mm d^{-1} ; the maximum simulated drain discharge amounted to roughly 11 mm d^{-1} . As at the experimental field Eastern Flevoland, the difference is mainly caused by the limited capacity of the pump, which pumps the water from the reservoir into the collector drain. During some periods the water level in the

collector drain rises above the level of the drain pipes. The drain water does not flow freely into the collector drain and the maximum drain discharge decreases. This was particularly the case during the spring. However, the observed cumulative drain discharge conforms to the simulated cumulative drain discharge. This is presented in figure 4.63.

Sensitivity analyses: Changes in the soil moisture content are mainly determined by the actual evapotranspiration and net precipitation. The redistribution of the net precipitation strongly influences soil moisture content during the summer period. Differences between the soil moisture content of dry and wet spots are highly variable within a few metres. The moisture content of the third layer is influenced by the saturated permeability of the second layer ($K_{sat,2}$), especially during the autumn (rewetting of the soil).

During the summer period the groundwater levels in the soil matrix are sensitive for the spatial inhomogeneity.

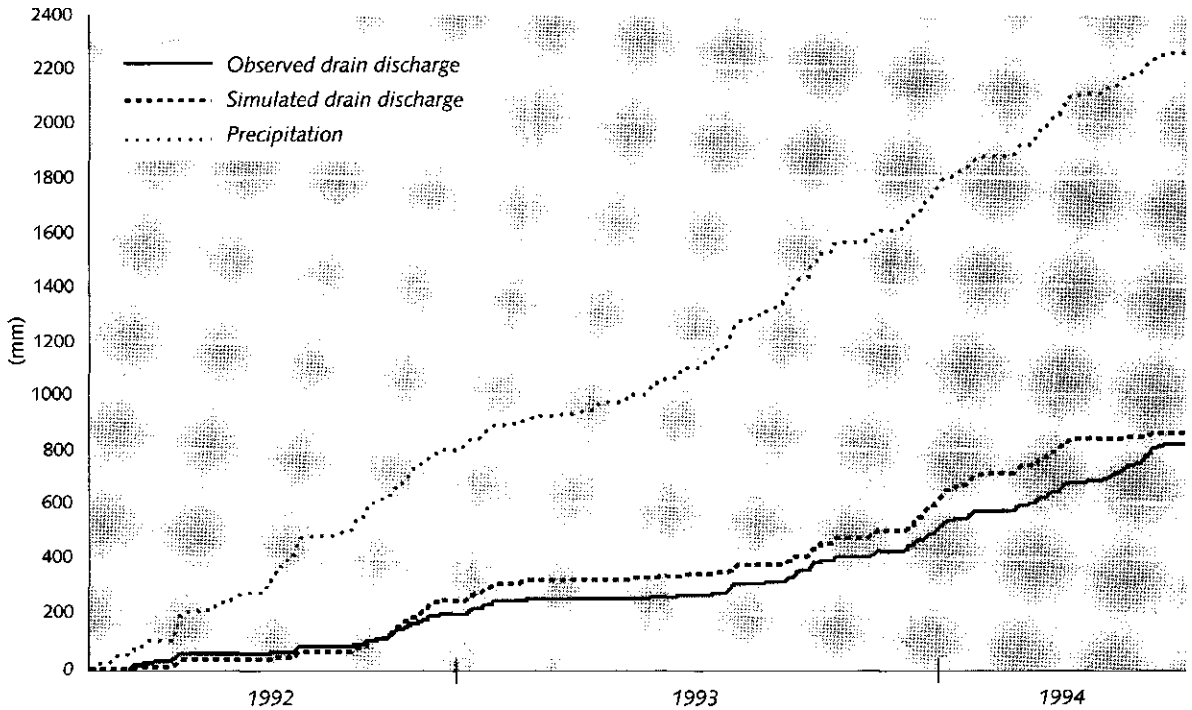


Figure 4.63. Observed and simulated cumulative drain discharge and cumulative precipitation from March 1992 until June 1994 at the experimental field *Southern Flevoland*.

geneity of the net downward flux. Due to the soil characteristics of the unripened clay, small changes in soil moisture content strongly influence groundwater levels. As the saturated permeability of the third layer ($K_{sat,3} = 150 \text{ m d}^{-1}$) is extremely high, the convexity between the drain pipes hardly exceeds 0.15 m. During periods of drain flow, groundwater levels vary between 0.90 and 1.05 m below the soil surface.

The drain flow depends on the height of the groundwater table, the saturated permeability of the soil (K_{sat}) and the redistribution of the precipitation, represented by the parameters a_1 , a_2 , a_3 and a_4 . Drain flow during the summer period is mainly defined by magnitude of the parameter a_4 , which represents the area with the maximum throughfall. The influence of the remaining parameters a_1 , a_2 and a_3 on the drain flow is limited. Drain flow is also influenced by $K_{sat,2}$, which determines the distribution of the drainage flux over the first and second drainage level. If the value of $K_{sat,2}$ in-

creases, the drainage flux of the first drainage level decreases.

Conclusions: The actual flux through the soil surface (q_s) at the experimental field Southern Flevoland is strongly influenced by the spatial inhomogeneity of the net precipitation at the top of the soil, especially during the summer period. The inhomogeneity is caused by the fact that half of the surface of the orchard is cropped by apple trees and the other half consists of grass. In addition, the leaves of the apple trees strongly redistribute the precipitation with wet spots between the trees and dry spots below the leaves.

In order to describe the spatial inhomogeneity of the precipitation at the top of the soil without leaving the concept of one-dimensional flow, the orchard is subdivided in a number of sections. Net precipitation and area will vary for each section. The equations required to solve the flow of water in the unsaturated zone are

equal to the equations used for the experimental field Eastern Flevoland including the implementation of imaginary drains.

The distribution of the net precipitation at the section apple trees is calibrated using the observed drain discharge. The net precipitation at the section "apple trees" is segmented into four subsections of equal surface area, represented by the parameters a_1 , a_2 , a_3 and a_4 (equation 2.67). Results of the calibration procedure showed that the optimum values of a_1 , a_2 , a_3 and a_4 during the summer period are equal to 0.3, 0.7, 1.2 and 1.8. Drain flow during the summer period is mainly defined by magnitude of the parameter a_4 , which represents the area with the maximum throughfall. These values are in the same order of magnitude as the maximum observed throughfall, which was twice the net precipitation ($a_4 = 2.0$) and the minimum observed throughfall, which amounted to only 35% of the net precipitation ($a_1 = 0.35$).

The simulated drain flow is calculated as the weighted average of the separate simulated drain flow for each section. It shows good agreement with the observed drain flow. If the net precipitation is distributed uniformly, hardly any drain flow is simulated during the summer period.

4.3.2 Solute transport

As groundwater levels, moisture content and drain discharges could be simulated reasonably well, an attempt was made to simulate the solute fluxes of the inert ion bromide. The soil water fluxes for the concept with imaginary drains and segmentation of the upper boundary conditions, as determined in the previous section, are used to simulate bromide fluxes. The results of the simulation model will be compared with the concentration profiles of bromide sampled at particular time intervals. Bromide was only applied at the section "apple trees".

Model: At the experimental field Southern Flevoland, flow of solutes is assumed to take place according to the convection-dispersion equation (equation 2.43). The dispersion coefficient is calculated according to equation 2.40. Solute uptake by plant roots is calculated according to equation 2.60. The additional set of

equations used for the transport of bromide is the same as for the experimental field in the North-East Polder (table 4.6).

Input: For the calculation of bromide flow, additional input is needed on the applied load, the date of application, bromide uptake by plants and the estimated dispersion length. Table 3.14 gives information on the date of bromide application, the quantity applied and the period of the field measurements for bromide.

In comparison with the effect of preferential flow through cracks and spatial inhomogeneity of the precipitation on the leaching of bromide, the effect of root uptake by the roots of apple trees was considered to be of minor importance. Therefore, the model was not calibrated for bromide uptake by roots. The value of F was assumed to be 0.5. Reported values of the dispersion length (L_{dis}) in literature vary considerably from less than 1 cm up to more than 20 cm (section 4.1.2). As the value of L_{dis} was unknown and may vary considerably, L_{dis} was determined by calibration.

Optimization criteria: For the transport of bromide through the soil the Root-Mean-Square ($RMS_{[Br]}$) is used as an optimization criterium. $RMS_{[Br]}$ are formulated in the same way as the Root-Mean-Square for groundwater levels (equation 4.2). The calculated concentration of bromide in the drain pipes is compared with the observed concentration of bromide.

Parameters to optimize: Model simulations were undertaken in order to acquire the best possible fit between observed and simulated bromide concentrations in the drains pipes. Calibration of the model for bromide showed that the best fit was obtained for $L_{dis} = 6$ cm, which conforms to results obtained at the experimental field Eastern Flevoland. The optimum value of $RMS_{[Br]}$ is calculated at 0.55 mg l^{-1} .

Results 1992/1993: The results of the concentration of bromide in the drain pipes in 1992/1993 showed a good agreement between the observed and simulated values (figure 4.64). The simulated concentration level of bromide in the drain pipes strongly depended on the distribution of the lateral soil water fluxes. In general, if the drain water originates from the upper soil layers

Date of application 9 June 1992: amount applied 16.8 kg ha^{-1}

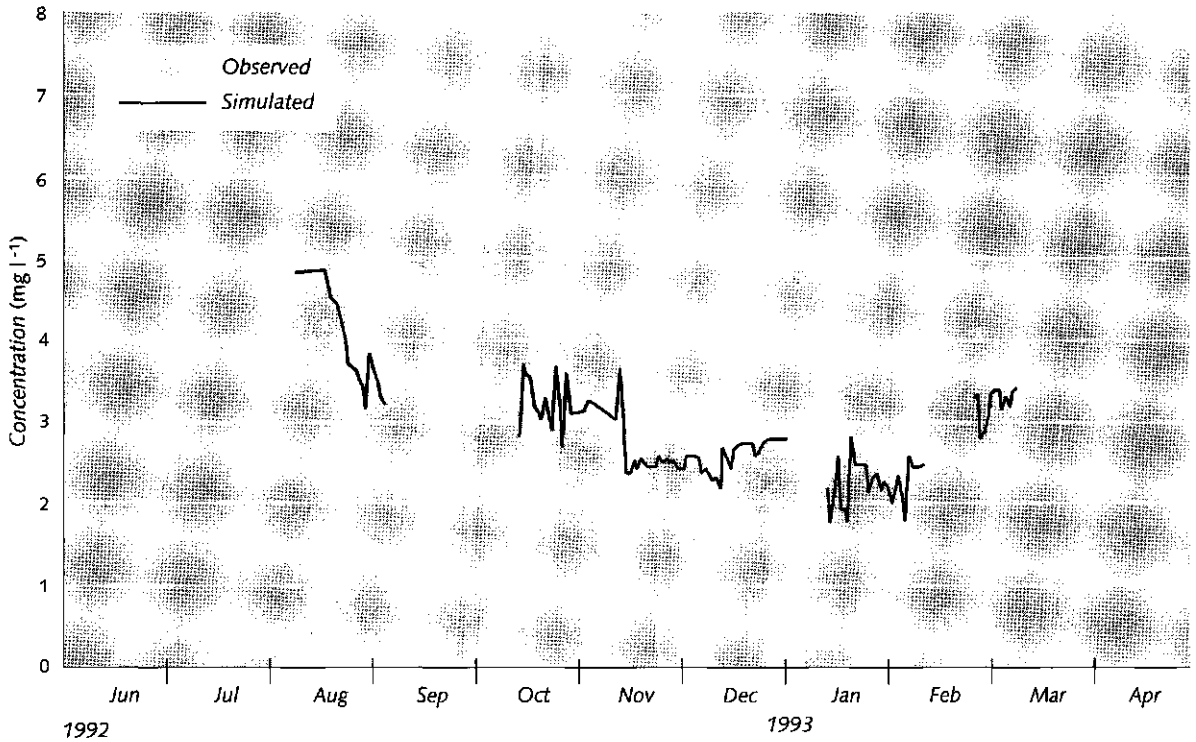


Figure 4.64. Observed and simulated concentration of bromide in the drain pipes at the experimental field Southern Flevoland in 1992/1993 ($L_{dis} = 6 \text{ cm}$, $F = 0.5$).

of the strip under the apple trees, concentrations are high during the first months after application. After the winter period concentration levels are high if the drain water originates from the lower soil layers of the strip under the apple trees (0.9 - 1.0 m below soil surface). However, concentration levels will be diluted as lateral soil water fluxes from the section "grass" also contribute to the drain flow. Drain water originates from the upper soil layers if precipitation intensity is very high. It should be noted that the high background concentration of 0.9 - 1.5 mg l^{-1} makes it more difficult to interpret the measurements.

Figure 4.65 presents the observed and simulated amount of bromide leaching through the soil into the drain pipes ($L_{dis} = 6 \text{ cm}$, $F = 0.5$). The observed amount of bromide in the drain pipes from 9-6-1992 until 21-4-1993, was 6.1 kg ha^{-1} . This is equal to approximately

16% of the amount applied, taking into account background concentrations (subsection 3.2.10.4). The simulated load of bromide, which leached through the drain pipes in 1992/1993, was 8.7 kg ha^{-1} . Approximately 3.5 kg ha^{-1} of this load originates from the background concentration. In figure 4.66 the simulated content of bromide is compared with the observed content of bromide in the soil. The observed data agree with the simulated data particularly at the fourth sampling date (9 March 1993). It shows that after one winter period 45% of the load applied is still present in the soil.

Results 1993/1994: At the second experimental field the applied amount of bromide was increased by approximately a factor 2. The observed concentration in the drain pipes also rose by a factor 2. Results show that the similarity between the simulated values and the

Date of application 9 June 1992: amount applied 16.8 kg ha^{-1}

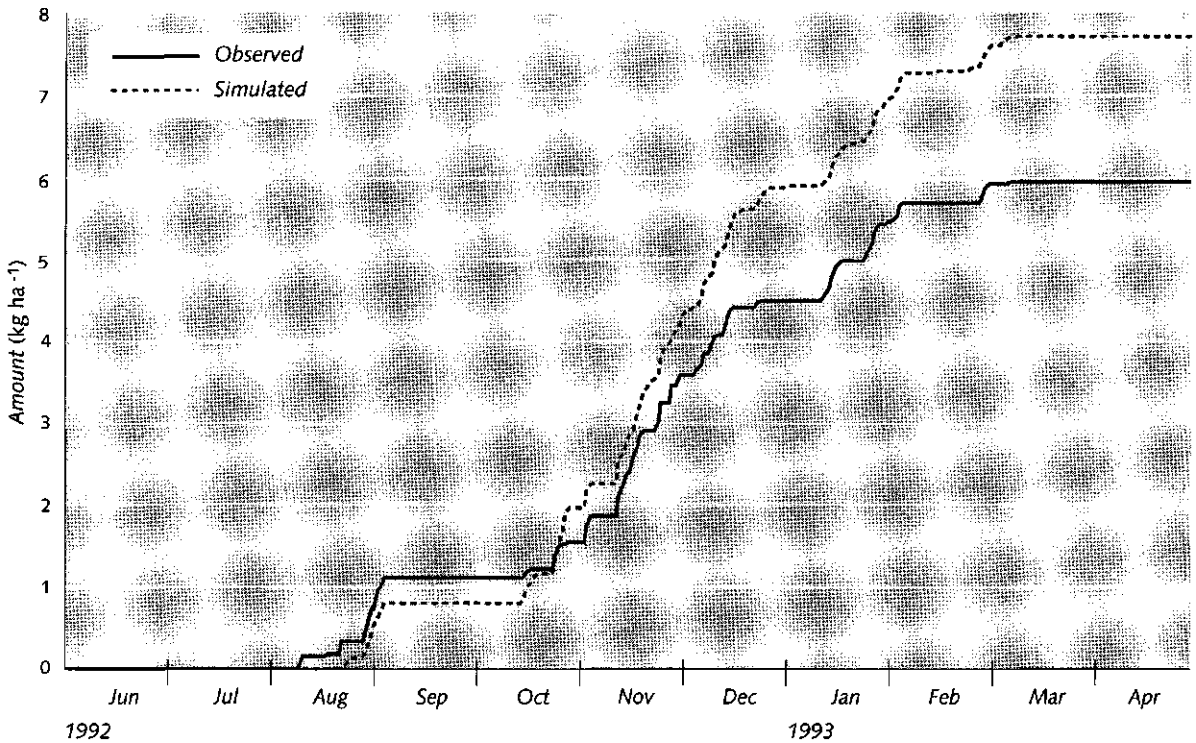


Figure 4.65. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field *Southern Flevoland* in 1992/1993 ($L_{dis} = 6 \text{ cm}$, $F = 0.5$).

observed values is moderate (figure 4.67). As in the previous year, the concentration level of bromide in the drain pipes strongly depends on the distribution of the lateral soil water fluxes and the net precipitation at the top of the soil. Again, background concentrations of bromide made it difficult to interpret the measurements.

The observed load of bromide, which leached through the drain pipes from 21-4-1993 until 29-6-1994, was 19.6 kg ha^{-1} (figure 4.68). This is equal to 33% (taking into account background concentrations) of the amount applied. It corresponded fairly well with the simulated load of bromide leached, which amounts to 21.7 kg ha^{-1} . In figure 4.69 the simulated content of bromide is compared with the observed content of bromide in the soil. The observed data agree fairly well

with the simulated data. Approximately one year after application, 30% of the initial bromide content (e.g. one day after application) is still present in the soil.

Sensitivity analyses: Calibration showed that the influence of the dispersion length on the concentration levels of bromide in the drain pipes is limited. This is mainly caused by the fact that the bromide concentration is more sensitive to preferential flow of water. Results were similar as for the experimental field Eastern Flevoland.

Bromide uptake by roots of the apple trees decreases the concentration of bromide in the drain pipes. If $F = 0.5$ (assumed root uptake), root uptake from June 1992 until April 1993 and from April 1993 until 1993/1994 amounted to 3.5 kg ha^{-1} and 7.7 kg ha^{-1} respectively,

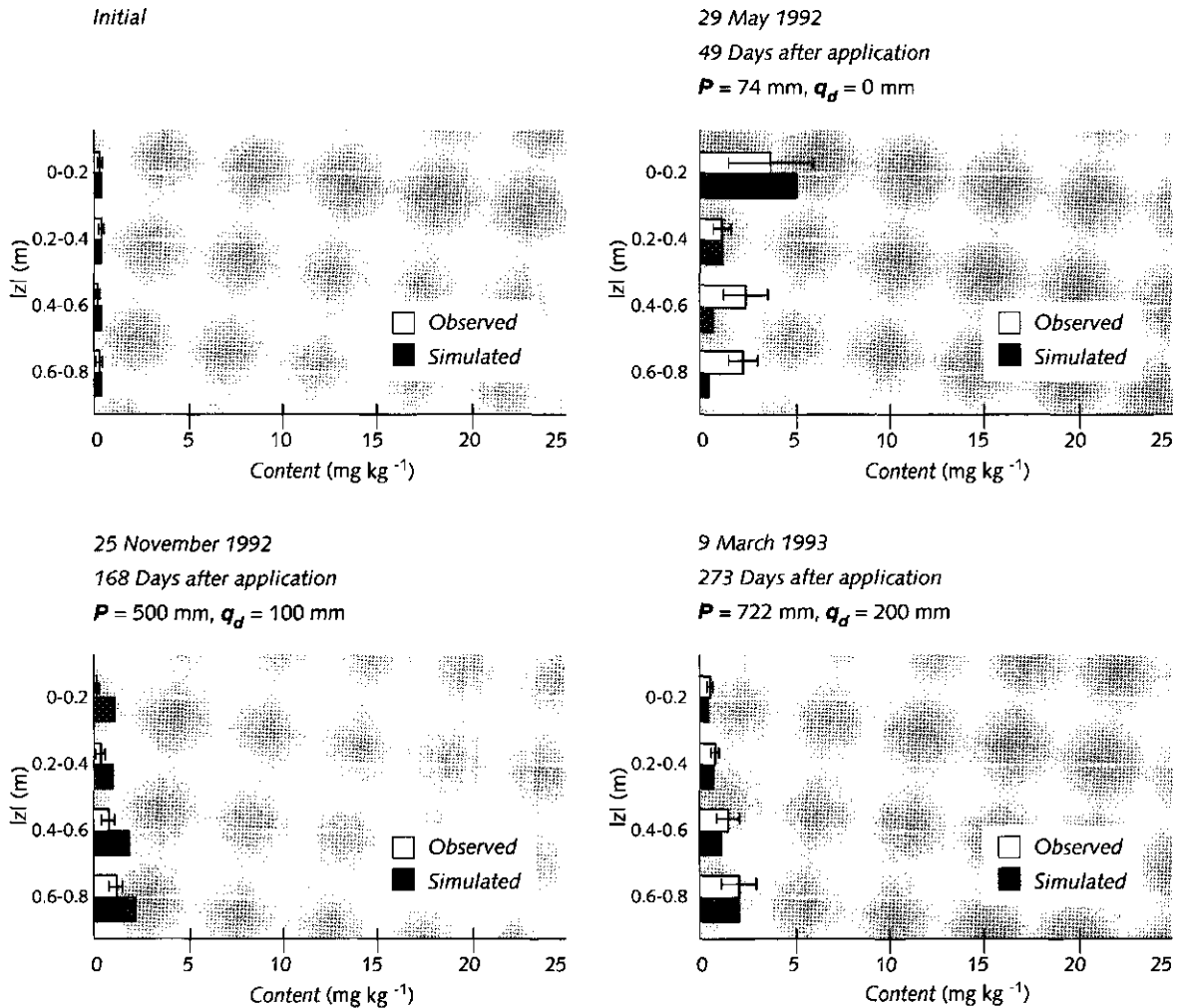


Figure 4.66. Observed (including standard deviation) and simulated movement of bromide through the soil profile in 1992/1993 at the experimental field *Southern Flevoland* (P = cumulative precipitation, q_d = cumulative drain discharge rate; $L_{dis} = 6$ cm, $F = 0.5$).

which is 20 - 25% of the dosage. If the bromide uptake is increased to $F = 1$, root uptake amounts to 30 - 35% of the dosage.

Sensitivity analyses showed that the spatial inhomogeneity of the net precipitation at the top of the soil has an enormous impact on the concentration levels of bromide in the drain pipes. If the parameter a_z , which represents the maximum throughfall (see previous section), is reduced from 1.8 to 1.0, the rise of concentra-

tion levels of bromide in the drain pipes can be delayed by several months, depending on the time of application.

Conclusions: In 1992/1993 the observed concentration of bromide in the drain pipes could be reasonably well calculated with model convection-dispersion equation. In 1993/1994 similarity between observed and calculated values was moderate. Observed concentrations are a mixture of concentrations of bromide originating

Date of application 21 April 1993: amount applied 33.6 kg ha^{-1}

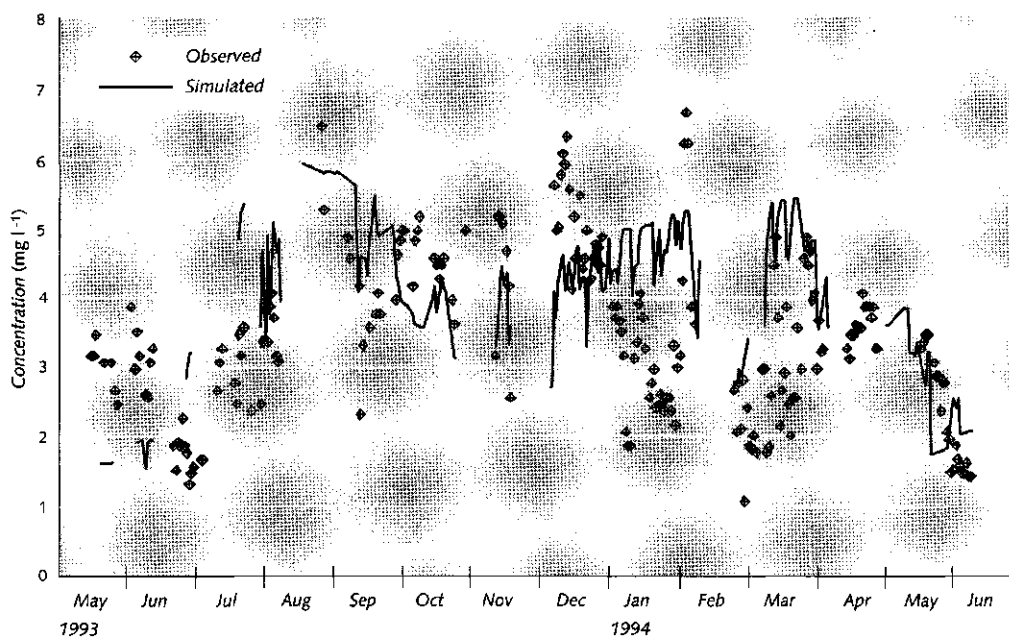


Figure 4.67. Observed and simulated concentration of bromide in the drain pipes at the experimental field *Southern Flevoland* in 1993/1994 ($L_{dis} = 6 \text{ cm}$, $F = 0.5$).

Date of application 21 April 1993: amount applied 33.6 kg ha^{-1}

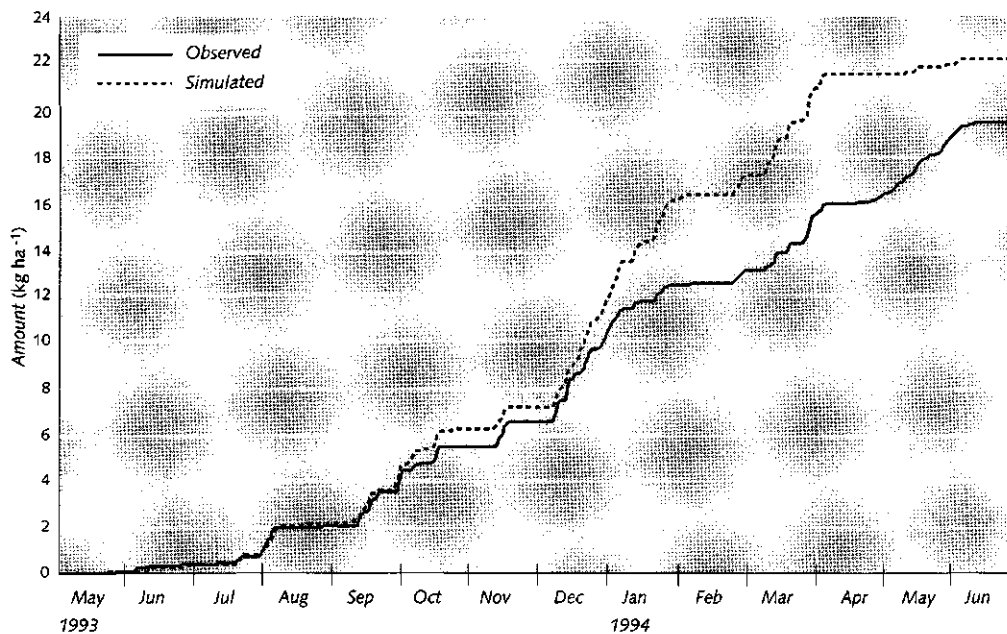


Figure 4.68. Observed and simulated amount of bromide leaching through the drain pipes at the experimental field *Southern Flevoland* in 1993/1994 ($L_{dis} = 6 \text{ cm}$, $F = 0.5$).

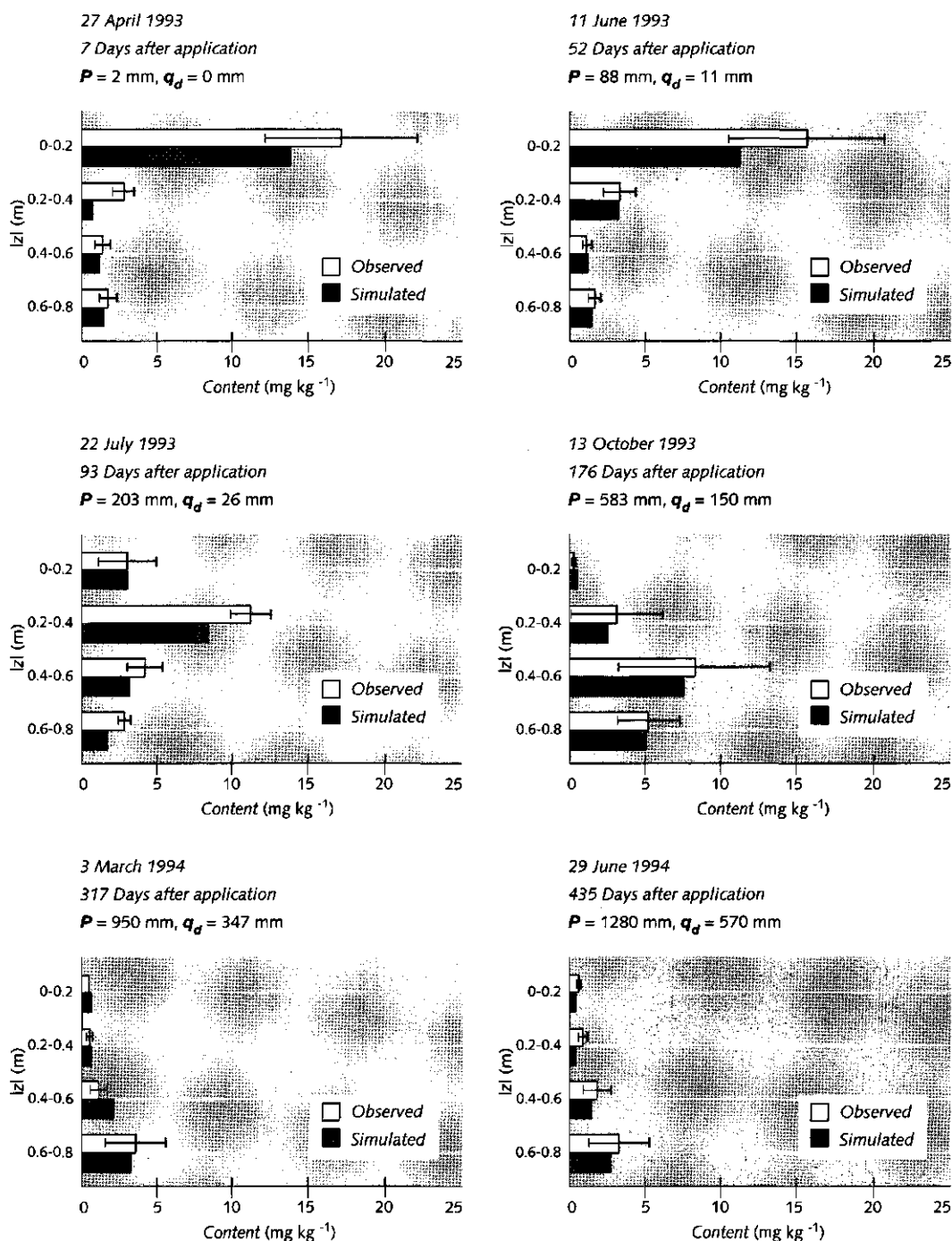


Figure 4.69. Observed and simulated movement (including standard deviation) of bromide through the soil profile in 1993/1994 at the experimental field *Southern Flevoland* (P = cumulative precipitation, q_d = cumulative drain discharge rate; $L_{dis} = 6 \text{ cm}$, $F = 0.5$).

from the soil layers above the cracks and the soil layer below the cracks. If the drain water originates from the upper soil layers, the concentrations are high during the first months after application. After the winter period, concentration levels are high if the drain water originates from the lower soil layers. Furthermore, spatial inhomogeneity of the net precipitation at the top of the soil strongly influences the concentration levels of bromide in the drain pipes. The parameter a_4 , which represents the maximum throughfall at the strip under the apple trees, strongly determines the concentration levels of bromide in the drain pipes during the summer period. The best fit is achieved if $L_{dis} = 6$ cm. If the parameter F is fixed at 0.5, root uptake amounts to 20 - 25% of the dosage.

The observed load of bromide, which leached through the drain pipes, corresponded fairly well with the simulated load. Differences were mainly caused by the deviation between simulated and observed drain discharges (figures 4.65 and 4.68). The simulated content of bromide agreed fairly well with the observed content of bromide in the soil.

Two years after application of 50.4 kg bromide ha^{-1} (9-6-1992 - 16.8 kg ha^{-1} ; 21-4-1993 - 33.6 kg ha^{-1}) approximately 30% of the applied bromide was still present in the soil. The major part of the bromide was located in the deeper soil layers. Root uptake was calculated at 10.2 kg ha^{-1} , which is 20% of the applied bromide. The observed and simulated load of bromide leaching through the drain pipes amounts to 25.7 and 30.4 kg ha^{-1} respectively, which is equal to 51% and 60% of the applied bromide (or 32% and 36% if corrected for background concentrations).

4.3.3 Pesticide transport

The next step in the calibration is an attempt to simulate the behaviour of pesticides under the orchard. The soil water fluxes were calculated for the concept with imaginary drains and segmentation of the upper boundary conditions. The same fluxes were used to simulate pesticide transport. Apart from the soil water fluxes, the applied load and time of application, parameters that are related to transformation, pesticide uptake by plants, sorption and soil temperatures are needed. The results of the simulation model are com-

pared with the concentration level of simazine in the drain pipes. Simazine is applied directly to soil at the strip under the apple trees.

Model: The flow of pesticides is partly described with the same equations as the flow of solutes. Equations to describe the transport of pesticides are summarized in table 4.1 (flow of water), table 4.6 (flow of solutes) and table 4.7 (flow of pesticides).

Input parameters: Data on the time of application, quantity applied and period of field measurements for simazine have already been presented in table 3.14. In 1992 simazine was applied twice (11 April: 0.5 kg ha^{-1} and 9 June: 0.25 kg ha^{-1}), in 1993 once (21-4-1993). Input parameters to determine soil water fluxes are given in table 4.18. This table is supplemented with parameters which were obtained from the optimization of water fluxes ($a_1 = 0.3$, $a_2 = 0.7$, $a_3 = 1.2$ and $a_4 = 1.8$ (during the summer period), $K_{sat,2} = 0.005$ m day^{-1} and solute fluxes ($L_{dis} = 6$ cm).

The transformation of simazine was analyzed in laboratory experiments, as described in subsection 3.1.2.4. Results of this experiment showed that transformation of simazine in the plough layer is strongly influenced by soil temperatures. Simazine is applied during the summer period when soil temperatures are high. The influence of the temperature on the rate of transformation is presented by equation 2.47. The coefficient γ_a was established at 0.07 ± 0.02 $^{\circ}\text{C}^{-1}$. The influence of the soil moisture content is given by equation 2.49. The parameters θ_{ref} and b_1 were set at 0.35 and 0.7 respectively. The influence of the soil depth on the rate of transformation is presented by a factor, f_z . This factor is equal to 1 in the plough layer and normally decreases with depth. It is assumed that f_z is 0.5 beneath the plough layer. However, no data on the transformation of simazine were available for the deeper soil layers.

Sorption is calculated according to equation 2.57. The Freundlich coefficient (K_F) and exponent ($1/n$) were obtained by laboratory experiments as presented in subsection 3.1.2.4.

Plant uptake is calculated according to equation 2.60. It was assumed that $F = 0.5$. Sensitivity analyses for the

Table 4.22. Input parameters to determine the leaching of simazine.

TRANSFORMATION AND UPTAKE			
Symbol	Parameter	Value	Equation
$k_{l,ref}$	Reference coefficient for first-order transformation rate	0.13 d ⁻¹	2.44
γ_a	Coefficient	0.07 °C ⁻¹	2.47
T_{ref}	Reference soil temperature	20 °C	2.47
θ_{ref}	Soil moisture content at reference level	0.35	2.49
b_i	Parameter	0.7	2.49
f_z	Coefficient for the influence of the soil depth on the rate of transformation	1.0-0.5	2.46
F	Constant for selective uptake of the pesticide by the root system	0.5	2.60
SORPTION			
Symbol	Parameter	Value	Equation
K_F	Freundlich coefficient	4.0 cm ³ g ⁻¹	2.57
$(1/n)$	Freundlich exponent	0.77	2.57
$c_{l,ref}$	Reference concentration in the liquid phase	10 µg l ⁻¹	2.57
ρ	Dry soil bulk density	1200 kg m ⁻³	2.32
SOIL TEMPERATURE			
Symbol	Parameter	Value	Equation
T_m	Average soil temperature	11.4 °C	2.56
T_a	Amplitude of the soil temperature at the soil surface	7.7 °C	2.56
d	Damping depth	3.6 m	2.56

concentration simazine have been performed for plant uptake. The parameters to determine the behaviour simazine are summarized in table 4.22.

Results 1992/1993: Traces of simazine are observed in the drain pipes in the first months after the first application. The maximum concentration level amounted to 7 µg l⁻¹. After the second application no drain discharge is observed until two month after application. After this period, observed concentration of simazine in the drain pipes were low. During the winter period no leaching was observed.

Computer simulations showed concentrations of simazine in the drain pipes during the summer period approximately two months after application (figure 4.70). This is not in agreement with the observed concentration of simazine, which started to rise directly after application. Apparently preferential flow through

the cracks is faster than predicted. Also the observed amount of simazine leaching through the drain pipes was higher than predicted (figure 4.71). It was simulated that after August the concentration of simazine was below the detection limit due to transformation (figure 4.72). Less than 1% of the amount applied, was transported from the plough layer into the deeper layers. Field measurements showed that simazine was only observed in the upper part of the soil. The presence of simazine in the soil could not be demonstrated below 0.2 m. This corresponds to the simulated movement of simazine in the soil. The model predicted that simazine was almost completely transformed after August. However, the observed remaining part was higher (figure 4.72). $RMS_{[Sim]}$ was calculated at 1.12 µg l⁻¹.

Results 1993/1994: The leaching of simazine into the drain pipes was observed until March 1994. The highest concentrations were observed in June and July

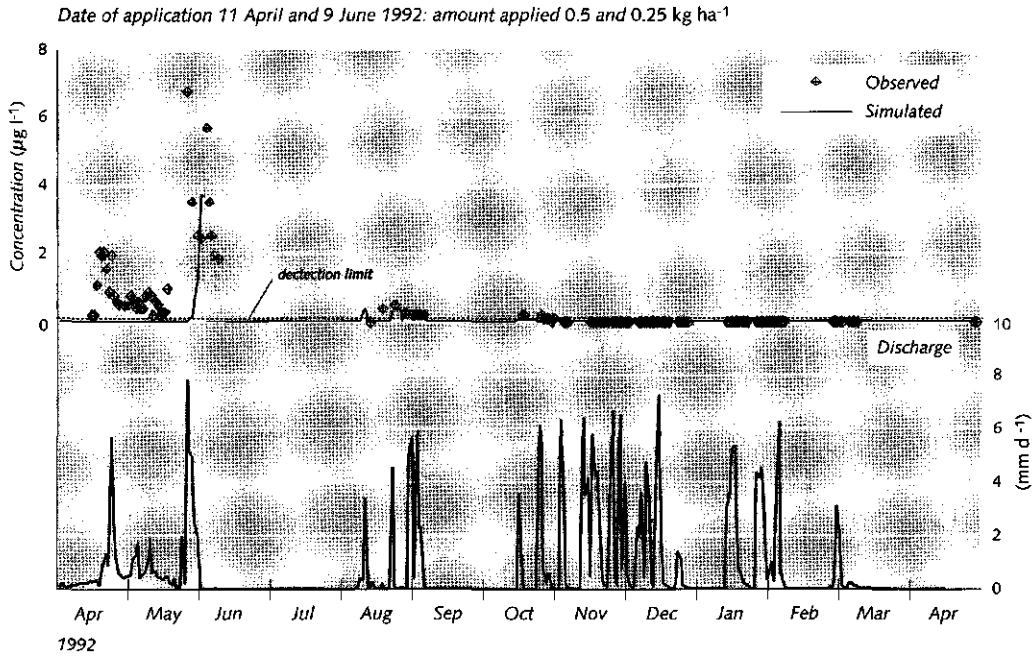


Figure 4.70. Observed and simulated concentration of simazine in the drain pipes at the experimental field *Southern Flevoland* in 1992/1993 (parameters according to table 4.22).

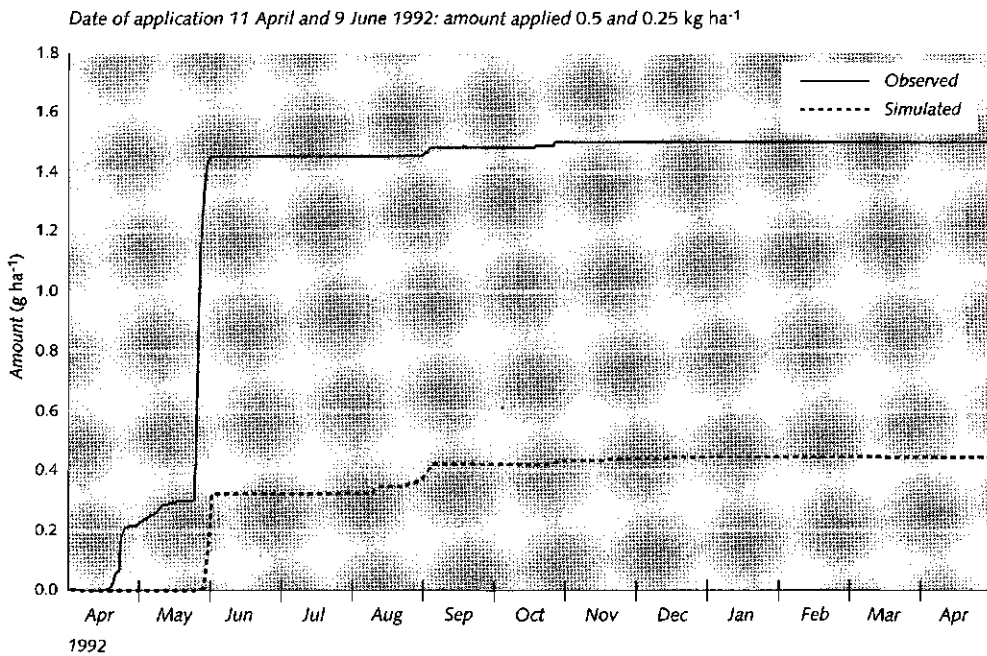


Figure 4.71. Observed and simulated amount of simazine leaching through the drain pipes at the experimental field *Southern Flevoland* in 1992/1993 (parameters according to table 4.22).

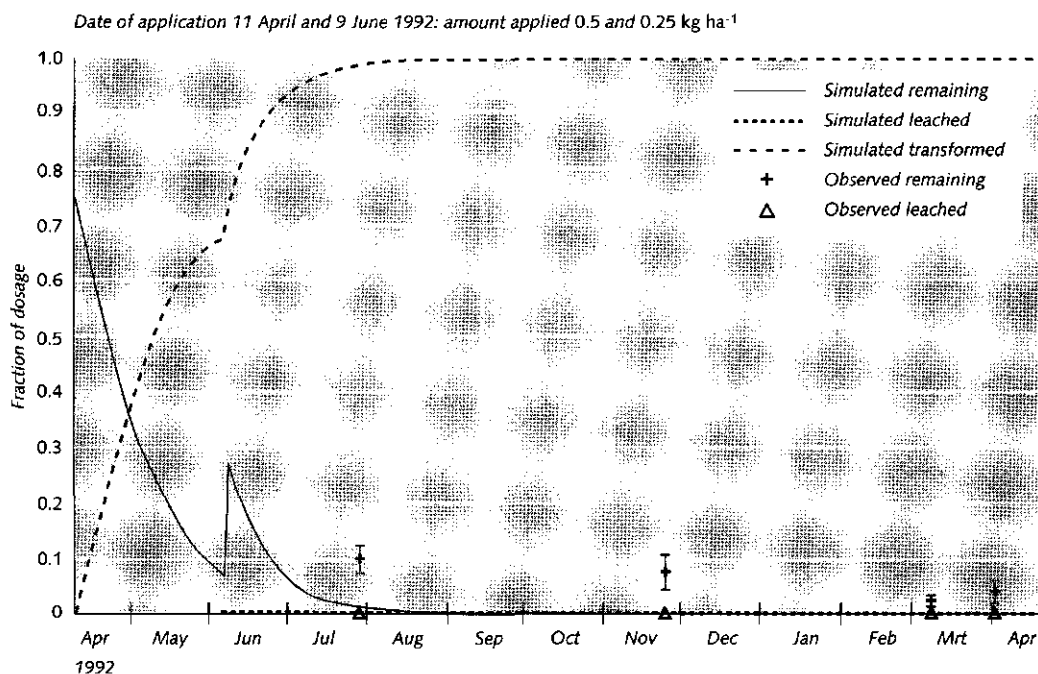


Figure 4.72. Simulated fate of simazine in the soil at the experimental *Southern Flevoland* in 1992/1993 (parameters to table 4.22).

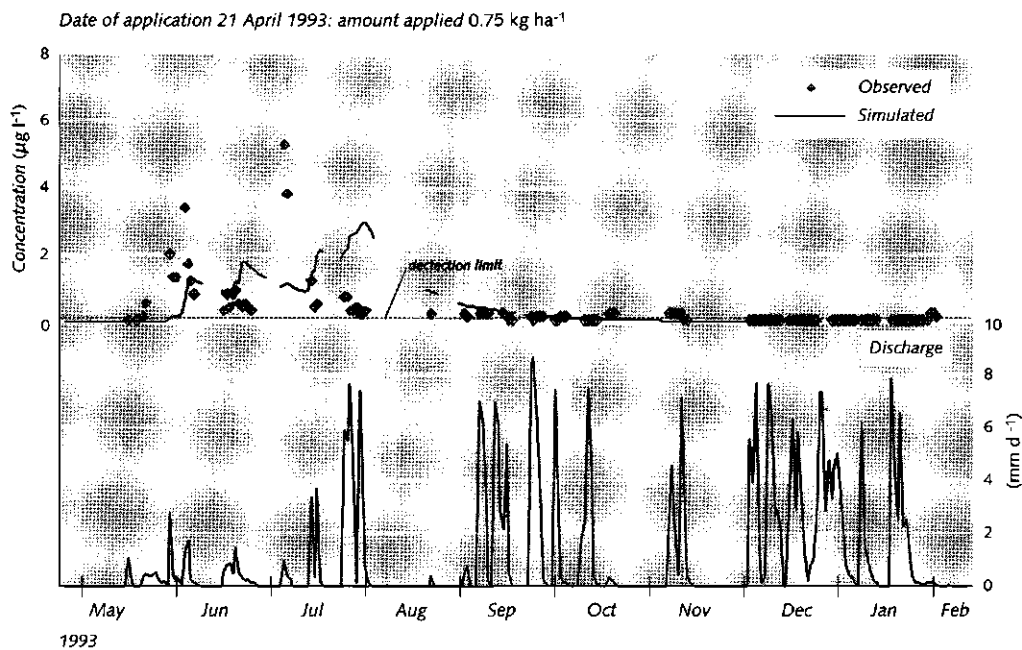


Figure 4.73. Observed and simulated concentration of simazine in the drain pipes at the experimental field *Southern Flevoland* in 1993/1994 (parameters according to table 4.22).

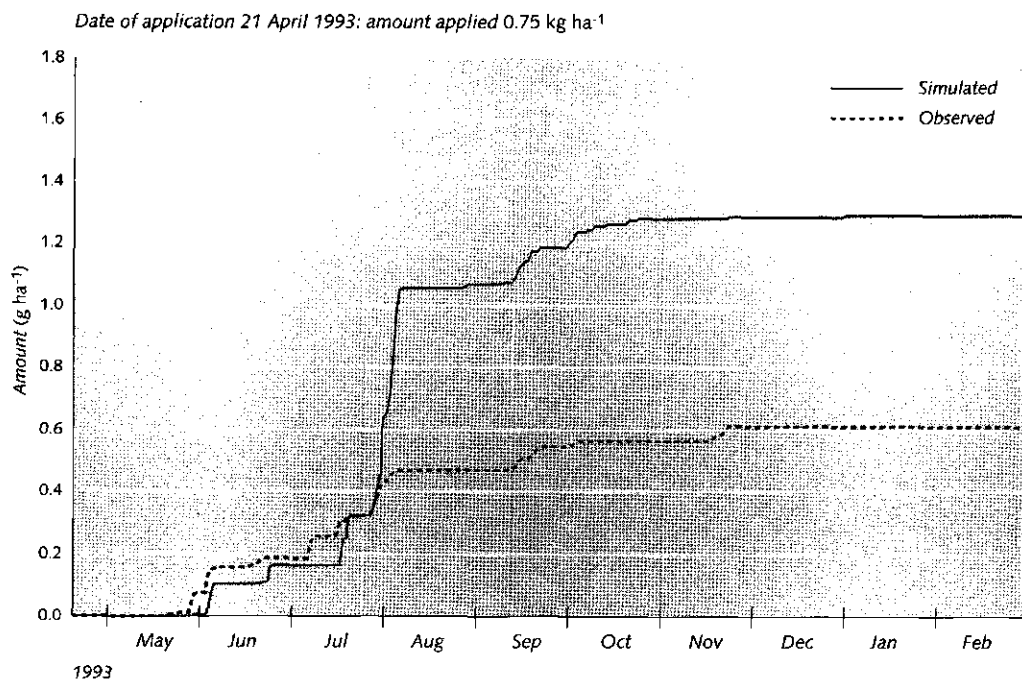


Figure 4.74. Observed and simulated amount of simazine leaching through the drain pipes at the experimental field *Southern Flevoland* in 1993/1994 (parameters according to table 4.22).

1993. The observed concentration of simazine in the drain pipes varied from 0 up to 5 $\mu\text{g l}^{-1}$.

Computer simulations showed concentrations of simazine in the drain pipes during the months June until September (figure 4.73). The concentration of simazine was below the detection limit due to transformation after October (figure 4.75). It was calculated that less than 1% of the amount applied, was transported from the plough layer into the deeper layers. $RMS_{[Sim]}$ was calculated at 0.78 $\mu\text{g l}^{-1}$. The observed and simulated amount of simazine leaching through the drain pipes in 1993/1994 is presented in figure 4.74. Figure 4.75 presents the simulated fate of simazine in the soil. It corresponds fairly well with the observed data.

Sensitivity analyses: Both the value of the Freundlich coefficient and the Freundlich exponent have a considerable impact on leaching and the concentration of

simazine in the drain pipes. If the Freundlich coefficient was reduced to 1.5 $\text{cm}^3 \text{g}^{-1}$ the concentrations of simazine in the drain pipes increased by a factor 15 to 20. The same effect was simulated if the Freundlich coefficient was lowered to 0.65 (-). In this case concentration of simazine in the drain pipes increases by a factor 10 - 15.

Results of sensitivity analyses show that the temperature has an enormous impact on the leaching of simazine. If the average soil temperature was lowered by 5 °C, the maximum concentration of simazine in the drain pipes increased by a factor 10 to 15.

The sensitivity of F (constant for selective uptake of simazine by the root system) for leaching is relatively low, because sorption and temperature influence are dominant. If $F = 0$, the maximum concentration in the drain pipes increases by factor 1.02 - 1.05. Conversely, the concentration in the drain pipes decreases by factor

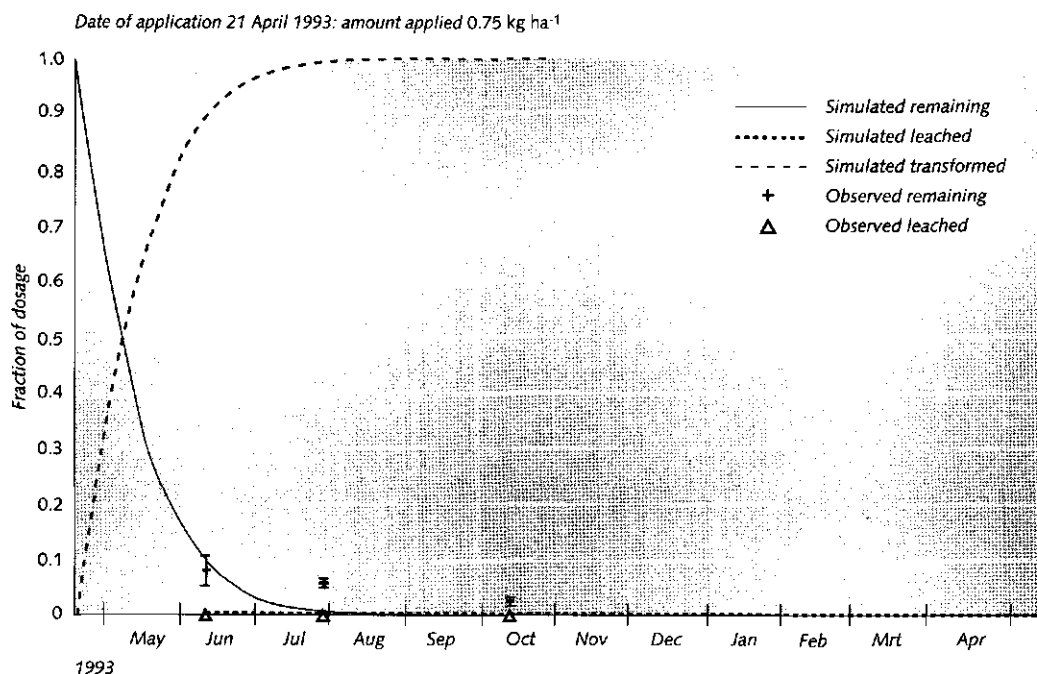


Figure 4.75. Simulated fate of simazine in the soil at the experimental field *Southern Flevoland* in 1993.1994 (parameters according to table 4.22).

0.98 - 0.95 if $F = 1$. If $F = 1$ the calculated root uptake amounts to less than 5% of the dosage applied.

If concentration levels of simazine in the drain pipes are calculated without the concept for imaginary drains or segmentation of the upper boundary conditions, simulations showed that simazine will not reach the drain pipes.

Conclusions: Concentration levels of simazine in the drain pipes could be reasonably well simulated with the model SWACRO, if the model is extended to a concept for imaginary drains and segmentation of the upper boundary conditions. Concentration levels of simazine in the drain pipes were only observed and simulated during the summer period. After the summer the percentage of the dose remaining was less than 1%.

Chapter 5

Scenario analysis

Scenario analysis

5.1 Introduction

The extended version of the *SWACRO* model, as presented in chapter 2, was calibrated in chapter 4, using data from the laboratory experiments (section 3.1) and three experimental fields (section 3.2). Results of the calibration, which was undertaken in three steps (water flow, solute transport and pesticide transport) showed that pesticide transport could be reasonably well calculated with the *SWACRO* model, either with (experimental fields Eastern and Southern Flevoland) or without (experimental field North-East Polder) a concept for preferential flow.

As stated in chapter 1 the objective of the research is formulate drainage design and management criteria for pesticide application in polder areas in order to develop an integrated pest management. The scenarios as presented in this chapter will show a few examples on how the extended *SWACRO* model can be used to formulate design and management criteria. These scenarios are limited to the leaching of pesticides through drain pipes.

Sensitivity analysis in chapter 4 showed that pesticide characteristics (sorption, transformation and volatilisation), time of application of the pesticide, soil characteristics, organic matter content, preferential flow, lateral and lower boundary conditions and weather conditions define the concentration of the pesticide in the drain pipe and thereby the fraction of the dosage of the pesticide leaching through drain pipes.

One or more of these aspects are incorporated in the scenario analyses. The following four scenarios were selected:

- Influence of the time of application on leaching of the fumigant 1,3-dichloropropene;

- Influence of pesticide characteristics on leaching in loamy sands and cracked clay soils;
- Potential pesticide leaching map of the IJsselmeerpolders;
- Future design criteria for subsurface pipe drains and the effect of plough depth on leaching of pesticides.

Results of the selected scenario analyses will be presented in this chapter. Stemming from these scenarios, recommendations for drainage design and management criteria for pesticide application are presented in the last paragraph.

5.2 Dichloropropene: time of application

In the IJsselmeerpolders the soil fumigant 1,3-dichloropropene is mainly applied to calcareous sand and loamy sand to control nematodes, such as *Trichodorus teres* (Kuiper, 1977). The fumigant is applied after harvesting during the autumn period (from August until the end of November) at a depth of approximately 0.2 m below the soil surface. Technical 1,3-dichloropropene is an equal mixture of (E)- and (Z)-isomer (subsection 3.2.2), of which the (Z)-isomer is the most effective isomer to control nematodes. For this reason, the Board for Authorization of Pesticides in the Netherlands decided that from 1997 only the use of the (Z)-isomer is permitted (Commissie Toelating Bestrijdingsmiddelen, 1997). It may be expected that this decision will reduce the amount of 1,3-dichloropropene applied by roughly 50%. In this scenario only the application of the (Z)-isomer is considered.

As time passes during the autumn period, the soil temperatures decrease and the precipitation surplus increases, thus the chance of leaching. As already observed at the experimental field North-East Polder and

later simulated during the sensitivity analyses (subsection 4.1.3.2), the fraction of dichloropropene which leaches through the drain pipes strongly depends on the time of application. Differences between the concentrations of (Z) 1,3-dichloropropene in the drain pipes between application in September and November varied over a factor 1000. Therefore in present legislation, the application of 1,3-dichloropropene is prohibited after 15 November. In this scenario we analyze the suitability of this date with respect to leaching of (Z) 1,3-dichloropropene.

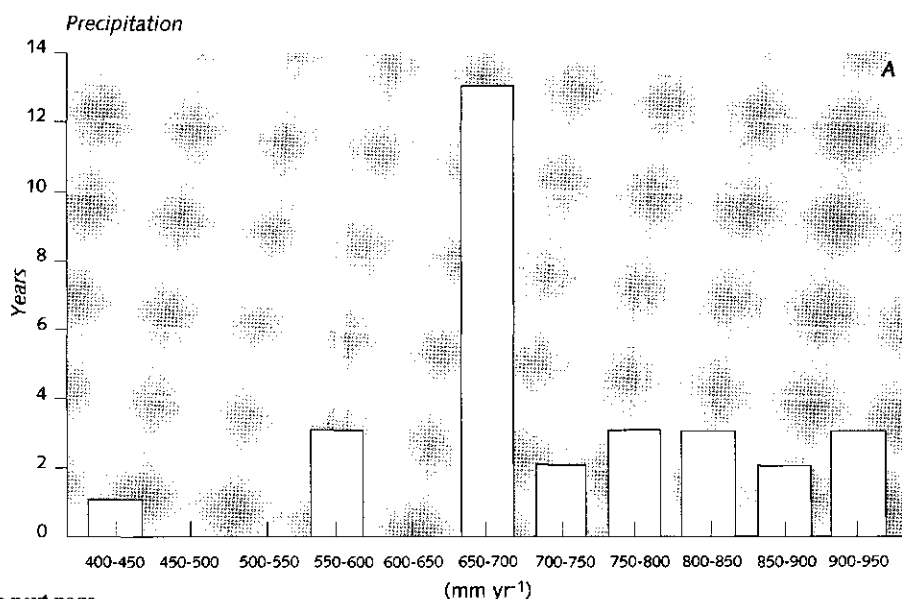
Model: In order to simulate the leaching of dichloropropene for various circumstances, the *SWACRO* model was used. Calibration of the model, as presented in the previous chapter, showed that the transport of (Z) 1,3-dichloropropene could be reasonably well described with the convection-dispersion equation, assuming a soil without an immobile phase. Soil temperatures were calculated according to equation 2.56.

Input parameters: Input parameters to determine soil water fluxes and the leaching of dichloropropene are presented in table 3.2 (soil water retention curve and hydraulic conductivity curve), 4.2 (numerical method, upper and lateral boundary conditions), 4.8 (soil temperatures) and 4.10 (transformation, distribution and

diffusion in the gas phase). The dispersion length is set to 16 cm. The Freundlich coefficient and Freundlich exponent amount to $1.1 \text{ cm}^3 \text{ g}^{-1}$ and 0.74.

To study the effect of the time of application on the leaching of dichloropropene, 30 years of daily data on precipitation and potential evapotranspiration were used. Data on precipitation were collected at the experimental field North-East Polder during the period 1960 - 1989; data on the potential evapotranspiration according to Makkink for the same period were collected at a weather station in Leeuwarden. These data differed only slightly from the data which were collected at a weather station in Lelystad. However, data from Leeuwarden were available for the entire period 1960 - 1989. Calculations are undertaken for a bare loamy sand similar to the loamy sand of the experimental field North-East Polder. It is assumed that for a bare soil the crop factor f is equal to 1 and therefore the reference evapotranspiration equals the potential evapotranspiration. The actual soil evaporation rate is reduced as described according to Boesten (1986; equation 2.22). The parameter β is set at $1.7 \text{ mm}^{0.5}$.

Yearly precipitation during the period 1960 - 1989 varied from 430 to 920 mm with an average of 752 mm (figure 5.1A). Monthly precipitation amounted to



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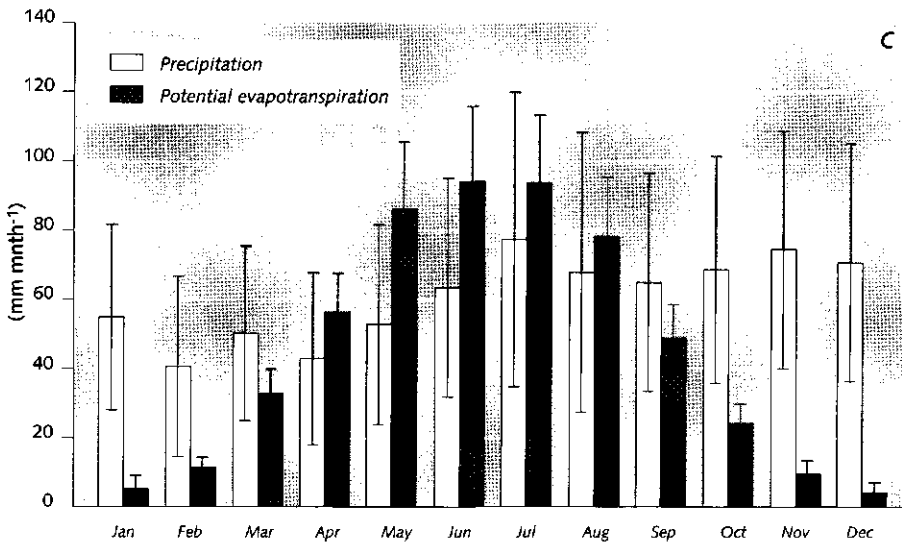
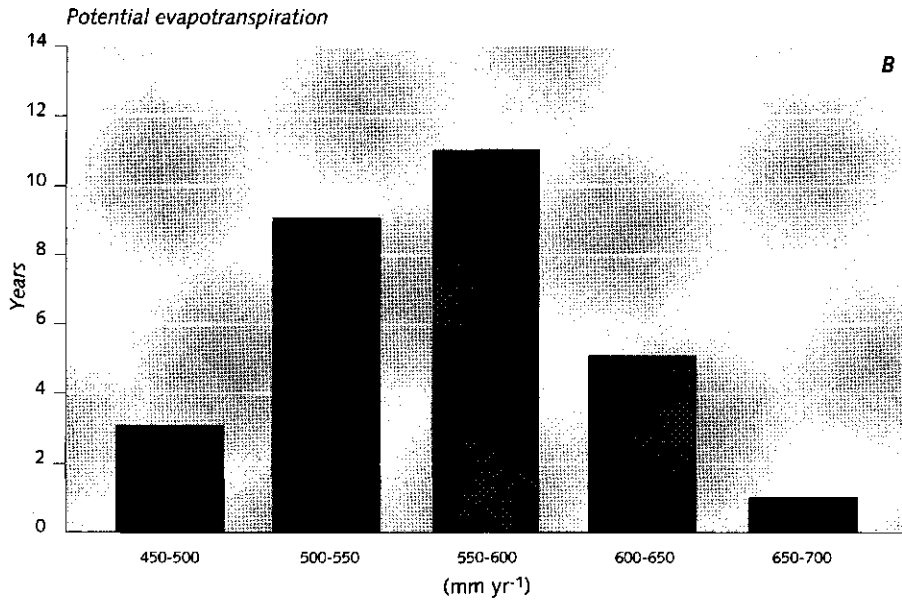


Figure 5.1. Distribution of the yearly precipitation (A) and potential evapotranspiration (B) in number of years over the hydrological period 1960 - 1989: (C) average monthly precipitation and potential evapotranspiration including standard deviation over the hydrological period 1960 - 1989.

roughly 60 mm; the winter and spring were slightly drier than the summer and autumn period (figure 5.1B). The yearly reference evapotranspiration (according to Makkink) varied from 460 mm to 675 mm (figure 5.1B). Monthly evapotranspiration varied from

5 mm in January up to roughly 95 mm in June and July (figure 5.1C).

During the period 1960 - 1989 it is simulated that 85 kg ha⁻¹ (Z) 1,3-dichloropropene is injected at a depth of

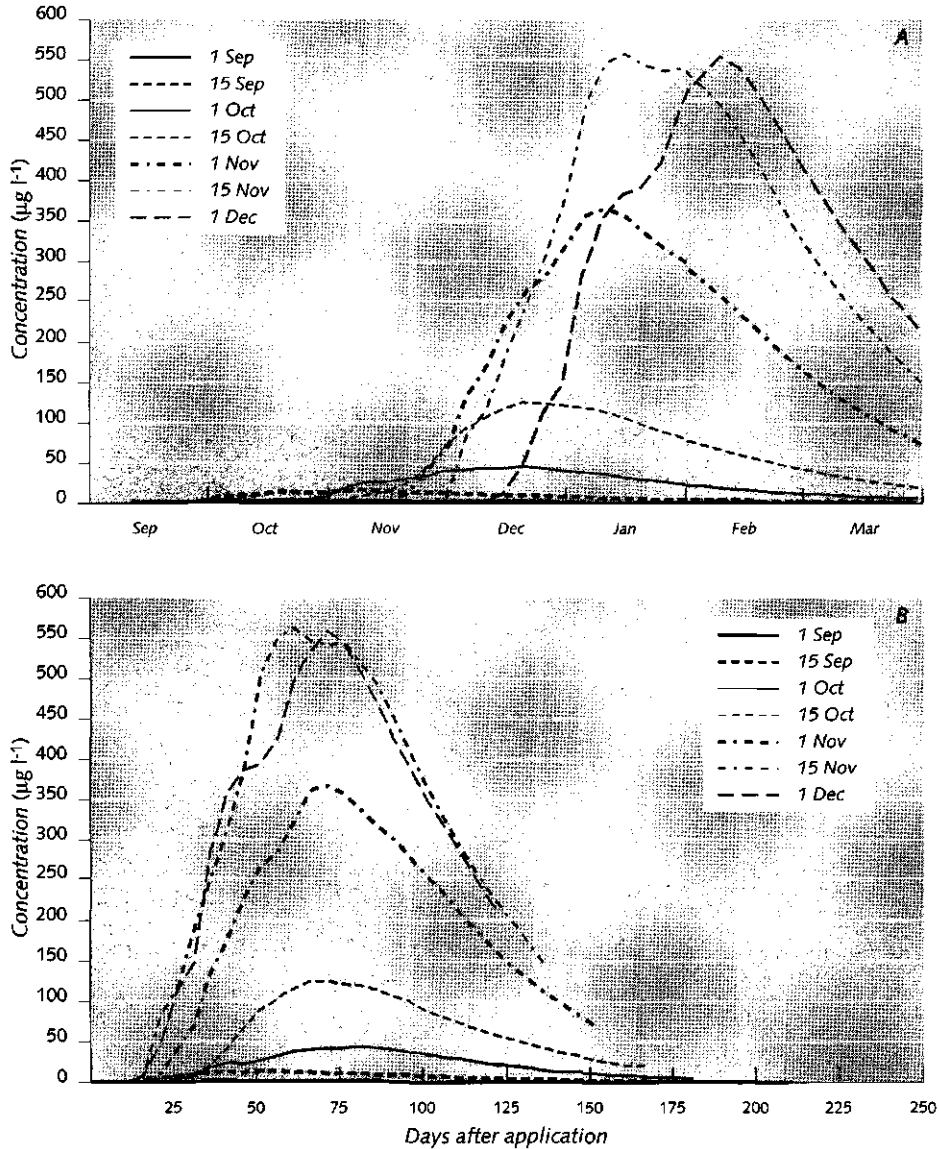


Figure 5.2. Average concentration of (Z) 1,3-dichloropropene in the drain pipes over the period 1960 - 1989 after application of 85 kg ha⁻¹ (Z) 1,3-dichloropropene on respectively 1 September, 15 September, 1 October, 15 October, 1 November, 15 November and 1 December respectively for the loamy sand soils of the North-East Polder as a function of time (A) and days (B) after application

0.2 m on 7 different dates: 1 August, 15 August, 1 September, 15 September, 1 October, 15 October, 1 November, 15 November, 1 December. This results in 210 (7*30) data sets, which are analyzed for concentration levels in the pipe drains and the fraction of the dosage leached.

Results: The leaching of dichloropropene into the drain pipes mainly takes place during the winter season. After 1 April the precipitation surplus is generally negative; the drain pipe discharge drops to zero. Moreover, soil temperatures rise sharply during the spring period, which causes an accelerated transformation of dichloropropene. Normally, leaching of dichloropropene after 1 April can be neglected.

The concentration of dichloropropene in the drain pipes strongly depends on the time of application and the precipitation surplus after application. Figure 5.2 shows the average concentration in the drain pipes as a function of time (A) and days after application (B) for various moments of application. Results of the simula-

tions show that the increase in the concentration of (Z) 1,3-dichloropropene is simulated after approximately 130 mm of drain discharge. Yearly variations in the concentration levels are enormous and depend strongly on the precipitation surplus.

Figure 5.2 shows that over the period 1960 - 1989 the average concentration in the drain pipes rises if (Z) 1,3-dichloropropene is applied at a later stage in the autumn. The maximum concentration is simulated approximately 75 days after application (figure 5.2B). The simulated maximum concentration in the drain pipe may be as high as 3.2 mg l^{-1} if (Z) 1,3-dichloropropene is applied on 15 November (figure 5.3). After November the concentration starts to decline as the precipitation surplus decreases. The precipitation surplus in the period from 1 December until 1 April is often inadequate to achieve leaching of (Z) 1,3-dichloropropene through the drain pipes.

In order to calculate the fraction of the dosage which leaches through the drain pipes into the collector drain,

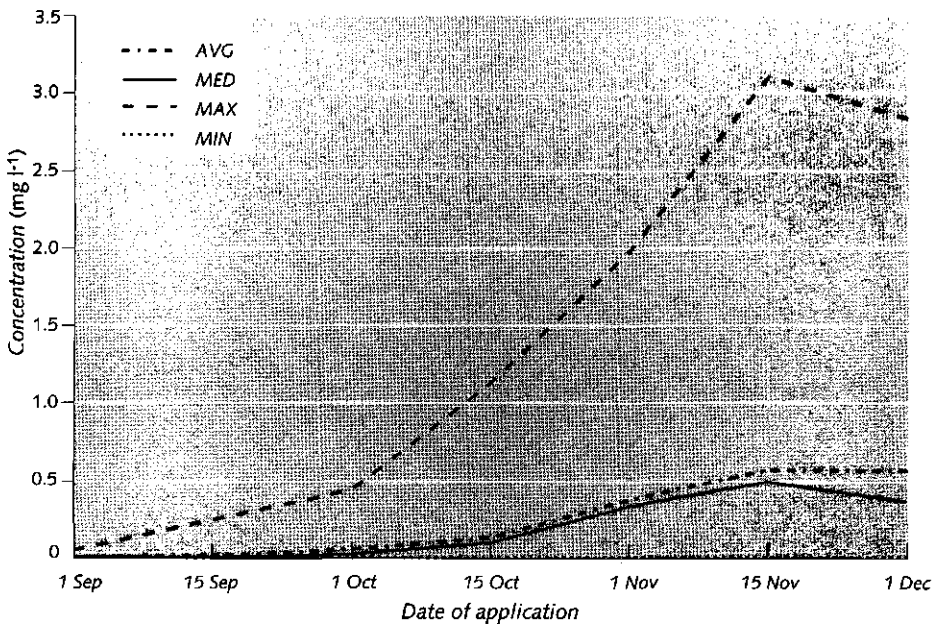


Figure 5.3. Average of maximum concentration (AVG), median of maximum concentration (MED) and maximum concentration (MAX) of 1,3-dichloropropene in the drain pipes in the period 1960 - 1989 after application of 85 kg ha^{-1} (Z) 1,3-dichloropropene on 1 September, 15 September, 1 October, 15 October, 1 November, 15 November and 1 December for the loamy sands of the North-East Polder.

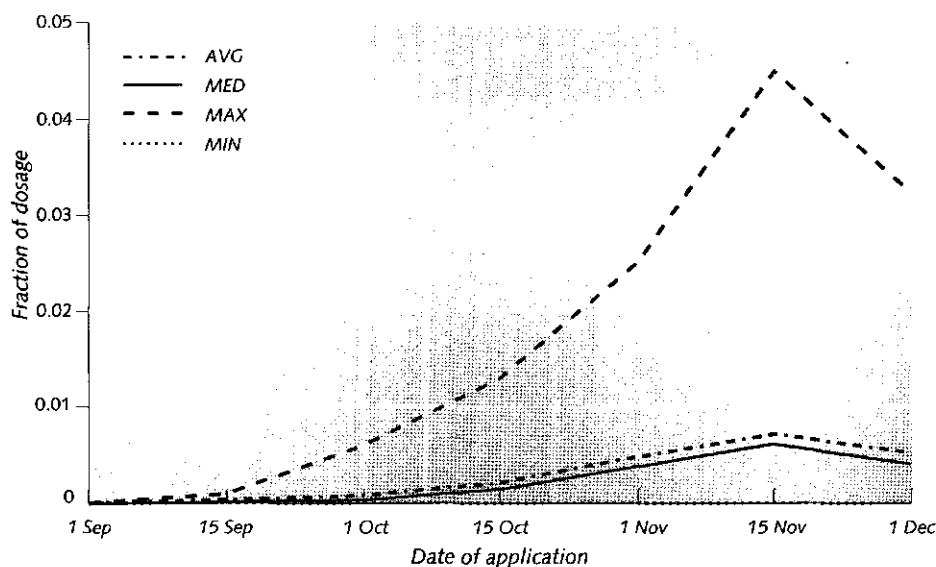


Figure 5.4. Average, median, maximum and minimum fraction of 1,3-dichloropropene leached through the drain pipes into the collector drain for the period 1960 -1989 after application of 85 kg ha^{-1} (Z) 1,3-dichloropropene on 1 September, 15 September, 1 October, 15 October, 1 November, 15 November and 1 December for the loamy sands of the North-East Polder from the date of application until April.

the drain discharge is multiplied by the concentration of (Z) 1,3-dichloropropene in the drain pipes from the day of application up to 1 April. The simulated average, median and maximum fraction of the dosage of (Z) 1,3-dichloropropene leaching through the drain pipes for the period 1960 - 1989 is presented in figure 5.4. It shows that the average fraction leaching through the drain pipe rises from less than 0.001 for application on 1 September up to 0.008 for application on 15 November. If (Z) 1,3-dichloropropene is applied on 15 November the maximum fraction leached amounts to 0.045.

The remaining part of (Z) 1,3-dichloropropene in the soil profile after one winter season at 1 April depends on the date of application and rises from 0 (Date of application: 1 September) up to approximately 0.01 (Date of application: 1 December) as fraction of the initial amount applied. The major part of the dichloropropene injected in the soil is transformed. The fraction of (Z) 1,3-dichloropropene transformed varies from 98 - 99% of the dosage in September to 88 - 95% of the dosage in November.

Volatilization of (Z) 1,3-dichloropropene strongly depends on precipitation, particularly directly after application and soil temperatures. It was calculated that volatilization during the period 1960 - 1989 amounted to 1 - 3% of the dosage if (Z) 1,3-dichloropropene is injected in September and 4 - 9% if dichloropropene is injected in November. The main reason for a higher degree of volatilization in November is the residence time of (Z) 1,3-dichloropropene in the soil, which is much shorter if (Z) 1,3-dichloropropene is injected in September.

Conclusions:

- the fraction of (Z) 1,3-dichloropropene which leaches through the drain pipes strongly depends on the precipitation, evapotranspiration and time of application. This fraction rapidly increases if application takes place after 1 October;
- the concentration of (Z) 1,3-dichloropropene in the drain pipes is strongly related to the time of application. The highest concentrations of (Z) 1,3-dichloropropene in the drain pipes were calculated for application on 15 November and the lowest for

- application on 1 September;
- high concentrations of (Z) 1,3-dichloropropene are simulated during the months December, January and February;
- the influence of the variation in meteorological conditions from year to year on the relation between the leaching of (Z) 1,3-dichloropropene and time of application is very large; therefore a statistical approach is needed to assess this relationship.

5.3. Effect of sorption and transformation of different pesticides on leaching for loamy sands and cracked clay soils

In this scenario we consider the relative effect of transformation and sorption on leaching in loamy sand and cracked clay soils in the IJsselmeerpolders. The surface of both soils amounts to roughly 75% of the IJsselmeerpolders. Pesticide characteristics, such as sorption, transformation and volatilization vary strongly for each pesticide.

The aim of this scenario is to indicate the relative effect of sorption and transformation on leaching for a soil with preferential flow (cracked clay) and without preferential flow (loamy sands). The organic matter content is set at 2% for both loamy sands and cracked clay soils. For this scenario volatilization of pesticides is ignored. The extent of leaching is characterized by the fraction of the dosage leached through the drain pipes.

Model: In order to simulate pesticide leaching, the extended SWACRO model was used. Calibration of the model, as presented in the previous chapter, showed that the transport of pesticides in loamy sands could be reasonably well described with the convection-dispersion equation, assuming a soil without an immobile phase. For the cracked clay soils, model simulations were undertaken for the concept with imaginary drains, as described in section 2.3.2.

Input: Input parameters for the SWACRO model are summarized in table 5.1. Simulations were executed from the date of application up to 2 years after application. This was necessary as the more persistent pesticides will also leach during the second winter period.

During the summer period both soils are cropped with potatoes, a widespread crop in the IJsselmeerpolders.

Simulations were performed for:

- 2 different soils: loamy sand and cracked clay;
- 12 different pesticides. These pesticides varied in sorption and transformation. The Freundlich coefficient (K_F) amounted to 0, 1, 2 and 3 cm³ g⁻¹ and half-life time (DT_{50}) amounted to 10, 50 and 100 d. Other parameters which characterize transformation and sorption were kept constant for all scenarios. The value of these parameters are presented in table 5.1;
- 30 different meteorological years with daily precipitation, potential evapotranspiration (period: 1960-1989). Data on precipitation were collected at the experimental field North-East Polder during the period 1960-1989; data on the potential evapotranspiration according to Makkink for the same period were collected at a weather station in Leeuwarden. These data have already been presented in section 5.2;
- spring (1 May) and autumn (1 September) application.

Results: Results are presented in figure 5.5 for cracked clay soils and in figure 5.6 for loamy sands. The results of the simulations were averaged over 30 years. They show that both transformation and sorption have an enormous impact on leaching. However, for pesticides with a small half-life time (e.g. $DT_{50} < 10$ d at 20 °C) leaching as a fraction of the dosage is very small and can usually be neglected. For loamy sands the same applies for K_F values above 3 cm³ g⁻¹. For the cracked clay soil the fraction of the dosage leached is higher than for the loamy sand, especially for K_F values above 2 cm³ g⁻¹. However, for $K_F < 1$ cm³ g⁻¹ and $DT_{50} < 10$ d, the fraction of the dose leached is higher for the loamy sands than for the cracked clay soils. Differences between application in May or September with respect to the fraction of the dosage leached are moderate for K_F values above 2 cm³ g⁻¹ or DT_{50} smaller than 50 d.

For weakly sorbing ($K_F < 2$ cm³ g⁻¹) and persistent ($DT_{50} > 50$ d) pesticides, differences between application in May or September are considerable. For a

cracked clay soil with $K_F = 1 \text{ cm}^3 \text{ g}^{-1}$ and $DT_{50} = 100 \text{ d}$, the fraction of the dosage leached amounted to 0.03 - 0.25, if the pesticide was applied in May and 0.05 - 0.35, if the pesticide was applied in September. Differences between the fraction of the dosage leached for various years were considerable, due to differences in weather conditions. Generally it can be concluded that

leaching is low in dry years and high in wet years. These differences become smaller for pesticides with a higher sorption and/or higher degree of transformation. E.g. for $K_F = 1 \text{ cm}^3 \text{ g}^{-1}$ and $DT_{50} = 100 \text{ d}$, the fraction of the dosage leached amounted to 0.00 - 0.07 if the pesticide was applied in May and 0.00 - 0.08 if the pesticide was applied in September. For $K_F = 1 \text{ cm}^3 \text{ g}^{-1}$ and

Table 5.1. Input parameters for the simulation of the influence of sorption, transformation and time of application on leaching for loamy sands and cracked clay soils in the IJsselmeerpolders

	LOAMY SAND	CRACKED CLAY
Soil physical properties	Soil schematisation according to figure 4.1; Van Genuchten parameters are presented in table 3.2	Soil schematisation according to figure 4.37; Van Genuchten parameters are presented in table 3.4
Upper boundary conditions / crop parameters	Field is cropped with potatoes; crop factors are presented in table 4.13. Homogeneous distribution of the maximum water uptake by roots; maximum rooting depth 0.3 m (from May until October); Soil cover as function of time is presented in figure 4.38; the parameter for actual soil evaporation amounts to $1.7 \text{ mm}^{0.5}$ other parameters are presented in table 4.12.	Field is cropped with potatoes; crop factor are presented in table 4.13. Possible water uptake by roots diminishes with depth according to Prasad (1988); Rooting depth as function of time is presented in figure 4.39; Soil cover as function of time is presented in figure 4.38; other parameters are presented in table 4.12.
Lateral boundary conditions	Values for lateral boundary conditions are presented in table 4.2	At a depth of 0.35 m imaginary drains are implemented representing cracks. Values for lateral boundary conditions are presented in table 4.12
Lower boundary conditions	Zero flux at the lower boundary (no upward or downward seepage)	Zero flux at the lower boundary (no upward or downward seepage)
Dispersion	$L_{dis} = 16 \text{ cm}$ (equation 2.40)	$L_{dis} = 5 \text{ cm}$ (equation 2.40)
Root uptake	$F = 0.5$ (equation 2.60)	$F = 0.5$ (equation 2.60)
Pesticide application	Amount applied is 1 kg ha^{-1} ; dates of application are 1 May and 1 September; pesticide is applied on the surface	Amount applied is 1 kg ha^{-1} ; dates of application are 1 May and 1 September; pesticide is applied on the surface
Transformation	First-order transformation is assumed with $k_{1,ref} = 0.069 \text{ d}^{-1}$ ($DT_{50} = 10 \text{ d}$), $k_{1,ref} = 0.014 \text{ d}^{-1}$ ($DT_{50} = 50 \text{ d}$) and $k_{1,ref} = 0.007 \text{ d}^{-1}$ ($DT_{50} = 100 \text{ d}$) at $T_{ref} = 20^\circ \text{C}$; $\gamma_a = 0.05 \text{ K}^{-1}$; $\theta_{ref} = 0.32$; $b_1 = 1$; f_z according to figure 4.21	First-order transformation is assumed with $k_{1,ref} = 0.069 \text{ d}^{-1}$ ($DT_{50} = 10 \text{ d}$), $k_{1,ref} = 0.014 \text{ d}^{-1}$ ($DT_{50} = 50 \text{ d}$) and $k_{1,ref} = 0.007 \text{ d}^{-1}$ ($DT_{50} = 100 \text{ d}$) at $T_{ref} = 20^\circ \text{C}$; $\gamma_a = 0.05 \text{ K}^{-1}$; $\theta_{ref} = 0.32$; $b_1 = 1$; $f_z = 1$ for the plough layer and 0.5 below the plough layer
Soil temperatures	Soil temperatures calculated according to equation 2.56 with $T_m = 11^\circ \text{C}$, $T_a = 9^\circ \text{C}$ and $d = 2.4 \text{ m}$	Soil temperatures calculated according to equation 2.56 with $T_m = 11^\circ \text{C}$, $T_a = 9^\circ \text{C}$ and $d = 2.4 \text{ m}$
Sorption	Sorption according to Freundlich equation with $K_F = 0$, $K_F = 1$, $K_F = 2$ and $K_F = 3 \text{ cm}^3 \text{ g}^{-1}$ and $(1/n)$ constant at 0.9 with $c_{1,ref} = 10 \mu\text{g l}^{-1}$	Sorption according to Freundlich equation with $K_F = 0$, $K_F = 1$, $K_F = 2$ and $K_F = 3 \text{ cm}^3 \text{ g}^{-1}$ and $(1/n)$ constant at 0.9 with $c_{1,ref} = 10 \mu\text{g l}^{-1}$

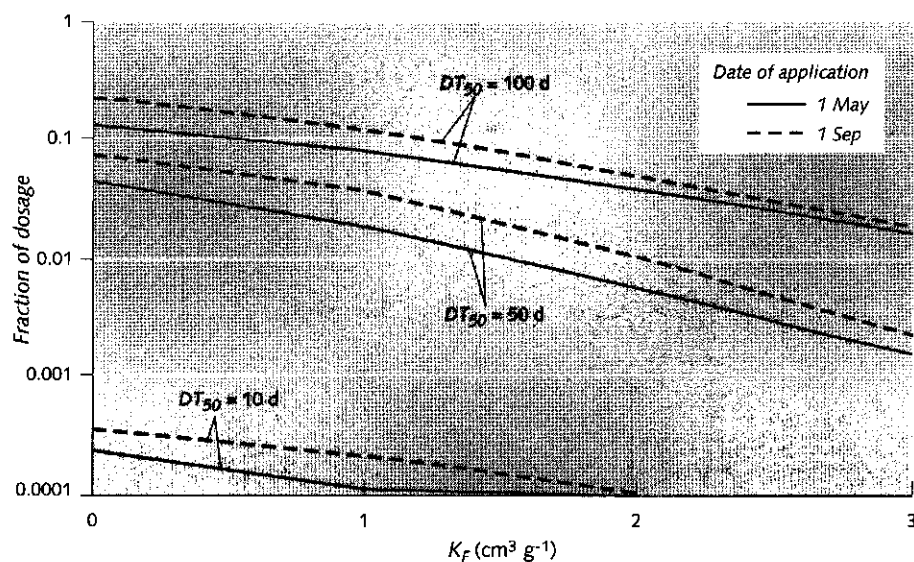


Figure 5.5. Fraction of the dosage leached through the drain pipes two years after date of application in cracked clay soils in the IJsselmeerpolders for application in May and September with $DT_{50} = 10, 50$ and 100 d and $K_F = 0, 1, 2$ and $3 \text{ cm}^3 \text{ g}^{-1}$. For $DT_{50} = 10$ d and $K_F > 2 \text{ cm}^3 \text{ g}^{-1}$ the fraction of the dosage leached was smaller than 0.0001 .

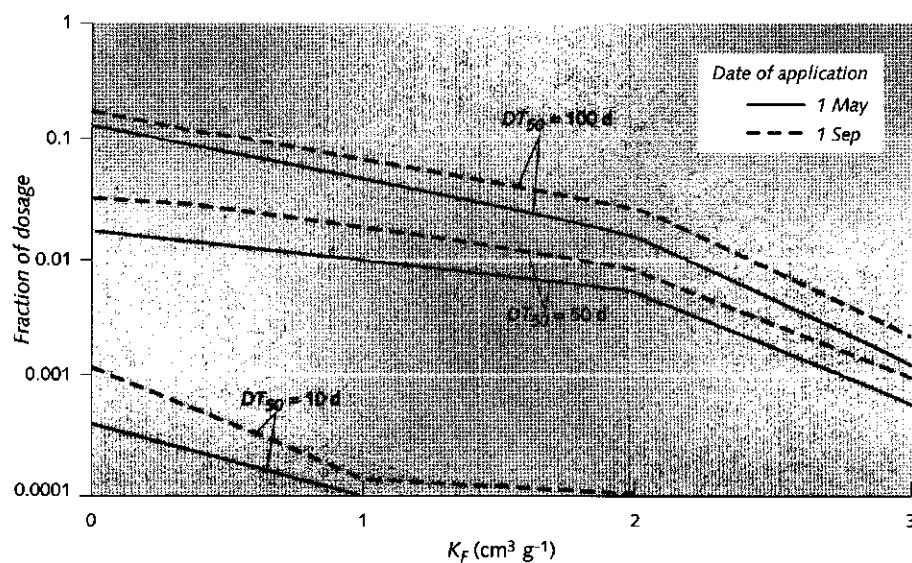


Figure 5.6. Fraction of the dosage leached through the drain pipes in loamy sands in the IJsselmeerpolders for application in May and September with $DT_{50} = 10, 50$ and 100 d and $K_F = 0, 1, 2$ and $3 \text{ cm}^3 \text{ g}^{-1}$. For $DT_{50} = 10$ d and $K_F > 2 \text{ cm}^3 \text{ g}^{-1}$ the fraction of the dosage leached was smaller than 0.0001 .

$DT_{50} = 50$ d, the fraction of the dosage leached amounted to 0.01 - 0.07 both for application in May and September.

The same results were observed for loamy sands as for the cracked clay soils, however both the fraction of the dosage leached and the difference between the maximum and minimum fraction of the dosage leached was smaller. In the simulations it was observed that for the cracked clay soils roughly 25 - 50% of the drain discharge flowed through the imaginary drains. For $K_F < 2 \text{ cm}^3 \text{ g}^{-1}$, $DT_{50} = 10$ d and spring application, the fraction of the dosage leached flowed through the cracks. However, for $K_F = 0 \text{ cm}^3 \text{ g}^{-1}$, $DT_{50} = 100$ d and autumn application, roughly half of the fraction of the dosage leached flowed through the cracks; the other half flowed through the soil matrix.

Conclusions:

- For pesticides applied under the same conditions, the fraction of the dose leached is higher for the cracked clay soils than for the loamy sands. However, for $K_F < 1 \text{ cm}^3 \text{ g}^{-1}$ and $DT_{50} < 10$ d, the fraction of the dose leached is higher for the loamy sands than for the cracked clay soils;
- The effect of application in autumn on leaching is

found to be large for weakly sorbing and persistent pesticides and low for strongly sorbing pesticides;

- For weakly sorbing (e.g. $K_F = 1 \text{ cm}^3 \text{ g}^{-1}$) and persistent (e.g. $DT_{50} = 100$ d) pesticides, the fraction of the dosage leached on cracked clay soils amounted to 0.03 - 0.25 if the pesticide was applied in May and 0.05 - 0.35 if the pesticide was applied in September. For loamy sands both the fraction of the dosage leached and the difference between the maximum and minimum fraction of the dosage leached was smaller;
- For non-sorbing ($K_F = 0 \text{ cm}^3 \text{ g}^{-1}$) and persistent ($DT_{50} = 100$ d) pesticides, roughly half of the fraction of the dosage leached on cracked clay soil flowed through the cracks, the other half flowed through the soil matrix. For pesticides with a low DT_{50} the fraction of the dosage leached flowed through the cracks.

5.4 Soil map for potential leaching in het IJsselmeerpolders

In order to mark the most vulnerable areas for pesticide leaching in the IJsselmeerpolders, soil maps for potential leaching are created. These maps can be used both

Table 5.2. Surface area of various soil pedons in the IJsselmeerpolders

Soil pedons	North-East Polder (ha)	Eastern Flevoland (ha)	Southern Flevoland (ha)
Cracked clay - organic matter content < 3%	4690	16890	4880
Cracked clay - organic matter content 3 - 5%	1250	14780	31250
Cracked clay - organic matter content > 5%			5640
Loamy sand - organic matter content < 3%	20100	11430	1010
Loamy sand - organic matter content 3 - 5%	9410	730	360
Loamy sand - organic matter content > 5%	1170	560	250
Loamy clay - organic matter content < 3%	8530	9710	
Loamy clay - organic matter content 3 - 5%	2120	30	
Loamy clay - organic matter content > 5%			
TOTAL	47260	54100	43390

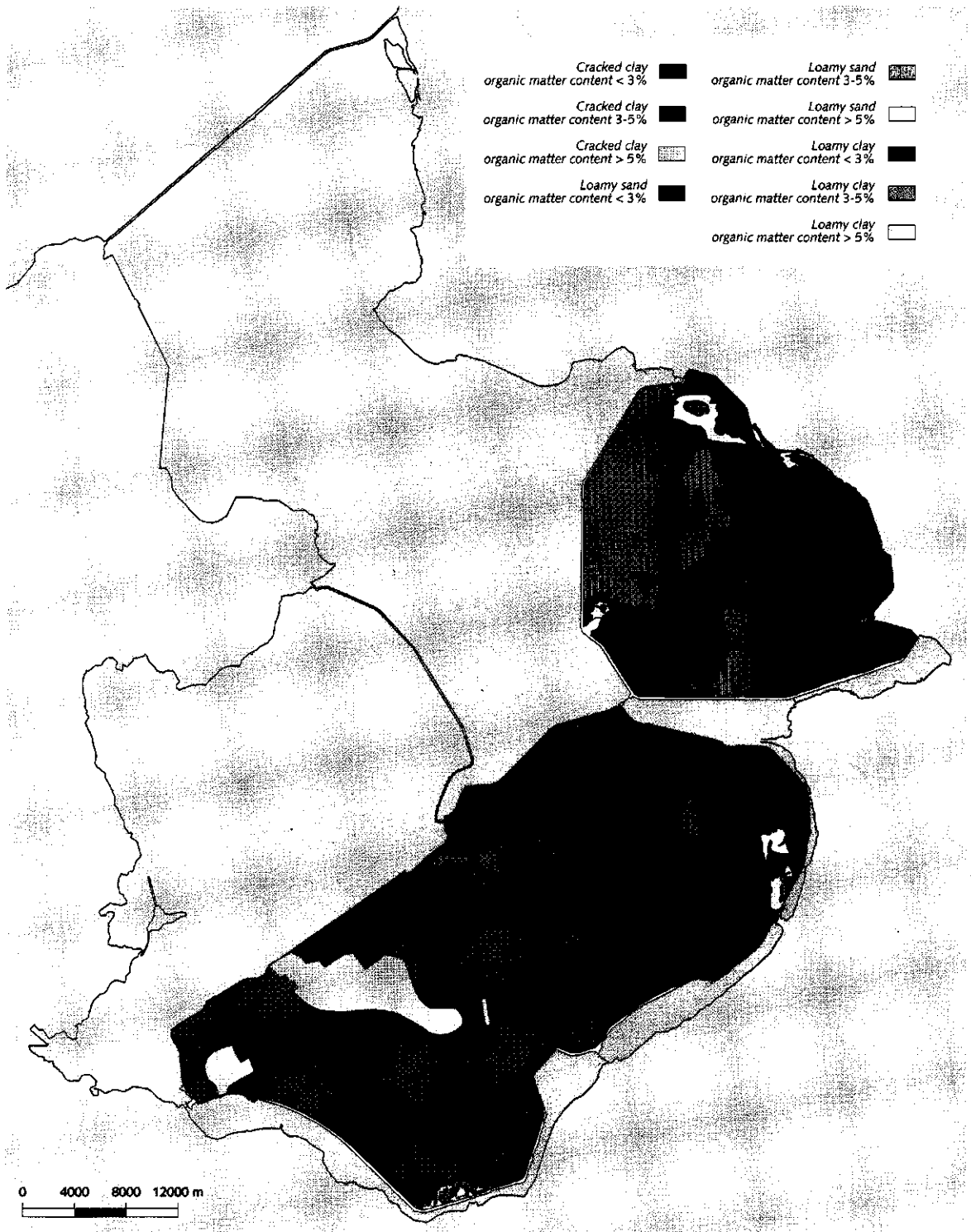


Figure 5.7. Soil map of the IJsselmeerpolders.

Table 5.3. Surface area of defined seepage areas in the IJsselmeerpolders

Seepage condition	North-East Polder (ha)	Eastern Flevoland (ha)	Southern Flevoland (ha)
No seepage	16630	35860	36750
Upward seepage 0 - 1 mm d ⁻¹	25630	8390	6210
Upward seepage 1 - 5 mm d ⁻¹	880	3700	370
Upward seepage >5 mm d ⁻¹	940	240	
Downward seepage	3190	5910	60
Total	47270	54100	43390

for planning and management objectives. As it is impossible to calculate all the various combinations of pesticides, time of application, soil characteristics, crops, weather conditions, lateral and lower boundary conditions, various simplifications were made.

Model: Pesticide leaching was calculated with the extended *SWACRO* model. Pesticides leaching in loamy sands was described with the convection-dispersion equation. For the cracked clay soils, model simulations were undertaken for the concept with imaginary drains, as described in subsection 2.3.2. The maps were created with a GIS (ARCINFO).

Input: In ARCIINFO two input coverages are distinguished:

- **Soil map** (figure 5.7; table 5.2). Nine different categories are classified: 3 * cracked clay soil (with an average of 2, 4 and 8% organic matter content), 3 * loamy clay soils (with an average of 2, 4 and 8% organic matter content) and 3 * loamy sands (with an average of 2, 4 and 8 % organic matter content). The surface area of each category is presented in table 5.2;
- **Seepage Map** (figure 5.8; table 5.3). Three different categories are classified: no seepage, upward seepage and downward seepage. For areas with downward seepage it was assumed that the drainage water flows through the subsoil into the collector or submain drains. Upward seepage usually influences the concentration level in the drain pipes but hardly influences the fraction of the dosage leached. The surface area of each category is presented in table 5.3.

Thus, three different soil types are distinguished: loamy sand, loamy clay and cracked clay. Soil characteristics for loamy clay were obtained from the Staring series (Wösten, 1987). Soil characteristics for the loamy sand and cracked clay originate from the experimental fields North-East Polder (table 3.2) and Eastern Flevoland (table 3.4) respectively.

The organic matter content of the soils varies from 0 to more than 10%. Three categories are distinguished: < 3%, 3 - 5% and >5% with an average of 2%, 4% and 8% respectively. It is assumed that the Freundlich coefficient is linearly correlated with the organic matter content.

It is assumed that the drain spacing and depth are related to the soil type (table 5.4). The lateral boundary conditions for cracked clay soils originate from the experimental field Eastern Flevoland. At a depth of 0.35 m imaginary drains were implemented. In the loamy clay no cracks are observed. For loamy clay, drain pipes were implemented at a depth of 1 m, drain distance is 24 m. At the lower boundary three options are taken into account: upward seepage, downward seepage and no seepage.

The soil is cropped with potatoes. Various input parameters with relation to the upper boundary conditions, dispersion and root uptake in loamy sands and cracked clay soils are presented in table 5.1. Input parameters with relation to the upper boundary conditions and root water uptake in loamy clay soils are assumed to be equal to the cracked clay soils, except

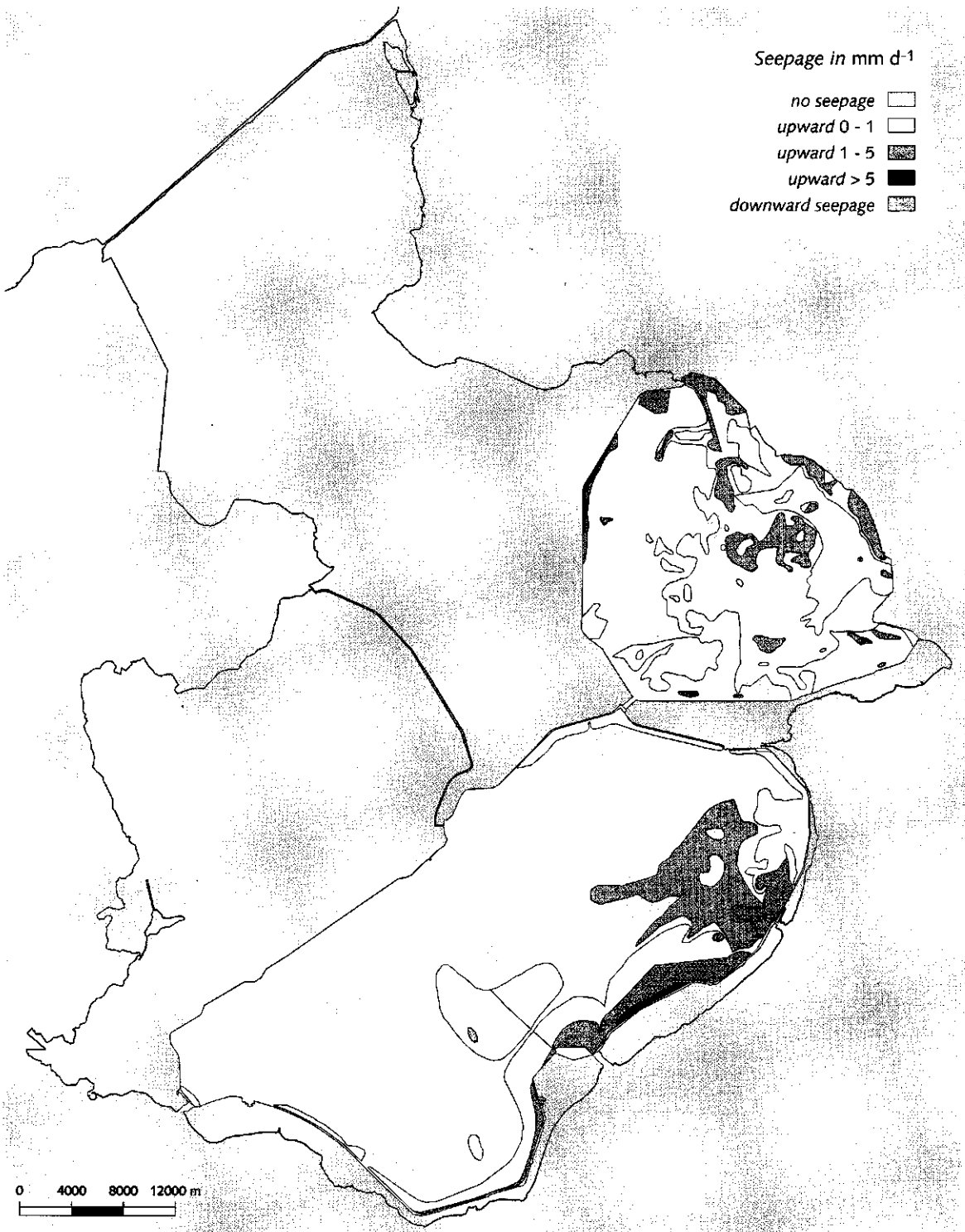


Figure 5.8. Seepage map of the IJsselmeerpolders.

Table 5.4. Input parameters for various soil types in the IJsselmeerpolders

Soil type	Drain spacing (m)	Drain depth (m)	Dispersion length (cm)	Preferential flow	Crop
Loamy sand	8	0.85	16	no	potatoes
Loamy clay	24	1.00	10	no	potatoes
Cracked clay	48	1.00	5	yes	potatoes

for the dispersion length which was set at 16 cm. The date of application of the pesticide is set at 1 May and 1 September. The quantity applied amounts to 1 kg ha⁻¹.

In the first scenario the sorption coefficient and exponent are set at 1 cm³ g⁻¹ and 0.9 for a soil with an organic matter content of 2%. The sorption coefficient increases linearly with increasing organic matter content. The transformation coefficient is set at $DT_{50} = 50$ d. In the second scenario the sorption coefficient and exponent are set at 1.5 cm³ g⁻¹ and 0.9 for a soil with organic matter content of 2% (relatively weak sorption). The transformation coefficient is set at $DT_{50} = 100$ d.

Simulations were undertaken for a May and September application over a period of 30 years (1960-1989) from the date of application up to 2 years after application. Meteorological data have already been presented in section 5.2. The results of the simulations were averaged over 30 years.

Results: Figure 5.9, 5.10, 5.11 and 5.12 show the potential leaching maps for the IJsselmeerpolders for two different pesticides with both a spring and autumn application. On these maps four categories are presented:

- Fraction leached through the drain pipes < 0.1%
- Fraction leached through the drain pipes 0.1 - 1.0%
- Fraction leached through the drain pipes 1.0 - 2.5%
- Fraction leached through the drain pipes > 2.5%

Comparison of figure 5.9 and 5.10 (Scenario I) shows that the sensitivity for leaching of a pesticide with moderate transformation ($DT_{50} = 50$ d) and low sorption ($K_F = 1$ cm³ g⁻¹) increases if the pesticide is ap-

plied after the summer period for nearly all soil types. Highest leaching is observed in areas with cracked clay soils with a low organic matter content. For areas with downward seepage, leaching is low due to the fact that the route for the pesticide to reach the collector or submain drains is much longer. For areas with downward seepage, it was calculated that the fraction leached through the drain pipes was always lower than 0.1%.

For loamy sands the sensitivity for leaching is high if the organic matter content amounts to 2% and the selected pesticide is applied in September. In other circumstances leaching in loamy sands and loamy clay soils is moderate to low. The sensitivity for leaching for cracked clay soils varied from low (for areas where downward seepage is observed) to very high. High to very high vulnerability for leaching is calculated for most cracked clay soils if the pesticide is applied in September.

In scenario II the half-life time of the pesticide is increased from 50 to 100 d and K_F increased from 1 to 1.5 cm³ g⁻¹ for a organic matter content of 2%. Figure 5.11 and 5.12 show that the sensitivity for leaching of the selected pesticide increases only slightly if the pesticide is applied in September. Generally vulnerability for leaching is low to moderate for areas without preferential flow (loamy sands and loamy clay soils) and high to very high for areas with preferential flow (cracked clay soils).

If the pesticide is more strongly adsorbed to the soil (e.g. $K_F = 3$ cm³ g⁻¹ for 2% organic carbon), it was simulated that leaching will become low for all soil types. The same results are obtained if $DT_{50} < 10$ d.

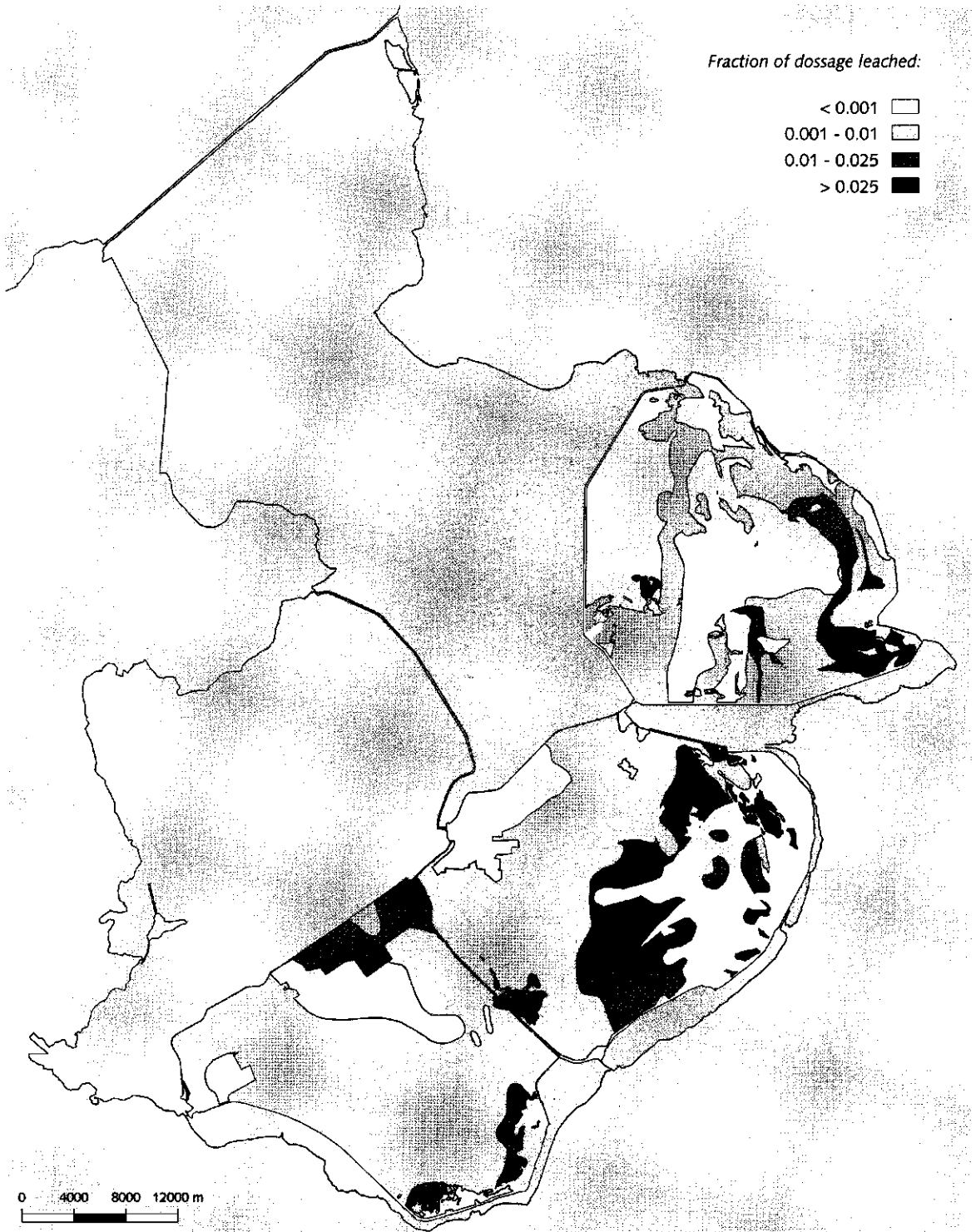


Figure 5.9. Potential leaching map for the IJsselmeerpolders for a pesticide with moderate transformation ($DT_{50} = 50$ d), low sorption ($K_f = 1 \text{ cm}^3 \text{ g}^{-1}$) and application in the spring (1 May).

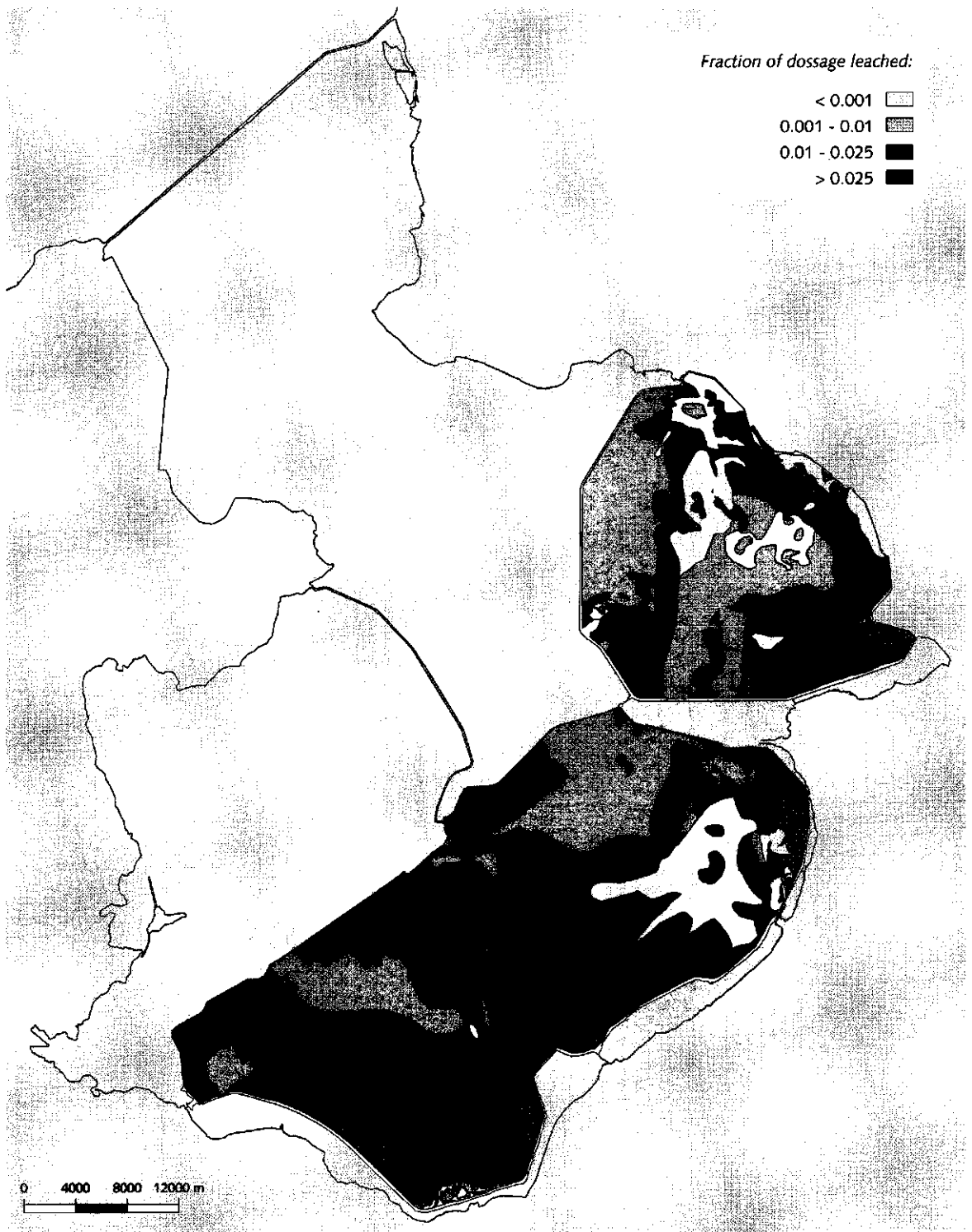


Figure 5.10. Potential leaching map for the IJsselmeerpolders for a pesticide with moderate transformation ($DT_{50} = 50$ d), low sorption ($K_F = 1 \text{ cm}^3 \text{ g}^{-1}$) and application in the autumn (1 September).

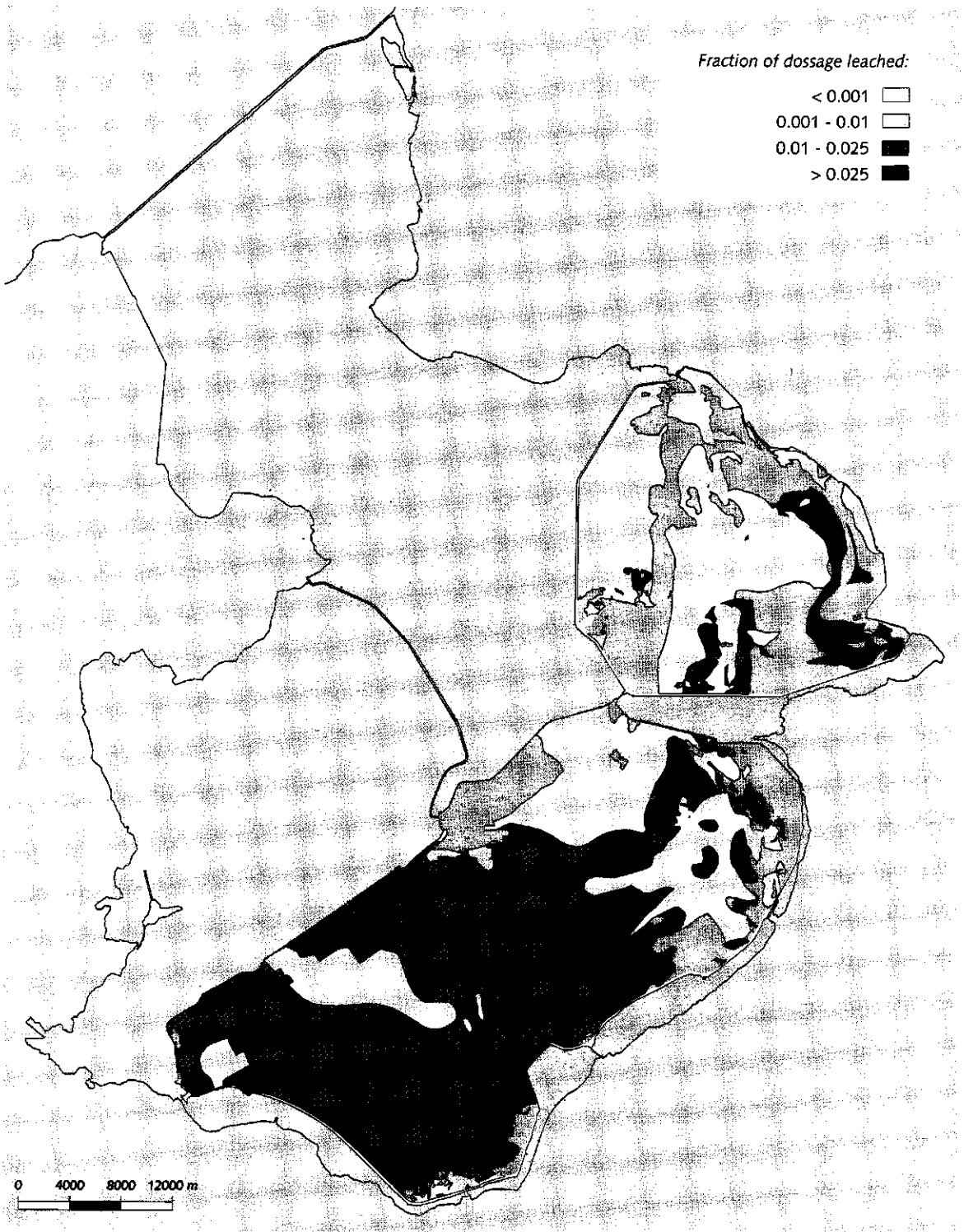


Figure 5.11. Potential leaching map for the IJsselmeerpolders for a pesticide with moderate transformation ($DT_{50} = 100$ d), low sorption ($K_F = 1.5 \text{ cm}^3 \text{ g}^{-1}$) and application in the spring (1 May).

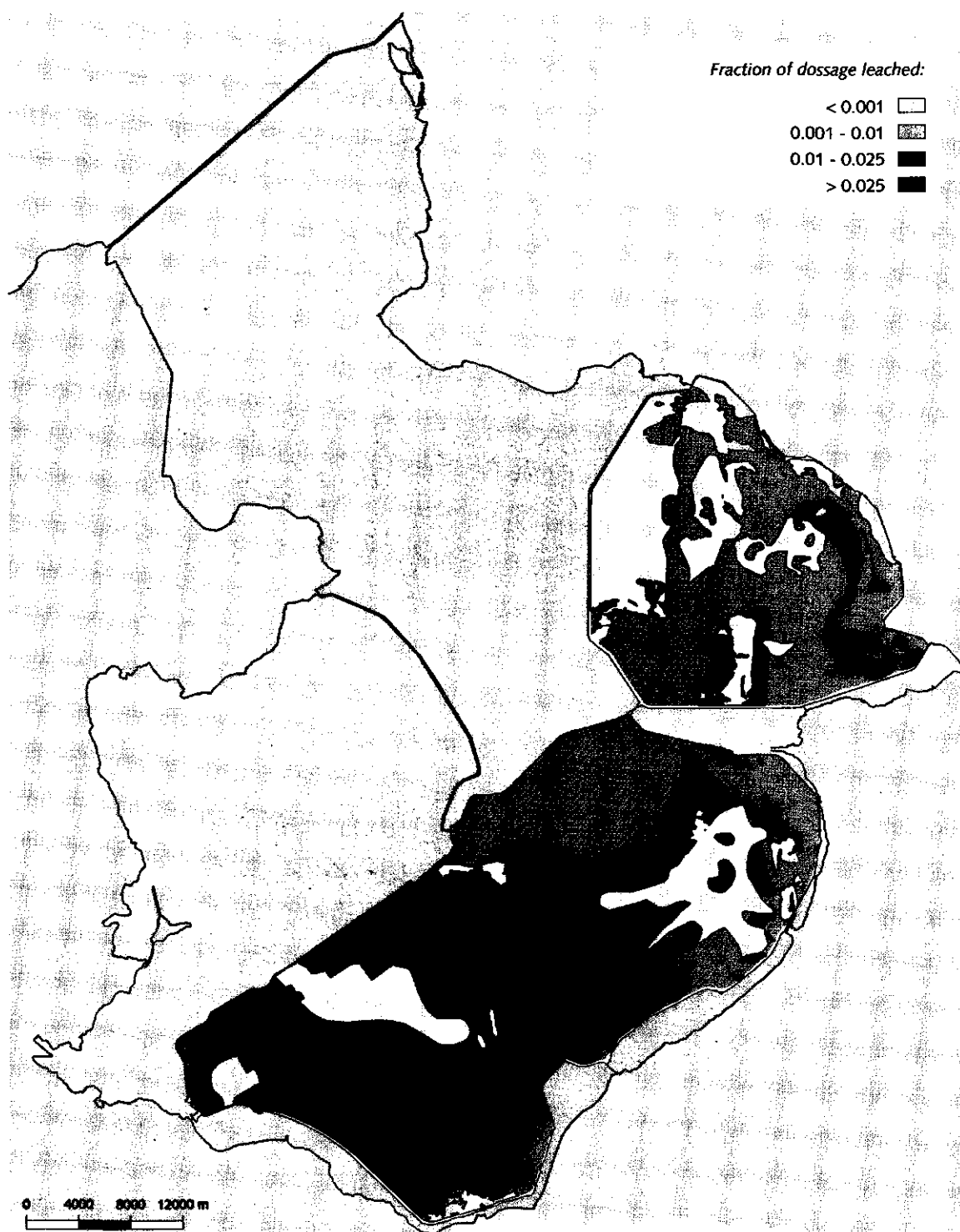


Figure 5.12. Potential leaching map for the IJsselmeerpolders for a pesticide with moderate transformation ($DT_{50} = 100$ d), low sorption ($K_f = 1.5 \text{ cm}^3 \text{ g}^{-1}$) and application in the autumn (1 September).

Conclusions:

- Sensitivity for leaching of a specified area does not depend on soil characteristics only, but also on pesticide characteristics, weather conditions and time of application;
- Leaching of pesticides in the IJsselmeerpolders is simulated for persistent pesticides ($DT_{50} > 50$ d) with a weak sorption ($K_F < 1.5 \text{ cm}^3 \text{ g}^{-1}$ for 2% organic matter). If the pesticides are more strongly adsorbed to the soil (e.g. $K_F > 3 \text{ cm}^3 \text{ g}^{-1}$ for 2% organic matter), it was simulated that leaching will become low for all soil types. The same results are obtained if transformation of the pesticide is high (e.g. $DT_{50} < 10$ d at 20°C);
- Sensitivity for leaching is higher for cracked clay soils than for loamy sands and loamy clay soils. The lowest sensitivity for leaching was simulated for loamy clay soils;
- For persistent pesticides (e.g. $DT_{50} = 100$ d), differences between application in May and September are small;
- For areas with downward seepage, sensitivity for leaching is low due to the fact that the route for the pesticide to reach the collector or submain drains rather than the drain pipes, is much longer.

5.5 Future design criteria for implementation of drain pipes in loamy sands and ploughin in cracked clay soils

In this scenario we consider the future design criteria for drain pipes in areas with loamy sand and cracked clay soils in the IJsselmeerpolders. On the one hand, these design criteria include a design discharge rate of 10 mm d^{-1} and a maximum groundwater level of 0.5 m below the soil surface (for arable land); on the other hand they take into account a reduction of pesticide leaching.

During the field experiments on heavy clay soils, it was observed that leaching of pesticides is mainly caused by preferential flow through cracks. Due to this preferential flow, the depth of the drain pipes have hardly any effect on the leaching of pesticides. Pesticides reach the drain pipes through the cracks, which run from the bottom of the plough layer to the depth of the pipe

drains. The concentration of pesticides in the drain pipes is influenced by the thickness of the plough layer. Thus, for the cracked clay soils in the IJsselmeerpolders reducing the leaching of pesticides by increasing the residence time can be obtained if the size of the plough layer is increased. This can be acquired by increasing the depth of ploughing.

For soils without preferential flow such as the loamy sands in the IJsselmeerpolders, the depth of the drain pipes has a direct impact on pesticide leaching. Generally, pesticide leaching will be reduced if the drain pipes are implemented at a deeper level as the residence time of the pesticide in the soil will be increased.

Model: Pesticide leaching was calculated with the extended SWACRO model. Pesticide leaching in loamy sands was described with the convection-dispersion equation. For the cracked clay soils, model simulations were undertaken for the concept with imaginary drains, as described in section 3.2.

Input: Input parameters for the SWACRO model are summarized in table 5.1. Simulations were carried out from the date of application up to 2 years after application. This was necessary as the more persistent pesticides will also leach during the second winter period. During the summer period both soils are cropped with potatoes, a widespread crop in the IJsselmeerpolders.

Simulations were performed for:

- Cracked clay soils: 2 different sizes for the thickness the plough layer (0.35 to 0.45 m respectively).
- Loamy sands: 3 different drain depths. The drain depth is increased from 0.85 m to 1.05 m and 1.25 m respectively. As a consequence the drain spacing is increased from 4 m to 8 m and from 4 m to 12 m respectively;
- Cracked clay soils and loamy sands: 12 different pesticides. These pesticides varied in sorption and transformation. The Freundlich coefficient (K_F) amounted to = 0, 1, 2 and $3 \text{ cm}^3 \text{ g}^{-1}$ and half-life time (DT_{50}) amounted to 10, 50 and 100 d. Other parameters which characterize transformation and sorption are constant for all scenarios. The value of these parameters are presented in table 5.1;
- Cracked clay soils and loamy sands: 30 different

meteorological years with daily average precipitation, potential evapotranspiration (period: 1960 - 1989). Data on precipitation were collected at the experimental field North-East Polder during the period 1960 - 1989; data on the potential evapotranspiration according to Makkink for the same period were collected at a weather station in Leeuwarden. These data were already presented in section 5.2;

- Cracked clay soils and loamy sands: spring (1 May) application.

During the summer period both soils are cropped with potatoes. Other input parameters, such as soil physical properties, upper boundary conditions and crop parameters, lower boundary conditions, dispersion, root uptake and soil temperatures are summarized in table 5.1.

Results: Figure 5.13 gives the results of the simulations for cracked clay soils with cracks starting at a depth of 0.35 m and 0.45 m. It shows that leaching is strongly reduced if the thickness of the plough layer is increased by 0.1 m. Reduction in the fraction of the dosage leached of roughly 15% up to 70% can be achieved. The largest reduction in the fraction of the dosage

leached is obtained if sorption is strong ($K_F > 2 \text{ cm}^3 \text{ g}^{-1}$) or if the half-life time of the pesticide is low ($DT_{50} < 50 \text{ d}$). For weakly sorbing pesticides reductions in the fraction of the dosage leached are less extreme.

Figure 5.14 presents the results of the simulations for loamy sands with drain pipes at a depth of 0.85 m, 1.05 m and 1.25 m respectively. It shows that leaching is strongly reduced if the drain depth is expanded. Reduction in the fraction of the dosage leached of roughly 25% up to 60% can be achieved if the drain pipes are implemented at a depth of 1.05 m. If the drain pipes are implemented at a depth of 1.25 m reduction amounted to 50% up to 90%. The highest reductions are accomplished for weakly sorbing pesticides ($K_F < 2 \text{ cm}^3 \text{ g}^{-1}$).

Conclusions:

- *Leaching of pesticides in cracked clay soils can be strongly reduced if the thickness of the plough layer is increased by 0.1 m from 0.35 m to 0.45 m. Reduction in the fraction of the dosage leached of roughly 15% up to 70% can be achieved. The largest reduction in the fraction of the dosage leached is obtained if sorption is strong or if the*

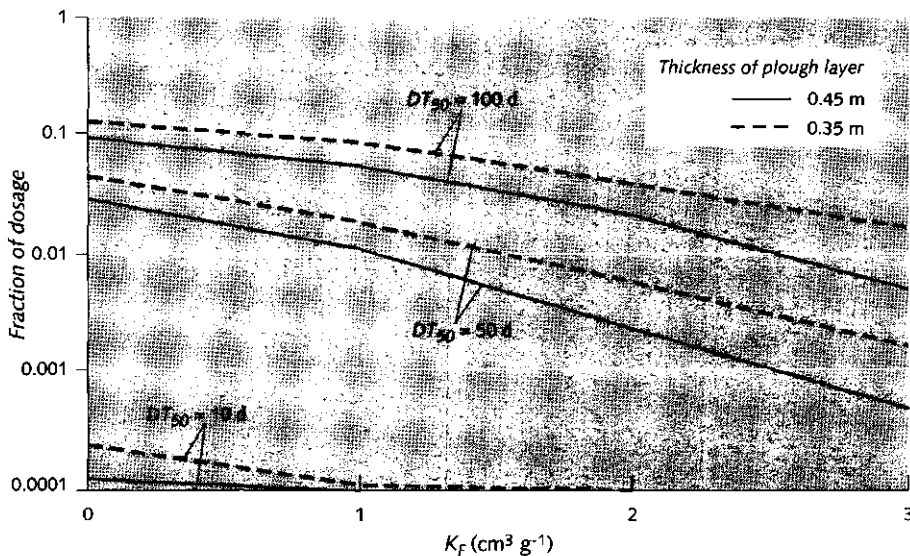


Figure 5.13. Influence of the plough layer on the fraction of the dosage leached through drain pipes in cracked clay soils in the IJsselmeerpolders with cracks starting at a depth of 0.45 m for application in May and September with $DT_{50} = 10, 50$ and 100 d and $K_F = 0, 1, 2$ and $3 \text{ cm}^3 \text{ g}^{-1}$. For $DT_{50} = 10 \text{ d}$ and $K_F > 2 \text{ cm}^3 \text{ g}^{-1}$ the fraction of the dosage leached was smaller than 0.0001.

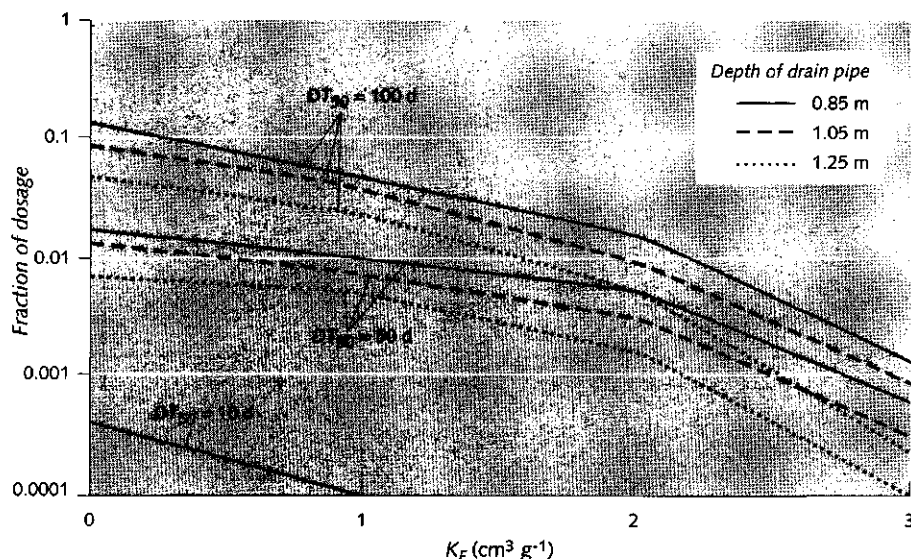


Figure 5.14. Influence of the plough layer on the fraction of the dosage leached through drain pipes in loamy sands in the IJsselmeerpolders with drain pipes at 1.05 m depth for application in May and September with $DT_{50} = 10, 50$ and 100 d and $K_F = 0, 1, 2$ and $3 \text{ cm}^3 \text{ g}^{-1}$. For $DT_{50} = 10$ d and $K_F > 1 \text{ cm}^3 \text{ g}^{-1}$ the fraction of the dosage leached was smaller than 0.001.

half-life time of the pesticide is moderate;

- *Leaching of pesticides in loamy sands can be strongly reduced if the drain pipes are implemented at a depth of 1.05 m with reduction in the fraction of the dosage leached of roughly 25% up to 60% with respect to the presented depth of 0.85 m. If the drain pipes are implemented at a depth of 1.25 m reduction was even stronger and amounted to 50% up to 90% with respect to the presented depth of 0.85 m. The highest reductions are accomplished for weakly sorbing pesticides.*

5.5 Recommendations for drainage design and management criteria for pesticide application

The objective of the scenario studies was to formulate design and management criteria for polder areas in order to reduce pesticide leaching. The scenarios as presented in this chapter show a few examples which constitute a basis for the formulating of new recommendations for design and management. Generally, all scenarios showed that pesticide characteristics (sorption,

transformation and volatilisation), time of application of the pesticide, soil characteristics, organic matter content, lateral boundary conditions and weather conditions define the final concentration of the pesticide in the drain pipe and thereby the fraction of the dosage of the pesticide leaching through drain pipes into the collector drains.

Leaching is strongly influenced by soil and pesticide characteristics and weather conditions. For most pesticides used in the IJsselmeerpolders, the pesticide and soil characteristics and weather conditions are such that the fraction of the dosage leached will be low. However, some design and management criteria can be formulated in order to reduce the leaching of weakly sorbing and/or highly persistent pesticides.

A few important design criteria to reduce pesticide leaching in polder areas could be extracted from the scenario studies:

- *Leaching of pesticides at cracked clay soils can be strongly reduced if the thickness of the plough layer is increased by 0.1 m from 0.35 m to 0.45 m;*
- *Leaching of pesticides at loamy sands can be*

strongly reduced if the drain pipes are implemented at a greater depth than present. Local circumstances such as the permeability of the deeper soil layers determine the practicability of this option. If the drain depth is increased, the drain distances will also be enlarged;

- *Future design of new polders should incorporate criteria which identify potential sensitive areas for leaching for cultivation with low pesticides use. For areas with downward seepage, sensitivity for leaching is low due to the fact that the route for the pesticide to reach the collector or submain drains is much longer. The precipitation surplus flows both through the cracks and the soil matrix into the subsoil. In areas with downward seepage, discharge of the precipitation surplus through the drain pipes hardly occurs. These areas are more suitable for cultivation with crops, where weakly sorbing and/or highly persistent pesticides are applied.*

Moreover, a few important management criteria for

pesticide application could be obtained from the scenario studies:

- *Weakly sorbing pesticides with short half-life times, which are applied after the summer period, should be applied as early as possible after harvesting the preceding crop. An example of such a pesticide is 1,3-dichloropropene. Legislation should prohibit application of dichloropropene after October 1st in order to prevent extreme leaching;*
- *Vulnerability for leaching is higher for cracked clay soils than for loamy sands and loamy clay soils. The lowest sensitivity for leaching was observed for loamy clay soils. For persistent pesticides differences between application in May or September are small.*

The presented design and management criteria, with the objective to reduce pesticide leaching in polder areas, are related to pesticide leaching through drain pipes and restricted to the results of the scenario studies. In the next chapter more recommendations for design and management criteria will be presented.

Chapter 6

Conclusions, evaluation and recommendations

Conclusions, evaluation and recommendations

In this thesis the leaching of pesticides on loamy sands and cracked clay soils in the IJsselmeerpolders has been analyzed. An extensive field study was performed at three experimental fields in the North-East Polder, Eastern Flevoland and Southern Flevoland respectively. Four pesticides were incorporated in the research program: 1,3-dichloropropene, metamitron, aldicarb and simazine. Among others reasons, these pesticides were selected on the basis of leachability and representativity.

In this chapter the results of the field study, the simulation model and the scenario analyses will be evaluated and recommendations given for making some adjustments to the current policy related to pesticides. Related to this latter aspect, the prevailing policy in the Netherlands concerning the admission of pesticides will be briefly reviewed. In addition attention is paid to a related research project, undertaken at the pumping stations in Eastern and Southern Flevoland. At the end of this chapter some recommendations for future research projects are presented.

Conclusions of this study

In this study the extended *SWACRO* model was developed and used to describe the flow of water, solutes and pesticides in the (un)saturated zone. Results of the experimental fields and laboratory studies were used to calibrate the model. After calibration, various scenario analyses were performed with the objective of formulating adapted design and management criteria for polder areas. The most important conclusions of this research are:

- *Laboratory experiments:* Parameters to describe the soil water characteristics for each experimental field and the sorption and transformation character-

istics for each pesticide were determined. Transformation could either be described by first-order transformation or microbial transformation. For all pesticides, transformation was strongly influenced by the soil temperatures. Laboratory studies showed that the selected pesticides transformed faster than was observed in other studies;

- *Field experiments:* Concentrations of (Z) and (E) 1,3-dichloropropene and metamitron were measured in the drainage water of the experimental field North-East Polder. Significant leaching was observed for dichloropropene applied in November. High concentrations (more than $1200 \mu\text{g l}^{-1}$) of (Z) and (E) 1,3-dichloropropene were mainly caused by an increasing precipitation surplus and decreasing soil temperatures. Metabolites of aldicarb, aldicarb-sulphoxide/sulphone were measured in the drainage water of the experimental field Eastern Flevoland. During the first year of the experiment, aldicarb was applied in the ridges where the potatoes were planted and aldicarb-sulphoxide/sulphone was transformed before it could reach the drain pipes. During the second year of the experiment, aldicarb was applied differently (full field application) and concentrations of aldicarb-sulphoxide/sulphone in the drainage water amounted to $0 - 4 \mu\text{g l}^{-1}$ and $0 - 1 \mu\text{g l}^{-1}$ respectively. Simazine was applied at the experimental field Southern Flevoland in the period April to July. Concentrations above $5 \mu\text{g l}^{-1}$ were observed for simazine during the spring and summer period. Due to preferential flow through cracks and the spatial inhomogeneity of the precipitation, simazine was able to reach the drain pipes. However, the field research generally showed that pesticide concentrations in the drain pipes were low and the fraction of the applied dosage leaching through the drain pipes was small;

- *Model development:* For each experimental field the model was calibrated in three steps: calibration of soil water fluxes, bromide fluxes and pesticide fluxes. Parameters optimized in the first calibration step were applied repeatedly in the following step of the calibration. This strategy gave good results. At all experimental fields preferential flow of solutes and pesticides was anticipated. At the experimental field North-East Polder preferential flow was calculated according to the mobile/immobile concept. Partitioning soil water fluxes gave accelerated break through, lower maximum concentrations and longer tailing effects. However, the same effect can be accomplished by increasing the dispersion length. At the experimental fields Eastern Flevoland and Southern Flevoland preferential flow in the cracked clay soils was anticipated by implementing imaginary drains at a depth of 0.35 m. This gave a better description of the soil water flow compared to the conventional one-dimensional concept. Additional to the cracks, for experimental field Southern Flevoland the actual flux through the soil is strongly influenced by the spatial inhomogeneity of the precipitation at the top of the soil. Redistribution of the precipitation causes preferential flow. Results of the calibration showed that preferential flow of water solutes and pesticides has a major impact on leaching;
- *Sensitivity analysis:* Both sorption and transformation of the pesticide have a strong impact on leaching. The soil temperature highly influences transformation and consequently on the leaching of pesticides. Thus, the fraction of the dosage leached depends on the time of application. Additionally, preferential flow has an important influence on leaching of solutes and pesticides;
- *Scenario analyses:* The first scenario showed that the fraction of the dosage of (Z) 1,3-dichloropropene which leaches through the drain pipes strongly depends on the time of application (soil temperatures) and weather conditions. The relation between the fraction of the dosage leached on the one hand and the soil temperatures and weather conditions on the other hand is strongly non-linear. The second scenario showed that leaching can be considerable if the half-life of the pesticide is more than 50 days and the Freundlich coefficient (K_F) is

smaller than $2 \text{ cm}^3 \text{ g}^{-1}$. Especially for cracked clay soils with a low organic matter content ($< 3\%$) the fraction of the dosage leached was calculated to be more than 2.5%. The simulated fraction leached is much higher than was observed in the field studies. Laboratory study showed that the selected pesticides were generally transformed rapidly. Furthermore, the experimental fields were situated in areas with a relatively high organic matter content in the plough layer. The last scenario showed that leaching of pesticides on loamy sands can be reduced if the drain pipes are installed at a greater depth. Leaching of pesticides at cracked clay soils can be strongly reduced if the thickness of the plough layer is increased (reduction of preferential flow).

Current policy

Since 1975, the Dutch Pesticide Act (which originates from 1962) requires an evaluation of the hazards of pesticides with regard to the environment before pesticides can be registered. In order to reduce the negative side effects of the use of pesticides, new strategic objectives were formulated in the Crop Protection Policy (1991). More stringent rules for the admission of pesticides are mentioned as a possibility to reduce the emission of pesticides to the environment. In 1995, the general administrative order (Besluit Milieutoelatingseisen Bestrijdingsmiddelen (AMvB-3a), 1995) was issued in which more stringent guidelines concerning leaching to groundwater, persistency in the soil and toxicity for aquatic organisms were embedded. Risk evaluation for aquatic organisms is included and based upon comparison of the estimated exposure concentration in the field with laboratory toxicity data (both acute and chronic toxicity). Basically two different routes of emission are classified: leaching of pesticide residues to groundwater and drift of pesticide towards collector drains.

The criterion with respect to pesticide residues in groundwater is that at 10 m below soil surface the concentration of a residue due to application in a certain crop should be less than the EC limit of $0.1 \mu\text{g l}^{-1}$. The assessment of leaching to groundwater is based on a stepwise scheme which is presented in a simplified

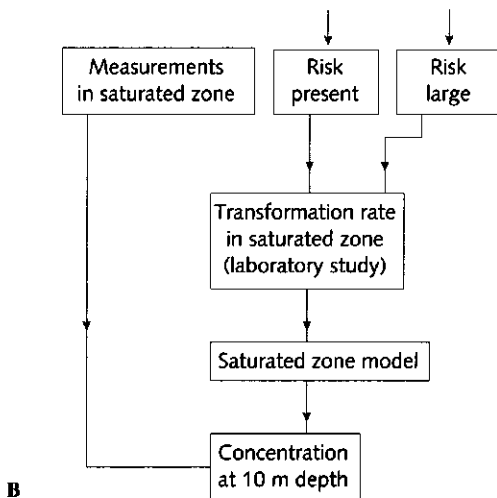
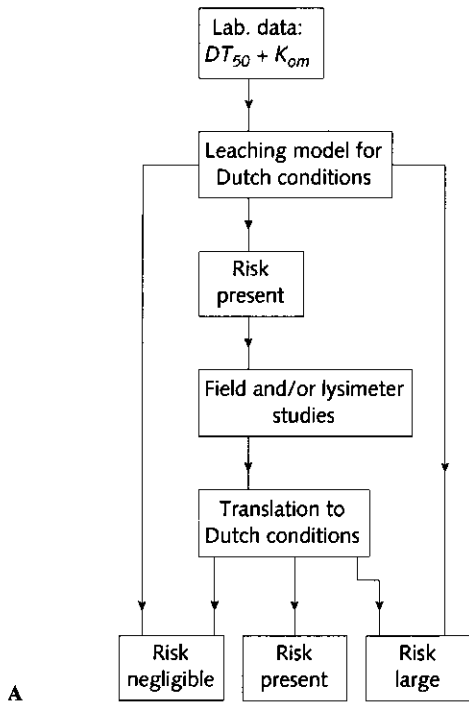


Figure 6.1. Simplified representation of the assessment scheme for leaching to groundwater (A) and the behaviour in the saturated zone (B) as used in the Netherlands (Boesten, 1993).

way in figure 6.1A. In this scheme the model for the leaching to groundwater plays an important role. Standard calculations for this scheme are performed for the worse case with respect to leaching to groundwater: a soil with 5% organic matter content in the top 0.3 m and less than 1% below 0.3 m in combination with a 75% wet year. In the standard calculations the pesticide is applied on 25 May and 1 November.

The assessment of behaviour in the saturated zone will be carried out according the scheme that is presented in figure 6.1B (in simplified form). The model used in this scheme is simple: transformation follows first-order kinetics and the residence time between 1 and 10 m depth amounts to 4 years. The concentration at 10 m depth is calculated with a simple exponential equation.

In the IJsselmeerpolders this assessment procedure is relevant for areas with downward seepage (figure 5.8). For the remaining part of the IJsselmeerpolders, which is 94% of the surface area, the assessment scheme for the saturated zone is less relevant.

At this moment, the assessment scheme of Dutch Pesticide Act does have various limitations. With respect to the IJsselmeerpolders the most important limitation were found to be:

- the Pesticide Act does not account for leaching of pesticide residues to surface water;
- the leaching model used in the assessment scheme does not take into account microbial transformation related to microbial activity and preferential flow;
- the half-life (DT_{50}) and sorption characteristics (K_{OM}) are collected for a limited number of soils and temperatures. Data available in literature were not representative for the soils in the IJsselmeerpolders;
- most parameters are obtained in laboratory columns and lysimeters, which were not necessarily representative for field conditions;
- standard calculations with the leaching model are only undertaken for a limited number of cases;
- the Pesticide Act does not make allowance for the fact that in some cases surface water may be used for drinking water purposes. The excess of water for the IJsselmeerpolders is drained of to the IJs-

selmeer (figure 1.1), which is used for drinking water;

Concentration of pesticides at the pumping stations

From May 1993 until May 1994, the concentration of several pesticides were measured in the water drained at the pumping stations of Eastern and Southern Flevoland (Kuiper, 1996). Approximately 70 different pesticides were included in the research program, which amounts to roughly 85% of the types of pesticides used in the IJsselmeerpolders. Despite all processes occurring from the moment the pesticide enters the open drains, such as sorption, transformation, transport (e.g. dilution and dispersion) and volatilization until reaching the pumping station, the existence of several pesticides at the pumping stations could still be demonstrated. During the summer period the average sum of pesticides at the pumping station amounted to approximately $2.0 \mu\text{g l}^{-1}$, during the winter period $0.4 \mu\text{g l}^{-1}$. Some pesticides which were detected regularly in high concentrations are MCPP (herbicide), MCPA (herbicide), 2,4-D (herbicide), bentazone (herbicide), 2,4-DB (herbicide), simazine (herbicide), mevinphos (insecticide), parathion (insecticide), isoproturon (herbicide) and dichlorvos (insecticide). The concentration of simazine observed at the pumping stations during the summer period varied from 0.05 to $0.20 \mu\text{g l}^{-1}$. During the winter period the concentration was below $0.05 \mu\text{g l}^{-1}$. This agrees with the tendency of the concentration levels observed at the experimental field Southern Flevoland. Dichloropropene was observed at the pumping stations incidentally during the autumn period in very low concentrations. As dichloropropene is very volatile, it is most likely that dichloropropene evaporated during the transport to the pumping station. Aldicarb-sulphoxide/sulphone was observed irregularly at the pumping stations at very low concentrations. Metamitron was not observed. Thus, the selected pesticides were less representative leachers than expected initially.

Based on these data, it may be roughly estimated that the load of pesticides that are discharged to the surrounding lakes of the IJsselmeer amounted to 500-

1000 kg yr^{-1} . This is 0.3-0.5% of the amount of pesticides applied in the IJsselmeerpolders. For some pesticide (e.g. bentazone) concentrations were high during the winter period. This may indicate that bentazone enters the collector drain by leaching.

It can be concluded that the results of the above study conform to the results of this study. Metamitron, metabolites of aldicarb (aldicarb-sulphoxide/sulphone) are observed in the drain pipes and at the pumping stations in very low concentrations. The concentration of simazine observed at the pumping stations was at the highest level during the summer period and varied from 0.05 to $0.20 \mu\text{g l}^{-1}$. This agrees with the results of the experimental field, where concentrations varied from 0.0 to $7.0 \mu\text{g l}^{-1}$. In addition the scenario studies showed that the concentrations in the drain pipes would be much higher for weakly sorbing and more persistent pesticides, particularly in areas with cracked clay soils with a low organic carbon content.

Recommendations for adaptation of the current policy

It has already been indicated that the current Dutch Policy Act has various limitations with regard to the prevention of pesticide emission to the environment. Based on this study some recommendations using the assessment scheme for leaching to groundwater and the behaviour of pesticides in the IJsselmeerpolders can be made:

- Due to upward seepage in polder areas, leaching of pesticides to deep groundwater (10 m below soil surface) can be ignored. In the IJsselmeerpolders, water found at a depth of 10 m below soil surface was not infiltrated from the soil surface at this point, but originated from another source. In the present assessment of leaching to groundwater, the hydrology of the system is not considered adequately;
- It was detected that pesticide leaching to groundwater is very sensitive to meteorological conditions. Both the scenario studies and the sensitivity analyses of this study showed that the concentration at approximately 1 m below soil surface may vary by a factor 10 to 100 depending on the

weather conditions. For example, intensive rainfall directly after the application of the pesticide may strongly influence leaching. In the current policy, leaching is calculated for a 75% wet year, which is assumed to be a realistic "worst case". Instead of using a 75% wet year as a standard input for the model, it would be more appropriate to use a statistical approach with a number of years (e.g. 30) and various times of application. Identical results were presented by Van Veen and Boesten (1996). It is recommended to adjust the current calculation scheme and use a statistical approach;

- Soil temperatures have a major impact on the transformation of the pesticide. Testing the vulnerability of the model with respect to yearly variations in soil temperatures is recommended;
- In the standard procedure as used in the assessment scheme, leaching to groundwater is calculated for an assumed worse case. However, in these calculations preferential flow is not considered. In this study it was concluded that preferential flow may have a major impact on the leaching of pesticides. Therefore the recommendation is to implement preferential flow of pesticides in future calculations for certain soils;
- It was observed that laboratory data on the transformation and sorption characteristics often did not coincide with literature data (e.g. curvature of the sorption isotherm, microbiological transformation). In order to obtain reliable results, the sorption and transformation characteristics for each pesticide should be collected for different soils.

The present assessment of pesticide residues in collector drains is defined only by spray drift deposition. The amount of spray drift is defined as a fraction of the dosage applied. Among others factors, this fraction depends on the way the pesticide is applied and the type of crop (e.g. for simazine applied in an orchard, spray drift is assumed to be 10% of the dosage applied (of which 1% is assumed to be effective); for aldicarb (granules) applied on arable land, spray drift is assumed to be 0%). This spray drift deposition is applied to a standard collector drain. As both the amount of spray drift and the content of the collector drain are known, the concentration may then easily be calculated. In this study it was demonstrated that pesticides

may enter the collector drains not only by drift, but also through drain pipes. The fraction of the dosage leached may be in the same order of magnitude as is assumed for spray drift, if sorption is weak ($K_F \leq 1 \text{ cm}^3 \text{ g}^{-1}$) and transformation is low ($DT_{50} \geq 50 \text{ days}$). This fraction will even increase if preferential flow occurs.

It should be noted that exposure of pesticides to aquatic organisms is not the only criterium. Water from the IJsselmeer is extracted for drinking water purposes. This water should meet the EC standards for drinking water. This may indicate that the allowed limits should be more uncompromising.

Recommendation for reduction of the emission of pesticides in the IJsselmeerpolders

If the pesticide concentration in the collector drains often exceeds the formulated limits for surface water, different action can be taken:

- Legislation. More strict conditions for pesticide use or even a ban of the pesticide;
- Design criteria:
 - (1) Reducing leaching: for soils without preferential flow, the depth of the drain pipes has a direct impact on leaching. If the depth of the drain pipes is increased, leaching can be reduced. For cracked clay soils, it was observed that leaching is mainly caused by preferential flow through cracks below the plough layer. If the depth of the plough layer is increased, leaching can be reduced.
 - (2) Realization of permanent spray-free zones along collector drains such as strips planted with trees;
- Management criteria:
 - (1) Reducing spray drift by new application techniques or spray-free zones;
 - (2) Reducing leaching by allowing pesticides to be applied only during a certain period;
 - (3) Reducing leaching by new application techniques (e.g. application of aldicarb in the furrows instead of full field application).

In 1996 the TOXSWA model was introduced and will have to be applied in the Dutch pesticide registration

procedure in the near future (Adriaanse, 1996). This program simulates the fate of pesticides in collector drains and estimates acute and chronic exposure to pesticides of aquatic organisms. The model incorporates the entry of pesticides in collector drains by drift or atmospheric deposition, surface runoff and leaching. Four processes are included: transport, transformation, sorption and volatilization.

For the collector drains in the IJsselmeerpolders, it is therefore recommended that both the output of the extended *SWACRO* model (both the drain pipe discharge and the concentration in the drain pipes) and the estimated spray drift as an input for the new *TOXSWA* model are used in order to calculate the fate of pesticides in the collector drains of the IJsselmeerpolders.

Recommendations for future research

The objective of this research project was to formulate design and management criteria for polder areas in order to develop an integrated pest management: effective and controlled application with few adverse effects on the surrounding environments. Due to the enormous variety in different types of pesticides, crops, hydrological and soil conditions and application time of pesticides, the use of computer simulation models is inevitable. The computer simulation model *SWACRO* was extended in order to calculate pesticide transport. The model was calibrated using field and laboratory data from three different experimental fields and four different pesticides. The project was limited to soil-applied pesticides in the IJsselmeerpolders. Processes such as wind erosion, drift and surface runoff were ignored. Recommendations for future research related to experience gained from this research project and up-scaling of the use of the models for regional and rural applications are:

General

- Application of statistics. In the present day assessment scheme "worst case scenarios" are used to calculate leaching of pesticides to groundwater. Instead of using the "worst case scenarios" it would be more appropriate to use a statistical approach. However, more research is needed to indicate in

which way this can be accomplished;

- Supplementary research on preferential flow. In this research it was indicated that preferential flow may have a major impact on leaching. In order to present an estimation of the impact of preferential flow on different soils, more research is needed;
- Intensification of regional and rural monitoring programs. It is recommended that the research on pesticides which are detected in surface water in high concentrations is intensified. This research should concentrate on the route they enter the surface water (e.g. leaching, spray drift, surface runoff). On the other hand, results of monitoring studies can be used to validate the results of computer simulations;
- Additional field research in vulnerable areas for pesticide leaching. Scenario analysis showed that the experimental fields presented in this thesis were not situated in the most vulnerable areas for pesticide leaching in the IJsselmeerpolders (chapter 5). It is therefore recommended to undertake additional field research in these areas;
- More research on the metabolites of pesticides. Very little is known about the metabolites (e.g. appearance, leachability and toxicity) of the pesticides used.

Model development

- Extension of models used for admission of pesticides. In the present day models used for admission of pesticides, preferential flow and microbial transformation related to microbial activity is not accounted for;
- Extension of the number of high quality data. More high quality data are needed to calibrate and validate the available models.

Upscaling of the use of models for regional and rural applications

- More research on the sorption and transformation of pesticides for various soils and soil temperatures;
- More research regarding transformation, sorption and transport processes in collector drains, secondary drains and field drain.

Concluding remark

Pesticides are very effective in controlling or preventing pests and have become indispensable in modern agriculture. However, the adverse effects of the use of pesticides on the environmental quality have been recognized for some time and are still not solved today. In order to reduce the negative side effects of the use of

pesticides several measures have already been taken and some others have already been mentioned in this chapter. The routes in which pesticides enter the environment strongly depend on local circumstances. In order to come to environmentally sound agricultural practices at acceptable costs, monitoring programs, research and guidelines will be required, resulting in adapted watermanagement and agricultural practices.

Summary

Summary

General

The hazards of pesticides with regard to public health and the environment have been recognized for some time. Traces of pesticides are found in groundwater, drainage systems, lakes and coastal waters. These traces may have a strong impact on aquatic ecosystems and/or on the quality of drinking water supplies. In the Dutch Crop Protection Policy, the following important strategic objectives for the use of pesticides were formulated: reduction of the dependency, the use and the emission of pesticides to groundwater, surface water and air.

The present study focuses on the use and the emission of pesticides to groundwater, surface water and air. The goals are to formulate management and design criteria in order to develop an integrated pest management with reduced emission of pesticides to the environment. An additional objective is the development and calibration of a computer-simulation model. The model is calibrated for the IJsselmeerpolders: reclaimed polder areas in the central part of the Netherlands.

In this thesis the effects of pesticide application on leaching in loamy sands and cracked clay soils in polder areas are analyzed. Data to determine the fate of water, solutes and pesticides were collected in the IJsselmeerpolders at the experimental fields North-East Polder, Eastern Flevoland and Southern Flevoland. Four different pesticides were used on the various fields: (E)/(Z) 1,3-dichloropropene and metamitron on the experimental field North-East Polder, aldicarb on the experimental field Eastern Flevoland and simazine on the experimental field Southern Flevoland. Bromide was used as a tracer and applied together with the pesticides at all locations. These data were used to calibrate the extended *SWACRO* computer simulation

model, which can simulate the fate of water, solutes and pesticides in the (un)saturated zone. The calibrated model was used to perform scenario analyses and evaluate the use of pesticides in the IJsselmeerpolders.

Development of the extended *SWACRO* simulation model

The model *SWACRO* was selected to describe water flow in the (un)saturated zone. *SWACRO* is a one-dimensional, dynamic, deterministic model, based on the differential equation for unsaturated soil water flow in porous media, the Richards equation. The soil is divided in a number of compartments, with variable sizes. One or more compartments form a soil layer having a specific soil-moisture retention curve and (un)saturated hydraulic conductivity curve. At the upper boundary the interception, actual soil evaporation and actual transpiration are calculated. In the unsaturated zone the movement of water is considered to occur in the vertical direction only, while for the saturated zone or at perched water tables, both vertical and horizontal flow is taken into account. Vertical flow at the lower boundary is dependent on the hydraulic head and the permeability of the subsoil.

The *PESTLA* model was selected to simulate pesticide behaviour in the soil. *PESTLA* is based on the concept of the convection/dispersion equation for solute transport, non-linear sorption according to the Freundlich equation, temperature dependent first-order transformation rates and passive plant uptake. This concept has been extended to transport of pesticides in the gas phase and microbiological transformation. The extended model concept of *PESTLA* for pesticide fate has been adapted and implemented as a subroutine in the *SWACRO* model. The extended *SWACRO* model

can describe soil water flow, crop water use, crop yield, pesticide fate and lateral transport of solutes and pesticides. Furthermore, the *SWACRO* model is extended with an option for the calculation of preferential flow according to the concept of mobile/immobile transport.

Data collection

Parameters to describe the soil characteristics such as the soil-moisture retention curve and the unsaturated hydraulic conductivity curve for each experimental field were determined in the laboratory. These parameters were used in the *SWACRO* model.

Sorption and transformation characteristics of each pesticide were determined in laboratory experiments under various physical conditions:

- *Metamitron*: transformation of metamitron could be described by first-order kinetics. For the plough layer the reference coefficient for first-order transformation, $k_{f,ref}$ (at 20 °C), amounted to 0.1 d⁻¹. The rate of transformation is strongly influenced by the soil depth and soil temperature. Sorption increases with depth. The K_{om} -value (Freundlich coefficient divided by organic matter content) amounted to 42 - 91 cm³ g⁻¹;
- (E)/(Z) *1,3-Dichloropropene*: transformation is described by microbial transformation in the top soil (0 - 0.4 m - soil surface) and first-order transformation in the subsoil. The rate of transformation is strongly influenced by the soil temperature. Depending on temperature, concentration and soil depth, the K_{om} -value amounted to 52 - 156 cm³ g⁻¹;
- *Aldicarb-sulphoxide/sulphone*: transformation of aldicarb-sulphoxide/sulphone was studied for the plough layer and appeared to be a very complex process. Accelerated transformation was observed, presumably due to microbial adaptation. Roughly half of the amount of aldicarb is transformed into aldicarb-sulphoxide and less than 3% into aldicarb-sulphone. The K_{om} -value amounted to 22 cm³ g⁻¹;
- *Simazine*: Transformation could be described by first-order kinetics. For the plough layer the reference coefficient for first-order transformation at 15 °C, $k_{f,15}$, amounted to 0.09 d⁻¹. The K_{om} -value amounted to 30 cm³ g⁻¹.

Parameters on transformation and sorption of the four pesticides, which were incorporated in this study, were derived from the laboratory studies and are used as input for the *SWACRO* model.

At the experimental field North-East Polder, data were collected at three different plots where tulips were grown. The soil is classified as a loamy sand. About 0.9 m below soil surface a nearly impermeable layer of detritus-gytta occurs. The drainage system is situated on top of this layer and the drain spacing amounts to 4 m.

At the experimental field Eastern Flevoland, data were collected on two experimental plots where potatoes were grown. The soil is classified as a heavy clay soil. Below the homogeneous plough layer up to a depth of 1.0 m below soil surface, cracks are found. These cracks are interconnected resulting in a very high saturated permeability (300 - 500 m d⁻¹). Below 1 m the soil consists of soft clayey sediments which have a very high water content and are practically impermeable. The depth of the drainage system amounts to 0.95 m below soil surface. Due to the high permeability of the soil above the drain pipes, the drain spacing amounts to 48 m.

At the experimental field Southern Flevoland, data were collected in an orchard where apples were grown. The soil is classified as a heavy clay soil. Characteristics of this soil are comparable to the experimental field Eastern Flevoland, only the drainage criteria differed. Drain depth and spacing amounted to 1.1 m and 24 m respectively. As the subsoil below the drain pipes is practically impermeable at all experimental fields, it was assumed that the precipitation surplus runs through the drainage system into the collector drain. However, some upward and downward seepage was observed at the experimental field North-East Polder and Eastern Flevoland.

Basically two types of data were collected at the experimental fields:

- *Data related to soil water fluxes*: precipitation, irrigation, groundwater levels, drain discharges, soil moisture content, potential evapotranspiration and interception;

- *Data related to solute and pesticide fluxes:* preferential flow, concentration of solutes and pesticides in drainage water, concentration profiles of solutes and pesticides.

Discharge proportional samples were taken from a number of drains on each plot and analyzed for the concentration of the selected pesticides and bromide. Concentration depth profiles of solutes and pesticides were measured. Soil samples were collected at increasing time intervals after application and analyzed for bromide and pesticide content.

Results of the field experiments showed differences between the soil characteristics of loamy sands of the experimental field North-East Polder and the heavy clay soils of the experimental fields Eastern and Southern Flevoiland. At the experimental fields North-East Polder (drain spacing 4 m), Eastern Flevoiland (drain spacing 48 m) and Southern Flevoiland (drain spacing 24 m) the height of the phreatic surface midway between the drain pipes amounted to a drain discharge rate of 8 mm d⁻¹ to 0.5 m, 0.1 m and 0.1 m respectively. Soil moisture storage from the soil surface to a depth of 1.2 m at the experimental field Eastern and Southern Flevoiland varied from roughly 500 to 760 mm. At the experimental field North-East Polder the soil moisture storage only varied from 500 to 575 mm. At the experimental field North-East Polder and Southern Flevoiland drain discharges occurred both during the summer and winter periods. At the experimental field Eastern Flevoiland drain discharges during the summer period were highly exceptional.

Concentration levels of (E)/(Z) 1,3-dichloropropene and metamitron were measured in the drainage water of the experimental field North-East Polder. When 1,3-dichloropropene was injected in September, the concentration in the drain pipes varied from 0.0 to 1.0 µg l⁻¹. However, if 1,3-dichloropropene was injected in November, the concentration of (Z)/(E) 1,3 dichloropropene rose to a level of 1200 µg l⁻¹ approximately 60 days after application. Metamitron was applied in the early spring (February/March). The concentration of metamitron in the drain pipes varied from 0.0 - 0.5 µg l⁻¹. The highest concentrations were measured during the summer period. Metabolites of aldicarb, aldicarb-sulphoxide/sulphone, were measured in the

drainage water of the experimental field Eastern Flevoiland. Aldicarb-sulphoxide/sulphone were not observed in the drainage water during the first year of the experiment. During the second year of the experiment, the highest concentration of aldicarb-sulphoxide/sulphone amounted to 0 - 4 µg l⁻¹ and 0 - 1.0 µg l⁻¹ respectively. Simazine was applied at the experimental field Southern Flevoiland in the period April to July. The concentrations of simazine in the drain pipes varied from 0 to 7.0 µg l⁻¹. The highest concentrations were measured during the summer period. Simazine remained traceable until approximately 150 days after application.

Concentration profiles of bromide and the selected pesticides in the soils were measured. For dichloropropene applied in September, accelerated transformation was observed after 4 days. After approximately 2 months, the content of 1,3-dichloropropene was equal to the initial content. Metamitron was only observed in the upper part of the soil (0 - 0.2 m - surface). Approximately 50 days after application roughly 15% of the dose applied was still detectable in the soil. Bromide was applied simultaneously with metamitron. About 400 days after application and 400 mm of drain discharge, half of the bromide leached through the drain pipes and half of the bromide was still present in the soil profile. At the experimental field Eastern Flevoiland only two weeks after application, no traces of aldicarb-sulphoxide/sulphone could be detected in the soil profile. Measurements on the movement of bromide in the soil profile were unreliable. Roughly 30% of the amount of bromide applied could be traced in the drainage water after 500 mm of drain discharge. At the experimental field Southern Flevoiland approximately 40% of the bromide leached through the drain pipes after 570 mm of drain discharge. Simazine was only detected in the upper part of the soil (0 - 0.3 m - soil surface). Generally, the average concentration during the summer and winter period amounted to 0.05 and 0.02 mg kg⁻¹ dry matter respectively.

For the experimental field North-East Polder and Eastern Flevoiland additional field experiments were undertaken to demonstrate preferential flow paths. At the experimental field North-East Polder no preferential flow path could be visualized. At the experimental

field Eastern Flevoland preferential flow was observed below the homogeneous plough layer, in the soil layer where the cracks are found. If the flux of water from the top soil exceeds the infiltration capacity of this layer, water starts to flow in the cracks. At the experimental field Southern Flevoland, the influence of the apple trees on the spatial inhomogeneity of the throughfall of precipitation was studied. Results showed that due to the redistribution of the precipitation by apple trees, permanent dry and wet spots are observed underneath the trees, particularly during the summer period.

Calibration of the extended *SWACRO* model

Results of the three field experiments were used to calibrate the *SWACRO* model. The collected data were either used as input for the model or as observed values which were compared with the calculated values. Each experimental field was calibrated in three steps:

- Calibration of soil water fluxes;
- Calibration of the concentration of bromide in the drain pipes and the concentration depth profiles of bromide;
- Calibration of the concentration of pesticide in the drain pipes and the concentration depth profiles of the pesticide.

Parameters optimized in the first calibration step were

applied repeatedly in the following step of the calibration.

Experimental field North-East Polder: Here the soil water fluxes were optimized for the lower boundary conditions. Results of the calibration of soil water fluxes showed good agreement between observed and simulated groundwater levels and observed and simulated drain discharges. The average simulated soil water fluxes are presented in table 1.

At the experimental field North-East Polder preferential flow of bromide and pesticides was anticipated. Preferential flow of bromide was calculated according to the mobile/immobile concept. Bromide fluxes were optimized for the partitioning between mobile and immobile fractions, the exchange coefficient and the dispersion length. These simulations showed that partitioning of the soil water in mobile and immobile fractions gave minor changes in the concentration of bromide in the drain pipes. Generally, partitioning of soil water fluxes gave accelerated breakthrough, lower maximum concentrations and longer "tailing" effects. However the same effect can be accomplished by increasing the dispersion length. This indicated that the mobile/immobile concept is exchangeable for a higher dispersion coefficient. For the conventional convection-dispersion equation, the dispersion length L_{dis} amounted to 16 cm. Results showed that both the

Table 1. Average yearly soil water fluxes for the experimental fields *North-East Polder*, *Eastern Flevoland* and *Southern Flevoland*.

Experimental field	Precipitation (including irrigation)	Actual evapotranspiration	Flux through bottom of soil profile (- = out)	Lateral drainage (- = out)
	(mm)	(mm)	(mm)	(mm)
North-East Polder (1989 - 1992)	850	523	31	-296
Eastern Flevoland (March 1992 - March 1994)	962	541	-63	-358
Southern Flevoland apple trees (1993)	925	600	0	-325
Southern Flevoland grass (1993)	925	560	0	-365

observed amount of bromide leaching through the drain pipes and the observed movement of bromide through the soil profile corresponded reasonably well with the simulated values.

The concentration of metamitron in the drain pipes was calculated using the Freundlich parameters from the laboratory experiments. Both in 1990 and 1991 the calculated concentration of metamitron in the drain pipes was equal to 0. Therefore, the model was calibrated for the Freundlich coefficient. The Freundlich exponent was set at 0.74, as was determined in the laboratory experiments. The optimum value of the Freundlich coefficient amounted to $3.1 \text{ cm}^3 \text{ g}^{-1}$, which approximated the average value determined in the laboratory experiments. The observed concentration of dichloropropene in the drain pipes could be reasonably well simulated, using the Freundlich parameters from the laboratory experiments. Optimization of the Freundlich coefficient and exponent showed that the optimum value correspond to the average of the values established in the laboratory experiments. Both field experiments and sensitivity analyses showed that both soil temperature and precipitation surplus have an enormous impact on the concentration of 1,3-dichloropropene in the drain pipes. Due to the relatively high soil moisture content, volatilization to air never amounted to more than 10% of the dose applied. If (Z) 1,3-dichloropropene was injected in September, volatilization to air was approximately 1 - 2% of the dose applied. For injection in November, volatilization to air approximated 6% of the dose applied. Differences between the (E) and (Z)-isomer can be ignored as far as sorption and transformation are concerned. However, losses due to volatilization are substantially lower for the (E)-isomer and amounted to approximately two thirds of the size of the (Z)-isomer.

Experimental field Eastern Flevoland: In order to describe the flow of water in the cracked clay soil at the experimental field Eastern Flevoland, without leaving the concept of one-dimensional flow, imaginary drains were implemented at a depth of 0.35 m. These imaginary drains represent the cracks, present just below the plough layer. In order to show the effect of the implementation of imaginary drains, simulations were undertaken for two concepts: with and without imagi-

nary drains. The model was calibrated for the lower boundary conditions and the saturated permeability of the layer just below the imaginary drains. Results of simulations showed that the implementation of imaginary drains gave a better description of the soil water flow. Drain discharges calculated without imaginary drains, deviate strongly from the observed drain discharges during the summer and autumn period. If simulations are undertaken for the concept without imaginary drains, the soil moisture content is replenished to field capacity before the drain pipes start to discharge. This does not correspond with observation where drain pipes start to discharge long before the cracked soil below the plough layer reaches field capacity. Roughly one third of drain discharge descends directly from the cracks, as two thirds of the drain discharge flows through the soil matrix before entering the drain pipe. The average simulated soil water fluxes for the period March 1992 until March 1994 are presented in table 1.

Implementation of imaginary drains strongly influences the concentration of bromide in the drain pipes. At the experimental field Eastern Flevoland, the concentration of bromide in the drain pipes could be reasonably well calculated with the concept of imaginary drains. Observed concentrations were a mixture of concentrations of bromide originating from the plough layer and concentrations at a depth of 0.95 m below soil surface. The model was calibrated for plant uptake F and the dispersion length L_{dis} . The best fit was obtained for $L_{dis} = 5 \text{ cm}$ and $F = 0$. An experiment with a rainfall simulator showed that the major part of the soil water flux flows through the cracks (imaginary drains) if rainfall intensity is high.

At the first experimental plot, the simulated concentration of aldicarb-sulphone/sulphoxide in the drain pipes amounted to $1 \mu\text{g l}^{-1}$ in September. However, observed concentrations were below the detection limit. This is most likely caused by the fact that at the first experimental plot, aldicarb is applied in ridges. In the computer simulations the flow of water is assumed to be uniform. In reality, infiltration of precipitation will be far from uniform due to surface runoff from the ridges into the furrows. Thus, the downward flux in the furrows is higher compared to the flux in the ridges. At the second experimental plot, aldicarb was applied before

planting of the potatoes as a full-field application. Leaching of aldicarb-sulphoxide/sulphone was observed up to 450 days after application. This did not correspond to the simulated values, where it was assumed that aldicarb-sulphoxide/sulphone was transformed very rapidly into other compounds. A possible explanation may be the reduced transformation of aldicarb in the deeper soil layers. Unfortunately, in the laboratory, the transformation of aldicarb-sulphoxide/sulphone was studied for the plough layer.

Experimental field Southern Flevoland: In order to describe the flow of water in the cracked clay soil at the experimental field Southern Flevoland, without leaving the concept of one-dimensional flow, imaginary drains were implemented at a depth of 0.35 m similar to the experimental field Eastern Flevoland. Due to the impermeability of the subsoil, the flux through the lower boundary could be ignored. Additional to the cracks, the actual flux through the soil surface is strongly influenced by the spatial inhomogeneity of the net precipitation at the top of the soil. This inhomogeneity is caused by the fact that half of the surface of the orchard is cropped by apple trees and half consists of grass. In addition, the leaves of the apple trees strongly redistribute the precipitation. Redistribution and throughfall were examined at the experimental field. In order to simulate soil water fluxes, the orchard was subdivided in a number of sections. The simulated drain flow is calculated as the weighted average of the separate simulated drain flow for each section. It showed good agreement with the observed drain flow. If the net precipitation is distributed uniformly, hardly any drain flow is simulated during the summer period. The simulated value for the section with the highest throughfall amounted to roughly twice the average value of the net precipitation. This agrees with observed values. The average simulated soil water fluxes for 1993 are presented in table 1.

The simulated values of bromide concentrations in the drain pipes and the content of bromide in the soil profile corresponded reasonably well with the observed values. The model was calibrated for the dispersion length L_{dis} and plant uptake F was set at 0.5. The best fit was obtained for $L_{dis} = 6$ cm.

Concentration levels of simazine in the drain pipes could be reasonably well simulated, if the model was extended to a concept for imaginary drains and segmentation of upper boundary conditions. Simazine was only observed and simulated in the drain pipes during the summer period. The concentration level varied from $0.1 \mu\text{g l}^{-1}$ to $7 \mu\text{g l}^{-1}$.

Scenario analyses with the extended SWACRO model

The objective of the scenario analysis is to formulate design and management criteria for polder areas in order to reduce pesticide leaching. The scenario analyses were undertaken with the extended, calibrated SWACRO model. Generally, the scenario analysis showed that pesticide characteristics (sorption, transformation and volatilisation), time of application of the pesticide, soil characteristics (e.g. type of soil, preferential flow, organic matter content) lateral boundary conditions and weather conditions define the concentration of pesticides in the drain pipes and thereby the fraction of the dosage leached.

In the first scenario the influence of the time of application of soil fumigants, such as 1,3-dichloropropene, on leaching in loamy sands was studied for the period 1960 - 1989. Results show that differences between the concentration in the drain pipes between application in September or November may vary over a factor 1000. Both precipitation and soil temperatures strongly influence the concentration in the drain pipes and the fraction of the dosage leached. If 1,3-dichloropropene is applied in November, the average fraction of the dosage leached was calculated at 1%. Under very wet weather conditions the maximum fraction of the dosage leached was calculated at 5%. Leaching is reduced considerably if the latest application date is set at October 1st.

In the second scenario, the influence of sorption and transformation at loamy sands and cracked clay soils was studied for the period 1960 - 1989. Important conclusions of this scenario are that under the same conditions (sorption and transformation characteristics, organic matter content) the fraction of the dosage leached

is higher for cracked clay soils than for loamy sands, especially if sorption is significant. For weakly sorbing ($K_F = 1 \text{ cm}^3 \text{ g}^{-1}$) and persistent pesticides ($DT_{50} = 100$ days) the fraction of the dosage leached amounted to 3 - 25% if the pesticide is applied in May and 5 - 35% if the pesticide is applied in September. The yearly variations in leaching were generated by differences in weather conditions.

In order to mark the most vulnerable areas for pesticide leaching in the IJsselmeerpolders, soil maps for potential leaching were created. Three different soil types were distinguished: loamy sand, loamy clay and cracked clays with an organic matter content varying from 0 to 10%. With relation to seepage, three different categories were distinguished: upward, downward and no seepage. Leaching was calculated for two theoretical pesticides ($K_F = 1 \text{ cm}^3 \text{ g}^{-1} / DT_{50} = 50$ days: $K_F = 1.5 \text{ cm}^3 \text{ g}^{-1} / DT_{50} = 100$ days) and application in May and September. Generally, sensitivity for leaching is low to moderate for areas without preferential flow and a high organic matter content (loamy sands and loamy clay soils) and high to very high for areas with preferential flow and a low organic matter content (cracked clay soils).

In the last scenario, the impact of new design criteria on leaching of pesticides was studied. For soils without preferential flow, the depth of the drain pipes has a direct impact on leaching. If the depth of the drain pipes is increased 0.2 m (from 0.85 to 1.05 m below soil surface), leaching is reduced by 25 - 65%. However, if the drain pipes are installed at a depth of 1.25 m, reduction is even stronger and amounts to 50 - 90%. For cracked clay soils, it was observed that leaching is mainly caused by preferential flow through cracks. The concentration of the pesticides in the drain pipes is mainly influenced by the depth of the plough layer. If this depth is increased by 0.1 m from 0.35 to 0.45 m - soil surface, reductions of 15% up to 70% can be reached. The largest reductions are achieved if sorption is high.

Evaluation and recommendations

The scenario analysis indicated that the leaching of

pesticides can be very high, especially for cracked clay soils with a low organic matter content. However, the observed concentration of the selected pesticides at the experimental fields was usually low. Generally, the transformation rate of the selected pesticides was high compared to data mentioned in literature. Only for simazine and 1,3-dichloropropene (applied in November) could significant leaching be observed.

According the Pesticide Act of 1975 registration of pesticides is only allowed if the pesticide meets two criteria:

- Concentration of pesticide residues in the ground-water at 10 m below soil surface should be less than $0.1 \mu\text{g l}^{-1}$;
- Exposure concentrations in collector drains caused by drift should be lower than a formulated maximum concentration (short-term effects on aquatic organisms).

The present legislation for the registration of pesticides is not satisfactory because of the following reasons:

- It is assumed that drift is the only way for a pesticide to enter the collector drain. In this thesis, it was indicated that leaching also contributes significantly to presence of pesticides in collector drains, secondary and main drains;
- In the calculation of concentration of pesticide residues in the groundwater at 10 m below soil surface, the local hydrological conditions are not taken into account. Due to upward seepage it is most unlikely that traces of pesticides will be detected at 10 m below soil surface in the IJsselmeerpolders;
- For the calculation of the concentration of pesticides at 1 m below the soil surface only a standard meteorological year is used. In this thesis, it was demonstrated that leaching is highly influenced by meteorological conditions;
- For the calculation of the concentration of pesticides at 1 m below the soil surface, preferential flow is not taken into account. In this study, it was demonstrated that leaching is highly influenced by preferential flow;
- Transformation and sorption characteristics used for the calculation of the concentration of pesticides at 1 m below the soil surface do not coincide with local circumstances. In this study, it was

observed that sorption and transformation characteristics did not agree with data mentioned in literature.

Measurements of concentrations of pesticides at the pumping stations of the IJsselmeerpolders in 1992 - 1994 indicated that traces of several pesticides were present. The sum of pesticides during the summer and winter period amounted to 2.0 and 0.4 $\mu\text{g l}^{-1}$ respectively. These pesticides enter the surface water by drift, atmospheric deposition and leaching.

For the IJsselmeerpolders, the use of the *TOXWA* model (behaviour of pesticides in collector drains) in combination with the *SWACRO* model is recommended. If the estimated concentration of the pesticides is above the standard limits, several measures can be taken (which may depend on the local circumstances, the type of pesticide and the method of application):

- Prohibition of the use of the pesticide;
- Reduction of leaching by introducing new application techniques, such as application of granules in the ridges;
- Reduction of leaching by allowing pesticide application only during a certain period;
- Introduction of new drainage criteria with increasing drain depths;

- Decreasing preferential flow (e.g. by ploughing).
- The effect of these measures can be calculated with *SWACRO / TOXWA*.

Some recommendations for additional research in the future are presented:

- Further calibration and validation of the model *SWACRO*;
- Research on the predicting value of simulation models for the calculation of the leaching of pesticides;
- Additional research on preferential flow, different routes of emission such as drift and surface runoff, sorption, transformation of pesticides and its metabolites for various soils;
- Additional field research for areas in the IJsselmeerpolders which are vulnerable for pesticide leaching;
- Intensification of monitoring programs for pesticides and metabolites in surface water;
- Research on the performance and effects of pesticides in surface water;
- Research on the use of *SWACRO* regional objectives.

Samenvatting

Samenvatting

In dit proefschrift wordt verslag gedaan van een onderzoek naar de emissie van bestrijdingsmiddelen naar het oppervlaktewater via drainagebuizen. Het onderzoek is verricht in de IJsselmeerpolders op gescheurde kleigronden en lichte zavelgronden. In het eerste hoofdstuk is een overzicht gegeven van het gebruik van bestrijdingsmiddelen in Nederland en de gevolgen van het gebruik voor de waterkwaliteit van het oppervlaktewater. Daarnaast wordt een overzicht gegeven van het studiegebied, de IJsselmeerpolders. Het tweede hoofdstuk beschrijft het computersimulatiemodel *SWACRO*, waarmee het gedrag van water, conservatieve stoffen en bestrijdingsmiddelen in de onverzadigde zone beschreven wordt. In het derde hoofdstuk worden het laboratorium- en het veldonderzoek beschreven. Veldonderzoek is uitgevoerd op drie verschillende proefvelden in respectievelijk de Noord-oostpolder, Oostelijk Flevoland en Zuidelijk Flevoland. Laboratorium- en velddata zijn gebruikt voor de calibratie van het model *SWACRO*. Het gecalibreerde model is vervolgens gebruikt voor het verrichten van scenario studies. Het laatste hoofdstuk bevat een evaluatie en een aantal aanbevelingen.

Algemeen

In 1994 werden in Nederland ongeveer 300 verschillende bestrijdingsmiddelen gebruikt met een verbruik van ongeveer 20.000 ton actieve stof. Het gemiddeld gebruik van bestrijdingsmiddelen is hoog in vergelijking met de ons omringende landen en bedroeg in 1994 ongeveer 8 kg ha⁻¹. Vijf belangrijke groepen kunnen worden onderscheiden: bodemontsmettingsmiddelen (42%), fungiciden (26%), herbiciden (19%), insecticiden/araciden (4%) en overige bestrijdingsmiddelen (9%) (NEFYTO, 1994).

Nadelige gevolgen van het gebruik van deze middelen op de volksgezondheid en het milieu worden reeds gedurende geruime tijd onderkend. Een aantal bestrijdingsmiddelen zijn teruggevonden in het grond- en oppervlaktewater en zelfs in de Noordzee. Hun aanwezigheid kan grote gevolgen hebben voor het ecosysteem of voor de kwaliteit van drinkwatervoorraden. In het Meerjarenplan Gewasbescherming zijn een drietal doelstellingen geformuleerd: reductie van de afhankelijkheid, het gebruik en de emissie van bestrijdingsmiddelen naar het grond- en oppervlaktewater en de atmosfeer.

Het huidige onderzoek richt zich op de laatste doelstelling van het Meerjarenplan Gewasbescherming en dan met name op de emissie van bestrijdingsmiddelen naar grond- en oppervlaktewater. Doel is te komen tot maatregelen met betrekking tot ontwerp en beheerscriteria voor het waterbeheerssysteem. Hiermee kan tevens een bijdrage worden geleverd aan een geïntegreerd bestrijdingsmiddelenbeleid met een afname van de emissie van bestrijdingsmiddelen naar het milieu. Een aanvullende doelstelling is het ontwikkelen en de calibratie van een computersimulatiemodel.

Ontwikkeling van een computersimulatiemodel

Voor de waterbeweging in de (on)verzadigde zone is in deze studie het model *SWACRO* gebruikt. *SWACRO* is een eendimensionaal, dynamisch, deterministisch model. De basis van het model wordt gevormd door de partiële differentiaalvergelijking voor onverzadigde stroming in poreuze media, de Richards vergelijking. De bodem is onderverdeeld in een aantal compartimenten die kunnen verschillen in hoogte. Eén of meer compartimenten vormen een bodemlaag met een voor

elke laag specifieke waterretentiekarakteristiek en onverzadigde-doorlatendheidscurve. Voor de bovenrand worden de interceptie, de actuele bodemverdamping en de actuele transpiratie berekend. In de onverzadigde zone treedt alleen de stroming in verticale richting op, terwijl voor de verzadigde zone of bij het optreden van schijnwaterspiegels het watertransport zowel in verticale als horizontale richting optreedt. De grootte van de flux aan de onderrand is afhankelijk van het verschil in stijghoogte tussen het grondwater in de Holocene bovengrond en de Pleistocene ondergrond enerzijds en de doorlatendheid van de ondergrond anderzijds.

Voor het gedrag van bestrijdingsmiddelen in de onverzadigde zone is het model *PESTLA* gebruikt. *PESTLA* gaat uit van de convectie/dispersievergelijking, niet-lineaire sorptie volgens de Freundlich vergelijking, temperatuurafhankelijke eerste-orde afbraak en passieve opname door de plant. Dit model is uitgebreid met het transport van pesticiden in de gasfase en microbiële afbraak. Het op deze wijze uitgebreide model *PESTLA* is geïmplementeerd als subroutine in het model *SWACRO*. Het uitgebreide model *SWACRO* beschrijft de stroming van water door de bodem, de gewasopname van water, gewasopbrengst en het gedrag van conservatieve stoffen en bestrijdingsmiddelen in de (on)verzadigde zone. Daarnaast bestaat thans een optie voor het berekenen van preferente stroming en transport volgens het concept van mobiel/immobiel bodemwater.

Laboratorium en veldexperimenten

De veldexperimenten zijn uitgevoerd op drie proefvelden in de IJsselmeerpolders: proefveld Noordoostpolder, proefveld Oostelijk Flevoland en proefveld Zuidelijk Flevoland. Op deze drie proefvelden is het gedrag van water, conservatieve stoffen en bestrijdingsmiddelen in de bodem gevolgd. Vier verschillende bestrijdingsmiddelen zijn in het onderzoek opgenomen:

- Cis en trans 1,3-dichloorpropeen en metamitron op het proefveld Noordoostpolder (lichte zavel);
- Aldicarb op het proefveld Oostelijk Flevoland (zwarte klei);

- Simazine op het proefveld Zuidelijk Flevoland (zwarte klei).

De parameters die de waterretentiekarakteristiek, onverzadigde doorlatendheidscurve en andere specifieke kenmerken voor de verschillende onderscheiden bodemlagen van de proefvelden beschrijven, zijn bepaald in het laboratorium. Deze parameters dienen als input voor het model *SWACRO*.

Sorptie- en afbraakkarakteristieken van de in het onderzoek betrokken bestrijdingsmiddelen zijn bepaald in het laboratorium. Deze parameters zijn als input voor het model *SWACRO* gebruikt. Het betreft hier:

- *Metamitron*: de afbraak kan worden beschreven met een eerste orde vergelijking. De referentie afbraakcoëfficiënt voor de ploeglaag ($k_{1,ref}$ bij 20 °C) bedroeg 0,1 d⁻¹. De afbraaksnelheid wordt sterk beïnvloed door de bodemlaag en de bodemtemperaturen. De K_{om} waarde (Freundlich coëfficiënt gedeeld door organische stof gehalte) bedraagt 42 - 91 cm³ g⁻¹. Sorptie neemt toe met de diepte;
- *Cis en trans 1,3-dichloorpropeen*: de afbraak wordt beschreven met een vergelijking voor de microbiële afbraak in de ploeglaag en met een eerste orde vergelijking voor de bodem onder de ploeglaag. De afbraaksnelheid wordt sterk bepaald door de bodemtemperatuur. Afhankelijk van bodemtemperatuur, concentratie en bodemdiepte, varieert de K_{om} van 52 - 156 cm³ g⁻¹;
- *Aldicarb-sulfoxide/sulfon*: de afbraak van aldicarb-sulfoxide/sulfon werd bestudeerd voor de ploeglaag en bleek zeer complex te zijn. Ook hier werd versnelde afbraak waargenomen, waarschijnlijk door microbiële adaptatie. Ongeveer de helft van de hoeveelheid aldicarb werd omgezet in aldicarb-sulfoxide en minder dan 35% in aldicarbsulfon. De K_{om} bedraagt 22 cm³ g⁻¹;
- *Simazine*: de afbraak wordt beschreven met een eerste orde vergelijking. De referentie afbraakcoëfficiënt voor de ploeglaag bij 15 °C ($k_{1,15}$) bedraagt 0,09 d⁻¹. De K_{om} bedraagt 30 cm³ g⁻¹.

Op het proefveld Noordoostpolder zijn data verzameld op drie verschillende veldjes waar tulpen werden verbouwd. De bodem bestaat uit lemig zand. Op een diepte van ongeveer 0,9 tot 1,2 m - maaiveld wordt een

vrijwel ondoorlatende detrituslaag aangetroffen. De drainbuizen met een drainafstand van 4 m liggen bovenop deze detrituslaag. Op het proefveld Oostelijk Flevoland werden de data verzameld op twee verschillende velden waar aardappelen werden verbouwd. De bodem kan worden geclassificeerd als een zware, gescheurde kleigrond. Onder de bouwvoor tot een diepte van ongeveer 1 m worden grote scheuren aangetroffen. Deze scheuren staan onderling met elkaar in verbinding, waardoor de verzadigde doorlatendheid zeer hoog is en ongeveer 300 - 500 m d⁻¹ bedraagt. Beneden 1 m - maaiveld wordt ongerijpte klei aangetroffen met een zeer hoog watergehalte en een zeer lage doorlatendheid. De drainage ligt op een diepte van 0,95 m - maaiveld. Door de grote doorlatendheid van de bodem boven de drains bedraagt de drainafstand 48 m. Op het proefveld Zuidelijk Flevoland werden data verzameld onder een appelboomgaard. Ook hier kan de bodem worden geclassificeerd als een zware, gescheurde kleigrond. Draindiepte en -afstand bedragen hier respectievelijk 1,1 m en 24 m. Omdat de bodem onder de drainage vrijwel ondoorlatend is op alle proefvelden, is verondersteld dat het neerslagoverschot door de drainage wordt afgevoerd. Later is echter gebleken dat enige kwel en/of wegzijging is waargenomen op de proefvelden Noordoostpolder en Oostelijk Flevoland.

Twee verschillende type data kunnen worden onderscheiden:

- *Data betreffende bodemwaterfluxen:* neerslag, beregning, interceptie, grondwaterstanden, drainafvoeren, bodemvocht en evapotranspiratie;
- *Data betreffende fluxen van bromide en bestrijdingsmiddelen:* preferente stroming, concentratie van bromide en bestrijdingsmiddelen in het drainwater, concentratieprofielen van bromide en bestrijdingsmiddelen.

Op elk proefveld zijn van een aantal drains debietsproportionele monsters genomen, die zijn geanalyseerd voor het betreffende bestrijdingsmiddel en de bromideconcentratie. Op elk proefveld zijn eveneens bodembemonsteringen uitgevoerd om het gedrag van bestrijdingsmiddelen en bromide in de bodem te kunnen volgen.

Resultaten van de veldproeven laten duidelijk de ver-

schillen in de bodemkarakteristieken van de lichte zavelgronden in de Noordoostpolder en de gescheurde kleigronden in Oostelijk en Zuidelijk Flevoland zien. Voor het proefveld Noordoostpolder (drainafstand 4 m), Oostelijk Flevoland (48 m) en Zuidelijk Flevoland (24 m), bedroeg bij een maatgevende afvoer van 8 mm d⁻¹ de opbolling tussen de drains respectievelijk 0,5 m, 0,1 m en 0,1 m. De berging (van het maaiveld tot een diepte van 1.2 m) varieerde op de proefvelden Oostelijk en Zuidelijk Flevoland van 500 mm in de zomer tot 760 mm in de winter. Voor het proefveld Noordoostpolder varieerde de berging van 500 mm in de zomer tot 575 mm in de winter. Drainafvoeren worden op de proefvelden Noordoostpolder en Zuidelijk Flevoland zowel in de zomerperiode als in de winterperiode waargenomen. Op het proefveld Oostelijk Flevoland worden bij hoge uitzondering drainafvoeren in de zomer gemeten.

In het drainwater van het proefveld Noordoostpolder zijn concentraties van 1,3-dichloorpropeen en metamitron in het drainagewater gemeten. Bij injectie van 1,3-dichloorpropeen in de maand september, varieerde de concentratie van de cis- en trans-isomeer in het drainagewater van 0 tot 1 µg l⁻¹. Echter, indien 1,3-dichloorpropeen werd toegediend in november, nam de concentratie in het drainage water zeer sterk toe tot ongeveer 1200 µg l⁻¹ voor zowel de cis- als de trans-isomeer. De maximale concentratie werd ongeveer 60 dagen na injectie gemeten. Metamitron werd toegediend in het vroege voorjaar (februari/maart). De concentraties van metamitron in het drainagewater varieerden van 0 tot 0,5 µg l⁻¹. De hoogste concentraties werden gemeten in de zomerperiode. Op het proefveld Oostelijk Flevoland zijn de concentraties van aldicarb-sulfoxide/sulfon in het drainagewater gemeten. In het eerste meetjaar (1992/1993) werd aldicarb-sulfoxide/sulfon niet aangetoond. In het tweede meetjaar bedroegen de concentraties van aldicarb-sulfoxide/sulfon in het drainagewater respectievelijk 0 - 4 µg l⁻¹ en 0 - 1 µg l⁻¹. In het drainagewater van het proefveld Zuidelijk Flevoland zijn de concentraties simazine gemeten. Simazine werd toegediend in de periode maart t/m juli. De concentratie in het drainagewater varieerde van 0 tot 7 µg l⁻¹. De hoogste concentraties zijn gemeten gedurende de zomerperiode. Simazine werd aangetroffen tot 150 dagen na toediening.

De concentratie van bromide en de geselecteerde bestrijdingsmiddelen werd eveneens gemeten in de bodem. Bij injectie van 1,3-dichloorpropeen in de maand september, werd een versnelde afbraak waargenomen na 4 dagen. Ongeveer 2 maanden na toediening was de concentratie in het bodemprofiel gedaald tot de initieel gemeten concentratie. Metamitron is alleen gemeten in de bouwvoor (0 tot 0,2 m - maaiveld). Ongeveer 50 dagen na de toediening kon ruwweg 15% van de toegediende hoeveelheid nog worden aangetoond in de bodem. Bromide werd tegelijk met metamitron toegediend. Na 400 dagen en 400 mm drainafvoer, was ongeveer de helft van de toegediende bromide uitgespoeld. De andere helft kon worden aangetoond in het bodemprofiel. Op het proefveld Oostelijk Flevoland kon aldicarbulsulfoxide/sulfon tot twee weken na toediening nog worden aangetoond. Metingen betreffende de verplaatsing van bromide in het profiel bleken onbetrouwbaar. Ongeveer 30% van de toegediende hoeveelheid bromide werd teruggevonden in het drainagewater na 500 mm drainafvoer. Op het proefveld Zuidelijk Flevoland spoelde 40% van de toegediende hoeveelheid bromide uit via het drainagewater na 570 mm drainafvoer. Simazine werd alleen aangetoond in de bouwvoor (0 tot 0,3 m - maaiveld). De concentratie gedurende de winter en de zomer bedroeg respectievelijk 0,05 en 0,02 mg kg⁻¹ droge stof.

Op de proefvelden Noordoostpolder en Oostelijk Flevoland zijn aanvullende experimenten uitgevoerd om het eventueel voorkomen van preferente stroming na te gaan. Op het proefveld Noordoostpolder werd geen preferente stroming aangetoond. Op het proefveld Oostelijk Flevoland werd het voorkomen van preferente stroming aangetoond in de gescheurde laag beneden de bouwvoor. Indien de flux vanuit de bouwvoor (bij hoge neerslagintensiteit) de infiltratiecapaciteit van de ondergrond overtrof, liep het water de scheuren in. Door deze preferente stroming bereikten het water en de daarin opgeloste stoffen de drainbuizen veel sneller dan wanneer er geen scheuren in het profiel voorkamen. Ook op het proefveld Zuidelijk Flevoland werd dit preferent transport door scheuren aangetoond. Hier speelt bovendien dat de neerslag door de appelbomen ongelijk verdeeld wordt over het maaiveld. Hierdoor werden onder de appelbomen, vooral tijdens de zomerperiode, permanent natte en droge plekken

gevonden. Op de natte plekken lag de neerslagintensiteit ongeveer twee keer zo hoog als het gemiddelde.

Calibratie van het uitgebreide model SWACRO

De resultaten van de drie proefvelden zijn gebruikt voor de calibratie van het uitgebreide model SWACRO. De verzamelde data zijn gebruikt als input data en als data voor calibratie. De calibratie is uitgevoerd in drie stappen:

- *Calibratie van bodemwaterfluxen;*
- *Calibratie van de concentratie van bromide in het drainagewater en verplaatsing van bromide in het bodemprofiel;*
- *Calibratie van de concentratie van bestrijdingsmiddelen in het drainagewater en de verplaatsing van bestrijdingsmiddelen in het bodemprofiel.*

Parameters die werden geoptimaliseerd in de eerste calibratiestap werden constant gehouden in de tweede en derde calibratiestap.

Proefveld Noordoostpolder: Voor het proefveld Noordoostpolder zijn de bodemwaterfluxen gecalibreerd voor de grootte van de flux aan de onderrand van het gedefinieerde profiel. Resultaten van de calibratie laten een goede overeenstemming zien tussen de gemeten en berekende grondwaterniveaus en de gemeten en berekende drainafvoeren. Een waterbalans voor de periode 1989 - 1992 is te zien in tabel 1.

Ondanks het feit dat op het proefveld Noordoostpolder preferente stroming van water en transport van stoffen in de bodem niet werden aangetoond, kan het voorkomen van ruimtelijke variabiliteit in de stroming van water en het stoffentransport in de bodem niet worden uitgesloten. Preferent transport van bromide is berekend volgens het concept van mobiel en immobiel water. De bromide fluxen zijn geoptimaliseerd voor de verdeling van de bodem in een mobiele en immobiele fase, de uitwisselingscoëfficiënt tussen de mobiele en immobiele fase en de dispersiecoëfficiënt. Deze optimalisatie liet zien dat de verdeling van de bodem in een mobiele en een immobiele fractie een versnelde doorbraak van bromide geeft. Daarnaast wordt een lagere

Tabel 1. De waterbalans voor de proefvelden Noordoostpolder, Oostelijk Flevoland en Zuidelijk Flevoland

Proefveld	Neerslag (inclusief irrigatie)	Actuele evapotranspiratie	Flux door de bodem van het profiel (- = uit)	Laterale drainage (- = uit)
	(mm jr ⁻¹)	(mm jr ⁻¹)	(mm jr ⁻¹)	(mm jr ⁻¹)
Noordoostpolder (1989 - 1992)	850	523	-31	-296
Oostelijk Flevoland (maart 1992 - maart 1994)	962	541	-63	-358
Zuidelijk Flevoland appelbomen 1993	925	600	0	-325
Zuidelijk Flevoland gras 1993	925	560	0	-365

maximumconcentratie in de drains gesimuleerd en is bromide gedurende een veel langere periode in de drains waar te nemen. Ditzelfde effect kan echter worden bereikt wanneer de dispersielengte groter wordt gekozen. Voor de conventionele convectie/dispersie-vergelijking bedraagt de optimale dispersielengte 16 cm. Resultaten van de simulaties tonen aan dat zowel de emissie van bromide via de drains als het gedrag van bromide in de bodem redelijk goed overeenkomen met de waarnemingen.

Als eerste werd de concentratie van metamitron in de drains berekend met behulp van de Freundlich parameters, zoals vastgesteld in de laboratoriumproeven. De berekende concentratie was zowel bij toediening in 1990 als 1991 gelijk aan 0. Daarnaast werd het model gecalibreerd voor de Freundlich coëfficiënt. Voor de Freundlich exponent werd een waarde gekozen van 0,74, zoals was vastgesteld in de laboratorium experimenten. Nu kwam de gemeten waarde van metamitron in de drains redelijk goed overeen met de berekende waarde. De optimale waarde van de Freundlich coëfficiënt werd vastgesteld op 3,1 cm³ g⁻¹. Deze waarde is ongeveer gelijk aan de gemiddelde waarde die werd gevonden voor de verschillende bodemlagen zoals bepaald in de laboratorium experimenten.

De concentratie van 1,3-dichloorpropeen in de drains kon redelijk goed worden voorspeld wanneer gebruik

werd gemaakt van de Freundlich parameters zoals vastgesteld in de laboratoriumproeven. Daarnaast werd het model gecalibreerd voor de Freundlich exponent en coëfficiënt. De optimale waarden kwamen overeen met de waarnemingen in de laboratoriumexperimenten. Zowel de veldexperimenten als de gevoeligheidsanalyse toonden aan dat de bodemtemperatuur en het neerslagoverschot een grote invloed hebben op de toestroming van 1,3-dichloorpropeen naar de drains. Door een relatief hoog vochtgehalte in de bodem, bedroeg de vervluchtiging naar de atmosfeer nooit meer dan 10% van de toegediende dosis. Indien cis 1,3-dichloorpropeen wordt toegediend in september bedraagt de emissie naar de atmosfeer 1 - 2% van de toegediende dosis. Bij toediening in november neemt de vervluchtiging toe en bedraagt ongeveer 6%. De reden hiervoor is dat de afbraak in november veel trager verloopt. Verschillen tussen de cis- en trans-isomeer kunnen worden verwaarloosd voor wat betreft sorptie, afbraak en concentratie in het drainagewater. Echter, vervluchtiging naar de atmosfeer is aanzienlijk lager voor de trans-isomeer en bedraagt ongeveer tweederde van de emissie van de cis-isomeer.

Proefveld Oostelijk Flevoland: Om de stroming van water in de gescheurde gronden van Oostelijk Flevoland goed te kunnen beschrijven zonder het eendimensionale concept van het model *SWACRO* te verlaten, werden direct onder de bouwvoor op een

diepte van 0,35 m denkbeeldige drains gelegd. Deze drains karakteriseren de scheuren die direct onder de bouwvoor worden aangetroffen. Om het effect van de installatie van deze drain te kunnen aangeven werden berekeningen uitgevoerd voor zowel het conventionele concept alsmede het concept met de denkbeeldige drains. Het model is gecalibreerd voor de grootte van de flux aan de onderrand van het gedefinieerde profiel en de verzadigde doorlatendheid van de laag direct onder de denkbeeldige drains. Resultaten van de berekeningen geven aan dat de implementatie van de denkbeeldige drains een betere beschrijving van de bodemwaterfluxen geeft.

Wanneer de drainafvoeren worden berekend zonder de denkbeeldige drains, treden grote verschillen op tussen de berekende en de gemeten drainafvoer vooral in de zomer en herfst. Het verschil ontstaat mede omdat voor het conventioneel concept het vochtgehalte in de bodem eerst wordt aangevuld tot veldcapaciteit alvorens de drains tot afvoer komen. Dit komt niet overeen met de waarnemingen, waarbij al drainafvoeren worden waargenomen voordat de ondergrond verzadigd is. Er werd berekend dat ongeveer éénderde deel van het water door de scheuren naar de drains loopt. Het overige deel komt via de bodemmatrix in de drainbuizen terecht. Een waterbalans voor de periode maart 1992 t/m maart 1994 staat gepresenteerd in tabel 1.

De implementatie van de denkbeeldige drains heeft een sterke invloed op de concentratie van bromide in het drainagewater. Deze concentratie kon redelijk worden berekend voor het concept met de denkbeeldige drains. De bromide concentraties in de drainagebuizen waren een menging van de concentratie aan de onderkant van de bouwvoor en op een diepte van 0,95 m - maaiveld. Het model is gecalibreerd voor opname door de plant F en de dispersielengte L_{dis} . De beste resultaten werden gevonden voor $F = 0$ en $L_{dis} = 5$ cm. Het experiment met een neerslagsimulator liet zien dat wanneer de neerslagintensiteit groot is, het grootste deel van het bodemwater door de scheuren loopt.

Voor het eerste meetjaar (1992/1993) bedroeg de gesimuleerde concentratie van aldicarb-sulfoxide/sulfon $1 \mu\text{g l}^{-1}$. De gemeten concentraties waren echter

beneden de detectie limiet. Dit wordt waarschijnlijk veroorzaakt door het feit dat aldicarb wordt toegediend in de bouwvoor. In de berekeningen werd er van uitgegaan dat de neerwaartse flux van water en stoffen uniform is voor het hele proefveld. In werkelijkheid zal de verdeling van de neerslag over maaiveld en de infiltratie van water in de bodem verre van uniform zijn, ondermeer door oppervlakkige afstroming van neerslag vanaf de ruggen naar de voren. In het tweede meetjaar (1993/1994) werd aldicarb toegediend volgens de volleveldsmethode en daarna ingewerkt in de bodem. Aldicarb-sulfoxide/sulfon werd in het drainagewater teruggevonden tot 450 dagen na toediening. De gemeten concentratie van aldicarb-sulfoxide/sulfon in het drainagewater bedroeg respectievelijk $0 - 4 \mu\text{g l}^{-1}$ en $0 - 1 \mu\text{g l}^{-1}$. Dit kwam niet overeen met de gesimuleerde waarnemingen, waarbij er van uitgegaan werd dat aldicarb-sulfoxide/sulfon zeer snel werd afgebroken. Mogelijk wordt de afbraak van aldicarb in de lagen beneden de bouwvoor sterk vertraagd. In de laboratoriumexperimenten werd de afbraaksnelheid alleen bepaald voor de bouwvoor.

Proefveld Zuidelijk Flevoland: Om de stroming van water in de gescheurde gronden van Zuidelijk Flevoland goed te beschrijven zonder het eendimensionale concept van het model SWACRO te verlaten, werden opnieuw direct onder de bouwvoor denkbeeldige drains gelegd conform het concept van het proefveld Oostelijk Flevoland. Door de aanwezigheid van een dik pakket ongerijpte klei direct onder de (echte) drains trad geen kwel of wegzijging op. Naast de aanwezigheid van scheuren in het profiel, werd het preferent transport van water en stoffen extra versterkt door het optreden van een grote ruimtelijke variabiliteit in de verdeling van de neerslag op het maaiveld. Deze variabiliteit wordt veroorzaakt door verschil in begroeiing: de helft van het oppervlak in de boomgaard bestaat uit appelbomen, de andere helft uit gras, terwijl de appelbomen de neerslag sterk herverdelen. Op het proefveld zijn metingen verricht naar de interceptie en de herverdeling van de neerslag door de appelbomen. De grootste verschillen in de verdeling van de neerslag traden op gedurende de zomerperiode. Om de stroming van water goed te kunnen beschrijven zonder het eendimensionale concept van het model SWACRO te verlaten, werd het proefveld onderverdeeld in vier

secties van gelijke grootte. De drainafvoer werd berekend als een gemiddelde van de gesimuleerde drainafvoeren per sectie. Het resultaat gaf goede overeenkomsten tussen gemeten en berekende drainafvoeren. Wanneer de neerslag uniform over het maaiveld werd verdeeld, trad geen drainafvoer op gedurende de zomerperiode. Dit werd echter wel waargenomen. Berekend werd dat in de natste sectie ongeveer twee keer de gemiddelde hoeveelheid neerslag was gevallen. Dit kwam overeen met de gemeten waarden. Een waterbalans voor de sectie met appels en gras staat weergegeven in tabel 1.

De gesimuleerde concentraties van bromide in de drains en de verplaatsing van bromide in het bodemprofiel konden redelijk goed worden gesimuleerd. Het model werd gecalibreerd voor de dispersielengte L_{dis} en de opname door de plant, F , werd vastgezet op 0,5. De beste resultaten werden gevonden voor $L_{dis} = 6$ cm. De concentratie van simazine in de drains kon goed worden gesimuleerd voor het modelconcept met denkbeeldige drains en de segmentatie van de neerslag. Simazine werd alleen in de drain waargenomen gedurende de zomerperiode. De concentratie in het drainagewater varieerde van 0 tot $7 \mu\text{g l}^{-1}$.

Scenariostudies met het uitgebreide model SWACRO

Het doel van de scenariostudies is om voor een aantal situaties voorschriften te formuleren met betrekking tot een geïntegreerd bestrijdingsmiddelenbeleid met een afname van de emissie van bestrijdingsmiddelen naar het milieu. Deze scenario's hebben zowel betrekking op aspecten van inrichting, als op de toepassing van bestrijdingsmiddelen in de polder. De scenariostudies werden uitgevoerd met het gecalibreerde model SWACRO. Over het algemeen lieten de scenariostudies zien dat de karakteristieken van de bestrijdingsmiddelen (sorption, afbraak en vervluchtiging), het tijdstip van toediening, bodemkarakteristieken (bodemfysische functies, preferente stroming, organische stofgehalte), de drainage omstandigheden, het gewas en het weer, de concentratie bestrijdingsmiddelen in de drains en daarmee de fractie van de toegediende hoeveelheid die uitspoelt naar het oppervlaktewater bepalen.

In het eerste scenario is gekeken naar het effect van het tijdstip waarop grondontmettingsmiddelen, zoals 1,3-dichloorpropeen, worden geïnjecteerd op de uitspoeling. De berekeningen zijn uitgevoerd voor een lichte zavelgrond gedurende de periode 1960 - 1989. Resultaten van de berekeningen lieten zien dat bij toediening in november in plaats van september, de concentratie in het drainagewater meer dan 1000 keer hoger kan liggen. Zowel het neerslagoverschot als de bodemtemperaturen beïnvloeden de concentratie in de drains en de uitgespoelde fractie van de toegediende hoeveelheid sterk. Bij toediening in november spoelde gemiddeld ongeveer 1% en maximaal 5% van de toegediende hoeveelheid uit. De uitspoeling wordt sterk beperkt wanneer dichloorpropeen wordt geïnjecteerd voor 1 oktober.

In het tweede scenario is gekeken naar de invloed van sorptie en afbraak voor zowel lichte zavelgronden als gescheurde kleigronden voor de periode 1960 - 1989. Een belangrijke conclusie van de berekeningen is dat onder dezelfde condities (sorption, afbraak, organische stofgehalte) de fractie die uitspoelt via de drains voor gescheurde kleigronden hoger is dan voor lichte zavelgronden, vooral wanneer de sorptie sterk is. Voor zwak sorberende ($K_F \leq 1 \text{ cm}^3 \text{ g}^{-1}$) en persistente bestrijdingsmiddelen (DT_{50} (= halfwaardetijd) ≥ 100 dagen) bedroeg de uitgespoelde fractie bij toediening in mei 3 - 25% en bij toediening in september 5 - 35%. Jaarlijkse verschillen werden veroorzaakt door verschillen in meteorologische omstandigheden.

Om de meest kwetsbare gebieden voor de emissie van bestrijdingsmiddelen via de drains naar het oppervlaktewater aan te geven, zijn potentiële uitspoelingskaarten voor de IJsselmeerpolders gemaakt. Hiervoor werden de bodem- en kwelkaart van de polder enigszins gesimplificeerd. Drie verschillende bodemtypes werden onderscheiden: lichte zavelgronden, zware zavelgronden en gescheurde kleigronden. Daarnaast werden drie verschillende kwelklassen onderscheiden: kwel, wegzijging, geen kwel/wegzijging. Uitspoeling werd berekend voor twee theoretische bestrijdingsmiddelen ($K_F = 1 \text{ cm}^3 \text{ g}^{-1} / DT_{50} = 50$ dagen en $K_F = 1,5 \text{ cm}^3 \text{ g}^{-1} / DT_{50} = 100$ dagen) met twee verschillende toedieningstijdstippen (mei en september). Over het algemeen kan worden vastgesteld dat de uitspoeling

laag tot matig is in gebieden waar het organische-stof gehalte hoog is en geen preferente stroming voorkomt. De uitspoeling is hoog tot zeer hoog in gebieden waar het organische stof gehalte laag is en preferente stroming voorkomt.

In het laatste scenario is gekeken naar de invloed van nieuwe drainagecriteria op de emissie van bestrijdingsmiddelen. Voor gronden zonder preferent transport, heeft de diepte waarop de drains worden gelegd een directe invloed op de emissie van bestrijdingsmiddelen via de drains. Wanneer draindiepte toeneemt van 0,85 tot 1,05 m - maaiveld, neemt de emissie af met 25 - 65%. De reductie wordt groter naarmate de drains dieper worden gelegd. Bij een draindiepte van 1,25 m bedraagt de reductie 50 - 90%. Voor de gescheurde kleigronden is waargenomen dat emissie via de drains voornamelijk plaatsvindt door preferent transport via de scheuren. Hier wordt de grootte van de emissie voornamelijk bepaald door de diepte waarop de scheuren in het profiel beginnen. Indien de dikte van de bouwvoor wordt vergroot met 0,1 m, zodat de scheuren beginnen op een diepte van 0,45 m, kan een reductie van de emissie met 15 - 70% worden bereikt. De grootste reducties worden bereikt indien de sorptie hoog is.

Evaluatie en aanbevelingen

In dit proefschrift werd een uitgebreid veldonderzoek verricht naar de emissie van vier verschillende bestrijdingsmiddelen naar het oppervlaktewater. In een aantal situaties werd aangetoond dat een aanzienlijk deel van de toediende hoeveelheid via de drains in de kavelsloten terecht komt (1,3-dichloorpropeen bij toediening in november en simazine bij toediening op gescheurde kleigronden). Over het algemeen waren de concentraties van de gemeten bestrijdingsmiddelen in het drainagewater laag. Metingen in het laboratorium gaven aan dat de geselecteerde bestrijdingsmiddelen over het algemeen sneller afbreken dan in de literatuur werd aangegeven. Voor dichloorpropeen en aldicarb is waarschijnlijk sprake van microbiële afbraak. De scenariostudies geven echter aan dat emissie van bestrijdingsmiddelen aanzienlijk kan zijn. Vooral op de gescheurde kleigronden met een laag organische stof

gehalte werden vanwege preferent transport hoge emissiepercentages berekend.

Van 1992 tot 1994 zijn bij de gemalen van Oostelijk en Zuidelijk Flevoland de concentratie van ongeveer 70 verschillende bestrijdingsmiddelen in het uitgeslagen water debietproportioneel gemeten. In dit water werden verschillende bestrijdingsmiddelen teruggevonden. Van de bestrijdingsmiddelen die in het kader van dit onderzoek zijn onderzocht is alleen simazine in relatief hoge concentraties teruggevonden. De gemiddelde som van de concentratie bestrijdingsmiddelen bedroeg 's zomers ongeveer $2,0 \mu\text{g l}^{-1}$ en 's winters $0,4 \mu\text{g l}^{-1}$. Dit geeft aan dat een aantal bestrijdingsmiddelen via drift en/of atmosferische depositie en/of uitspoeling in oppervlaktewater terecht komen (oppervlakkige afstroming mag in de IJsselmeerpolders worden verwaarloosd).

De wetgeving voor toelating van bestrijdingsmiddelen in Nederland schrijft voor dat er een risicobeoordeling moet plaatsvinden, waarbij onder gestandaardiseerde omstandigheden de concentratie van residuen van bestrijdingsmiddelen in grondwater op een diepte van 10 m - maaiveld berekend wordt. Deze concentratie mag niet groter zijn dan $0,1 \mu\text{g l}^{-1}$. Daarnaast worden voor kavelsloten eveneens berekeningen uitgevoerd waarbij wordt verondersteld dat bestrijdingsmiddelen alleen via drift in het oppervlaktewater kunnen komen. Bij de toelating wordt bij de modelmatige risicobeoordeling voor het oppervlaktewater gerekend met bepaalde driftpercentages, welke voornamelijk afhangen van toepassingswijze, type teelt en gewas. Deze studie heeft aangetoond dat de bovengenoemde wetgeving voor wat betreft de IJsselmeerpolders op een aantal punten niet voldoet:

- In het huidige toelatingsbeleid wordt geen rekening gehouden met plaatselijke hydrologische omstandigheden. Door de optredende kwel geldt voor een groot deel van de IJsselmeerpolders dat het zeer onwaarschijnlijk is dat bestrijdingsmiddelen op een diepte van 10 m zullen worden teruggevonden;
- In deze studie werd aangetoond dat de emissie van bestrijdingsmiddelen via de drains sterk afhankelijk is van meteorologische condities. In het huidige toelatingsbeleid wordt gerekend met een "standaard" hydrologisch jaar. Gebleken is echter dat het

- beter is om uit te gaan van het gemiddelde van een aantal hydrologische jaren;
- In het huidige toelatingsbeleid wordt geen rekening gehouden met preferent transport. Deze studie heeft echter aangetoond dat preferent transport een zeer grote invloed heeft op de uitspoeling van pesticiden;
 - Transformatie- en sorptiekenarakteristieken kwamen vaak niet overeen met de literatuurgegevens. Om betrouwbare resultaten voor de berekeningen te krijgen, dienen transformatie- en sorptiekenarakteristieken voor de betreffende gronden te worden vastgesteld;
 - Behalve via drift kunnen bestrijdingsmiddelen ook via de drains in het oppervlaktewater terecht komen. Hier dient in de toekomst rekening mee te worden gehouden. Vooral voor middelen waarvoor lage driftpercentages worden aangehouden, kan de emissie via de drains een belangrijke bijdrage leveren.

In 1996 werd het model *TOXSWA* geïntroduceerd. Dit model berekent het gedrag van bestrijdingsmiddelen in het oppervlaktewater en schat de chronische en acute toxiciteit van bestrijdingsmiddelen bij blootstelling aan aquatische organismen. Voor de kavelsloten in de IJsselmeerpolders wordt aanbevolen dit model toe te passen en als input de resultaten van het model *SWACRO* en de geschatte driftemissies te gebruiken. Indien bestrijdingsmiddelen worden aangetroffen boven de vastgestelde normen, kunnen de mogelijk volgende acties worden ondernomen (afhankelijk van het type bestrijdingsmiddel, de toepassing en de grondsoort):

- Verbieden van het gebruik van het betreffende bestrijdingsmiddel;
- Toestaan van het gebruik alleen binnen een bepaalde periode of binnen een bepaalde zone;
- Toediening van granulaten (b.v. aldicarb) in de ruggen in plaats van volleldstoepassing;
- Aanpassen van de draindiepte in nieuw te draineren gebieden;
- Beperken van preferente stroming (b.v. in de IJsselmeerpolders door het vergroten van de ploeglaag).

Tenslotte worden een aantal aanbevelingen gedaan voor aanvullend onderzoek. De belangrijkste aanbevelingen zijn:

- Verdere calibratie en validatie van het model *SWACRO*;
- Onderzoek naar de voorspellende waarde van modellen bij de berekening van de emissie;
- Aanvullend onderzoek naar preferent transport, andere emissieroutes dan uitspoeling, sorptie en transformatie van pesticiden en metabolieten voor verschillende gronden;
- Intensivering van monitoringsprogramma's betreffende bestrijdingsmiddelen en metabolieten op regionale schaal;
- Aanvullend veldonderzoek naar de emissie van bestrijdingsmiddelen in de meest kwetsbare gebieden in de IJsselmeerpolders;
- Meer onderzoek naar het gedrag en de effecten van bestrijdingsmiddelen in oppervlaktewater;
- Onderzoek naar het gebruik van modellen zoals *SWACRO* voor regionale toepassingen.

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List of Symbols

LIST OF SYMBOLS

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SYMBOL	DEFINITION	DIMENSION
a	regression coefficient	(-)
a_{dev}	parameter	L^{-1}
a_i	parameter representing crop dependant saturation value	$(L\ T^{-1})$
a_k	parameter representing the segmentation of the precipitation	(-)
a_m	constant	(-)
a_r	geometry factor for radial flow depending on the flow conditions	(-)
b	regression coefficient	(-)
b_1	parameter	(-)
b_2	parameter	(-)
b_3	parameter	(Θ^{-1})
C	differential soil moisture capacity	(L^{-1})
c	regression coefficient	(-)
c^*	total solute concentration in all phases	$(L^{-3}\ M)$
c_g	concentration in the gas phase	$(L^{-3}\ M)$
c_l	concentration in the liquid phase	$(L^{-3}\ M)$
$c_{l,n}$	concentration in the liquid phase for compartment n	$(L^{-3}\ M)$
$c_{l,ref}$	reference concentration in the liquid phase	$(L^{-3}\ M)$
$c_{l,m}$	concentration in the mobile fraction of the liquid phase	$(L^{-3}\ M)$
$c_{l,i}$	concentration in the immobile fraction of the liquid phase	$(L^{-3}\ M)$
D_{dif}	diffusion coefficient	$(L^2\ T^{-1})$
$D_{dif,air}$	vapour diffusion coefficient in air	$(L^2\ T^{-1})$
$D_{dif,w}$	diffusion coefficient in water	$(L^2\ T^{-1})$
$D_{dif,\theta}$	effective diffusion coefficient for the liquid phase	$(L^2\ T^{-1})$
$D_{dif,e}$	vapour diffusion coefficient in the gas phase	$(L^2\ T^{-1})$
D_{dis}	dispersion coefficient	$(L^2\ T^{-1})$
D_r	thickness of layer over which radial flow is considered	(L)
D_v	thickness of layer over which vertical flow is considered	(L)
d	damping depth over a year	(L)
d_{eq}	equivalent depth	(L)
d_m	distance between phreatic surface and impervious layer	(L)
E	molar activation energy	$(L^2\ M\ N^{-1}\ T^{-2})$
E_a	actual evapotranspiration	$(L\ T^{-1})$
E_{ex}	exchange between mobile and immobile fraction	$(L^{-3}\ M\ T^{-1})$
E_{grass}	reference grass evapotranspiration	$(L\ T^{-1})$
E_i	interception rate	$(L\ T^{-1})$

LIST OF SYMBOLS

SYMBOL	DEFINITION	DIMENSION
E_{max}	maximum evapotranspiration rate	(L T ⁻¹)
E_p	potential evapotranspiration rate	(L T ⁻¹)
E_r	reference crop evapotranspiration rate	(L T ⁻¹)
E_s	actual soil evaporation rate	(L T ⁻¹)
$E_{s,k}$	actual soil evaporation rate at section k	(L T ⁻¹)
E_{sp}	potential soil evaporation rate	(L T ⁻¹)
E_t	actual transpiration rate	(L T ⁻¹)
E_{tp}	potential transpiration rate	(L T ⁻¹)
F	transpiration stream concentration factor	(-)
f	crop factor	(-)
f_m	fraction of the liquid phase present in the mobile region	(-)
f_T	coefficient for the influence of the soil temperature on the rate of transformation	(-)
f_z	coefficient for the influence of soil depth on the rate of transformation	(-)
f_θ	coefficient for the influence of the soil moisture content on the rate of transformation	(-)
h	pressure head	(L)
$ h_1 $	absolute value soil water pressure head (oxygen deficiency)	(L)
$ h_2 $	absolute value soil water pressure head (maximum extraction)	(L)
$ h_3 $	absolute value soil water pressure head (maximum extraction)	(L)
$ h_4 $	absolute value soil water pressure head (wilting point)	(L)
h_m	height of the phreatic surface midway between the drain pipes above the water levels in the drain pipes (= total hydraulic head loss)	(L)
h_{phr}	height of phreatic surface	(L)
h_{pl}	hydraulic head in Pleistocene subsoil	(L)
I	irrigation rate	(L T ⁻¹)
i	number of sections	(-)
J	total solute flux density	(L ⁻² M T ⁻¹)
J_{cl}	convective flux density in the liquid phase	(L ⁻² M T ⁻¹)
J_{dg}	diffusive flux density in the gas phase	(L ⁻² M T ⁻¹)
J_{dl}	diffusive flux density in the liquid phase	(L ⁻² M T ⁻¹)
K	hydraulic conductivity	(L T ⁻¹)
K^\downarrow	global solar radiation flux density	(M T ⁻³)
K_i	hydraulic conductivity of the layer above the drain pipes	(L T ⁻¹)
K_b	hydraulic conductivity of the layer below the drain pipes	(L T ⁻¹)
K_F	Freundlich coefficient	(L ³ M ⁻¹)
K_g	ratio for partitioning of the fumigant between liquid and gas phase	(-)
K_L	critical concentration level for microbial growth	(L ⁻³ M)
K_M	saturation constant of Monod's equation	(L ⁻³ M)
K_r	hydraulic conductivity in layer with radial flow	(L T ⁻¹)
K_s	saturated hydraulic conductivity	(L T ⁻¹)
$K_{s,avg}$	average saturated permeability for the compartments between phreatic surface and impervious layer	(L T ⁻¹)
$K_{s,n}$	saturated permeability of soil compartment n	(L T ⁻¹)
K_v	hydraulic conductivity in layer with vertical flow	(L T ⁻¹)

SYMBOL	DEFINITION	DIMENSION
$(KD)_{hor}$	transmissivity of the soil layers trough which horizontal flow is considered	(L)
k_1	first-order transformation rate coefficient	(T ⁻¹)
$k_{1,ref}$	reference coefficient for first-order transformation	(T ⁻¹)
L	drain spacing	(L)
L_{dis}	dispersion length	(L)
LAI	Leaf Area Index	(-)
m	shape parameter	(-)
M	microbial activity	(L ⁻³ M)
n	shape parameter	(-)
$1/n$	Freundlich exponent	(-)
P	(gross) precipitation rate	(L T ⁻¹)
Q	net upward flow rate through the bottom	(L T ⁻¹)
Q_{10}	increase of decay rate by increase of temperature of 10 °C	(T ⁻¹)
q	macroscopic soil water flux density	(L T ⁻¹)
q_b	flux at bottom of the profile	(L T ⁻¹)
q_d	drain discharge rate per unit surface area	(L T ⁻¹)
$q_{s,k}$	actual flux density through the soil at section k	(L T ⁻¹)
R	universal gas constant	(L ² M N ⁻¹ T ⁻² Θ ⁻¹)
R_t	sink term for degradation	(L ⁻³ M T ⁻¹)
R_u	sink term for root uptake	(L ⁻³ M T ⁻¹)
R_d	sink term for lateral drainage	(L ⁻³ M T ⁻¹)
S	sink term for root water extraction	(T ⁻¹)
S_c	soil cover	(-)
S_{max}	maximum possible water extraction by roots	(T ⁻¹)
s	saturated vapour pressure	(L ⁻¹ M T ⁻² Θ ⁻¹)
T	soil temperature	(Θ)
T_a	amplitude of the temperature at the soil surface	(Θ)
T_{dev}	possible deviation of the soil temperature al depth $ z $	(T)
$T_{dev,max}$	maximum deviation of the soil temperature al depth $ z $	(T)
T_m	average soil temperature	(Θ)
T_{max}	lethal temperature for micro-organisms	(T)
T_{min}	minimum temperature for microbial activity	(T)
T_{opt}	optimum temperature for maximum microbial activity	(T)
T_{ref}	reference temperature	(Θ)
$T(z , t)$	temperature of the soil at height z and time t	(Θ)
t	time	(T)
u	wet perimeter of drain	(L ² T ⁻¹)
v_e	effective pore water velocity (q/θ)	(L T ⁻¹)
X	sorbed-phase content	(-)
z	vertical coordinate taken positive upwards	(L)
z_r	lower limit of the root zone	(L)

LIST OF SYMBOLS

SYMBOL	DEFINITION	DIMENSION
α	shape parameter	(L^{-1})
α_{ex}	exchange coefficient	(T^{-1})
α_m	microbial mortality rate constant	(T^{-1})
$\alpha(h)$	reduction factor	(-)
β	soil dependent parameter	($L^{0.5}$)
β_m	microbial mortality rate constant	($L^3 M^{-1}$)
γ	psychometric coefficient	($L^{-1} M T^{-2} \Theta^{-1}$)
γ_a	coefficient	(Θ^{-1})
γ_b	gain factor for biomass production	(-)
ε	volumetric air content	(-)
θ	volumetric water content	(-)
θ_i	volumetric water content in immobile soil domain	(-)
θ_m	volumetric water content in mobile soil domain	(-)
θ_r	residual volumetric water content	(-)
θ_s	saturated volumetric water content	(-)
θ_{ref}	soil moisture content at a reference level	(-)
λ	shape parameter depending on dK/dh	(-)
λ_w	latent heat of vaporization of water	($L^{-1} M T^{-2}$)
$\mu(T)$	rate of a microbial temperature dependant reaction	(T^{-1})
μ_{max}	maximum rate of growth	(T^{-1})
ρ	dry soil bulk density	($L^{-3} M$)
τ_l	tortuosity factor for diffusion in the liquid phase	(-)
τ_g	tortuosity factor for diffusion in the gas phase	(-)
Y	drainage resistance	(T)
ω	angular frequency of the temperature wave	(T^{-1})

Curriculum Vitae

Klaas P. Groen werd geboren op 2 juli 1961 te Westeremden. Na het behalen van zijn VWO-diploma in 1980, begon hij zijn studie aan de Landbouwniversiteit in Wageningen. Tijdens zijn studie bracht hij zijn praktijktijd door aan het Drainage Research Institute in Cairo. In november 1987 studeerde hij af in de richting cultuurtechniek met de hoofdvakken hydrologie, hydraulica, wiskunde en economie. Na zijn studietijd vervulde hij zijn dienstplicht als Officier bij de Aan- en Afvoertroepen. Sinds 1989 is hij via de Landbouw-

universiteit werkzaam bij de wetenschappelijke afdeling van de Rijksdienst IJsselmeerpolders (RIJP), welke in 1990 tijdelijk werd ondergebracht bij Rijkswaterstaat Directie IJsselmeergebied. De voormalige wetenschappelijke afdeling van de RIJP maakt sinds 1996 deel uit van het Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling (RIZA). Betrokkene is hier thans werkzaam op het gebied van integraal waterbeheer.