Behaviour of herbicides in soil: simulation and experimental assessment

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BEHAVIOUR OF HERBICIDES IN SOIL: SIMULATION AND EXPERIMENTAL ASSESSMENT

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ABSTRACT

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The mathematical models of the transport and the transformation rate of herbicides in soil that are available in the literature and the tests done on them are reviewed.

A simulation model of the transport of herbicides in field soil, based on the best model available in the literature, was developed. The detailed field experiments carried out on a bare loamy sand soil with two soil-applied herbicides (cyanazine and metribuzin) in spring and summer to test this model are described.

A new sub-model for the evaporation of water from bare soil was developed and tested in the field, with acceptable results. Testing the herbicide transport model against the concentration profiles measured in the field, showed that calculated penetration of the two herbicides in soil at a few months after application was much deeper than that measured.

To elucidate the cause of the discrepancy between calculations and measurements, the sorption of the two herbicides onto soil collected from the experimental field was studied in detail in laboratory experiments. Based on these studies a new model for the sorption of the herbicides was developed and incorporated into the transport model. The main new element in this model was a sorption process that equilibrates at a time scale of months. A comparison between concentration profiles calculated with the new model and those measured in the field showed that the new model successfully explained the field measurements.

STELLINGEN

1. Het optreden van een lange-termijn sorptie-proces kan een grote invloed hebben op het transport en de beschikbaarheid van bestrijdingsmiddelen in de bodem.

   Dit proefschrift.

2. Zowel uit practische als uit theoretische overwegingen verdient de Freundlich-vergelijking de voorkeur boven de Langmuir-vergelijking voor de beschrijving van het sorptie-evenwicht van ongeladen bestrijdingsmiddelen in de bodem.

3. De sorptie van het onkruidbestrijdingsmiddel paraquat aan de vaste bodembestanddelen is een omkeerbaar proces.

4. Het begrip 'gebonden residu' ('bound residue', IUPAC Commission on Pesticide Chemistry) heeft voor bodem-bestrijdingsmiddel systemen geen theoretische basis.

   IUPAC Commission on Pesticide Chemistry, 1984. Pure & Applied Chemistry 56: 945-956.

5. Er dienen internationale afspraken gemaakt te worden over de betekenis van de begrippen 'afbraak' ('degradation') en 'omzetting' ('transformation') voor bodem-bestrijdingsmiddel systemen.

6. Er is geen aanleiding om een verband te veronderstellen tussen de dispersielengte van een bodem en zijn textuur.

   Dit proefschrift (Hoofdstuk 6).

7. Er is geen aanleiding om een verband veronderstellen tussen snelheid waarmee de bovenste millimeters van een bodem onder veldomstandigheden uitdrogen en zijn textuur.

   Dit proefschrift (Hoofdstuk 5).

8. Het formuleren van een wiskundig model van het transport van opgeloste stoffen in de bodem uitsluitend in de vorm van een computer-programma (zoals b.v. gedaan door Frissel et al., de Wit & van Keulen, Addiscott en Nicholls et al.) moet worden afgeraden.

   Addiscott, T.M., 1977. Journal of Soil Science 28: 554-563.
   Frissel, M.J., P. Poelstra & P. Reiniger, 1970. Plant and Soil 33: 161-176.
   Nicholls, P.H., A. Walker & R.J. Baker, 1982. Pesticide Science 13: 484-494.
   Wit, C.T. de & H. van Keulen, 1972. Simulation of transport processes in soils. Pudoc, Wageningen.

9. In de literatuur over het transport van opgeloste stoffen in de bodem komt het regelmatig voor dat de term 'voorspelling' ('prediction') gebruikt wordt om de beschrijving van meetwaarden met een model aan te geven. Dit gebruik is in strijd met de betekenis van de term en zeer misleidend.

10. De opmars van de rekenautomaat in het wetenschappelijk onderzoek brengt het risico met zich mee dat te veel nadruk wordt gelegd op het gebruik van dit hulpmiddel en te weinig op een adequate onderzoeksmethodiek.

11. In het onderwijs aan de Landbouwuniversiteit te Wageningen wordt onvoldoende aandacht besteed aan een systematische nomenclatuur van grootheden en aan een goed gebruik van eenheden.

12. Het gebruik van de term 'reversibel' in fysisch-chemische literatuur zowel voor 'omkeerbaar' als voor 'oneindig dicht bij evenwicht verlopend' (in de thermodynamica), is verwarrend.

13. Ambtenaren die betrokken zijn bij de wetenschappelijke evaluatie van het gedrag en de effecten van bestrijdingsmiddelen in het milieu ten behoeve van de wettelijke toelating van deze middelen, zouden voor de financiering van hun onderzoeksprojecten niet afhankelijk moeten zijn van de opdrachten van producenten van bestrijdingsmiddelen.

14. De analogie die voorstanders van plaatsing van kruisraketten in Nederland veelal zien tussen de huidige internationale situatie en die voor de tweede wereldoorlog, is niet op zijn plaats: de huidige internationale situatie vertoont dan nog eerder overeenkomsten met de situatie voor de eerste wereldoorlog.

15. De opvallende overeenkomst tussen officiële wetenschappelijke plechtigheden (zoals b.v. een promotie) en religieuze plechtigheden, doet vermoeden dat wetenschap en religie enigszins gelijksoortige zaken zijn.

J.J.T.I. Boesten
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1 INTRODUCTION

Herbicides are essential for agriculture as practised in the Netherlands today: Dutch farmers use approximately 5 Gg (5 000 tonnes) of herbicides (active ingredients) per year (as estimated from data given for the year 1976 by Besemer, 1984) and 90 different herbicides (active ingredients) are currently registered in the Netherlands for agricultural use (van Rijn, 1985). About half of the herbicides registered act mainly via the foliage, and the other half act mainly via the soil. The present study considers the behaviour of soil-applied herbicides in soil. These herbicides are taken up by the sub-surface part of the weeds and exert their action after transport within the plant.

After soil-applied herbicides have been sprayed, a number of agricultural problems may occur. For instance, the efficacy of the herbicides may be too low if no rain falls in the first weeks after application (Walker, 1980). The herbicides are usually sprayed as an aqueous suspension or emulsion. The spray liquid usually amounts to an areic volume[1] of less than 0.1 mm. Some movement into the top layer of soil is therefore essential for uptake by the weeds and thus for good herbicidal activity. However, if the herbicide penetrates too deeply into soil, crop roots may take up sufficient herbicide for the plant to become damaged. If soil-applied herbicides are persistent, there is also a risk of damage to subsequent crops.

The activity of herbicides against weeds (and also their possible undesirable effects on crops) is tested by the producing firms and by governmental institutions before the herbicides are put on the market. In the final stage of testing, several field experiments are carried out. Often, the field experiments are continued even after the herbicide has been registered. In the field, usually only the effects of the herbicides on plants are considered and not their behaviour in soil. Soil and climatic factors have a large influence on the behaviour of the herbicides, and therefore the effects observed in the field experiments may vary considerably (Gerber et al., 1983). Knowledge of the behaviour of herbicides in soil under the specific conditions of the field experiments may result in a better interpretation of the effects observed and may lead to

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[1] For the nomenclature used for derived quantities (such as areic volume) see Rigg et al. (1985).

better founded advice for the farmer.

The environmental aspects of the use of herbicides also require attention. Residues in soil may be taken up by crops and thus may arrive in food chains. Persistent and weakly sorbed compounds may leach to the ground water and thus damage the quality of drinking water. Residues may also leach to surface water, for instance via tile drains. Processes important for soil fertility may be disturbed via the influence of herbicides on micro-organisms.

Both the performance of herbicides and the significance of adverse effects (agricultural or environmental) largely depend on the physico-chemical behaviour of the herbicide in the soil system (in the first instance, in the plough layer). This behaviour depends on properties of the active ingredients, the formulation of the herbicide, the way it is applied, and on soil characteristics and climatic conditions. Experimental study of the behaviour of a herbicide under the full range of soil and climatic conditions would be a tremendous task. Meteorologists use measuring periods of some 30 years to characterize climatic conditions, and a similar period may be needed to characterize herbicide behaviour. It seems more efficient to measure the interactions between herbicides and soils in some well-defined laboratory experiments and to use simulation models to evaluate the behaviour of the herbicide under the range of soil and climatic conditions it can be expected to encounter. However, a prerequisite for such a procedure is that the simulation models be valid for the field conditions encountered.

For a herbicide to be registered in the Netherlands, certain data on its behaviour in soil are required (Commissie Toelating Bestrijdingsmiddelen, 1985). In the first stage of the procedure, well-defined laboratory experiments on the interactions between the herbicide and some soils are required (e.g. experiments on sorption and on transformation rates). After the first evaluation, further research under field conditions may be requested. The basic data determined in the laboratory should be used optimally. This may be done by using them as input in computer models that can simulate the behaviour of the herbicide in soil under the range of climatic conditions to be expected.

The present study concentrates on the possibilities for simulating the movement and transformation of herbicides in field soil. The starting point of the study was the state of knowledge on the behaviour of herbicides in soil as described by a number of European researchers in Hance's review (1980). The study was restricted to non-ionic herbicides with vapour pressures that are so low that movement in the vapour phase is negligible. These are by far the most numerous of the herbicides registered in the Netherlands. Furthermore the study was restricted to natural weather conditions in a maritime temperate climate.

Following the basic ideas of de Wit (1982), simulation models can be divided into two types: descriptive models and explanatory models. Descriptive models are used to describe a series of measurements in a convenient way. Explanatory models are used to explain certain phenomena and require research at at least two levels. At the first level (the level used for explanation) knowledge is gained that can be used to explain phenomena at the second level (the level to be explained).

It seems most appropriate to use explanatory models for the simulation of herbicide behaviour in field soils. In such models well-defined laboratory experiments with herbicides and soils constitute the research level used for explanation. The level to be explained is the behaviour of herbicides in field soils under the varying climatic conditions. Both levels are linked by the model as schematized in Figure 1.1.

The first advantage of an explanatory over a descriptive model is that for the former fewer field tests are necessary to validate the model for a certain herbicide/soil combination. A second advantage of the use of an explanatory model is that it yields knowledge that is more general: one may expect that an explanatory model validated for a certain herbicide/soil combination can also be applied to some extent to other herbicides and soils that have similar physico-chemical properties. This advantage is important, given the large number of different herbicides registered. It also enables a preliminary evaluation of the probable field behaviour of newly introduced herbicides to be quickly obtained.

The results of measurements in the laboratory (the level used for explanation) are often conveniently summarized by a descriptive model. The explanatory

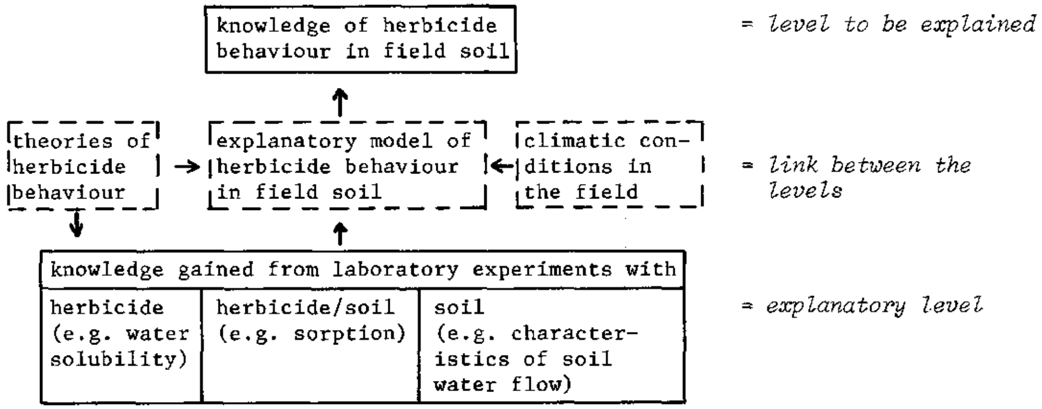

Figure 1.1. Scheme of a simulation model explaining the behaviour of herbicides in field soil from knowledge gained from laboratory experiments.

model will then contain a number of descriptive sub-models whose parameters were determined in laboratory experiments.

The properties 'descriptive' or 'explanatory' are not necessarily linked to a certain mathematical structure of the simulation model: the same computer program can be used as a descriptive or as an explanatory model. The way the values of the parameters in a model are selected determines wether a certain phenomenon is explained or described: only if values of essential parameters have been derived from measurements at the level used for explanation can one use the term 'explanation' (or 'prediction' if calculations were carried out before the measurements were done). Therefore it is very important to document how the values of all parameters are selected.

The research method described above considers properties measured in the laboratory as basic data that need no explanation. One may question whether it would be appropriate to explain these properties quantitatively. For instance, sorption onto a soil could possibly be explained quantitatively from knowledge of sorption of the herbicide onto pure soil components such as clay minerals, oxides and soil organic matter. Another example may be to explain quantitatively a transformation rate in soil in the laboratory from knowledge of the concentration of relevant micro-organisms in soil and from knowledge of the availability of the herbicide to these organisms. Such explanations are rarely available in literature. They may be rather important for a thorough theoretical basis for the measuring methods currently used to perform the experiments in the laboratory and the models currently used to describe their results.

It is always possible to define a more basic research level that can be used to explain the results obtained at the research level considered. For instance, one may attempt to explain sorption onto pure soil components quantitatively from knowledge about properties of the atoms constituting sorbent and sorbate. In the research method used in the present study only the last link in the chain of explanations was considered, namely the link between field and laboratory, because this link is most relevant for evaluating field behaviour of a herbicide. Explanation of results of laboratory experiments was only exceptionally attempted.

The present report begins with reviews of the models available for simulating the transport and transformation of herbicides in soil, and of the available tests of these models. Next, the detailed field experiments that were carried out with 2 soil-applied herbicides (cyanazine and metribuzin) are described. A model, based on the best model available in the literature, was developed to simulate the transport of herbicides: it is described in Chapter 6. However, to develop this model, much effort had to be devoted to the sub-models of evaporation of water and of flow of water in soil. This is explained in Chapter 5. Chapter 6 also reports on the outcome of testing the model against the results of the field experiments. Discrepancies were found between simulated and measured concentration profiles and these provided a motive to study the adsorption/desorption kinetics of the herbicides in soil in detail (Chapters 7 and 8). The latter study enabled the sub-model for adsorption/desorption to be improved. In Chapter 9 the results of simulations using this improved model are compared with the results of the field experiments.

2 AVAILABLE MODELS OF THE TRANSPORT OF HERBICIDES IN SOIL

2.1 INTRODUCTION

Various mathematical models of the transport of herbicides and other substances in soil have been described in the literature. In this chapter the most important of these models are described and discussed, together with the tests of the models as described in the literature. Special attention will be devoted to the ability of the models to simulate the transport of herbicides in field soil.

The transport models can be divided into deterministic and stochastic models (see, for instance, Addiscott & Wagenet, 1985). Only deterministic models will be considered here in detail. Stochastic models have been developed for irrigation situations where water ponds on the soil surface (Dagan & Bresler, 1979; Amoozegar-Fard et al., 1982). In these models the rate of liquid flow in soil is a random variable determined by the saturated hydraulic conductivity of the soil. The variability of the transport of substances in these models is mainly caused by the variability of the rate of liquid flow and thus of the saturated hydraulic conductivity of the soil. As the present study was restricted to natural weather conditions (i.e. no irrigation) with probably a random spatial variability of the rainfall, it was deemed appropriate to ignore these stochastic models.

All models to be discussed are based on the (one-dimensional) mass conservation equation for the substance in the soil system:

$$\frac{\partial c^*}{\partial t} = -\frac{\partial J}{\partial z} - R_{\mathrm{t}} \qquad (2.1)$$

in which

c^*	is mass concentration of substance in soil system	(kg m^{-3})
t	is time	(d)
J	is mass flux[2] of substance	(kg m^{-2} d^{-1})
z	is depth in soil	(m)
R_{t}	is volumic mass rate of transformation of the substance	(kg m^{-3} d^{-1})

---

[2] By flux is meant areic rate of transport.

In this chapter, only models for transport term $\partial J/\partial z$ will be discussed: models for the transformation term R_t will be discussed in Chapter 3.

In this chapter it will be assumed in all transport models that the herbicide/soil sorption isotherm is linear.

2.2 DESCRIPTION OF THE MODELS

2.2.1 Equilibrium transport model

Several authors have described the equilibrium transport model (e.g. Bolt, 1979, and Leistra, 1980). The basic assumptions in this model are that at any location (as specified by the space coordinate, z) and at any moment:

- the substance in the liquid phase is in equilibrium with that sorbed by the solid phase
- the concentration in liquid phase can be considered uniform.

In practice, this means that a sorption isotherm equation is used and so-called stagnant phase effects are ignored.

It is assumed in this model that the mass flux of the substance can be written as

$$J = J^V c - (D_{\text{dis}} + D_{\text{dif}})\, \partial c/\partial z \qquad (2.2)^3$$

in which

J^V	is volume flux of liquid	(m d^{-1})
c	is mass concentration of substance in the liquid phase	(kg m^{-3})
D_{dis}	is dispersion coefficient	$(\text{m}^2\ \text{d}^{-1})$
D_{dif}	is coefficient of diffusion through the liquid phase	$(\text{m}^2\ \text{d}^{-1})$

The dispersion coefficient D_{dis} is used to describe the spreading of the concentration profile as a result of the variability of liquid flow in the various soil pores. It is assumed that D_{dis} is proportional to J^V:

$$D_{\text{dis}} = L_{\text{dis}}\, |J^V| \qquad (2.3)$$

in which

L_{dis}	is dispersion length	(m)

---

[3] To avoid overuse of brackets, the sequence of mathematical operators in horizontal lines in formulas is specified: exponentiation, multiplication, division, addition, subtraction.

By the introduction of the dispersion process in the model, it is admitted that the concentration in the liquid phase at a microscale is not uniform for a given value of the space coordinate, z. The concentration in the liquid phase, c, in the model should be considered as the concentration averaged over a macroscopic surface area in a plane perpendicular to the direction of flow.

D_{dif} is calculated by

$$D_{\mathrm{dif}} = \lambda \, \theta \, D_0 \tag{2.4}$$

in which

λ	is tortuosity factor	(1)
θ	is volume fraction of liquid	$(\mathrm{m}^3\ \mathrm{m}^{-3})$
D_0	is coefficient for diffusion in water	$(\mathrm{m}^2\ \mathrm{d}^{-1})$

The concentration of substance in the soil system is the sum of the concentrations present in the liquid and the solid phases of the soil system:

$$c^* = \theta \, c + \rho_b \, X \tag{2.5}$$

in which

ρ_b	is dry soil bulk density (i.e. volumic mass of dry soil)	$(\mathrm{kg\ m}^{-3})$
X	is content of substance sorbed (i.e. the ratio of the mass of substance sorbed divided by the mass of dry soil)	$(\mathrm{kg\ kg}^{-1})$

Because it is assumed that sorption equilibrium exists, the value of X at each depth can be calculated from the sorption isotherm equation. The linear sorption isotherm is described by

$$X = K \, c \tag{2.6}$$

in which

K	is slope of linear sorption isotherm	$(\mathrm{m}^3\ \mathrm{kg}^{-1})$

2.2.2 Non-equilibrium transport models

Van Genuchten & Cleary (1979, p. 362) distinguished two possible reasons for non-equilibrium conditions during the transport of sorbing substances through soil. First, the herbicide molecules in the liquid phase near the sorption sites may not be in equilibrium with those sorbed at these sites. I shall call this 'chemical non-equilibrium'. Secondly, the concentration in liquid phase may not be uniform in a plane perpendicular to the direction of flow, because part of the soil liquid is stagnant in combination with a non-instantaneous transfer process between mobile and stagnant liquid. This will be termed 'physical non-equilibrium'. It is important to use the concepts of chemical and physical non-equilibrium, because chemical non-equilibrium only occurs with sorbing substances.

Van Genuchten & Cleary (1979, p. 362) denoted the first and second processes of non-equilibrium mentioned above as kinetic and physical non-equilibrium. I prefer to use the term 'chemical non-equilibrium' instead of 'kinetic non-equilibrium', because the former term is more in balance with the term 'physical non-equilibrium' than the latter term.

Let us first consider some models of chemical non-equilibrium. In these models the Equations 2.2 to 2.5 remain valid. The most simple model of chemical non-equilibrium was proposed by Lapidus & Amundson (1952). In this model it is assumed that all sorption sites have identical sorption properties and that the sorption rate is given by a reversible[4] first-order equation:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_{\mathrm{d}}(K\,c - X) \qquad (2.7)$$

in which

k_{d} is desorption rate constant (d^{-1})

Details of the derivation of Equation 2.7 will be discussed in Chapter 7.

In more extended models, two classes of sorption site are distinguished. Cameron & Klute (1977) suggested that class-1 sites are in equilibrium with the concentration in liquid phase:

$$X_1 = F\,K\,c \qquad (2.8)$$

in which

X_1 is content sorbed at class-1 sites ($\mathrm{kg\ kg^{-1}}$)

F is fraction of K to be attributed to class-1 sites (1)

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[4] In the context of the present study, 'reversible' always means 'ability to change and then return to the original condition by a reversal of the change'. Reversible is thus never used in its thermodynamic meaning.

In this model the sorption rate at class-2 sites is given by a rate equation similar to Equation 2.7:

$$\frac{dX_2}{dt} = k_{d,2} \{ (1 - F) K\, c - X_2 \} \tag{2.9}$$

in which

X_2	is content sorbed at class-2 sites	(kg kg^{-1})
$k_{d,2}$	is desorption rate constant for class-2 sites	(d^{-1})

In another model with two classes of sorption sites, sorption at both classes of site is described by a first-order rate equation (Leistra & Dekkers, 1977). The rate equation for class-1 sites reads

$$\frac{dX_1}{dt} = k_{d,1}(F\, K\, c - X_1) \tag{2.10}$$

in which

$k_{d,1}$	is desorption rate constant for class-1 sites	(d^{-1})

The rate equation for class-2 sites is equal to Equation 2.9.

Secondly, let us consider models of physical non-equilibrium. Van Genuchten & Wierenga (1976) proposed a model for pesticide transport in which both the liquid and solid phases in soil were divided into two zones. In the first zone the liquid is mobile, in the second one it is stagnant. Within each zone, equilibrium sorption occurs. The mass flux of the substance downward is then given by

$$J = J^V c_m - D_{dd,m}\, \partial c_m / \partial z \tag{2.11}$$

in which

c_m	is mass concentration in mobile liquid phase	(kg m^{-3})
$D_{dd,m}$	is coefficient for combined effects of diffusion and dispersion in mobile liquid phase	(m^2 d^{-1})

The equation for the concentration of substance in the soil system reads

$$c^* = \phi\, \theta\, c_m + f\, \rho_b\, X_m + (1 - \phi)\, \theta\, c_s + (1 - f)\, \rho_b\, X_s \tag{2.12}$$

in which

ϕ	is fraction of θ located in mobile zone	(1)
f	is mass fraction of solid phase assigned to the mobile zone	(1)
c_s	is mass concentration in stagnant liquid phase	(kg m^{-3})
X_m, X_s	are contents sorbed in mobile and stagnant zones, respectively	(kg kg^{-1})

Because equilibrium sorption exists in both zones, X_m and X_s are given by

$$X_m = K\ c_m \tag{2.13}$$

$$X_s = K\ c_s \tag{2.14}$$

To describe the exchange between mobile and stagnant liquid due to diffusion, van Genuchten & Wierenga (1976) used a first-order rate equation:

$$\frac{\partial\{(1 - \phi)\ \theta\ c_s + (1 - f)\ \rho_b\ X_s\}}{\partial t} = k_{m,s}(c_m - c_s) \tag{2.15}$$

in which

$k_{m,s}$	is coefficient for transfer of mass between mobile and stagnant zones	(d^{-1})

Nicholls et al. (1982a,b) adapted a model originally developed by Addiscott (1977) for the transport of anions in soil. Their model was developed to explain the transport of herbicides in field soil. The model can be considered to be a simplified version of that of van Genuchten & Wierenga (1976). The first simplification is that the volume fraction of liquid located in the stagnant zone, θ_s ($m^3\ m^{-3}$), is assumed to be constant for a certain soil: θ_s is assumed to be the volume fraction of liquid in equilibrium with a matric pressure of -200 kPa. The second simplification is that the mass fraction of solid phase assigned to the mobile zone, f, equals the fraction of θ located in the mobile zone, ϕ. The third simplification is that the diffusion/dispersion term in Equation 2.11 is introduced by an artifact called numerical dispersion caused by the use of a finite-difference approximation (see van Genuchten & Wierenga ,1974, for a thorough treatment of numerical dispersion). The fourth simplification is that the rate equation for exchange between stagnant and mobile zone (Equation 2.15) is replaced by a simple calculation procedure: for each day two calculation steps are made; in the first step the daily excess of rainfall over evaporation or vice-versa is assumed to carry the substance through the mobile zone without allowing any exchange between mobile and stagnant zones; in the second calculation step, equilibration is assumed to occur between mobile and stagnant zones and between liquid and sorbed phases.

I attempted to quantify the implicit assumptions associated with the calculation procedure of Nicholls et al. (1982a,b) in terms of the model of van Genuchten & Wierenga (1976). To do this, the rate of exchange between mobile and stagnant zones is considered for the situation in which c^* at a certain depth is constant with time (this situation is approached, for instance, during nights without rain). Then, a simple analytical solution can be given for the system of Equations 2.12 to 2.15 at a certain depth in soil:

$$\bar{c}_\mathrm{s} \equiv \frac{c_\mathrm{s} - c_\mathrm{s}(\infty)}{c_\mathrm{s}(0) - c_\mathrm{s}(\infty)} = \exp(-t/\tau_\mathrm{m,s}) \qquad (2.16)$$

in which

$\bar{c}_\mathrm{s}$	is fractional concentration in stagnant liquid phase	(1)
$c_\mathrm{s}(\infty)$	is equilibrium value of c_s $(t = \infty)$	(kg m^{-3})
$c_\mathrm{s}(0)$	is initial value of c_s $(t = 0)$	(kg m^{-3})
$\tau_\mathrm{m,s}$	is time constant for exchange of substance between mobile and stagnant zones	(d)

The equation for $\tau_\mathrm{m,s}$ is given by

$$\tau_\mathrm{m,s} = \frac{(\phi\,\theta + f\rho_\mathrm{b}\,K)\{(1-\phi)\,\theta + (1-f)\,\rho_\mathrm{b}\,K\}}{k_\mathrm{m,s}(\theta + \rho_\mathrm{b}\,K)} \qquad (2.17)$$

In the model of Nicholls et al. (1982a,b) it is assumed that the liquid flux in the soil is either high or zero. In terms of the model of van Genuchten & Wierenga (1976) this assumption implies that in periods with high liquid fluxes $\tau_\mathrm{m,s}$ is large enough to cause $\bar{c}_\mathrm{s}$ to drop appreciably. Periods with high liquid fluxes (because of rain or evaporation) usually last in the order of 0.1 d. Thus, the model of Nicholls et al. (1982a,b) implies that in these periods $\tau_\mathrm{m,s}$ should be greater than about 0.5 d. According to the model of Nicholls et al. (1982a,b), within 1 d again equilibration occurs. Thus, in periods of low liquid fluxes, $\tau_\mathrm{m,s}$ is assumed to be smaller than about 0.5 d.

Table 2.1 lists the parameters used in the non-equilibrium part of the models discussed. The table only shows those parameters that can be chosen independently. Nkedi-Kizza et al. (1984) have shown that for a soil system with constant θ and ρ_b the chemical non-equilibrium model of Cameron & Klute (1977) and the physical non-equilibrium model of van Genuchten & Wierenga (1976) result in identical dimensionless transport equations. This is remarkable because, according to Table 2.1, the model of Cameron & Klute has two independent variables, whereas that of van Genuchten & Wierenga has three. However, the analysis of Nkedi-Kizza et al. (1984) showed that ϕ and f depend on the same dimensionless transport parameter.

2.3 TESTS OF THE MODELS

2.3.1 Laboratory tests

Most of the models described have been used in attempts to describe results of laboratory experiments on the transport of pesticides in columns of sieved soil several decimetres long (for instance Kay & Elrick, 1967; Davidson & Chang, 1972; Davidson & McDougal, 1973; Hornsby & Davidson, 1973; van Genuchten et al., 1974; van Genuchten et al., 1977; Rao et al., 1979). These attempts have been reviewed by van Genuchten & Cleary (1979), Davidson et al. (1980a), Hartley & Graham-Bryce (1980, pp. 303-310) and Leistra (1980).

One may expect the validity of the equilibrium model for transport of substances to be determined by the liquid flux in soil. If the liquid flux is sufficiently low, the equilibrium model applies. If small non-equilibrium effects occur, the transport can still be described with the equations of the equilibrium model, the non-equilibrium effects being reflected in an apparent increase in the dispersion coefficient (Passioura, 1971). The volume flux of the soil liquid in the labor-

Table 2.1. Independent parameters in the non-equilibrium part of transport models.

Chemical non-equilibrium			Physical non-equilibrium	
Lapidus & Amundson (1952)	Cameron & Klute (1977)	Leistra & Dekkers (1977)	van Genuchten & Wierenga (1976)	Nicholls et al. (1982a,b)
k_d	$k_{d,2}$	$k_{d,2}$ $k_{d,1}$	$k_{m,s}$	
	f	f	f	
			ϕ	θ_s

atory experiments described in the literature was usually in the order of 100 mm d^{-1}. Usually, the validity of the equilibrium model was tested. The procedure for such a test was as follows: the parameters of the sorption isotherm equation were determined in an experiment with a suspension of the soil; the only unknown parameter remaining was the coefficient for the combined effects of diffusion and dispersion, which was ascertained by curve-fitting techniques. The general conclusion from these tests was that at the volume fluxes of liquid used, there was an appreciable deviation from the results calculated with the equilibrium model. Usually, one or more non-equilibrium models were then used in attempts to describe the effluent curves. Values of the parameters mentioned in Table 2.1 were derived from the experimental curves by curve-fitting techniques.

Some of the assumptions in the model of Nicholls et al. (1982a,b) can be tested against results obtained by van Genuchten et al. (1977) in laboratory experiments with the herbicide 2,4,5-T in a clay loam soil. Van Genuchten et al. (1977) found that the fraction of mobile liquid, ϕ, was around 0.9 for volume fluxes of liquid between 50 and 200 mm d^{-1}. They found that the mass fraction of solid phase assigned to the mobile zone, f, was around 0.4 in the same experiments. These figures contrast with the assumption in the model of Nicholls et al. (1982a,b) that f equals ϕ. Unfortunately, van Genuchten et al. (1977) did not give a water retentivity curve of their soil. Thus I cannot compare predicted and measured values of f and ϕ. Another implication of the model is that at high liquid fluxes the time constant, $\tau_{m,s}$, (Equation 2.17) should exceed 0.5 d. This was confirmed by values for $\tau_{m,s}$ of about 2 d calculated from the results of van Genuchten et al. (1977). Because van Genuchten et al. (1977) used sieved soil, the applicability of their results to field soils may be questioned.

Various researchers have attempted to distinguish between processes of physical and chemical non-equilibrium by describing results of column experiments with models for physical non-equilibrium and models for chemical non-equilibrium. In a review, van Genuchten & Cleary (1979) suggested that physical non-equilibrium processes have to be included to describe the observed experimental data. However, they only considered the model for chemical non-equilibrium developed by Lapidus & Amundson (1952) and compared it with the model for physical non--equilibrium of van Genuchten & Wierenga (1976). Table 2.1 shows that this is not a fair comparison: the model of van Genuchten & Wierenga (1976) has three adjustable parameters, whereas that of Lapidus & Amundson (1952) only has one. Rao et al. (1979) simulated the transport of three herbicides in soil columns and attempted to find out whether the model for chemical non-equilibrium of Cameron & Klute (1977) was to be preferred to the model for physical non-equilibrium of van

Genuchten & Wierenga (1976). Nkedi-Kizza et al. (1984) showed that the approach followed by Rao and his colleagues was inadequate, because the transport equations of both models are mathematically identical. Consequently, it cannot be concluded from a certain column experiment whether one of these models for chemical or physical non-equilibrium is to be preferred.

2.3.2 Field tests

Field tests of models for the transport of pesticides in soil have been carried out under natural rainfall in the Netherlands and in England. Leistra et al. (1980), Bromilow & Leistra (1980), Leistra & Smelt (1981), and Graham-Bryce et al. (1982) considered the equilibrium model. Nicholls et al. (1982a,b) considered both the equilibrium model and the non-equilibrium model they developed. Nicholls et al. (1984) considered only their own non-equilibrium model.

The procedure for testing the equilibrium model was usually as follows: the slope of the sorption isotherm was measured in the laboratory in a suspension of the soil in water; the coefficient for diffusion in the liquid phase in soil was estimated from molecular properties of the substance and from literature data and the value of L_{dis} was fitted to the results of the field measurements.

The procedures for testing the non-equilibrium model developed by Nicholls et al. (1982a,b) were: the slope of the sorption isotherm was estimated in the same way as for the equilibrium model; the combined effects of diffusion and dispersion in the mobile phase were introduced (accidentally) via numerical dispersion by 10 to 30 mm distance between the grid points used in the numerical solution; the volume fraction of stagnant liquid was derived from a measurement of water retentivity at a matric pressure of -200 kPa.

The field tests can be divided into two categories: those done in spring and summer and those done in autumn and winter. There is a large difference between the water flow regime in both periods: in spring and summer cumulative potential evaporation of water from soil is usually equal to or higher than cumulative rainfall, whereas in winter cumulative evaporation is only a small fraction of cumulative rainfall. I shall discuss the field tests done in autumn and winter first. Leistra & Smelt (1981) found that the movement of the nematicide ethoprophos, as calculated with the equilibrium model was somewhat greater than that measured. Nicholls et al. (1982a) tested both the equilibrium model and their non-equilibrium model for the movement of chloride ion, the insecticide aldoxycarb and the herbicide fluometuron in a structured clay loam soil. The non-equilibrium model somewhat overestimated movement of chloride ion, whereas the equilibrium model clearly underestimated movement. Both models overestimated movement of aldoxycarb after 2 and 3 months. Both models explained movement of fluometuron after 1 and 2 months satisfactorily, whereas after 3 and 4 months the movement of the major fraction of fluometuron was overestimated. However, measured penetration of small fractions of the fluometuron dose was deeper than calculated by either model. Nicholls et al. (1984) tested the non-equilibrium model of Nicholls et al. (1982a,b) for movement of simazine in a silty clay loam in winter. They found that the model calculated much more movement than was measured. When it was taken into account that part of the simazine was undissolved, the model only slightly overestimated movement.

Movement of herbicides in spring and summer can be expected to be roughly proportional to the excess of cumulative rainfall over cumulative actual evaporation. Thus, an accurate estimate of evaporation of water from soil is a prerequisite for a meaningful test of a transport model for a herbicide. Leistra et al. (1980), Bromilow & Leistra (1980), and Graham-Bryce et al. (1982) used the following procedure to estimate evaporation. They described water flow in soil with Darcy's law, which requires as input the water retentivity function and the relationship between hydraulic conductivity and volume fraction of liquid (cf. Koorevaar et al., 1983). They estimated potential evaporation from the Penman equation or from measurements of evaporation from a water surface. They assumed that the ratio between actual and potential evaporation was a function of the matric potential of the top layer, using the relationship derived by van Keulen (1975, p. 90). However, no reliable measurements of the hydraulic conductivity in the top few centimetres of the soil were available to them. Thus, they adjusted the relationship between hydraulic conductivity and volume fraction of liquid to obtain a good fit of soil moisture profiles measured on a few sampling dates. They assumed (without testing) that this procedure gave an accurate description of evaporation fluxes. Nicholls and his colleagues (Nicholls et al., 1982b, 1984) calculated evaporation with a simplified model that was calibrated on calculated results obtained by the procedure followed by Leistra et al. (1980), Bromilow & Leistra (1980) and Graham-Bryce et al. (1982).

Leistra et al. (1980) and Bromilow & Leistra (1980) tested the equilibrium model for the movement of two nematicides in sandy loam soils. Sorption of these nematicides was rather weak. In most cases they found reasonable agreement between calculated and measured movement. However, in some instances, differences were distinct.

Graham-Bryce et al. (1982) tested the equilibrium model for the movement of fluometuron and chloride ion in a sandy loam and in a clay soil. Differences between calculated and measured movement of chloride ion were large (especially for the sandy loam). Measured movement of fluometuron in the sandy loam soil could be described reasonably well by assuming values of about 60 mm for the dispersion length. Graham-Bryce and his co-workers suggested that these values for L_{dis} were in the range of those used by Frissel & Reiniger (1974), but the latter found values in the range of 2 to 25 mm. Graham-Bryce et al. (1982) found that calculated movement was greater for the clay than that measured. One may question the point of testing for fluometuron after it had been found that chloride movement could not be described by the model.

Nicholls et al. (1982b) tested both the equilibrium model and their own non--equilibrium model of the movement of atrazine and metribuzin in a sandy loam soil. They found that movement calculated with the equilibrium model was greater than that measured, whereas the movement calculated with the non-equilibrium model corresponded well with measured movement.

Nicholls et al. (1984) tested the non-equilibrium model developed by Nicholls et al. (1982a,b) for the movement of simazine in a silty clay loam soil in summer. After taking into account that part of the simazine was undissolved, calculated movement corresponded well with that measured. However, the measurement used for the evaporation from a water surface was probably wrong: according to their Figure 1, the averaged daily evaporation flux from a water surface in the summer of 1981 was about 1 mm d^{-1}. In the summers of 1944 and 1945, Penman (1948) measured average values of around 4 mm d^{-1} at the same location.

2.4 DISCUSSION

The non-equilibrium transport models described by Lapidus & Amundson (1952), Cameron & Klute (1977), Leistra & Dekkers (1977) and van Genuchten & Wierenga (1976) are incomplete: it is implicitly admitted in these models that the parameters in the non-equilibrium part (e.g. F, $k_{d,2}$, ϕ, $k_{m,s}$) are a function of the volume flux of liquid, but no relationships are proposed. As a consequence, these models cannot yet be used to calculate transport of herbicides in soils with varying liquid fluxes, as occurs in the field. In contrast to the non-equilibrium models mentioned above, the model developed by Nicholls et al. (1982a,b) is complete. Thus it is not surprising that only this non-equilibrium transport model has been used for calculations under field conditions.

Addiscott (1977) and Nicholls et al. (1982a,b) did not give a theoretical basis for the assumptions made in their model. Addiscott (1977) developed this model after finding that leaching of the main fraction of chloride ion in a structured soil proceeded much faster than expected from the equilibrium model. The resulting non-equilibrium model described the experimental results rather well (Addiscott et al., 1978). In the model, information from the water retentivity curve is used: the division between mobile and stagnant liquid is set at a matric pressure of -200 kPa. However, matric pressure is a static property and it seems more appropriate to use a dynamic property such as the relationship between hydraulic conductivity and volume fraction of liquid to distinguish mobile from stagnant liquid. Via this relationship, the liquid in soil could be divided into a number of classes with known mobility. An interesting point for further research would be to develop models that link information from soil water flow characteristics to solute flow.

Nicholls et al. (1982a,b) suggested that their model is 'empirical' as opposed to the equilibrium model which they designated 'theoretical'. But such a distinction, which was possibly prompted by the more complex submodel for water flow they used in connection with the equilibrium model, is unjustified.

The calculations done by Nicholls et al. (1982a) for the movement of fluometuron in a clay loam soil with both their non-equilibrium and the equilibrium model resulted in almost identical concentration profiles. The reason for this similarity for a clay soil is not clear and requires further investigation. In the non--equilibrium model the magnitude of the non-equilibrium effect is determined by the fraction of the liquid that is stagnant, i.e. θ_s/θ. During downward flow, θ is assumed to be equal to the volume fraction at a matric pressure of -5 kPa. θ_s is assumed to be equal to the value in equilibrium with a matric pressure of -200 kPa. The water retentivity curves of Koorevaar et al. (1983, p. 82) show that θ_s/θ ranges from 0.2 for sandy soils to 0.8 for clay soils. Thus, no large differences between the concentration profiles calculated with both models can be expected for sandy soils either. Consequently, for many pesticide/soil combinations, the results calculated with both models will be similar. In view of this similarity and the weak theoretical basis of the non-equilibrium model of Nicholls et al. (1982a,b), the equilibrium model is to be preferred.

It is stressed that the similarity in calculated profiles discussed above concerns the main fraction of the amount of herbicide in soil. The fraction of the dose that leaches to a depth below 1 m, as calculated with the non-equilibrium model, may be several orders of magnitude higer than that calculated with the equilibrium model.

In the research reports cited above, the aim of applying the models to the experiments with soil columns in the laboratory was usually to study the fundamentals of the transport mechanism. However, in view of the research method used the researchers did not explain the non-equilibrium effects; they merely described them.

Furthermore, the parameter values for the non-equilibrium models were usually found to vary with experimental conditions (van Genuchten et al., 1977; Rao et al., 1979). As a consequence, the models developed are not satisfactory. In reviews, Leistra (1980) and Davidson et al. (1980a) noted the need for independently estimated parameters in non-equilibrium models. The applications of the models to soil column experiments in the laboratory have shown that additional experimental techniques are required to elucidate the fundamentals of the transport mechanism. A promising development is the use of the experimental techniques developed and applied by Bouma (1984) to characterize the flow of water in structured soils.

As the transport equations in the main models for chemical and physical non-equilibrium were found to be mathematically identical (see Nkedi-Kizza et al., 1984), the question of how to operationalize the distinction between processes of chemical and physical non-equilibrium arises. One attempt could be to state that, by definition, there is physical equilibrium in experiments in which the transport of a non-sorbing substance can be described with the equilibrium transport model. However, if only a small fraction of the liquid is stagnant, the equilibrium model may still be adequate for description (Passioura, 1971; Bolt, 1979). One may expect that stagnant liquid is mainly located in the vicinity of the sorption sites. Consequently, the effects of physical non-equilibrium may be more severe for sorbing than for non-sorbing substances. This attempt to operationalize the distinction between processes of physical and chemical non-equilibrium, does not seem successful.

This can be illustrated by experiments done by van Genuchten & Cleary (1979) and Rao et al. (1979). Van Genuchten & Cleary (1979) stated that the results of certain percolation experiments with tritiated water could be described equally well with the equilibrium model and with a model for physical non-equilibrium. The description with the latter model indicated that ϕ was as large as 0.94. From percolation experiments with the herbicide 2,4,5-T they inferred that f was 0.4 and that $k_{m,s}$ was 0.2 d^{-1}. Rao et al. (1979) also found that under their experimental conditions, the movement of tritiated water could be described equally well by the equilibrium model and by a model for physical non-equilibrium. From the latter they derived that ϕ was equal to or larger than 0.99. They concluded that the physical non-equilibrium concept was not applicable, and attempted to use the model for chemical non-equilibrium developed by Cameron & Klute (1977) to describe the results of an experiment with the herbicide 2,4-D. They found that F was about 0.5 and that $k_{d,2}$ was about 0.2 d^{-1}. Although the results of the experiments of van Genuchten & Cleary (1979) and of Rao et al. (1979) were similar, the former concluded that the process was one of physical non-equilibrium and the latter that it was a process of chemical non-equilibrium.

In view of the problems described above, I propose a new operational definition of the distinction between processes of physical and chemical non-equilibrium (see Koningsveld, *1979*, p. *203*, for the definition of 'operational definition').

The new operational definition is that the rate of the chemical process is measured in a suspension of soil that is continuously being mixed. Thus, by definition, physical equilibrium exists in such a suspension of soil. This operational definition will be used in the chapters to follow.

The concepts of chemical and physical non-equilibrium processes introduced at the start of Section 2.2.2, imply that any operational definition for the distinction between the two types of processes has to specify the zones in the soil system in which the two processes take place: the qualification 'physical' implies that the rate-limiting step in the non-equilibrium process takes place 'far from' the sorption sites, whereas 'chemical' implies that this step takes place 'near' the sorption sites. The operational definition I proposed specifies the zones: chemical non-equilibrium processes take place in the zone between the sorption sites and the well-mixed bulk of the liquid phase in a soil suspension, and physical non-equilibrium processes take place in the remainder of the liquid phase.

The mathematical structure of a model does not specify the zones mentioned above. Thus, the attempts in the literature to use the mathematical structure as a basis for the operational definition were doomed to failure.

The new operational definition can be applied to the measurements for 2,4-D by Rao et al. (1979) discussed before. They reported that in suspension experiments, 2,4-D reached sorption equilibrium within a few hours. Consequently, the slow equilibration ($k_{d,2}$ = 0.2 d^{-1}) of about half of the sorption sites in the soil column is a physical non-equilibrium process.

In the field tests of the equilibrium model described in Section 2.3.2, the value of the dispersion length, L_{dis}, was not determined independently but was adjusted to obtain a good fit to the measurements. There is a risk that by this procedure the model used degenerates into a descriptive model. The risk is comparatively low if the effect of L_{dis} can be separated from the effect of other parameters. For instance, in periods with excess of rainfall over evaporation (winter), L_{dis} controls the spreading of an approximately Gaussian concentration distribution in soil. In periods without excess of rainfall over evaporation, a shorter L_{dis} or a steeper slope of the sorption isotherm or a higher cumulative evaporation all result in a steeper concentration profile. Then there is a large risk that adjusting L_{dis} will lead to a descriptive model.

From the field tests in autumn and winter of the equilibrium and non-equilibrium models (Section 2.3.2) it was concluded that both models tend to overestimate the movement of the main fraction of the amount of pesticide. However, there is evidence that in structured clay soils small fractions of the dose may move faster than calculated with either model.

The procedure used in the literature to estimate evaporation fluxes of water for the field tests of pesticide transport models, is rather speculative: in this procedure a dynamic quantity, such as evaporation flux is derived from static properties (moisture profiles at a few sampling dates) via a fitting procedure.

Thus, for the field tests in spring and summer described in the literature, there may be rather large uncertainties in the evaporation part of the model. This means that so far there are no reports of field tests in spring and summer in which the model for the pesticide transport has been tested accurately. In future field tests in spring and summer the sub-model for water evaporation should be tested.

3 AVAILABLE MODELS OF THE TRANSFORMATION RATE OF HERBICIDES IN SOIL

3.1 INTRODUCTION

In this chapter, models of the volumic mass rate of transformation, R_t (Equation 2.1), of herbicides in the plough layer of the soil are reviewed. The aim was to make an inventory of the models developed and to investigate their ability to simulate the transformation rate of herbicides in field soil. Only those models that attempt to explain herbicide transformation rates in the field from transformation rates measured in the laboratory were considered.

The definition of transformation is not straightforward. The usual procedure in the literature is to state that transformation of a herbicide molecule can either result in a molecule with a different molecular structure or in a molecule that has become soil-bound (non-extractable). This means that the definition of transformation is determined by the definition of a soil-bound herbicide residue. Various definitions of soil-bound pesticide residue have been given in the literature. One of the earliest definitions was: 'that unextractable and chemically unidentifiable pesticide residue remaining in fulvic acid, humic acid, and humin fractions after exhaustive sequential extraction with non-polar organic and polar solvents' (Environmental Protection Agency, 1975, p. 26893). A more recent definition was given by Anonymous (1982): 'nonextractable (or bound) pesticide residues in soils, plants, and food are defined as chemical species originating from pesticide usage that can not be extracted by methods commonly used in residue analysis and metabolism studies'. Another definition was recently given by the IUPAC Commission on Pesticide Chemistry (1984): 'non-extractable residues (sometimes referred to as "bound" or "non-extracted" residues) in plants and soils are defined as chemical species originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues'. According to the IUPAC Commission on Pesticide Chemistry (1984), in the context of their definition, methods 'refer to any procedures, such as solvent extraction and distillation, used to exhaustively remove chemical species from a soil or plant matrix'.

All definitions of soil-bound residues described above have in common that they only impose restrictions on the extraction method and thus are purely operational. It is not satisfactory to base the definition of a quantity such as the amount of herbicide transformed, on a quantity that has only an operational definition. It is generally observed that a small fraction of the soil-bound residue can be taken up by plants (IUPAC Commission on Pesticide Chemistry, 1984). This phenomenon may be caused by, for instance, a very steep sorption isotherm. It seems inappropriate to denote high affinity sorption as transformation. Therefore I propose to define that only that fraction of the soil-bound pesticide is transformed that is irreversibly bound. Furthermore the definition of 'irreversibly' should be directly linked to the system in which the reversibility of the soil-pesticide bond is actually important, i.e. in field soil. Thus, a pesticide molecule is said to be irreversibly soil-bound if it is no longer able to desorb into the liquid phase in soil under field conditions.

To illustrate the definition of transformation used above, Table 3.1 schematically shows the distribution of the properties 'transformed' and 'non-extractable' over the different phases and forms in which the residue of a certain amount of pesticide may occur in a closed soil system. Note that 'irreversibly bound' as defined above, does not necessarily imply 'non-extractable', because the soil system in the laboratory (i.e. soil subjected to extraction procedures commonly used in analytical chemistry) is not the same as the soil system in the field.

Admittedly, the proposed link between transformation and irreversibly soil-bound pesticide residue leaves unsolved the problem of how to measure whether or not a molecule is irreversibly bound. The procedures to be used will vary from herbicide to herbicide, and often the operational definitions of a soil-bound pesticide residue will also be acceptable to estimate the irreversibly soil-bound pesticide residue.

In the literature on transformation rate that will be discussed below, the distinction between irreversibly soil-bound (and thus transformed) herbicide and reversibly bound herbicide is based on an arbitrary extraction procedure (for instance, shaking for 1 h with some organic solvent). Usually, the research work-

Table 3.1. Schematic distribution of the properties transformed and non-extractable over the different phases and different forms in which a certain added amount of substance of a pesticide may occur in a closed soil system, some time after addition of the pesticide. The code is as follows: 1, transformed; 0, not transformed; +, extractable; -, non-extractable.

	Gas phase	Liquid phase	Solid phase	
			reversibly bound	irreversibly bound
Parent molecule	0, +	0, +	0, + or -	1, - or +
Other molecules or fractions of other molecules	1, +	1, +	1, + or -	1, - or +

ers concerned have checked that the extraction procedure used yields recovery values near 100 % if applied to a 1-day-old herbicide residue aged in the laboratory. It is known that the amount of field-aged herbicide residue recovered from soil depends on the extraction procedure (Smith, 1981). Thus, one must keep in mind that the somewhat arbitrary extraction procedure used may lead to an error in measuring transformation rate, if the procedure extracts only a fraction of the molecules that are able to desorb into the aqueous liquid phase.

3.2 DESCRIPTION OF THE MODELS

In all models considered, the transformation rate under constant conditions is described by a first-order rate equation:

$$R_{\mathrm{t}} = k_{\mathrm{t}}^{*}\, c^{*} \tag{3.1}$$

in which

k_{t}^{*} is transformation rate coefficient (d^{-1})

Theoretical considerations on the applicability of Equation 3.1 have been given by Hartley & Graham-Bryce (1980, pp. 206-207). Although other (more complex) rate equations have been proposed (see reviews by Hartley & Graham-Bryce, 1980, p. 208, and by Hurle & Walker, 1980), none of these equations has been used to simulate the transformation rate in field soil.

According to the review by Hurle & Walker (1980), both water content and temperature of the soil have a large influence on the value of the transformation rate coefficient, k_{t}^{*}. Walker (1974) proposed the use of the Arrhenius equation to describe the relationship between k_{t}^{*} and soil temperature:

$$k_{\mathrm{t}}^{*}(T) = C_{\mathrm{t},1} \exp\left(\frac{-U}{R\ T}\right) \tag{3.2}$$

in which

T	is soil temperature	(K)
$C_{\mathrm{t},1}$	is a coefficient	(d^{-1})
U	is molar energy of activation	(J mol^{-1})
R	is gas constant	(J mol^{-1} K^{-1})

To describe the relationship between k_{t}^{*} and water content of soil, Walker (1974) proposed an empirical equation:

$$k_t^*(w) = C_{t,2}\, w^B \tag{3.3}$$

in which

w	is water content of soil (i.e. the ratio of mass of water divided by mass of dry soil)	(kg kg^{-1})
$C_{t,2}$	is a coefficient	(d^{-1})
B	is a parameter	(1)

The effect of water content is thus reflected in the value of B.

Equations 3.2 and 3.3 can be combined to:

$$k_t^*(T,w) = C_{t,3}\, w^B \exp\left(\frac{-U}{R\ T}\right) \tag{3.4}$$

in which

$C_{t,3}$	is a coefficient	(d^{-1})

Walker (1974) developed a model of the transformation rate of herbicides in the top layer of field soil. The model is based on Equations 3.1 and 3.4. In Walker's approach the transformation rate coefficient for a certain herbicide/soil combination is measured in the laboratory over a range of temperatures and soil water contents. From these measurements the values of the parameters in Equation 3.4 ($C_{t,3}$, B and U) are derived. Walker's model contains sub-models for the simulation of water content and temperature in soil. In the model, only the uppermost centimetres of the soil are considered: it is assumed that the transformation rate is determined by average water content of the 0 to 25 mm soil layer and by temperature at 20 mm depth. In the model the water content increases during rainfall, the maximum being field capacity (defined in this model as the water content at a matric pressure of -10 kPa; personal communication A. Walker). The rate of decrease in water content caused by evaporation is calculated from the product of the flux of evaporation from a water surface and an evaporation reduction factor. No water is assumed to flow upward into the 0 to 25 mm layer from deeper layers. The sub-model for soil temperature requires daily averages of soil temperature at 100 mm depth as input. From these values, daily averages of the temperature at 20 mm depth are calculated, using an addition term that increases linearly with time from 0 °C on 1 April to 5 °C on 1 July and then decreases to 0 °C on 1 October. This addition term was based on field measurements by Walker (1974).

Walker & Barnes (1981) presented a revised version of Walker's 1974 model. Among the data required by the original model were records of the daily average of the soil temperature at 100 mm depth and the daily average of the flux of evaporation from a water surface. These requirements appeared to inhibit tests of the model, because such records are rarely available. Thus, Walker & Barnes (1981) revised the model to require only data on daily maximum and minimum air temperature, which are more readily available. In the new model, evaporation from a water surface is estimated from the daily maximum and minimum air temperatures and from the altitude and the latitude of the site, using a modified version of Linacre's equation (Linacre, 1977). The temperature of the top layer of soil is calculated from daily minimum and maximum air temperatures. The calculation is based on relationships between soil and air temperatures derived from measurements taken by Walker & Barnes (1981) in a sandy loam soil in England during one summer.

The models of Walker (1974) and Walker & Barnes (1981) are explanatory models to which the scheme of Figure 1.1 applies: transformation rates derived from laboratory experiments (summarized with help of the descriptive relationship of Equation 3.4) together with climatic data from the field are used to explain the transformation rate in the field.

3.3 TESTS OF THE MODELS

3.3.1 Laboratory tests

In a large number of experiments in the laboratory, various researchers have found that the transformation rate could be described well with the first-order rate Equation 3.1 (see references cited in Tables 3.2 and 3.3).

The vast majority of the laboratory measurements on the effect of soil temperature on the transformation rate coefficient reported in the literature have been described with the Arrhenius equation (Equation 3.2). Table 3.2 lists a number of values of the molar energy of activation, U, as found in the literature. All soil temperatures used in these experiments were in the range from 4 to 35 °C. All experiments were carried out in the laboratory at constant water content (most of them at one water content only). For a few herbicides Walker (1976b) and Kibler (1979) showed that U does not vary with water content. The range of U values in Table 3.2 is broad (27 to 92 kJ mol^{-1}). The value of U does not seem to be correlated with the type of herbicide: for instance, the range of 27 to 70 kJ mol^{-1} was found for simazine. On the other hand, the seven values of U found for propyzamide were in a narrower range: 60 to 75 kJ mol^{-1}. Soil texture does not seem to influence U strongly: the highest and the lowest values found in Table 3.2

Table 3.2. Effect of soil temperature on the transformation rate coefficient (expressed in the activation energy of the Arrhenius equation) as found in the literature, for different herbicides and soil textures.

Herbicide	Soil texture	Molar activation energy U (kJ mol^{-1})	Reference
Atrazine	sandy loam	70	Walker (1978)
Atrazine	sandy loam	51	Walker & Zimdahl (1981)
Atrazine	sandy loam	76	Hurle (1982)
Atrazine	loam	51	Walker & Zimdahl (1981)
Atrazine	silt loam	45	Walker & Zimdahl (1981)
Chlorsulfuron	sandy loam	67	Walker & Brown (1983b)
Chlorthal-dimethyl	sandy loam	92	Walker (1978)
Diuron	sandy loam	41	Hurle (1982)
Fluometuron	sandy loam	54	Graham-Bryce et al. (1982)
Fluometuron	clay	59	Graham-Bryce et al. (1982)
Isopropalin	loam	65	Gingerich & Zimdahl (1976)
Linuron	sandy loam	30	Walker (1976b)
Linuron	sandy loam	29	Walker (1978)
Linuron	sandy clay loam	50	Usoroh & Hance (1974)
Linuron	loam	37	Walker & Zimdahl (1981)
Linuron	silt loam	36	Walker & Zimdahl (1981)
Metamitron	sandy loam	47	Walker (1978)
Metolachlor	sandy loam	44	Walker & Zimdahl (1981)
Metolachlor	loam	50	Walker & Zimdahl (1981)
Metolachlor	silt loam	52	Walker & Zimdahl (1981)
Metribuzin	sandy loam	53	Hyzak & Zimdahl (1974)
Metribuzin	sandy loam	65	Walker (1978)
Napropamide	sandy loam	33	Walker (1974)
Oryzalin	loam	72	Gingerich & Zimdahl (1976)
Pendimethalin	sandy loam	52	Walker & Bond (1977)
Prometryne	sandy loam	56	Walker (1976a)
Propyzamide	sandy loam	73	Walker (1970)
Propyzamide	sandy loam	62	Walker (1976c)
Propyzamide	sandy loam	60	Walker (1976c)
Propyzamide	sandy loam	75	Walker (1978)
Propyzamide	clay loam	72	Walker (1976c)
Propyzamide	clay loam	63	Walker (1976c)
Propyzamide	clay	70	Walker (1976c)
Simazine	sand	51	Walker et al. (1983)
Simazine	sand	35	Walker et al. (1983)
Simazine	sand	34	Walker et al. (1983)
Simazine	loamy sand	45	Walker et al. (1983)
Simazine	loamy sand	69	Walker et al. (1983)
Simazine	sandy loam	62	Walker (1976a)
Simazine	sandy loam	57	Walker (1976b)
Simazine	sandy loam	70	Walker (1978)
Simazine	sandy loam	50	Walker et al. (1983)
Simazine	sandy loam	56	Walker et al. (1983)
Simazine	sandy loam	27	Walker et al. (1983)
Simazine	sandy loam	35	Walker et al. (1983)
Simazine	loam	58	Walker et al. (1983)
Simazine	clay loam	56	Walker et al. (1983)
Simazine	clay loam	64	Walker et al. (1983)

Simazine	clay loam	45	Walker et al. (1983)
Simazine	silty clay loam	62	Walker et al. (1983)
Simazine	clay	45	Walker et al. (1983)
Simazine	clay	39	Walker et al. (1983)
2,4,5-T	clay	85	Walker & Smith (1979)
Trifluralin	sandy loam	53	Walker (1978)

(27 and 92 kJ mol^{-1}) were measured using a sandy loam and a loamy sand soil, respectively. Thus, if one wants to estimate the U value of a specific herbicide/soil combination, all measured values of Table 3.2 are of identical weight. The frequency distribution of all values (Figure 3.1) shows that they may be treated as following a normal distribution. The average of all U values is 55 kJ mol^{-1} and the standard deviation is 15 kJ mol^{-1}. A 99 % confidence interval of the U values to be expected, embraces the range from 20 to 90 kJ mol^{-1}.

In a few cases (Smith & Walker, 1977; Kibler, 1979; Poku & Zimdahl, 1980) the dependence of the transformation rate coefficient on temperature could not be described satisfactorily by the Arrhenius equation: at temperatures in the range 20 to 40 °C the transformation rate coefficient no longer increased, or actually decreased with increasing temperature.

The vast majority of the laboratory measurements on the effect of soil water content on the transformation rate coefficient reported in the literature have been described with Equation 3.3. Table 3.3 lists a number of values of the exponent B as found in the literature. Water contents in the measurements reported were nearly always in the range between that corresponding to air-dry soil and that corresponding to a matric pressure of -10 kPa. Table 3.3 suggests that the value of B does not correlate with the type of herbicide or soil texture. The range of B values measured, for instance, for simazine was 0.0 to 1.3, and the frequency

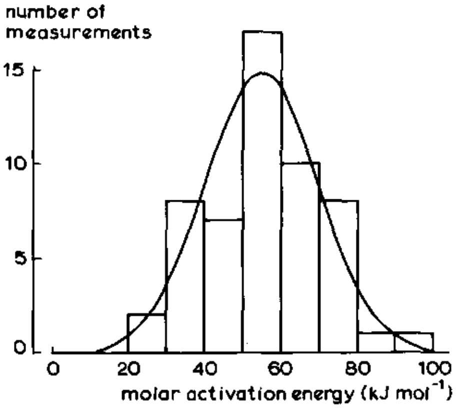


Figure 3.1. Frequency distribution of the molar activation energy, U, as found in the literature (Table 3.2). The smooth line is the probability density of the corresponding normal distribution.

Table 3.3. Effect of water content on the transformation rate coefficient (expressed in the exponent B of Equation 3.3) as found in the literature, for different herbicides and soil textures.

Herbicide	Soil texture	Exponent B(1)	Reference
Atrazine	sandy loam	0.2	Walker (1978)
Atrazine	sandy loam	0.5	Walker & Zimdahl (1981)
Atrazine	loam	0.8	Walker & Zimdahl (1981)
Atrazine	silt loam	0.6	Walker & Zimdahl (1981)
Chlorsulfuron	sandy loam	1.1	Walker & Brown (1983b)
Chlorthal-dimethyl	sandy loam	1.0	Walker (1978)
Chlortoluron	sandy loam	1.6	Hurle (1982)
Fluometuron	sandy loam	0.5	Graham-Bryce et al. (1982)
Fluometuron	clay	1.4	Graham-Bryce et al. (1982)
Linuron	sandy loam	0.5	Walker (1978)
Linuron	loam	0.9	Walker & Zimdahl (1981)
Linuron	silt loam	0.8	Walker & Zimdahl (1981)
Metamitron	sandy loam	1.0	Walker (1978)
Metolachlor	sandy loam	1.0	Walker & Zimdahl (1981)
Metolachlor	loam	0.8	Walker & Zimdahl (1981)
Metolachlor	silt loam	1.1	Walker & Zimdahl (1981)
Metribuzin	sandy loam	0.7	Walker (1978)
Napropamide	sandy loam	0.6	Walker (1974)
Prometryn	sandy loam	2.8	Walker (1976a)
Propyzamide	sandy loam	0.8	Walker (1973)
Propyzamide	sandy loam	0.6	Walker (1976c)
Propyzamide	sandy loam	0.8	Walker (1976c)
Propyzamide	sandy loam	0.7	Walker (1978)
Propyzamide	clay loam	1.0	Walker (1976c)
Propyzamide	clay loam	0.5	Walker (1976c)
Propyzamide	clay	0.8	Walker (1976c)
Simazine	sand	0.2	Walker et al. (1983)
Simazine	sand	0.2	Walker et al. (1983)
Simazine	sand	0.1	Walker et al. (1983)
Simazine	loamy sand	0.0	Walker et al. (1983)
Simazine	loamy sand	0.5	Walker et al. (1983)
Simazine	sandy loam	1.0	Walker (1976a)
Simazine	sandy loam	0.6	Walker (1978)
Simazine	sandy loam	0.7	Walker et al. (1983)
Simazine	sandy loam	0.2	Walker et al. (1983)
Simazine	sandy loam	1.3	Walker et al. (1983)
Simazine	sandy loam	0.2	Walker et al. (1983)
Simazine	loam	0.3	Walker et al. (1983)
Simazine	clay loam	1.0	Walker et al. (1983)
Simazine	clay loam	0.7	Walker et al. (1983)
Simazine	clay loam	0.1	Walker et al. (1983)
Simazine	clay	1.2	Walker et al. (1983)
Simazine	clay	0.4	Walker et al. (1983)
2,4,5-T	clay	0.7	Walker & Smith (1979)
Trifluralin	sandy loam	1.0	Walker (1978)

distribution of all B values (Figure 3.2) shows that this is almost the complete range. Furthermore, the highest and lowest values shown in Table 3.3 (2.8 and 0.0) were both measured using a loamy sand.

Using Equation 3.3 to describe the effect of soil water content on the transformation rate coefficient implies (for positive values of B) assuming that the transformation rate coefficient, k_t^*, approaches zero in completely dry soil and increases continuously with water content. In a laboratory experiment McAuliffe & Appleby (1981) found that ethofumesate disappeared much faster in air-dry silt loam soil than in the wet soil. Smelt et al. (1979) found that the rate coefficient for the nematicide oxamyl in a loamy sand soil at a water content of 0.03 kg kg^{-1} was higher than the coefficients at water contents between 0.06 and 0.2 kg kg^{-1}. Thus, extrapolation of Equation 3.3 to very dry situations is not always warranted.

In the experiments compiled in Table 3.3 the bulk density of the soil was not varied. Thus, for each experiment the water contents differed by a constant factor from the volume fractions of liquid. Consequently, for the experiments reported in Table 3.3, Equation 3.3 is equivalent to the equation:

$$k_t^*(\theta) = C_{t,4}\ \theta^B \qquad (3.5)$$

in which

$C_{t,4}$ is a coefficient (d^{-1})

3.3.2 Field tests

In 5 field experiments, Walker tested the sub-model he had developed to simulate the water content in the 0 to 25 mm layer (Walker, 1974, 1976c): these

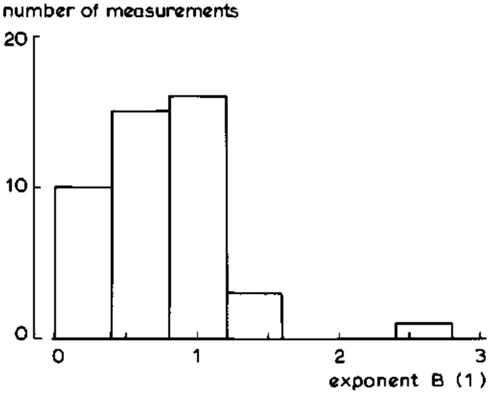


Figure 3.2. Frequency distribution of the exponent B of Equation 3.3 as found in the literature (Table 3.3).

tests showed that for each soil there were discrepancies between calculated and observed values, but that the model roughly simulated the general pattern of the fluctuation in soil water content. The sub-model for calculation of soil temperature at 20 mm depth was not tested. Walker's 1974 model has been tested some 50 times on different field plots or in different years for a series of herbicides (Walker, 1974, 1976a,b,c, 1978; Walker & Bond, 1978; Walker & Smith, 1979; Smith & Walker, 1977; Kibler, 1979). In these tests, measured decline of areic mass of herbicide in soil was compared with the decline simulated with the model. In about 3 out of 4 cases the model satisfactorily explained measured rates of decline. In the cases in which discrepancies were found, rates of decline measured in the field were nearly always higher than those calculated.

Walker & Barnes (1981) tested their sub-model for the simulation of water content in one field experiment in England and in two field experiments in Canada in two consecutive years. They found that generally there was good agreement between calculated and observed water contents. They also tested their sub-model for the simulation of soil temperature in two field experiments, one in Canada (clay soil) and one in the U.S.A. (silt loam soil) and found that the course of time of daily maxima and minima at a few centimetres depth in the soil was simulated reasonably by the relationships developed in England for a sandy loam soil, although deviations of 2-3 °C were common (Walker & Barnes, 1981). They calculated the decline in areic mass for a few field experiments with the revised model and found that these were similar to those calculated with Walker's original 1974 model. The model developed by Walker & Barnes (1981) was tested under a wide range of soil and climatic conditions by Poku & Zimdahl (1980), Walker & Zimdahl (1981), Walker & Brown (1983b) and Walker et àl. (1983). Poku & Zimdahl (1980) found reasonable agreement between calculated and measured areic mass of dinitramine in a clay loam soil. Sometimes, Walker & Zimdahl (1981) measured more loss of metolachlor and linuron than calculated, especially during the first 14 d. They argued that this may have been caused by processes other than transformation in soil, such as volatilization or photochemical transformation. Walker & Brown (1983b) found that the model explained chlorsulfuron persistence with reasonable accuracy. Walker et al. (1983) carried out a collaborative experiment on simazine persistence in soil (21 field experiments in 11 different countries) and found that in general the model overestimated areic masses in the field. According to Walker et al. (1983) deviations from first-order kinetics may be responsible for the discrepancy. They suggest further experiments to examine the transformation kinetics in more detail and also the factors that influence the kinetics, such as the microbial populations and the partition of the herbicide between solid and liquid phases during the course of prolonged incubation experiments.

Nicholls et al. (1982b) tested the model developed by Walker & Barnes (1981), using data from two field experiments with atrazine and metribuzin. They found good agreement for atrazine, but the measurements for metribuzin showed a faster decline than calculated. They also carried out calculations with a model in which the flow of water and the movement of herbicide were also simulated, and in which soil temperature was simulated in the same way as in the Walker & Barnes model. Calculations with both models for atrazine resulted in nearly identical results, whereas for metribuzin, calculations with the model that included movement resulted in areic masses that were 10-20 % lower than those calculated with the first model. However, discrepancies between measured and calculated areic masses of metribuzin were still large. Nicholls et al. (1982b) suggested that differences between soil conditions in the field and those in the laboratory were responsible for the discrepancies obtained with metribuzin.

Nicholls et al. (1984) measured rates of decline of simazine in a silty clay loam in the field in both summer and winter. They used a model similar to one they had used earlier (Nicholls et al., 1982b). A new assumption in the model was that a fraction of simazine occurred in undissolved state if the calculated concentration in the liquid phase in soil exceeded the solubility. It was assumed that undissolved simazine was neither degraded nor leached. Nicholls and his colleagues calculated soil temperature using the sub-model of Walker & Barnes (1981), but found that calculated soil temperatures were about 5 °C higher than those measured. From their own measurements they derived a new regression equation that relates air temperature to mean soil temperature. They found that the rate of decline of areic mass of simazine in winter was explained well by the model, whereas the rate of decline in summer was somewhat underestimated (Nicholls et al. 1984).

Graham-Bryce et al. (1982) carried out two field experiments with fluometuron. They used the model for the flow of water and the movement of fluometuron as developed by Leistra et al. (1980). Soil temperature was assumed to be constant with depth and equal to that measured at 100 mm depth 70-90 km away from their two experimental plots. The transformation rate was calculated with Equations 3.1, 3.2, and 3.3. In one field experiment the model only slightly overestimated the areic masses, but in the other it highly overestimated the areic masses.

3.4 DISCUSSION

The Arrhenius equation was developed to describe the effect of temperature on the rate coefficient of a chemical reaction. Obviously, this equation is not necessarily applicable to a combination of chemical and microbial transformation processes. For the microbial process the physical significance of an activation energy is not clear. Thus, there is no theoretical basis for the use of the Arrhenius equation to describe the effect of temperature on the rate coefficient of the transformation process of herbicides in soil. The only justification for its use is that it may give a good description of experimental data. It would be more appropriate to use the most simple equation that gives a good description of the experimental data. A simpler equation that satisfies the latter requirement, is

$$k_t^*(T) = k_t^*(T_0) \exp\{\gamma(T - T_0)\} \tag{3.6}$$

in which

T_0 is a reference temperature (K)
γ is a parameter (K^{-1})

From Equation 3.2 it can be derived that:

$$k_t^*(T_0) = C_{t,1} \exp\left(\frac{-U}{R\,T_0}\right) \tag{3.7}$$

With the help of Equation 3.7, $C_{t,1}$ can be eliminated from Equation 3.2 and Equation 3.2 can be rewritten in a form similar to that of Equation 3.6:

$$k_t^*(T) = k_t^*(T_0) \exp\{\frac{U}{R\,T_0\,T}(T - T_0)\} \tag{3.8}$$

which shows that

$$\gamma = \frac{U}{R\,T_0\,T} \tag{3.9}$$

In Equation 3.9, T is not constant, thus from a given value of U no exact corresponding value of γ can be derived. However, in practice T ranges from 273 to 308 K and if γ is calculated assuming T constant at 303 K, the maximum error in γ is only 10 %. Assuming T = 303 K and T_0 = 278 K (usually the lowest value at which transformation rates are measured in the laboratory), the value of the denominator of Equation 3.9 becomes 700 kJ K mol^{-1}. I calculated the quotient

$k_t^*(T)/k_t^*(278\ \mathrm{K})$ for a number of temperatures in the range from 5 to 35 °C using both Equation 3.2 and Equation 3.6 for $U = 60\ \mathrm{kJ\ mol^{-1}}$, and deriving γ from Equation 3.9 using the denominator value given above. Both quotients never differed more than 5 % from each other. Thus, for all practical purposes it is acceptable to convert U values into γ values using Equation 3.9 with a fixed denominator value of $700\ \mathrm{kJ\ K\ mol^{-1}}$. The average U value and the standard deviation of U as derived from the results in Table 3.2 (55 and 15 $\mathrm{kJ\ mol^{-1}}$, respectively), therefore correspond to an average γ value of $0.08\ \mathrm{K^{-1}}$ and a standard deviation of γ of $0.02\ \mathrm{K^{-1}}$.

The literature on the effect of water content on the transformation rate coefficient does not usually contain information about the relationship between matric potential and water content. Matric potential is a better characteristic of water availability than water content. Thus one would expect the relationship between k_t^* and matric potential to be less dependent on soil type than that between k_t^* and water content. The relationship between matric potential and water content is related to soil texture (see, for instance, Koorevaar et al., 1983). As soil texture does not seem to be related to the value of B, it may be expected that the relationship between k_t^* and matric potential is not unique.

The current literature contains reports of about 100 field tests of Walker's 1974 model and the similar model Walker & Barnes developed in 1981. Most of these tests showed that the models explained the observed decline of areic mass present in field soil reasonably well (e.g. Poku & Zimdahl, 1980; Walker & Zimdahl, 1981; Walker & Brown, 1983b; Walker et al., 1983; Nicholls et al., 1982b). In most of the remaining tests the model underestimated rates of decline in the field (e.g. Walker & Zimdahl, 1981; Walker et al., 1983; Nicholls et al., 1982b). Further testing of the models does not seem to be justified, as this will probably not alter this picture. At this stage, progress can only be made by examining quantitatively the causes of the discrepancies, but this is difficult because there are many possible causes. Processes other than transformation in soil may have caused loss of herbicide (for instance, volatilization, photochemical decomposition, or wind erosion). It is not easy to quantify these processes in field situations. Possible errors in the calculated temperatures should also be considered: at $U = 60\ \mathrm{kJ\ mol^{-1}}$ a temperature difference of 1 K corresponds with about 9 % difference in the rate coefficient. As shown by Nicholls et al. (1984) the relationship between the air and soil temperatures derived from measurements in England during one summer, is not generally applicable. Thus it seems more appropriate to use a physical (explanatory) sub-model for calculating the temperature in the soil. The estimation of the flux of evaporation of water from wet soil using the modified version of

Linacre's equation (Linacre, 1977) is probably not very reliable and has not been tested. Furthermore, as stated by Walker et al. (1983), conditions in soil in the laboratory may differ from those in the top layer of soil in the more dynamic field situation.

When comparing measured areic mass of herbicide with that calculated, one encounters the problem of variability in the field. From their variability measurements, Walker & Brown (1983a) calculated that the areic mass in a soil sample comprising 30 cores bulked and mixed together, has a 95 % probability of being only within 25 % of the true mean value. This was calculated assuming a normal distribution of the areic mass in the field. Data from Taylor et al. (1971) and Hörmann et al. (1973) suggest that this assumption is wrong (see Figures 3.3 and 3.4). A log-normal distribution seems more appropriate to describe their data. For problems in which the variability of the areic mass plays an important role, models that simulate the variability as well can be developed (for instance by Monte Carlo simulation). This merits further research.

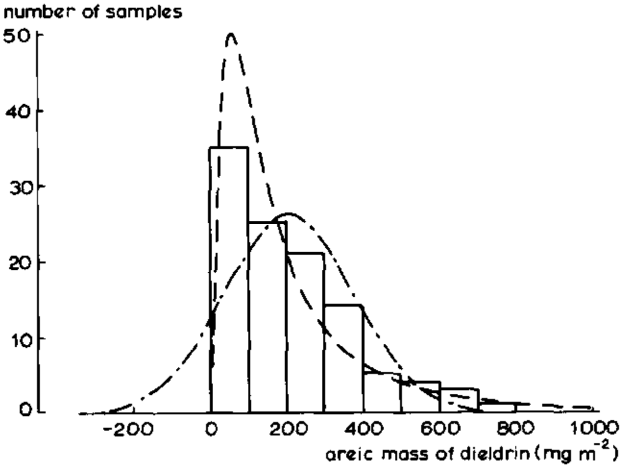


Figure 3.3. Frequency distribution of areic mass of dieldrin in soil as measured by Taylor et al. (1971) 530 d after application to a field plot of 6 m × 6 m. -·-·, --, probability densities of the corresponding normal and log-normal distributions, respectively.

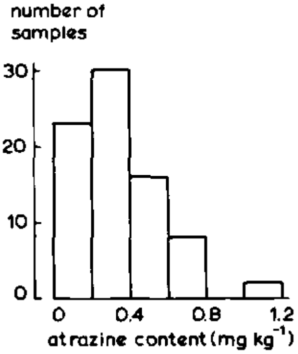


Figure 3.4. Frequency distribution of atrazine content in soil as measured by Hörmann et al. (1973) 136 d after application to a field plot of 1 m × 25 m.

4 FIELD EXPERIMENTS WITH HERBICIDES AND BROMIDE ION

4.1 INTRODUCTION

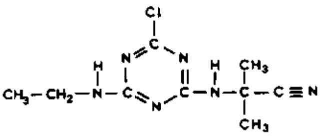
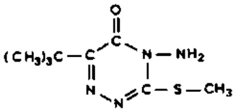
Field experiments with herbicides were carried out in spring and summer to test the equilibrium transport model (described by Equations 2.2 to 2.6) under these conditions. In Chapter 3 it was concluded that further field tests of the models for the transformation rate, R_t, were not justified. Thus the aim of the experiments was solely to test the model for the transport term $\partial J/\partial z$ (see Equation 2.1).

Back in 1971 and 1972 a few field experiments had been done by the Dutch Plant Protection Service on low-humic loamy sand soils in the Noord-Oost Polder of the former Zuyder Zee. In these experiments the herbicide cyanazine was applied on fields sown with peas before their emergence and it was found that damage occurred to the peas in both years (personal communication, H. Naber). This damage was possibly caused by herbicide penetrating too deeply into the soil, and the resulting uptake of too high amounts by the pea roots.

The experience obtained by the Dutch Plant Protection Service suggested that this herbicide/soil combination would be appropriate for a sensitive test of the transport model. Furthermore, of all soil types, in a sandy soil with a low organic matter content, leaching to groundwater and water courses occurs most rapidly, because such a soil sorbs herbicides most weakly.

In the first field experiment, in 1981, cyanazine movement in bare loamy sand soil was measured during two months in spring. As movement of cyanazine in 1981 was limited, in addition to cyanazine the more mobile herbicide metribuzin was applied in the second field experiment carried out in 1982. In Table 4.1 the structural formulas and other physico-chemical properties of both herbicides are given. In 1982 bromide was also applied: bromide as a negative ion is not sorbed by sandy soil, so its movement can be used to test the model for non-sorbing substances. In the 1982 experiment, the movement of the two herbicides and bromide ion in bare soil was measured over a period of 4 months in spring and summer.

Table 4.1. Physico-chemical properties of cyanazine and metribuzin (from Martin & Worthing, 1977).

	Cyanazine	Metribuzin
Structural formula		
Molecular formula	$C_9H_{13}ClN_6$	$C_8H_{14}N_4OS$
Relative molecular mass	240.7	214.3
Melting point	167 °C	125 °C
Saturated vapour pressure	0.2 μPa at 20 °C	30 mPa at 60 °C <1 mPa at 20 °C
Solubility in water	0.17 kg m^{-3} at 25 °C	1.2 kg m^{-3} at 20 °C

4.2 MATERIALS AND METHODS

4.2.1 Experimental field, application of herbicides, and sampling

The field experiments were done on experimental plots on 'de Waag' experimental farm near Creil (Noord-Oost Polder) about 1 km from the IJsselmeer dike.

The distance between the experimental plot of 1981 and that of 1982 was about 200 m. In 1981 the plot was 8 m × 25 m and in 1982 it was 12 m × 30 m. In spring 1981, after ploughing in winter, the soil was tilled with a cultivator-harrow, a float and a roller. This resulted in a very smooth and even surface of the soil. In spring 1982, after ploughing in winter, the soil was only tilled with a cultivator-harrow and the resulting surface was still cloddy and irregular. The soil was also tilled manually with a harrow and a Cambridge roller. This resulted in a regular surface, most of which was covered with clods some 10 mm in diameter.

In the field there were drains at about 0.9 m depth and the water level in the ditches was maintained at about 1.2 m below the surface of the field.

In both years, before the start of the experiments soil was sampled to 0.2 m depth by taking 40 cores in 1981 and 100 cores in 1982; the surface area of each core was about 5 cm^2. The soil was mixed and passed through a 4-mm sieve.

Characteristics of these soil samples are given in Table 4.2. The textural class of both plots was loamy sand.

In both years the herbicides were sprayed onto a dry soil surface. No rain fell in the 4 d prior to spraying in 1981. In 1982, 3 mm fell 2 d before spraying, and 0.1 mm fell on the day before and the day of spraying.

In both years the herbicides and bromide ion were sprayed on the plot from a boom with 6 nozzles (Birchmeyer-160) spaced 0.33 m apart. In 1981 spraying pressure was 0.2 MPa and spraying height was 0.5 m; in 1982 these values were 0.3 MPa and 0.7 m respectively. The coefficient of variation of the volumes of water sprayed by the 6 nozzles in a period of 15 s was found to be 5 % in 1981 and 3 % in 1982. Speed of walking during spraying was 0.5 m s^{-1} in 1981 and 1.3 m s^{-1} in 1982.

In the evening of 11 May 1981 cyanazine was sprayed at a dose (areic mass) of 58 mg m^{-2} in an areic volume of water of 0.07 mm. In the evening of 5 May 1982, cyanazine was sprayed at a dose of 164 mg m^{-2} in an areic volume of water of 0.04 mm. Only 1 h thereafter metribuzin and sodium bromide were mixed in the same tank and sprayed on the same plot, again in an areic volume of water of 0.04 mm. Metribuzin was sprayed at a dose of 99 mg m^{-2}, sodium bromide at a bromide dose of 9.9 g m^{-2}. In both years, cyanazine was applied as Bladex®, which is a wettable powder with a mass fraction of cyanazine of 0.5. Metribuzin was applied (in 1982) as Sencor®, which is a wettable powder with a mass fraction of metribuzin of 0.7.

Table 4.2. Characteristics of the soil in the 0 to 0.2 m layer of the experimental plots in 1981 and 1982.

	Plot in	
	1981	1982
Mass fraction of organic matter (kg kg^{-1})	0.017	0.018
Mass fraction (kg kg^{-1}) of particles with equivalent diameters between:		
0- 2 µm	0.06	0.03
2- 50 µm	0.12	0.20
50- 150 µm	0.81	0.76
150-2000 µm	0.01	0.01
Mass fraction of $CaCO_3$ (kg kg^{-1})	0.036	0.037
pH-KCl	7.4	7.4

In both 1981 and 1982, the variation in the deposition of cyanazine on the soil surface was measured. Polyurethane discs 30 mm thick and 110 mm in diameter were covered with aluminium foil. The foil was fixed to the disc by pushing a plastic ring about 10 mm wide and 110 mm in diameter onto the disc plus foil, leaving an area of 57 cm^2 of foil exposed to the spray. The foil-covered discs (26 *in* 1981 *and* 47 *in* 1982) were *regularly* spaced over the surface of the experimental plot before the cyanazine was sprayed. After spraying, the foil-covered discs were transferred to the laboratory for cyanazine extraction and analysis.

In 1981 the soil was sampled at 1, 16, 30, 45 and 64 d after spraying, in 1982 at 1, 14, 34, 56 and 121 d after spraying. On all dates samples were taken at 5 spots in the field. In 1981 the sampling spots at each sampling time were evenly distributed over the field. In 1982 sampling spots were selected at random: before the start of the experiment a rectangular grid pattern of 2 m × 2 m was defined. This resulted in 84 grid units. Using a table of random numbers the grid units sampled at the subsequent dates were determined.

In both years the 0 to 100 mm layer was sampled within a rectangular iron frame (see Figure 4.1). The size of the base of the frame was 500 mm × 100 mm and it was 100 mm deep. The longer sides were flanged at the top (the flanges were 40 mm wide). In 1981 the frame was pushed and hammered into the soil until the flanges were flush with the soil surface. Then, three wooden beams each 25 mm thick were stacked on each of the flanges. A rectangular scoop (100 mm deep) with flanges that slid over the wooden beams was then used to sample the 0 to 25 mm layer (see Figure 4.1). By removing one wooden beam from each of the flanges of the frame the 25 to 50 mm layer could be sampled; by removing another pair of wooden beams the 50 to 75 mm layer could be sampled, and so on. For accurate working, half of the frame was emptied before sampling. Thus the size of the area sampled was 100 mm × 250 mm.

In 1982 the sampling method was modified, using the same frame but using a steel frame instead of the wooden beams to regulate depth (see Figure 4.1). Three iron pins (250 mm high) were provided with a horizontal iron disc (80 mm in diameter) at a height of 100 mm. The pins with discs were welded onto iron bars. The pins were pushed into the soil up to the horizontal discs and the frame was screwed to the upper parts of the pins in such a way that the bottom of the frame was flush with the soil surface. The position of each of the three points of suspension of the frame were read on measuring tapes attached to the pins and they were lowered according to the desired thickness of the soil layer to be sampled (see Figure 4.1). After this, the soil was sampled in the same way as in 1981. In 1982 the following layers in the top 100 mm were sampled: 0 to 15 mm,

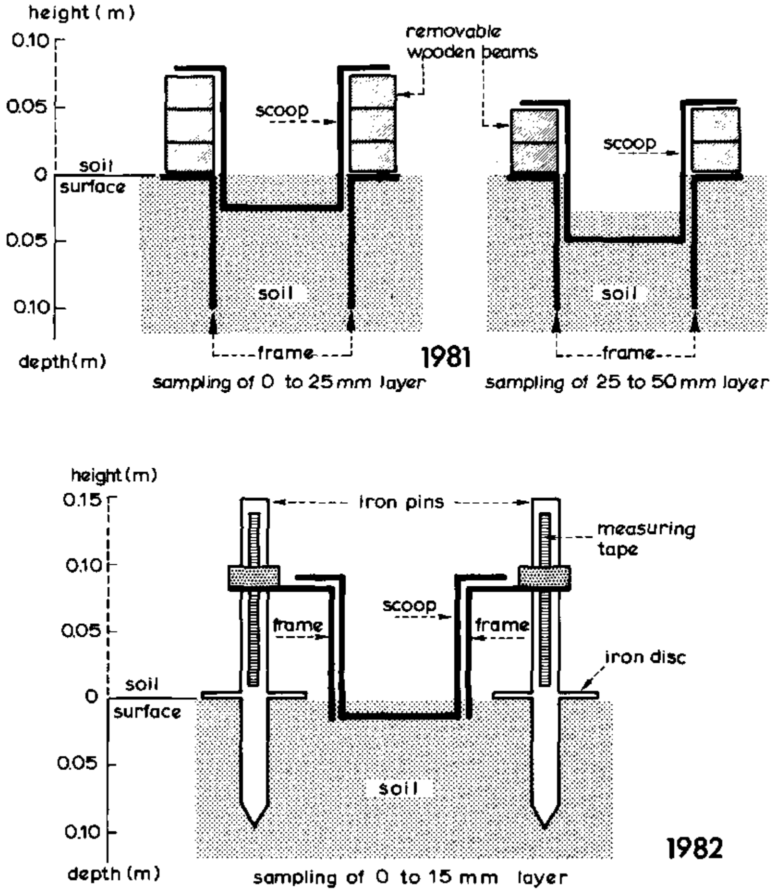


Figure 4.1. Schematic representation of the sampling procedures in 1981 and 1982.

15 to 30 mm, 30 to 50 mm, 50 to 75 mm and 75 to 100 mm. The main difference between sampling in 1981 and 1982 was that in 1981 the frame was pushed and hammered into the soil to a depth of 100 mm before sampling, whereas in 1982 the frame was only pushed to the lower depth of the next layer to be sampled.

In both years the 100 to 200 mm layer was sampled within the frame area using a cylindrical auger 150 mm long and 40 mm in diameter. The auger could be divided lengthwise into two halves. The soil core could then easily be divided crosswise into the 100 to 150 and 150 to 200 mm layers. In each frame area three soil cores were taken and the three samples per soil layer were bulked. Thus the sampled surface area of the 100 to 200 mm layer was only 15 % of that of the 0 to 100 mm layer.

After 121 d in 1982 the 200 to 400 mm layer was also sampled within the frame area using a cylindrical auger about 400 mm long with a sampling area of about 5 cm^2. In each frame area three soil cores were taken. Each soil core was divided into the 200 to 300 mm and 300 to 400 mm layers and the three samples per layer were bulked.

Each of the soil samples per layer and per sampling spot were collected in polyethene bags. They were transferred to the laboratory on the same day and stored for 1 to 3 d at 4 °C. The soil in the bags was weighed, sieved (4 mm mesh) and mixed. Larger solid particles, mostly shell remnants, were discarded. Water content was determined by drying a subsample of 60 to 200 g overnight at 105 °C. After subsamples had been taken for chemical analysis, a portion of the remaining soil was stored at -18 °C.

4.2.2 Meteorological measurements

Both in 1981 and 1982 rainfall was recorded continuously from the start of the experiments using a Lambrecht (type 1509-10H) rain gauge installed on the edge of the experimental plot. The speed of the recording paper was 0.24 m d^{-1} and 1 mm of rainfall corresponded with 10 mm on the paper. The surface area of the aperture was 200 cm^2 and the aperture was located 1.2 m above the soil surface.

In 1982 in some periods during the field experiment cumulative rainfall was also measured using a Lambrecht (type 1507C) rain gauge (0.45 m tall). The surface area of its aperture was also 200 cm^2 and the rim of this gauge was flush with the soil surface. Around this gauge a metal grid (0.8 m × 1.0 m) was placed on the soil surface to prevent rain splashing from the soil surface into the gauge. This grid consisted of iron strips, 20 mm high and 2 mm thick with a mesh width of 30 mm. In the centre of the grid there was a hole (250 mm in diameter), which was positioned above the gauge. In both years checks were made periodically to ensure that the apertures of the gauges were still water-level.

In 1981 soil temperature at 50 mm depth was measured with a thermocouple. In 1982 measurements were taken at depths of 10 and 50 mm. In both years the signal was recorded continuously with a 1 mV recorder.

4.2.3 Extraction and analysis of the herbicides

In the laboratory, each of the aluminium foils exposed to cyanazine spray was put into a glass jar (volume: 250 cm^3). The foils were washed by shaking with 50 cm^3 of ethyl acetate for 1 h. The cyanazine concentrations in the extracts were measured by gas-liquid chromatography (GLC).

Subsamples of 50 g of moist soil were weighed into 250 cm^3 jars. 25 cm^3 of water containing $CaCl_2$ at a concentration of 10 mol m^{-3} and 50 cm^3 ethyl acetate were added and the jars were shaken for 1 h on a reciprocating shaker. This single extraction with ethyl acetate was applied in 1981 for cyanazine and in 1982 for both cyanazine and metribuzin.

In 1981 25 cm^3 of the ethyl acetate layer were evaporated to dryness on a water bath (40 °C) under a gentle stream of air. Samples from the 0 to 50 mm layers contained high contents of the insecticide trichloronate (accidentally sprayed on the plot) which interfered with cyanazine measurement when using GLC. Therefore these samples were measured by high-pressure liquid chromatography (HPLC). The residues of the ethyl acetate extracts of the 0 to 50 mm layers were dissolved in 4 cm^3 of a water-methanol-acetonitrile mixture (75:20:5 by volume) by ultrasonic vibration for 1 h. The HPLC system consisted of a Waters WISP sample processor (sample volume 100 mm^3) and a Spectra Physics SP8000 liquid chromatograph equipped with a variable wavelength detector (Schoeffel SF770), set at 225 nm. A stainless steel precolumn (50 mm long; 4.6 mm inner diameter) packed with Copell ODS (37 μm), and an analytical column (250 mm long; 4.6 mm inner diameter) packed with Lichrosorb 10-RP-8 were used for separation. The temperature of the analytical column was maintained at 50 °C. The mobile phase was a water-methanol-acetonitrile mixture (70:25:5 by volume), pumped at a volume rate of 25 mm^3 s^{-1}. The retention time of cyanazine under these conditions was 18 min. Standard solutions with concentrations of 0.5 to 4 g m^{-3} were made from cyanazine (96 % pure) and injected regularly. Standard curves were made from peak areas or peak heights. Limit of detection was 0.01 mg per kilogram soil.

The residues of the ethyl acetate extracts of the 50 to 100 mm layers were dissolved in 4 cm^3 ethyl acetate by shaking manually. The cyanazine concentration was measured by injecting 3 mm^3 in a Tracor-550 gas chromatograph equipped with a Tracor-702 nitrogen phosphorus thermionic detector. The Pyrex glass column (400 mm long; 2 mm inner diameter) was packed with 4 % SE 30 / 6 % SP 2401 on Supelcoport (0.13-0.15 mm). The isothermal operating conditions were: inlet port 210 °C; column oven 190 °C; detector 260 °C. The carrier gas was helium at a volume rate of 0.8 cm^3 s^{-1}. Retention time of cyanazine under these conditions was 2.0 min. Standard solutions with concentrations of 0.1 to 10 g m^{-3} were made from cyanazine (96 % pure) and injected regularly. Standard curves were made from peak areas or peak heights. The limit of detection was 0.005 mg per kg soil.

In 1982 10 cm^3 of the ethyl acetate layer of the extracts were dried over

0.5 g anhydrous Na_2SO_4. The concentrations of both cyanazine and metribuzin were measured by injecting 3 mm^3 in a Tracor-550 gas chromatograph equipped with an electron capture detector (^{63}Ni). The Pyrex glass column (1.30 m long; 2 mm inner diameter) was packed with 1 % SP 2330 on Supelcoport (0.13-0.15 mm). The isothermal operating conditions were: inlet port 225 °C; column oven 210 °C; detector 300 °C. Nitrogen was used as carried gas at a volume rate of 1.5 cm^3 s^{-1}. The retention times for cyanazine and metribuzin under these conditions were 6.3 min and 2.0 min, respectively. Standard solutions with concentrations of 5 to 500 mg m^{-3} cyanazine and 5 to 50 mg m^{-3} metribuzin were made from cyanazine (96 % pure) and metribuzin (97 % pure) and they were injected regularly. Standard curves were made from peak heights or peak areas. Limits of detection were 0.002 and 0.001 mg per kilogram soil for cyanazine and metribuzin, respectively.

Recovery was tested by weighing 50 g portions of air-dried untreated soil into 250 cm^3 jars and adding 10 cm^3 solution of cyanazine, metribuzin or a mixture of both in water containing $CaCl_2$ at a concentration of 10 mol m^{-3} (all treatments in triplicate). After standing overnight at 4 °C, extractions and measurements were carried out as described above. Stock solutions of the herbicides in water were also extracted with ethyl acetate to check the masses of herbicides added. Recoveries of cyanazine at a content of 0.2 mg kg^{-1} were 101 % to 103 % with the GLC method in 1981 and 97 % to 101 % with the HPLC method. In 1982, recoveries of cyanazine were 102 % to 115 % in one experiment at a content of 0.2 mg kg^{-1} and they were 94 % to 97 % in a second experiment with contents ranging from 0.05 to 0.4 mg kg^{-1}. Recoveries of metribuzin were 89 % to 94 % in one experiment at a content of 0.27 mg kg^{-1} and they were 93 to 100 % in a second experiment with contents ranging from 0.02 to 0.4 mg kg^{-1}. Addition of 2 g NaBr per kilogram soil or storage of soil samples during 5 months at -18 °C did not affect recoveries of both herbicides. In view of these recovery percentages no correction factor for incomplete recovery was applied.

After the soil samples had been stored -18 °C for 1 to 5 months in 1981 and 1982, the analytical procedure was checked. All soil samples from one sampling spot at each sampling date were extracted and analysed once again as described above. In 1981 the second measurements (18 samples) resulted in cyanazine contents that were on average 105 % (with a standard deviation, s, of 9 %) of those of the first measurements. In 1982 the second measurements (20 samples for cyanazine and 22 for metribuzin) resulted in contents that were for cyanazine and metribuzin respectively, on average 95 % (s = 16 %) and 93 % (s = 18 %) of those of the first measurements. Thus in 1982, the first and second measurements corresponded well on average, but occasionally accuracy of a measurement was low.

4.2.4 Extraction and analysis of bromide ion

In 1982 bromide ion was extracted by shaking 25 g of moist soil with 25 cm^3 of water containing $CaCl_2$ at a concentration of 10 mol m^{-3} in a glass-stoppered flask on a rotating disk for 1 h. After centrifugation at a rotation frequency of 30 s^{-1} for 10 min a fraction of the supernatant was filtered through a Millipore filter (pore size 0.45 μm). The concentration of bromide ion was measured with a Varian-500 liquid chromatograph equipped with a precolumn (50 mm long; 4.6 mm inner diameter) packed with Bondapack-TM Phenyl/Corasil for protection of the analytical column and an analytical column packed with Bondapack-NH_2 (250 mm long; 4.6 mm inner diameter). The mobile phase, water containing KH_2PO_4 at a concentration of 10 kg m^{-3}, set at pH 3.0 with phosphoric acid, was pumped at a volume rate of 25 mm^3 s^{-1}. Retention time for the bromide ion was 3.9 min. A Varichrom U.V. detector, set at 210 nm, was used for detection. The detection signal was linear up to a bromide concentration of 100 g m^{-3}. Limit of detection was 1 g m^{-3}. More detailed information about this analytical procedure is given by Harmsen (1982).

In a recovery experiment 25 g untreated soil and 5 cm^3 water containing bromide ion at a concentration of 500 g m^{-3} were mixed (in triplicate). After standing overnight at room temperature (about 17 °C) bromide ion was extracted and measured as described above. Recoveries were measured to be 96 % to 98 %. In a long-term bromide ion recovery experiment the flasks containing the soil plus bromide ion were left open and kept in the laboratory for 3 months, near the windows so they were exposed to sunlight. Recoveries of these artificially aged bromide residues were found to be 92 % to 101 %. These recovery values were so high that no correction factor for incomplete recovery needed to be applied.

The bromide contents of all soil samples from one sampling spot at each sampling date were determined once again after the samples had been stored for 4 to 8 months at -18 °C, to check the extraction and analysis of bromide ion. The second measurements (23 samples) resulted in bromide contents that were on average 102 % (s = 5 %) of those of the first measurements.

4.3 RESULTS AND DISCUSSION

Figure 4.2 shows daily rainfall and cumulative rainfall as measured with the rain gauge with aperture at 1.2 m above the soil surface. The distribution of total rainfall over the hourly averages of the volume flux of rainfall is shown in Figure 4.3. From the original recordings it can be inferred that actual rainfall

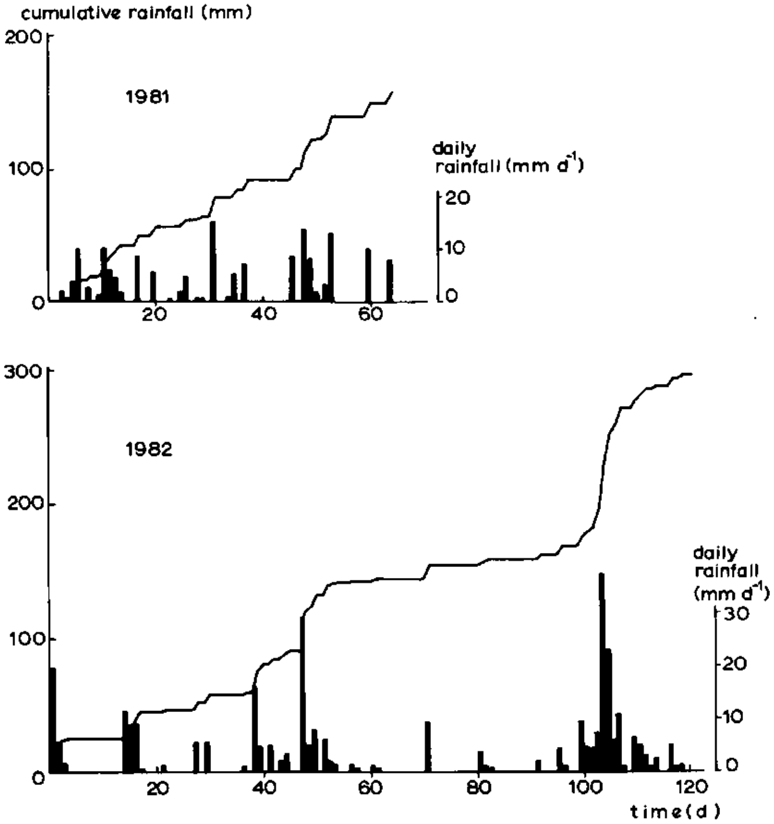


Figure 4.2. Rainfall measured at the experimental field in 1981 and 1982 with the rain gauge with aperture at 1.2 m above the soil surface. Vertical bars are daily averages of the volume flux of rainfall; ——, cumulative rainfall. Time zero on the graphs represents the end of the day on which the substances were sprayed (i.e. 11 May in 1981 and 5 May in 1982).

fluxes were sometimes 5 to 10 times the hourly average. Figure 4.3 shows that hourly averages of volume fluxes of rainfall of about 100 mm d^{-1} were common.

Rainfall measured at 1.2 m height and that measured at soil surface level are compared in Figure 4.4. Measurements at the soil surface were always slightly higher. A least-squares linear regression approximation of a line through the origin, resulted in a slope of 1.07 m m^{-1}. It is common that when measured flush with the soil surface, rainfall values are higher than those measured at a certain height (Beese & Van der Ploeg, 1978; Warmerdam, 1981). In all subsequent calculations for both 1981 and 1982 it is assumed that actual rainfall was equal to 1.07 times the rainfall measured at 1.2 m height.

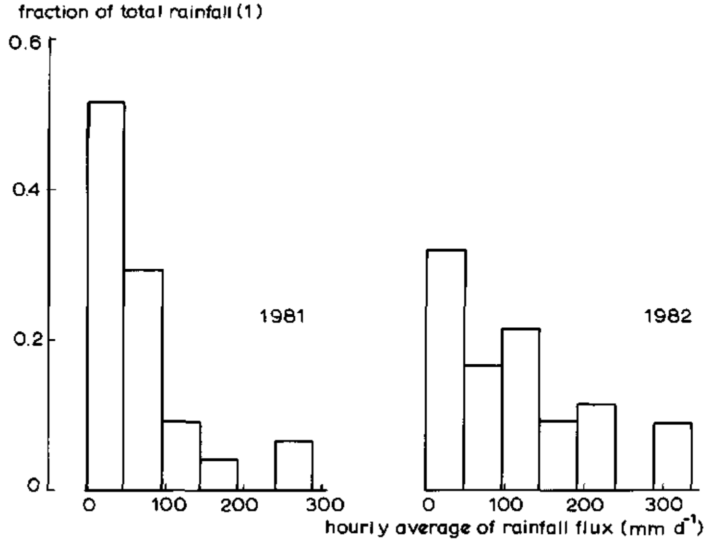


Figure 4.3. Distribution of total rainfall over the hourly average of the volume flux of rainfall as measured at the experimental fields in 1981 and 1982 with the rain gauge with aperture at 1.2 m above the soil surface.

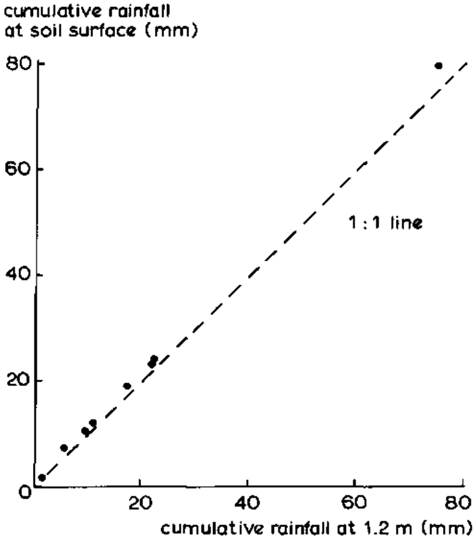


Figure 4.4. Cumulative rainfall measured with the rain gauge with aperture flush with the soil surface, plotted against that measured with the gauge with aperture at 1.2 m above the soil surface.

Figure 4.5 shows daily averages of soil temperature at 50 mm depth for both years. Soil temperature at 50 mm depth averaged over the whole experimental periods was 17 °C in 1981 and 19 °C in 1982. Daily averages of soil temperature

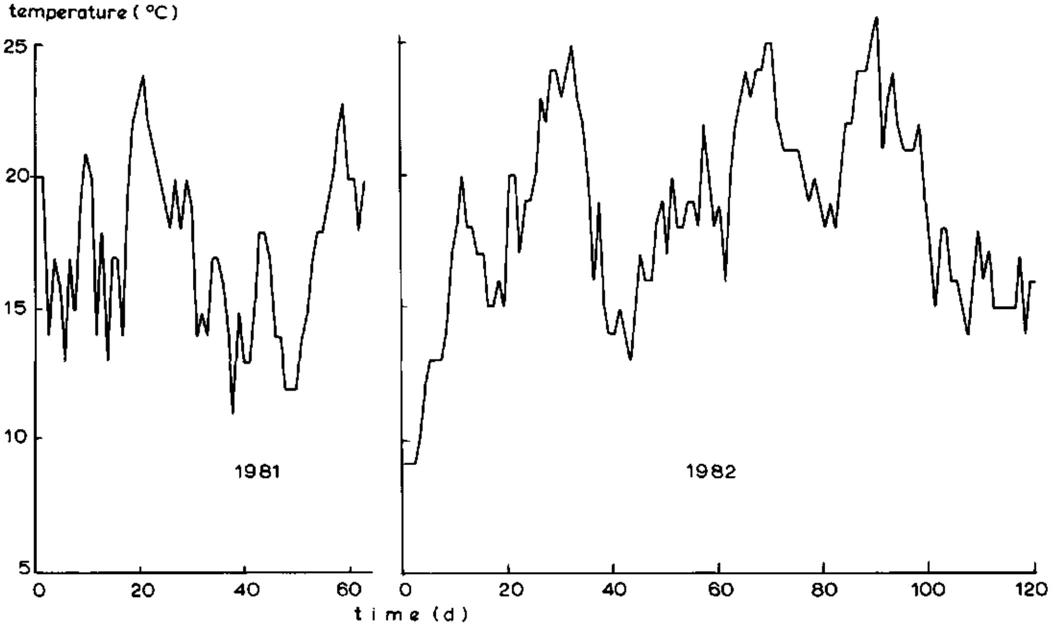


Figure 4.5. Daily average of soil temperature at 50 mm depth as a function of time at the experimental fields in 1981 and 1982. Time zero on the graphs represents the end of the day on which the substances were sprayed (i.e. 11 May in 1981 and 5 May in 1982).

measured at 10 and 50 mm depth were compared for ten days distributed over the experimental period in 1982: on average the temperature at 10 mm was 0.3 °C higher than that at 50 mm. The standard deviation of the differences between daily averages of soil temperatures at 10 and 50 mm was 0.5 °C. Thus, daily averages of soil temperatures at 10 and 50 mm depth usually differed less than 1 °C. Consequently, the daily average of soil temperature at 50 mm depth can be considered representative for the 10 to 50 mm layer.

Figure 4.6 shows frequency distributions of the areic mass of cyanazine recovered from the aluminium foils. In 1981 the average areic mass as calculated from the mass applied and from the surface area of the plot amounted to 58 mg m^{-2}, whereas the average areic mass as measured from the foils amounted to 52 mg m^{-2}, corresponding with a loss of 10 %. In 1982 these figures amounted to 164 and 152 mg m^{-2}, respectively, corresponding with a loss of 7 %. Such losses are small and may be due to e.g. spillage or spray drift. Figure 4.6 shows that the frequency distributions in both years are described reasonably by a normal distribution. Coefficients of variation of the frequency distributions shown in Figure 4.6 were estimated to be 18 % and 21 % in 1981 and 1982, respectively.

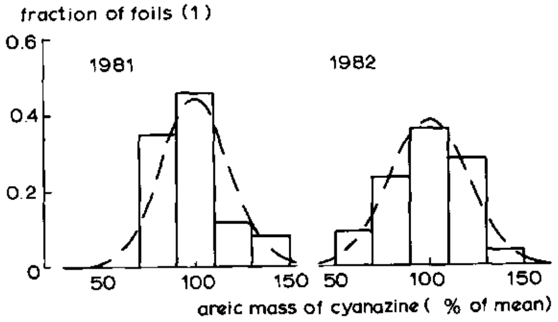


Figure 4.6. Frequency distributions of areic mass of cyanazine on the aluminium foils in 1981 and 1982. The averages correspond with areic masses of cyanazine of 52 and 152 mg m^{-2} in 1981 and 1982, respectively. Dashed lines indicate the probability densities of the corresponding normal distributions.

These estimates imply that more than 98 % of all values can be expected to be within the range of 50-150 % of the average.

Tables 4.3 and 4.4 show dry bulk density as a function of depth and time during the two field experiments. In both years, bulk density increased steadily with depth in the 0 to 100 mm layer, whereas the values for the 100 to 200 mm layer were often somewhat lower than those for the 75 to 100 mm layer. This is probably an artifact, caused by soil being lost when sampling the 100 to 200 mm layer with the auger. The variability of the bulk densities was low in the field: all coefficients of variation were lower than about 10 %, except for the coefficient for the 0-15 mm layer after 1 d in 1982, which was about 20 %. This high value can be attributed to the somewhat cloddy surface at the start of the field experiment in 1982. An increase in bulk density over time caused by compaction of the top layer did not occur (see Tables 4.3 and 4.4). Bulk densities in the 0 to 50 mm layer in 1982 were somewhat higher than those in 1981. This is probably the result of the additional tillage in 1982 with the harrow and the Cambridge roller.

Figure 4.7 shows some examples of the profiles of volume fraction of liquid measured in the field in 1981 and 1982. Variability of the volume fractions of liquid also was low: estimated coefficients of variation were usually 5-10 %. An exception is the top layer, which had coefficients of variation in the range of 10-40 %.

Table 4.5 shows that average areic mass of cyanazine recovered from the soil at 1 d after spraying both in 1981 and 1982 was almost equal to that recovered from the aluminium foils. Average areic mass of metribuzin recovered from the soil at 1 d after spraying in 1982 was only 8 % less than that calculated to have been applied.

Table 4.3. Average dry soil bulk density at the sampling dates as a function of depth during the field experiment in 1981. Figures in parenthesis indicate standard deviations.

Depth (mm)	Bulk density (Mg m^{-3}) after				
	1 d	16 d	30 d	45 d	64 d
0 - 25	1.03 (0.08)	1.14 (0.09)	0.97 (0.03)	1.09 (0.11)	1.11 (0.05)
25 - 50	1.13 (0.11)	1.20 (0.12)	1.20 (0.10)	1.17 (0.01)	1.20 (0.10)
50 - 75	1.40 (0.06)	1.35 (0.07)	1.37 (0.07)	1.35 (0.04)	1.38 (0.07)
75 - 100	1.43 (0.03)	1.46 (0.09)	1.45 (0.07)	1.45 (0.07)	1.50 (0.08)
100 - 150	1.38	1.43 (0.03)	1.44 (0.06)	1.41 (0.11)	1.40 (0.13)
150 - 200	1.40	1.42 (0.04)	1.42 (0.04)	1.41 (0.05)	1.41 (0.07)

Table 4.4. Average dry soil bulk density at the sampling dates as a function of depth during the field experiment in 1982. Figures in parenthesis indicate standard deviations.

Depth (mm)	Bulk density (Mg m^{-3}) after				
	1 d	14 d	34 d	56 d	121 d
0 - 15	1.27 (0.26)	1.23 (0.09)	1.29 (0.12)	1.14 (0.12)	1.33 (0.11)
15 - 30	1.25 (0.15)	1.22 (0.06)	1.27 (0.05)	1.42 (0.07)	1.27 (0.05)
30 - 50	1.27 (0.06)	1.27 (0.08)	1.32 (0.05)	1.28 (0.17)	1.37 (0.08)
50 - 75	1.31 (0.10)	1.41 (0.04)	1.39 (0.06)	1.40 (0.07)	1.41 (0.08)
75 - 100	1.39 (0.11)	1.40 (0.07)	1.43 (0.07)	1.49 (0.07)	1.41 (0.08)
100 - 150	1.37 (0.07)	1.36 (0.09)	1.41 (0.04)	1.54 (0.07)	1.42 (0.07)
150 - 200	1.39 (0.04)	1.32 (0.06)	1.32 (0.07)	1.38 (0.02)	1.28 (0.02)

Table 4.5. Areic mass of herbicide at the start of the field experiments as estimated with different methods. Figures in parenthesis indicate standard deviations.

Estimation method	Areic mass (mg m^{-2})		
	cyanazine		metribuzin
	1981	1982	1982
Calculated to have been applied	58	164	99
Recovered from the aluminium foils	52 (9)	152 (31)	
Recovered from soil after 1 d	49 (11)	152 (27)	91 (12)

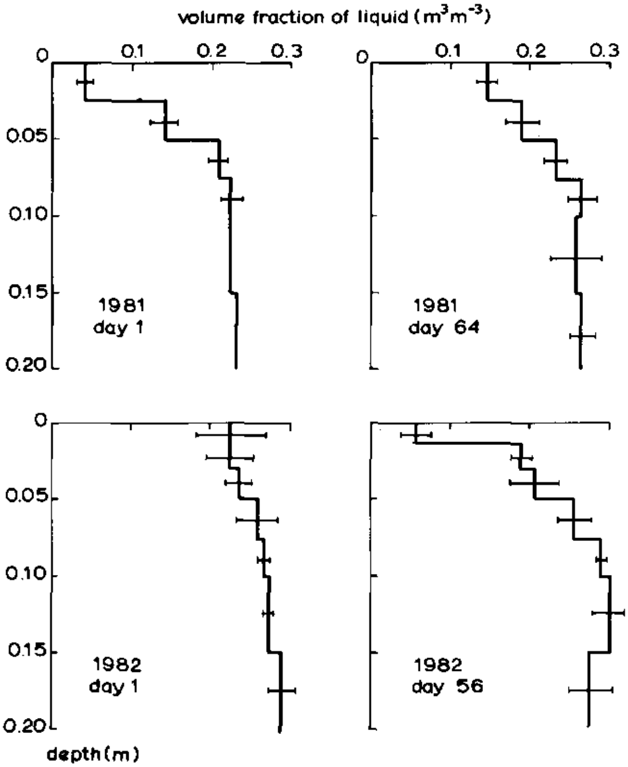


Figure 4.7. A few examples of moisture profiles measured in the field in 1981 and 1982. Vertical line segments are average values, horizontal bars standard deviations.

Figure 4.8 shows concentration profiles of cyanazine in the field experiment in 1981. After 1 d no movement had taken place because no rain fell in the night between application and first sampling. On 6 May the dry remnants of the spraying drops still could be seen on the soil surface. Nevertheless, the concentration profile measured after 1 d shows some apparent movement (concentrations in the 50 to 100 mm layers are from one sampling spot only). This apparent movement must be the result of contamination during sampling: in 1981 the frame was pushed and hammered into the 0 to 100 mm layer before sampling and it was observed in the field that soil particles from the dry surface layer had reached deeper layers along the wall of the frame. On other sampling dates in 1981 the effect of the contamination on measured concentration profiles was probably smaller than at 1 d, because on the other dates concentration profiles were much less steep.

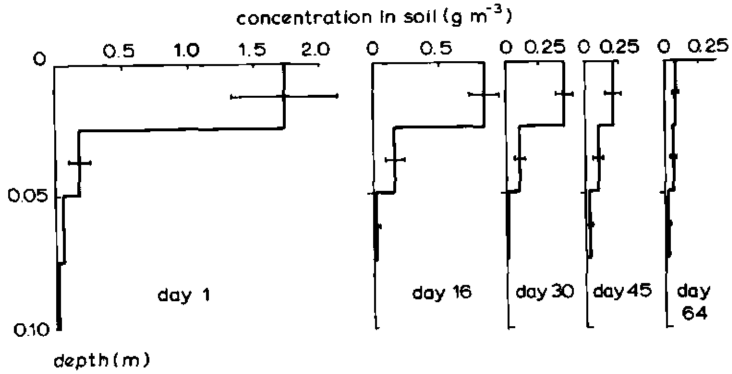


Figure 4.8. Concentration profiles of cyanazine measured at the sampling dates in 1981. Vertical line segments are average values, horizontal bars standard deviations.

Figure 4.9 shows concentration profiles of cyanazine in the field experiment in 1982. In this case 6 mm of rain fell between application and first sampling. In 1982 the frame was pushed into the soil no deeper than necessary for sampling of the next layer, so one may expect that this reduced mechanical contamination of deeper layers to a minimum. This was confirmed by the measurements: cyanazine concentrations in the deeper layers after 1 d in 1982 (Figure 4.9) were even smaller fractions of the top layer concentration than those after 1 d in 1981 (Figure 4.8), even though movement into deeper layers may have occurred in 1982 as a result of the rain.

Figure 4.10 shows concentration profiles of metribuzin as measured in the

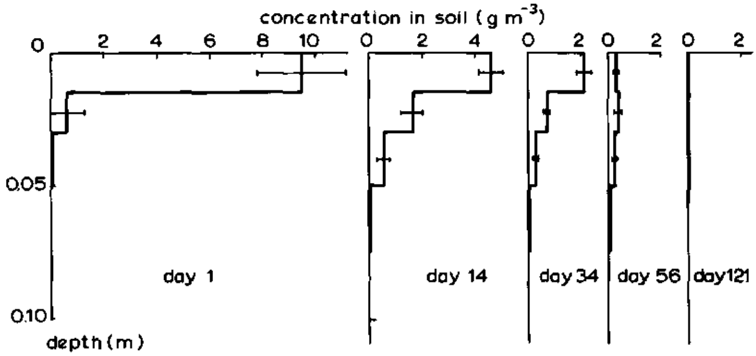


Figure 4.9. Concentration profiles of cyanazine measured at the sampling dates in 1982. Vertical line segments are average values, horizontal bars standard deviations.

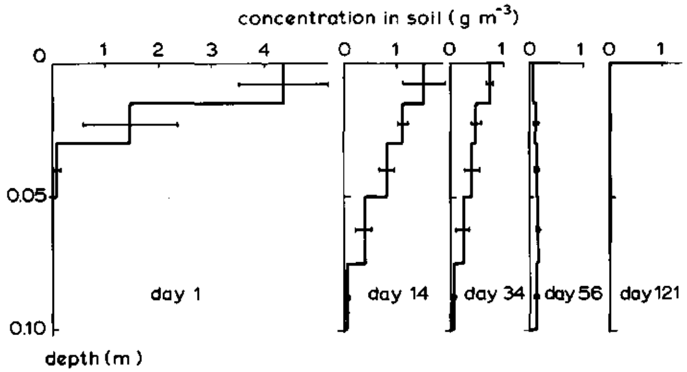


Figure 4.10. Concentration profiles of metribuzin measured at the sampling dates in 1982. Vertical line segments are average values, horizontal bars standard deviations.

field in 1982. This figure shows that penetration of metribuzin was deeper than that of cyanazine (Figure 4.9) on most of the sampling dates.

The areic mass of herbicide at each sampling spot in the field was calculated from the sum of the areic masses in all sampled layers that contained measurable concentrations of herbicide. Figure 4.11 shows areic mass of herbicides (logarithmic scale) as a function of time. The figure shows that the decreases of areic mass with time can be described reasonably well by an exponential relationship:

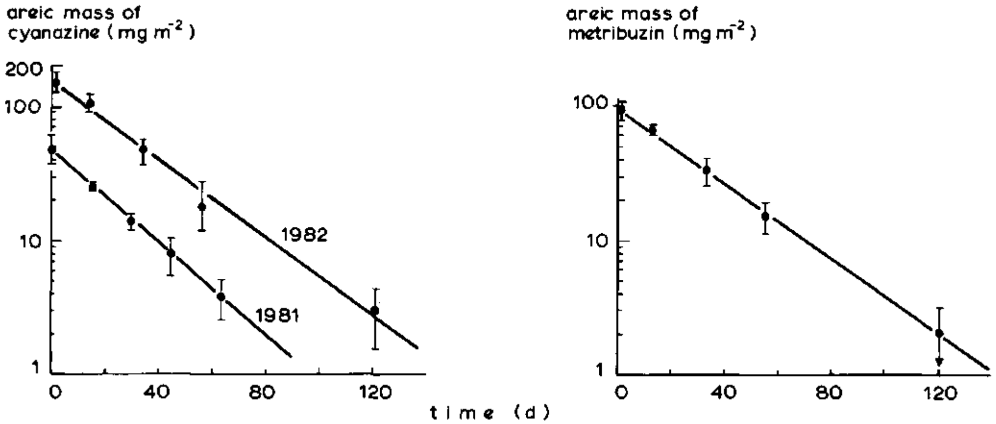


Figure 4.11. Areic mass of herbicide recovered from the soil as a function of time during the field experiments in 1981 and 1982. Points are averages, vertical line segments standard deviations. Lines are linear regression approximations.

$$\sigma^*(t) = \sigma^*(0)\ \exp(-k_{\mathrm{dec}}\ t) \qquad (4.1)$$

in which

σ^* is areic mass of herbicide in the soil system ($\mathrm{kg\ m^{-2}}$)

k_{dec} is rate coefficient for decline ($\mathrm{d^{-1}}$)

Values of $\sigma^*(0)$ and k_{dec} were estimated with a least-squares linear regression model. For the cyanazine measurements this resulted in $\sigma^*(0)$ values of 48 and 149 mg $\mathrm{m^{-2}}$ and k_{dec} values of 0.040 and 0.033 $\mathrm{d^{-1}}$ for 1981 and 1982, respectively. For metribuzin a $\sigma^*(0)$ value of 96 mg $\mathrm{m^{-2}}$ and a k_{dec} value of 0.032 $\mathrm{d^{-1}}$ was found.

The areic mass of herbicide at the various sampling spots at a certain moment will vary because of the variability of the deposition of the herbicides (see Figure 4.6) and because of the variability of the transformation rate in the field. Variability of the herbicide concentration at a certain depth is also influenced by the variability of the herbicide transport process. Figure 4.12 shows coefficients of variation of the areic masses as a function of time in 1981 and 1982 for both herbicides. As can be seen, most of the values range between 10-40 %. Figures 4.8 to 4.10 show that the coefficients of variation of the measured concentrations are also in the order of 10 %. Thus an important fraction of the variability of the herbicide concentration profiles of Figures 4.8 to 4.10 is attributable to the variability of the deposition and the transformation rate.

Figure 4.13 shows concentration profiles of bromide ion in the field experiment in 1982. After 1 d the bromide profile shows a peak in the 15 to 30 mm layer, whereas after 14 and 34 d concentrations were highest in the top layer;

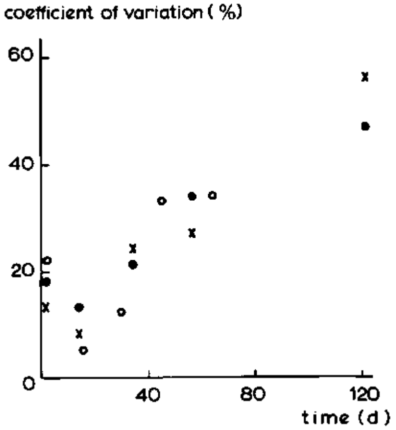


Figure 4.12. Coefficient of variation of the areic mass of herbicide as a function of time during the field experiments in 1981 and 1982. o, cyanazine in 1981; •, cyanazine in 1982; x, metribuzin in 1982.

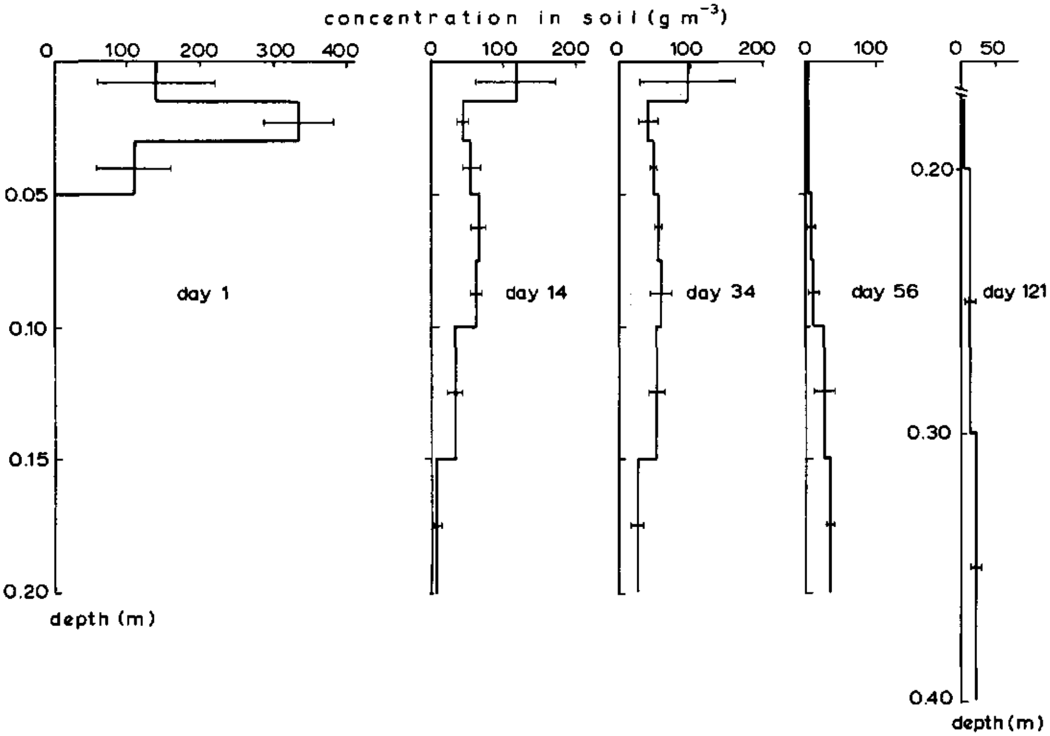


Figure 4.13. Concentration profiles of bromide ion measured at the sampling dates in 1982. Vertical line segments are average values, horizontal bars standard deviations.

this is probably because of evaporation of soil water. The concentration profile after 56 d indicates that leaching to below 200 mm depth had occurred. As the volumes of the samples from the 200 to 400 mm layer taken after 121 d were not known, the dry bulk density of this layer had to be estimated. From Table 4.4 it was calculated that average bulk densities of all sampling dates of the 75 to 100 mm, 100 to 150 mm and 150 to 200 mm layers were 1.42, 1.42, and 1.34 Mg m^{-3}, respectively. The value of the 150 to 200 mm layer was probably too low because of some soil loss during sampling; therefore the bulk density of the 200 to 400 mm layer was estimated to be 1.42 Mg m^{-3}. The concentration profile of bromide ion measured after 121 d indicates that leaching to below 400 mm depth had occurred.

Figure 4.13 shows that the variability of the transport of bromide ion was not very great. Bromide is much more mobile than the herbicides (compare Figures 4.9, 4.10 and 4.13) which illustrates the influence of the adsorption/desorption process on the movement of both herbicides.

Table 4.6. Average areic mass of bromide ion recovered from the 0 to 200 mm soil layer at the sampling dates in 1982. Figures in parenthesis indicate standard deviations.

Sampling date (d after spraying)	Areic mass of bromide ($g\ m^{-2}$)
1	9.2 (1.4)
14	8.8 (1.0)
34	9.7 (1.1)
56	3.6 (1.1)
121	0.3 (0.1)

Table 4.6 shows that average areic mass of bromide ion recovered from the 0 to 200 mm soil layer after 1, 14 and 34 d corresponded reasonably well with the calculated dose (9.9 $g\ m^{-2}$). After 56 and 121 d appreciable amounts of bromide had leached out of the 0 to 200 mm layer. The average areic mass of bromide recovered from the 0 to 400 mm layer after 121 d amounted to 3.6 $g\ m^{-2}$ (s = 1.2 $g\ m^{-2}$). Thus an appreciable fraction of the bromide dose had leached even deeper than 400 mm.

5 THE MODEL OF FLOW OF WATER IN FIELD SOIL, AND ITS TESTING

5.1 INTRODUCTION

Flow of water in soil is a very important process for herbicide transport in soil, as it is the main transport mechanism for herbicides that are not very volatile. Thus a model for herbicide transport always needs a sub-model that simulates water flow. In this chapter the sub-model used to simulate flow of water in soil during the field experiments reported in Chapter 4, is described.

In principle, flow of water in soil can be simulated with a mechanistic model that describes the water flux in both the liquid and vapour phases as induced by the gradient of the water potential, including the effect of temperature. This has been done, for example by van Keulen (1975), Rosema (1975), Hammel et al. (1981), Camillo et al. (1983) , and ten Berge (1986). Some of these models do not take into account the water flow that results from temperature gradients (e.g., van Bavel & Hillel, 1976; Bernard et al., 1981). However, all these models require input that is not readily available for field soils. Furthermore, as few of these models have been field-tested for the plough layer under spring conditions, their validity is questionable. A further problem is that they require time steps several orders of magnitude smaller than those required for the transport of the herbicides.

Wierenga (1977) and Beese & Wierenga (1980) simulated transport of solutes with a model similar to the equilibrium transport model. They carried out simulations with two types of sub-models of flow of water in soil. The first model was based on Darcy's law, the second was a more simple model in which the water flux was constant. They found that concentration profiles calculated with both sub-models were similar. Their simulations indicate that a simplified sub-model of water flow may be adequate in a model of transport of solutes.

For these reasons it was decided to use a simple sub-model of the flow of water in soil in this study.

In models for transport of herbicides it is more appropriate to talk about flow of liquid rather than about flow of water because not only the component 'water' flows! However, in the literature on soil physics it is common to speak of flow of water (for instance, Hillel, 1977; Koorevaar et al., 1983). The liquid phase is also termed water in generally accepted terms such as ground water and surface water. Water is the main component of the liquid in soil and the quantitative difference between liquid and water flow is of no concern in the models discussed above. It was decided to use the term 'liquid' in the names and symbols of the quantities occurring in the model. The model itself is described as a model of the flow of water in soil, in accordance with the nomenclature used in soil physics literature.

5.2 THE MODEL OF FLOW OF WATER IN SOIL

The model of flow of water simulates the redistribution of water resulting from infiltration (rainfall) and evaporation. It is an extension of a model described earlier by van Keulen (1975) and Stroosnijder (1982).

For calculations with the model, the depth in soil, z, and time, t, have to be discretized. In the (z,t) plane a rectangular grid of points is defined, numbered $i = 1, 2, \ldots$ along the z axis and numbered $j = 0, 1, 2, \ldots$ along the t axis. Downward direction of z is assumed to be positive. Δz_i (m) is defined as the thickness of a layer (compartment) around point i (see Figure 5.1). Δt (d) is defined as the time step.

In the model, on days of surplus rainfall (i.e. rainfall exceeds evaporation) the *infiltrating* water fills the layers from top to bottom to volume fractions of liquid at field capacity. It is assumed that thereafter no further redistribution takes place. This procedure is represented by the following algorithm:

$$(R_{1,\mathrm{p}})_i^j = \{(\theta_{\mathrm{max}})_i - (\theta)_i^j\} / \Delta t \qquad (5.1)$$

$$(J^V)_i^j = \max\{0 \, , \, (J^V)_{i-1}^j - \Delta z_{i-1} \, (R_{1,\mathrm{p}})_{i-1}^j\} \qquad (5.2)$$

in which

$R_{1,\mathrm{p}}$ is potential rate of change in volume fraction of liquid $(\mathrm{m}^3 \ \mathrm{m}^{-3} \ \mathrm{d}^{-1})$

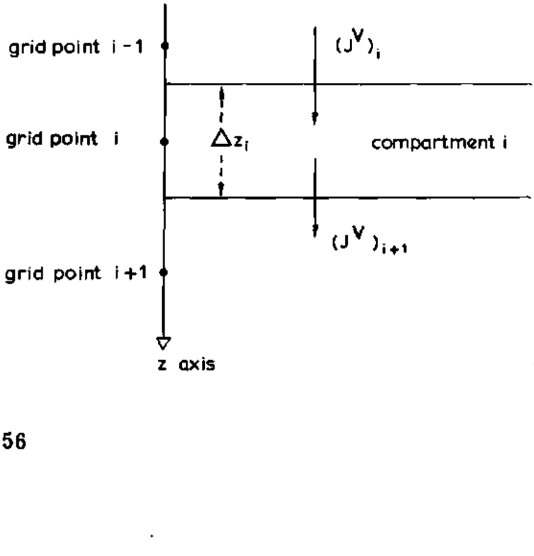


Figure 5.1. Discretization of the *z* axis in the model of flow of water in soil.

$\theta_{\max}$	is maximum volume fraction of liquid (field capacity value)	$(\mathrm{m}^3\ \mathrm{m}^{-3})$
max	means 'maximum of'	

On days of surplus evaporation (i.e. evaporation exceeds rainfall), the rate of change in volume fraction of liquid, R_1 $(\mathrm{m}^3\ \mathrm{m}^{-3}\ \mathrm{d}^{-1})$, is simulated by

$$(R_1)_i^j = (\Xi)^j\ (\xi)_i\ \max\left[0\ ,\ \{(\theta)_i^j - (\theta_{\min})_i\}\right] \tag{5.3}$$

in which

Ξ	is a coefficient	(d^{-1})
ξ	is withdrawal factor	(1)
$\theta_{\min}$	is minimum volume fraction of liquid (value for air-dry soil)	$(\mathrm{m}^3\ \mathrm{m}^{-3})$

The withdrawal factor, ξ, is a function of depth: this function is referred to as the withdrawal function. The coefficient Ξ is derived from the liquid flux at the soil surface and therefore applies to all compartments. Ξ is given by

$$\Xi = (J^V)_1 \Big/ \int_0^Z \xi \quad \max\{\,0\ ,\ (\theta - \theta_{\min})\}\ \ \mathrm{d}z' \tag{5.4}$$

in which

Z	is depth at lower boundary of the soil system	(m)
z'	is integration dummy for depth, z	(1)
$(J^V)_1$	is volume flux of liquid at soil surface	$(\mathrm{m}\ \mathrm{d}^{-1})$

It is assumed by using Equation 5.4 that during upward flow the volume flux of liquid at depth Z is negligible.

Equation 5.4 leads to the following approximation for Ξ :

$$(\Xi)^j = \frac{(J^V)_1^j}{\sum\limits_{i=1}^{I} (\xi)_i\ \max\{0\ ,\ (\theta)_i^j - (\theta_{\min})_i\}\ \Delta z_i} \tag{5.5}$$

in which

I	is number of compartments in the soil system	(1)

In the model of Stroosnijder (1982) the volume flux of upward liquid flow between compartments is not simulated. However, in a model for herbicide transport this simulation is essential. Thus the model had to be extended to include the upward liquid flow as well. This flux is calculated with the equation:

$$(J^V)_i^j = (J^V)_{i-1}^j - (R_1)_{i-1}^j \ \Delta z_{i-1} \tag{5.6}$$

The algorithm described by Equations 5.1 to 5.6 yields the volume flux of liquid, J^V, as a function of depth and time. The sub-model for water flow is completed by the conservation equation for the liquid in the soil system:

$$\frac{\partial \theta}{\partial t} = - \frac{\partial J^V}{\partial z} \tag{5.7}$$

Equation 5.7 was integrated by

$$(\theta)_i^{j+1} = (\theta)_i^j + \Delta t\{(J^V)_i^j - (J^V)_{i+1}^j\} / \Delta z_i \tag{5.8}$$

The model described above was translated into a computer program using the simulation language CSMP III (Speckhart & Green, 1976). The program is shown in Appendix A. The soil system considered in the program was 400 mm deep. The thickness of the compartments, Δz, was 5 mm for 0 to 50 mm depth, 10 mm for 50 to 200 mm depth and 20 mm for 200 to 400 mm depth. The time step was 0.05 d.

5.3 THE MODEL OF EVAPORATION AT THE SOIL SURFACE

The model of flow of water in soil presented in the preceding section requires the flux at the soil surface, $(J^V)_1$, as an input parameter. This flux depends on rainfall and evaporation. Data on rainfall were available (see Figures 4.2 and 4.3). Evaporation had to be estimated with a simulation model. It was first attempted to use existing simple evaporation models, and therefore the literature was searched for such models.

The simple evaporation models in literature usually only describe evaporation during a single drying cycle after the soil has been wetted to field capacity. In the evaporation process then three stages may be distinguished (Bond & Willis, 1970): stage 1, in which the actual volume flux of evaporation, E_{ac} (m d^{-1}), is equal to the potential flux, E_p (m d^{-1}); stage 2, in which the soil surface is gradually drying out and E_{ac} is a rapidly decreasing proportion of E_p; stage 3, in which E_{ac} is very low and relatively constant.

Black et al. (1969) formulated one of the earliest simple models to estimate evaporation. Cumulative actual evaporation during a drying cycle, ΣE_{ac} (m), was described by

$$\Sigma E_{ac} = \alpha_1 \sqrt{t} \tag{5.9}$$

in which

α_1 is a parameter ($\mathrm{m\ d^{-\frac{1}{2}}}$)

For sand in a lysimeter experiment over a period of 12 d, Black et al. (1969) obtained an α_1 value of 5 mm $\mathrm{d^{-\frac{1}{2}}}$. In a lysimeter over a period of 9 d, Klaghofer (1974) obtained an α_1 value of 7 mm $\mathrm{d^{-\frac{1}{2}}}$. Gill & Prihar (1983) measured evaporation from tilled soil in laboratory columns under various constant levels of E_p for 50 d. They found that the measurements could be described reasonably with Equation 5.9, but that α_1 increased from 7 to 13 mm $\mathrm{d^{-\frac{1}{2}}}$ when E_p increased from 4 to 16 mm $\mathrm{d^{-1}}$.

Equation 5.9 does *not* take stage 1 evaporation into account. Ritchie (1972) modified this equation to include both stage 1 and stage 2:

$$\Sigma E_{ac} = \Sigma E_p \qquad \text{for } t \leqq t_1 \text{ in which } \Sigma E_p \leqq \Sigma E_1 \tag{5.10}$$

$$\Sigma E_{ac} = \Sigma E_1 + \alpha_2 \sqrt{t - t_1} \qquad \text{for } t > t_1 \tag{5.11}$$

in which

ΣE_p is cumulative potential evaporation during a drying cycle (m)

t_1 is time at the end of stage 1 (d)

ΣE_1 is cumulative evaporation during a drying cycle at the end of stage 1 (m)

α_2 is a parameter ($\mathrm{m\ d^{-\frac{1}{2}}}$)

Ritchie (1972) reported α_2 values between 3 and 5 mm $\mathrm{d^{-\frac{1}{2}}}$ for four field experiments with sand, loam, clay loam and clay. In field experiments with loam, Jackson et al. (1976) found that α_2 was 2 mm $\mathrm{d^{-\frac{1}{2}}}$ in winter and 4 mm $\mathrm{d^{-\frac{1}{2}}}$ in summer.

Stroosnijder & Koné (1982) modified Equations 5.10 and 5.11 slightly:

$$\Sigma E_{ac} = \Sigma E_p \qquad \text{for } t \leqq t_1 \tag{5.12}$$

$$\Sigma E_{ac} = \Sigma E_1 + \alpha_3(\sqrt{t} - \sqrt{t_1}) \qquad \text{for } t > t_1 \tag{5.13}$$

in which

α_3 is a parameter (m $d^{-\frac{1}{2}}$)

In field experiments on sand and on clay soils in West Africa, they obtained t_1 = 2 d and α_3 = 3.5 mm $d^{-\frac{1}{2}}$.

Values of α_1, α_2 and α_3 reported in the literature indicate that the effect of soil texture on E_{ac} in stage 2 is small.

Measurements obtained by Jackson et al. (1976) and by Gill & Prihar (1983) indicate that E_p has an appreciable effect on E_{ac} in stage 2 and thus on α_1, α_2 and α_3.

The square root of time relationship in Equation 5.9 originates from the solution of the equation for horizontal isothermal flow assuming a constant initial moisture content and an instantaneous lowering of the moisture content at the evaporating soil surface (Gardner, 1959). Although these conditions are not completely fulfilled under evaporation conditions in the field, a square root type of equation usually describes soil evaporation reasonably.

In spring in the Netherlands, the daily average value of E_p may vary considerably: from 1 to 6 mm d^{-1}. Unfortunately, parameter values obtained with the models discussed are a function of E_p. Therefore a new model was developed based on the following criteria:

- it should contain one or two parameters only, and these should be easy to measure
- the parameter(s) should not depend on E_p
- the model should exploit the fact that for constant E_p a $\sqrt{t}$ type relationship fits most experimental data.

The new evaporation model is described as

$$\Sigma E_{ac} = \Sigma E_p \quad \text{for} \quad \Sigma E_p < \beta^2 \tag{5.14}$$

$$\Sigma E_{ac} = \Sigma E_p \quad \text{for} \quad \Sigma E_p = \Sigma E_1 = \beta^2 \tag{5.15}$$

$$\Sigma E_{ac} = \beta\sqrt{\Sigma E_p} \quad \text{for} \quad \Sigma E_p > \beta^2 \tag{5.16}$$

in which

β is a parameter ($m^{\frac{1}{2}}$)

Equations 5.14 to 5.16 contain only one parameter, β, which determines both ΣE_1 and the slope of the ΣE_{ac} versus $\sqrt{\Sigma E_p}$ relationship in stage 2.

In Equations 5.14 to 5.16, ΣE_{ac} depends on ΣE_p, not on time. This implies that to each day, a weight is attached that is directly proportional to the flux of potential evaporation for that day. To show that β is less dependent on E_p than α_1 is dependent on E_p, the data of Gill & Prihar (1983) were reanalysed. β values of 3.4, 3.1 and 3.2 $mm^{\frac{1}{2}}$ were obtained for E_p values of 4, 8, and 16 mm d^{-1}, respectively. Thus, whereas values of E_p differed by a factor of four, β values differed by only about 10 %; thus β can be considered to be a constant.

An implicit assumption in Equation 5.15 is that ΣE_1 (that is, $\int_0^{t_1} E_p \, dt'$) does not depend on E_p. This assumption was also made in Ritchie's model and confirmed in a laboratorium experiment by Bond & Willis (1970), who found that the time at the end of stage 1 (t_1) was directly proportional to $E_p^{-1.2}$. Thus ΣE_1 was almost constant.

The evaporation model developed (Equations 5.14 to 5.16) only specifies evaporation behaviour during a single drying cycle. Thus, Equations 5.14 to 5.16 have to be supplemented with a procedure for simulation of evaporation during periods with rainfall and during periods preceded by a rainfall event that was not sufficient to moisten a dried soil profile to field capacity. It is assumed that for days in which the volume flux of rainfall (precipitation), P (m d^{-1}), exceeds E_p, E_{ac} is equal to E_p, irrespective of the moisture status of the soil profile.

For days in which E_p exceeds P, it is assumed that the rain evaporates without infiltration. Furthermore, for these days it is assumed that the deficit in soil water throughout the soil profile (as compared with the situation at field capacity), determines E_{ac} uniquely. This deficit is equal to ΣE_{ac}. The corresponding calculation procedure is described below using a time axis, t, which is divided into time steps, Δt, as in Section 5.2. Between $t = j \Delta t$ and $t = (j+1) \Delta t$ the rate variables (P, E_{ac}, E_p) are assumed to be constant and equal to the values at $t = j \Delta t$. As described earlier, the time step Δt is 1 d in the procedure.

On days with no excess of rainfall over evaporation $\{(P)^j < (E_p)^j\}$, the value of ΣE_p is updated by

$$(\Sigma E_p)^{j+1} = (\Sigma E_p)^j + \Delta t\{(E_p)^j - (P)^j\} \tag{5.17}$$

$(\Sigma E_{ac})^{j+1}$ is calculated from $(\Sigma E_p)^{j+1}$ with the function described by Equations 5.14 to 5.16. Then $(E_{ac})^j$ is calculated from:

$$(E_{ac})^j = (P)^j + \{(\Sigma E_{ac})^{j+1} - (\Sigma E_{ac})^j\} / \Delta t \tag{5.18}$$

On days with excess of rainfall over evaporation $\{(P)^j > (E_p)^j\}$, E_{ac} is given by:

$$(E_{ac})^{i} = (E_{p})^{i} \tag{5.19}$$

and the excess in areic volume of rainfall is subtracted from ΣE_{ac}:

$$(\Sigma E_{ac})^{i+1} = (\Sigma E_{ac})^{i} - \Delta t\{(P)^{i} - (E_{p})^{i}\} \tag{5.20}$$

Thereafter, $(\Sigma E_{p})^{i+1}$ is calculated from $(\Sigma E_{ac})^{i+1}$ with the function described by Equations 5.14 to 5.16. If the excess in areic volume of rainfall of a day is greater than $(\Sigma E_{ac})^{i}$, then both $(\Sigma E_{ac})^{i+1}$ and $(\Sigma E_{p})^{i+1}$ are set at zero and the excess is considered to drain away.

The model described above was translated into a computer program using the simulation language CSMP III (Speckhart & Green, 1976). The program is shown in Appendix B.

5.4 APPLICATION OF THE EVAPORATION MODEL

5.4.1 Introduction

To be able to apply the evaporation model it is necessary to estimate the parameter β from a measurement of the relationship between ΣE_{ac} and ΣE_{p}, or from literature data. Thus first the literature about the relationship between ΣE_{ac} and ΣE_{p} was reviewed. For a first rough comparison, the cumulative evaporation at the end of stage 1, ΣE_{1}, was used as a characteristic of the relationships found.

Table 5.1 lists the results reported in the literature of a number of laboratory experiments with sieved soil. It may be concluded that ΣE_{1} is in the range of 20 to 60 mm and that stage 1 often lasts several days. Also, there seems to be no clear relationship between ΣE_{1} and soil texture.

In a computer simulation study, Hillel (1977) calculated ΣE_{1} for three soils at E_{p} = 14 mm d^{-1}. He found ΣE_{1} values for sand, loam and clay to be 20, 40 and 70 mm, respectively. These values are as high as those listed in Table 5.1 but show an unexpectedly strong effect of texture. The hydraulic properties of the soils used by Hillel (1977) were probably derived from sieved samples in the laboratory, and thus it is not surprising that the range of ΣE_{1} values obtained corresponds with those in Table 5.1.

However, field experiments have given considerably lower values for ΣE_{1}. Ritchie (1972) reported values of 6, 9, 12 and 6 mm for sand, loam, clay loam, and clay respectively. Al-Khafaf et al. (1978) obtained values between 6 and 8 mm

Table 5.1. Cumulative evaporation at the end of stage 1, ΣE_1, as reported in laboratory experiments with sieved soils.

Soil texture	Experimental conditions			Cumulative evaporation at the end of stage 1 (mm)	Reference
	column length (m)	average volume fraction of liquid at the start ($m^3\ m^{-3}$)	volume flux of potential evaporation ($mm\ d^{-1}$)		
Sandy loam	0.6	0.3	10	40	Gardner & Hanks (1966)
Sand	0.4	0.3	10	30	Hanks et al. (1967)
Loamy sand	0.4	0.3	10	25	Hanks et al. (1967)
Silt loam	0.4	0.4	10	40	Hanks et al. (1967)
Sandy loam	0.4	0.3	1 - 12	30 - 60	Bond & Willis (1970)
Sandy loam	0.6	0.3	8	40	Willis & Bond (1971)
Silt loam	0.9	0.3	15	60	van Keulen (1975)

for clay loam. Stroosnijder & Koné (1982) found values of 4-6 mm for sand and clay. Smelt (personal communication, 1983) obtained values of 0-4, 4-8 and 4-8 mm for sand, loamy sand and clay, respectively. From the ΣE_1 values reported in the literature for field experiments I concluded that there is no clear relationship between ΣE_1 and soil texture. Furthermore, as the values for field experiments were an order of magnitude lower than those reported for sieved soils in the laboratory, I concluded that data from laboratory experiments with sieved soils cannot be used to describe evaporation from soils under field conditions. The looser soil structure in the top few centimetres in the field is probably responsible for part of the discrepancy. Thus, evaporation characteristics should be measured in field soil.

In view of the foregoing, only the results of the field measurements were considered in more detail. It was attempted to estimate β values from the α_1 values derived from the slopes of the relationships between ΣE_{ac} and $\sqrt{t}$ reported in literature for field soils. If E_p is constant, β can be calculated (using Equations 5.9 and 5.16) from α_1 and E_p by

$$\beta = \alpha_1 / \sqrt{E_p} \tag{5.21}$$

From the measurements obtained by Black et al. (1969) with a sand, a β value of 2 $mm^{\frac{1}{2}}$ was derived. From data obtained by Ritchie (1972) a β value of 3 $mm^{\frac{1}{2}}$ was derived for a clay loam and of 2 $mm^{\frac{1}{2}}$ for a clay. From data given by

Al-Khafaf et al. (1978) for a clay loam, a β value of 3 $mm^{\frac{1}{2}}$ was derived. From data reported by Stroosnijder & Koné (1982) for a sand and a clay, a β value of 2 $mm^{\frac{1}{2}}$ was derived. Thus, β values derived from field measurements reported in literature varied between 2 and 3 $mm^{\frac{1}{2}}$. This implies that ΣE_1 values (i.e. β^2) varied by about a factor of two. Thus a rough estimate of the evaporation behaviour of a field soil can be derived from literature. However, for an accurate application of the model it seems advisable to measure β for the field being studied. Thus it was decided to carry out field experiments to determine β accurately and to test the evaporation model.

5.4.2 Estimation of values of parameters

5.4.2.1 Estimation of potential evaporation from soil

The volume flux of potential evaporation, E_p, was estimated from available meteorological data.

E_p largely depends on atmospheric evaporativity, that is mainly on the net radiation and vapour removal characteristics of the prevailing weather conditions: it depends on the properties of the soil to a small extent only (van Bavel & Hillel, 1976). One of the earliest methods of measuring atmospheric evaporativity (still widely used) is the volume flux of evaporation from an open water surface, E_o. Penman (1948) compared measured values for E_o and E_p. In lysimeter studies carried out in England in spring and summer (for two years), he found that monthly averages of E_p were, on average, 0.9 (range 0.8-1.0) times the monthly averages of E_o. McIlroy and Angus (1964) obtained the same result in similar studies in Australia. Penman (1948) devised a formula to calculate E_o from weekly or monthly averages of duration of sunshine, air temperature, wind speed and water vapour deficit. De Bruin & Lablans (1980) modified this formula to use daily averages to calculate E_o. In the Netherlands, daily values for E_o are calculated with their method by the Royal Netherlands Meteorological Institute (KNMI) for five weather stations.

In the model it was assumed that the daily average of E_p is 0.9 times the daily average of E_o as calculated by the KNMI. Since the experimental field was located between the meteorological stations at De Bilt, Eelde and De Kooy, an average value for these stations was taken as E_o at the experimental field.

5.4.2.2 Estimation of rainfall

Daily averages of the volume flux of rainfall were assumed to be equal to 1.07 times those measured at the experimental fields at 1.2 m height (see Section 4.3; Figures 4.2 and 4.4).

5.4.2.3 Estimation of β

The evaporation parameter, β, was determined using a method similar to the microlysimeter method proposed by Boast & Robertson (1982). In the morning of day 118 in the field experiment in 1982, 15 undisturbed soil columns were taken in PVC cylinders (0.07 m diameter, 0.12 m long). The average volume fraction of liquid of the columns was 0.26 $m^3 m^{-3}$ (the standard deviation, s, was 0.02 $m^3 m^{-3}$) which was very close to the field capacity of the soil of 0.27 $m^3 m^{-3}$ (s = 0.02 $m^3 m^{-3}$), as determined in the laboratory with four soil columns on a suction plate at -8 kPa. Field capacity was considered to be a good starting water condition for a measurement of β.

The columns were closed at the bottom and carefully replaced in the soil with their tops flush with the soil surface. Five columns were kept wet by adding water to their surfaces several times a day and the remaining ten columns were allowed to dry out. All cylinders were weighed several times per day for four consecutive days (days 118-121). They were covered with a glass lid in a few periods in which rain showers threatened. The measurements taken of the wet and drying columns were used to calculate E_p and E_{ac}.

At the end of the experiment (day 121), the ten dried soil columns were sliced into layers and the moisture profiles determined. On that day the moisture profile in the field soil was also measured and found not to differ from that in the dried columns. Only 15 % of the water in the soil columns had evaporated during the experiment.

Figure 5.2 shows the relationship between ΣE_{ac} and ΣE_p as measured on days 118-121. Up to ΣE_{ac} values of 3 to 4 mm, actual evaporation flux equalled the potential flux. Thereafter the actual flux became much lower than the potential flux, because a dry surface layer formed. Daily averages of the measured volume flux of potential evaporation were 3, 1 and 5 mm d^{-1} for the first three days of the experiment. It is remarkable that the surface layer of the soil dried out during the second day although the potential flux was low on that day. A ΣE_1 value of 3-4 mm is in the low range of the values for field soils as found in the literature study discussed in Section 5.4.1.

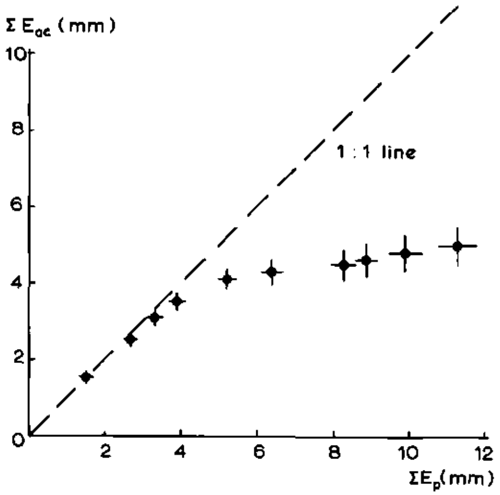


Figure 5.2. Relationship between cumulative actual evaporation, ΣE_{ac}, and cumulative potential evaporation, ΣE_p, as measured on days 118-121 in 1982. Points are averages; vertical and horizontal line segments are standard deviations.

In the model, values of E_o as calculated from the Penman equation are used to estimate E_p. In the experiment of Figure 5.2 values of E_p were measured. As long as the surface of the experimental field is wet, measured potential evaporation should correspond with the estimates from the Penman equation. However, the Penman equation was developed for wet surfaces in a wet environment and thus it may be expected to be invalid for small wet surfaces in a dry environment. This was checked in an experiment between days 9 and 14 in the experimental field in 1982. Evaporation was measured from a soil column (diameter: 0.11 m) whose surface was kept wet by maintaining a 'water table' in the column between 50 and 100 mm depth. The column was buried in the field with its top flush with the soil surface. In the measuring period the column was surrounded by dry bare soil for a distance of at least 20 m. It was found that cumulative evaporation from the column was 35 mm as compared with a cumulative evaporation of 18 mm as estimated from E_o values based on the Penman equation. Thus, evaporation from a wet column in a dry environment was found to be 1.9 times higher than the Penman equation predicted. This is probably because of an oasis effect. There are two methods of taking this oasis effect into account. The first is to leave the E_p values as estimated from E_o unchanged and to divide the E_p values of Figure 5.2 by 1.9 for the days on which the soil surface was dry (days 120 and 121). The second method is to leave the E_p values of Figure 5.2 unchanged and to multiply the E_p values as estimated from E_o by 1.9 on days with a dry field soil surface. The second method was not feasible as it was not known on which days the soil surface was dry. Thus the first method was applied.

Figure 5.3 shows the relationship between ΣE_{ac} and the square root of ΣE_p (E_p values were corrected as described above). Measuring points during stage 1 evaporation were omitted from the figure because then $\Sigma E_{ac} = \Sigma E_p$ (see Equation 5.14). Linear regression with least squares optimization yielded a value of 1.7 $mm^{\frac{1}{2}}$ for β. This value of β is low in the range of the values for field soils as found in the literature study discussed in Section 5.4.1.

It is interesting to know whether the correction for the oasis effect had a great influence on β. Thus β was also calculated without the correction. This resulted in a value of 1.6 $mm^{\frac{1}{2}}$ for β, which shows that the correction had only a minor influence on β.

In order to estimate the spatial variability of β within the experimental field, twice the standard deviation in the ΣE_{ac} measurements was added to each point in Figure 5.3, and twice the standard deviation subtracted. The resulting range of ΣE_{ac} values may then be expected to cover about 95 % of all possible variation. β values were obtained by a least-squares linear regression approximation, and upper and lower limits for β were found to be 2.0 and 1.4 $mm^{\frac{1}{2}}$, respectively. Thus, the effect of spatial variability of evaporation reduction properties of the soil was small. This agrees with results obtained by Lascano & van Bavel (1982) from a computer model.

In the model the value $\beta = 1.7$ $mm^{\frac{1}{2}}$, as determined in 1982, was used for both years.

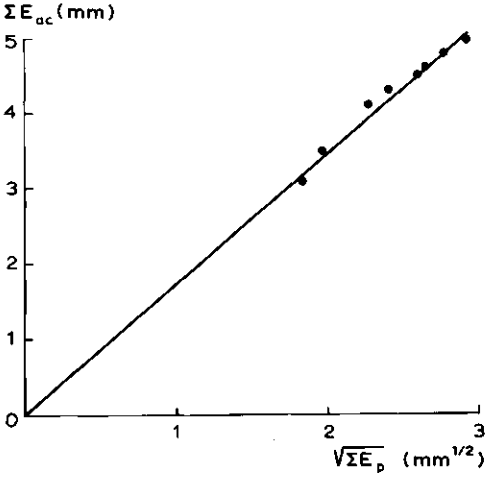


Figure 5.3. Relationship between cumulative actual evaporation, ΣE_{ac}, and the square root of cumulative potential evaporation, ΣE_p, as measured on days 118-121 in 1982 (corrected for the oasis effect). Points are averages, the line is the result of linear regression analysis.

5.4.3 Testing the evaporation model

Evaporation was calculated with the model during the full test periods of herbicide experiments carried out in 1981 and 1982. Calculated cumulative actual evaporation is shown for both years in Figure 5.4, together with cumulative rainfall and cumulative potential evaporation. Cumulative actual evaporation was usually between 40 % and 60 % of cumulative potential evaporation. Cumulative rainfall was usually greater than cumulative actual evaporation but less than cumulative potential evaporation. Thus there was mostly an excess of rainfall because of the reduction in evaporation by drying of the soil surface.

To test the evaporation model, experiments were carried out in the experimental field throughout spring and summer 1982. At various time intervals three soil columns were sampled at the experimental plot in steel cylinders (diameter 0.11 m; length 0.18 m). The columns could drain freely through a perforated bottom and percolated water was collected in a tray. The steel cylinders were sunk in other steel cylinders (diameter 0.12 m; length 0.20 m) which were buried in soil. The tops of the columns and cylinders were flush with the soil surface.

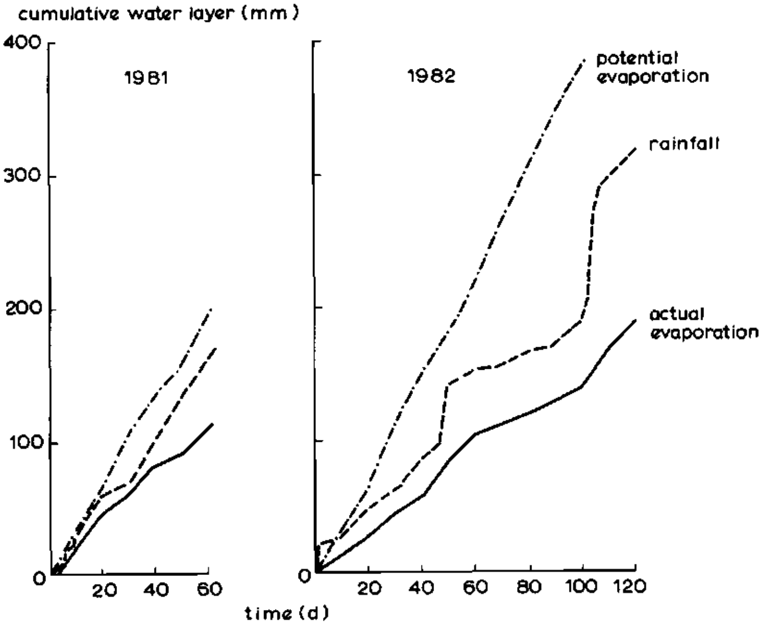


Figure 5.4. Cumulative rainfall and cumulative potential and actual evaporation from soil in the field experiments in 1981 and 1982. Actual evaporation was calculated with the evaporation model.

The columns were weighed on the sampling date and again at the end of the measuring period. At the end, the columns were sliced into layers and the moisture profiles determined. In cases where percolated water was found in the trays or where moisture profiles differed significantly from those in the field soil, the evaporation measurement was excluded as being not representative of field soil conditions. Duration of measuring periods varied from 5 to 34 d. The results for periods with accepted evaporation measurements are presented in Table 5.2 together with the calculated evaporation for these periods.

It is concluded from Table 5.2 that the calculated values correspond reasonably well with the measured values. However, it is recognized that the model requires further testing.

5.4.4 *Sensitivity analysis of the evaporation model*

In the experiment used to determine β, E_p was measured in the experimental field in order to obtain an accurate value for β. In the model, E_p was calculated from the average of the daily E_o values of the three nearest weather stations. Daily values of E_o as estimated for the experimental field are not accurate, because the values from the three weather stations often vary by a factor of 2 (average monthly values usually do not vary by more than 10 %). To assess the sensitivity to realistic changes in E_o values, cumulative actual evaporation was calculated using the values of E_o from each weather station seperately. This was done for the experimental period in 1982. Cumulative actual evaporation calculated with the individual E_o values usually differed less than 5 % from that calculated with the average E_o value (the standard procedure).

In another calculation, the effect of the spatial variability of β was considered. Calculations were done for the experimental period in 1982 with the

Table 5.2. Results of evaporation measurements for soil columns during the field experiment in 1982. Figures in parenthesis indicate standard deviations.

Length of measuring period (d)	Cumulative rainfall (mm)	Average volume fraction of liquid at the end of the period ($m^3\ m^{-3}$)		Cumulative evaporation (mm)	
		in columns	in the field (0 - 0.18 m)	measured	calculated
5	0	0.239 (0.003)	0.235 (0.005)	3.8 (0.3)	2.9
8	12	0.223 (0.005)	0.225 (0.004)	13 (0.4)	13
34	19	0.179 (0.008)	0.189 (0.003)	29 (1)	29

upper and lower limits of β (2.0 and 1.4 $\mathrm{mm}^{\frac{1}{2}}$) as estimated in Section 5.4.2. It was found that cumulative evaporation calculated with the upper and lower limits of β was usually only 6-7 % higher or lower than that calculated with the standard value of β (1.7 $\mathrm{mm}^{\frac{1}{2}}$).

5.5 EXTENSION OF THE EVAPORATION MODEL TO SIMULATE DIURNALLY FLUCTUATING FLUXES

In the evaporation model of Section 5.3 the time step, Δt, was 1 d. Thus, only daily averages of the volume fluxes of rainfall and potential evaporation can be used in this model. Daily averages of the rainfall flux are much lower than the actual flux: from Figures 4.2 and 4.3 it can be derived that the daily averages are an order of magnitude lower than the hourly averages. Models for transport of herbicides may be sensitive to the volume flux of liquid in soil. To be able to test the sensitivity of transport models of herbicides to the liquid flux in soil under field conditions, the evaporation model of Section 5.3 was extended to simulate evaporation with time steps smaller than 1 d.

The volume flux of potential evaporation in the model was simulated as a function of time of day, with a formula similar to that suggested by Hillel (1977, p. 44):

$$E_{\mathrm{p}} = E_{\mathrm{p,av}}\ \pi \left| \min\{\ 0,\ \cos(2\pi\ t)\ \}\right| \qquad (5.22)$$

in which

$E_{\mathrm{p,av}}$ is daily average of E_{p} (m d^{-1})
min means 'minimum of'

In the model, time is a multiple of 1.0 at midnight. Thus in Equation 5.22 it is assumed that E_{p} varies sinusoidally between 6.00 h and 18.00 h and is zero between 18.00 h and 6.00 h. Equation 5.22 was tested against field measurements carried out in the experimental field on days 120 and 121 in 1982. The results shown in Figure 5.5 show that Equation 5.22 can serve as a first estimate for the simulation of E_{p} as a function of time of day. Detailed measurements of E_{p} obtained by Fritschen & van Bavel (1962) and by van Bavel (1966) also indicate that Equation 5.22 is a reasonable approximation.

As was done in the model presented in Section 5.3, it is assumed that cumulative rain falling within a day evaporates without reduction if it does not exceed cumulative potential evaporation within the day. This assumption is operationalized

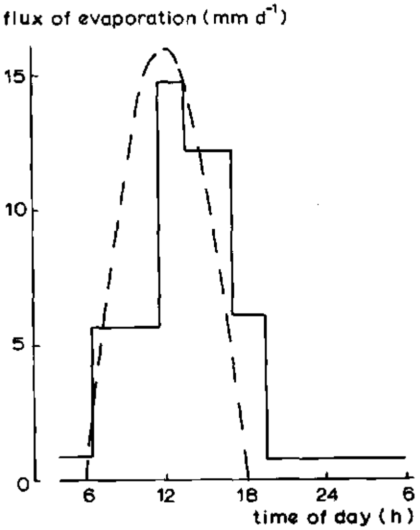


Figure 5.5. Volume flux of potential evaporation as a function of time of day (mid European time) on days 120 and 121 in 1982. The solid line is the flux measured in some periods, the dashed line is calculated with Equation 5.22.

with help of the quantity Q (m) i.e. the excess in cumulative rain over cumulative potential evaporation within a day. Q is given by

$$Q = \int_{t_{\mathrm{st}}}^{t} (P - E_{\mathrm{p}})\ \mathrm{d}t' \qquad (5.23)$$

in which

t_{st}	is time at which integration of $(P - E_{\mathrm{p}})$ starts	(d)
t'	is integration dummy for time, t	(1)

For each day the integration of $(P - E_{\mathrm{p}})$ starts at 18.00 h of the previous day and stops 24 h later. Thus, values of t_{st} are 0.75 d, 1.75 d, 2.75 d, 3.75 d, and so on. As long as Q is positive, actual evaporation flux equals the potential flux, and values of ΣE_{ac} and ΣE_{p} are left unchanged. Q is not allowed to become negative: if this threatens, Q is set at zero. If Q is zero, actual evaporation flux is calculated as described in Section 5.3 with Equations 5.17 and 5.18.

The above model was translated into a computer program using the simulation language CSMP III (Speckhart & Green, 1976). The program is shown in Appendix C. Calculations were carried out for the experimental field in 1982. 3 h-averages of rainfall flux were used in the model. The time step, Δt, was 0.005 d. Table 5.3 shows that calculated cumulative evaporation was only 0 to 4 % lower than that calculated with the model described in Section 5.3 based on daily averages. The lower values found with the model based on Equation 5.22 and on 3

Table 5.3. Cumulative evaporation calculated as a function of time for the experimental field in 1982 with the evaporation models based on daily averages of potential evaporation flux and on diurnally fluctuating potential flux, respectively.

Time (d)	Cumulative evaporation (mm) calculated with	
	daily average flux	diurnally fluctuating flux
20	28	28
40	57	55
60	103	99
80	119	116
100	139	133
120	186	179

h-averages of rainfall are more realistic, because they are based on the more realistic distribution of rainfall over the day. However, as differences were small, the model based on daily averages is acceptable.

5.6 TESTING THE MODEL OF FLOW OF WATER IN SOIL

The model of flow of water in soil, described in Section 5.2, requires the following input:

- volume fluxes of rainfall and actual evaporation
- the volume fraction of liquid at field capacity as function of depth
- the volume fraction of liquid of air-dry soil as a function of depth
- the initial volume fraction of liquid as a function of depth
- the withdrawal factor ξ as a function of depth (the withdrawal function).

Rainfall flux was assumed to be equal to 1.07 times the daily average flux measured in the experimental field at 1.2 m height (see Section 4.3; Figures 4.2 and 4.4). The actual evaporation flux was assumed to be equal to the daily average flux as calculated by the model discussed in Sections 5.3 and 5.4.

Only moisture profiles measured in the field were available for the estimation of the moisture profile at field capacity in 1981. The moisture profile at field capacity was assumed to be equal to that measured in the field after 64 d: on day 64 soil was sampled between 11.00 h and 14.00 h; 9 mm of rain fell on the site between 7.00 h and 8.00 h.

The moisture profile at field capacity for the field experiment in 1982 was estimated from a laboratory experiment. On day 121 in 1982 4 undisturbed soil columns were sampled in the field in PVC cylinders 0.07 m in diameter and 0.12 m long. In the laboratory the columns were placed on a suction table with a matric pressure established at -8 kPa. In the field there are drains at about 0.9 m depth, and thus this matric pressure roughly corresponds to that in the plough layer in the field after superfluous rain has drained away. A liquid layer of 28 mm was ponded on the surface of the columns to simulate excess rainfall. The columns were allowed to drain for 24 h and then divided into layers. The water content and dry bulk density of each layer were measured. Figure 5.6 shows the results. At all depths measured, average bulk densities were almost equal to the average bulk densities of the field experiment of 1982 calculated from the data in Table 4.4. The columns can thus be considered as representative for the experimental field. Figure 5.6 shows that the average volume fraction of liquid increased with depth; the depth-averaged value for the 4 columns was 0.27 $m^3\ m^{-3}$ (s = 0.02 $m^3\ m^{-3}$). Volume fraction of liquid at field capacity was assumed to be equal to the profile measured to 0.12 m depth shown in Figure 5.6. Below 0.12 m depth the volume fraction of liquid was assumed to be equal to 0.3 $m^3\ m^{-3}$ (the value of the deepest layer measured).

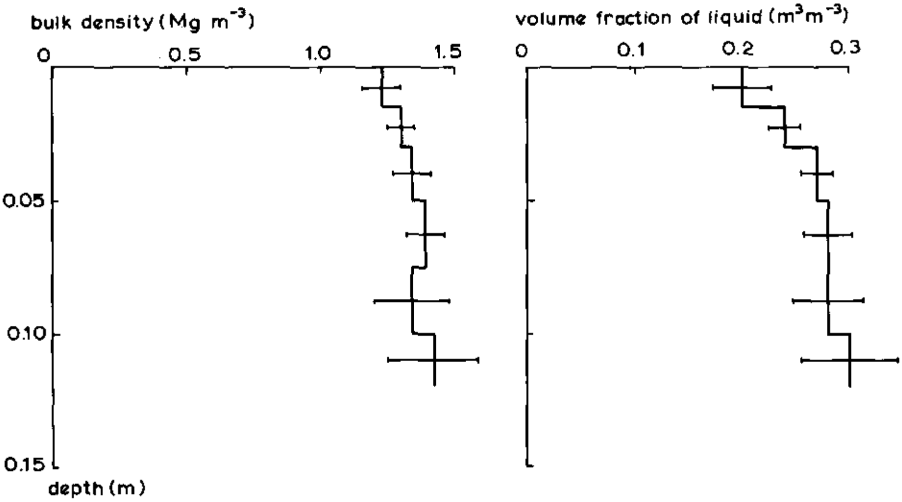


Figure 5.6. Average dry bulk density (left) and average volume fraction of liquid (right) as a function of depth as measured in the field capacity experiment with four soil columns in 1982. Horizontal bars indicate standard deviations.

The volume fraction of liquid at air-dryness was set at 0.01 m^3 m^{-3} for all depths and for both years. This was based on a laboratory measurement in 1981 of the water content at a relative humidity of about 60 %: at this relative humidity the water content was found to be 0.010 kg kg^{-1}.

In the simulations for 1981 the initial moisture profile was derived from the profile measured in the field the morning after spraying. In 1982 5 mm of rain fell between spraying and first sampling and the initial moisture profile was derived from that measured after 56 d. This sampling date was chosen because the rainfall pattern preceding day 56 was similar to that preceding the spraying date.

The withdrawal function was adjusted by trial and error to obtain the best fit of the moisture profiles as measured in the field in both 1981 and 1982. First it was attempted to use the withdrawal function described by Stroosnijder (1982):

$$\xi(z) = \exp(-z/z_w) \qquad (5.24)$$

in which

z_w is characteristic depth for withdrawal of water due to evaporation (m)

It was found that the measurements could not be described satisfactorily with

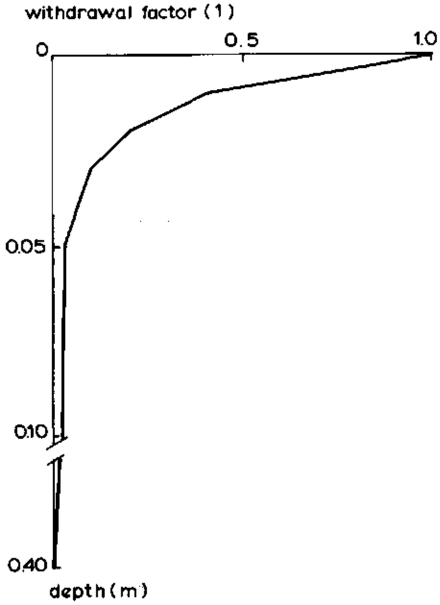


Figure 5.7. The withdrawal function, $\xi(z)$, used to describe water withdrawal from soil during evaporation.

Equation 5.24. Thus $\xi(z)$ was introduced with the FUNCTION statement in CSMP. The $\xi(z)$ function shown in Figure 5.7 was used to describe measured moisture profiles in both years. Measured and simulated moisture profiles for the 1981 and 1982 experiments are presented in Figures 5.8 and 5.9, respectively. It was concluded that an acceptable description of measured moisture profiles in both years was obtained using only one withdrawal function.

The influence of the magnitude of the time step, Δt, was investigated. Because of the structure of the infiltration algorithm of the water flow model, the time step has no influence on calculated volume fractions of liquid in infiltration situations. Thus, the effect of the time step was checked in a drying situation only. The moisture profile after 14 d in 1982 was calculated with a time step of 0.01 d and was compared with the result of the standard run (Δt = 0.05 d). It was found that volume fractions of liquid of corresponding layers always differed from each other by less than 1 %.

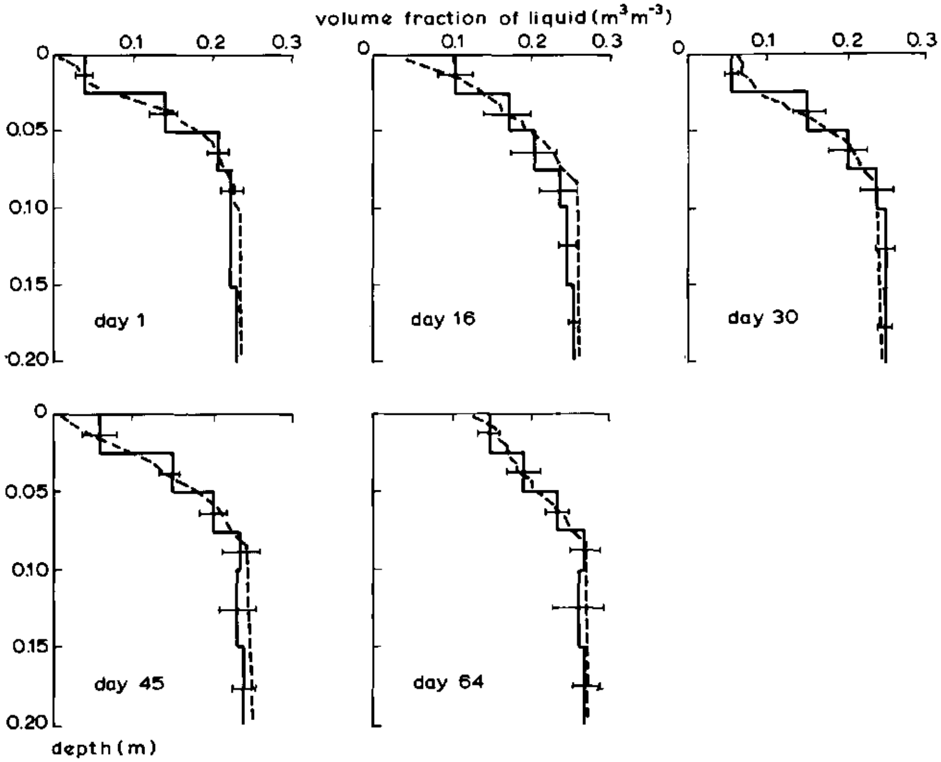


Figure 5.8. Moisture profiles on sampling dates in the field experiment in 1981. Vertical solid line segments are averages of 5 measured profiles; horizontal bars are standard deviations; and dashed lines are simulated profiles.

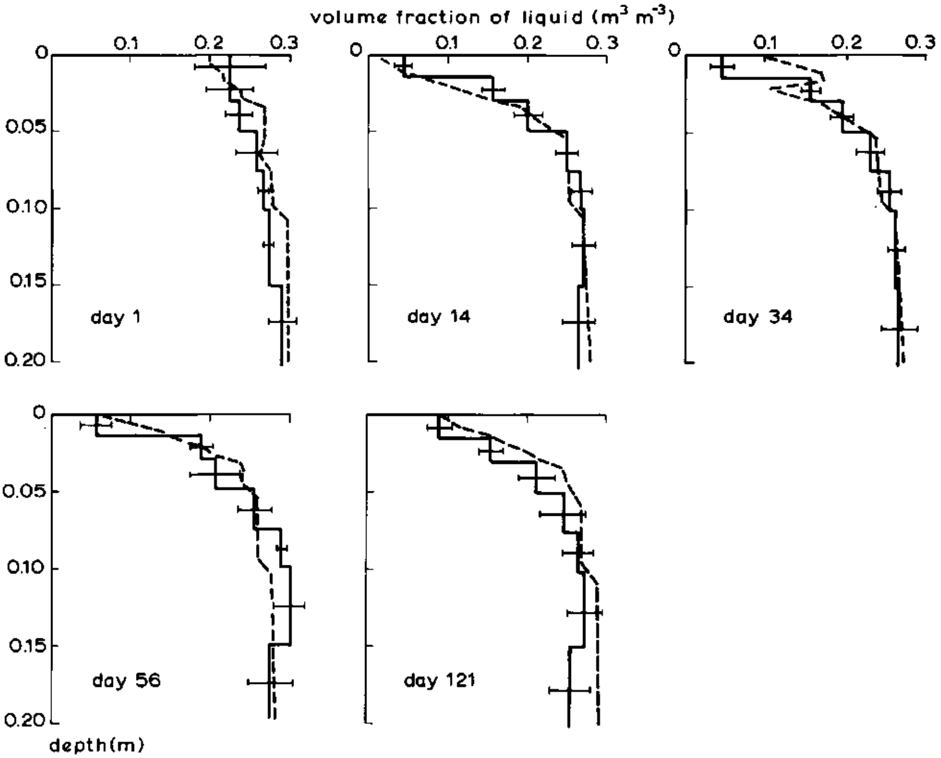


Figure 5.9. Moisture profiles on sampling dates in the field experiment in 1982. Vertical solid line segments are averages of 5 measured profiles; horizontal bars are standard deviations; and dashed lines are simulated profiles.

6 FIELD TEST OF THE EQUILIBRIUM TRANSPORT MODEL

6.1 MATHEMATICAL DESCRIPTION OF THE EQUILIBRIUM TRANSPORT MODEL

In Chapter 2 (Section 2.4) it was concluded that the equilibrium transport model is the best model available in the literature for simulating the transport of substances in the field. In this chapter the test of this model against the results of the field experiments (Chapter 4) is described. For this test the equilibrium transport model described in Section 2.2.1 was used. This model was modified so that instead of the linear sorption isotherm (Equation 2.6) the Freundlich sorption isotherm was used:

$$X = K_\mathrm{F}\, c^{1/n} \tag{6.1}$$

in which

K_F	is the Freundlich coefficient	$(m^{3/n}\ \mathrm{kg}^{-1/n})$
$1/n$	is the Freundlich exponent	(1)

The Freundlich equation was used because it has commonly been found to describe the results of sorption experiments with soils and pesticides well (Calvet et al., 1980c, p. 240). Table 6.1 lists the set of equations of the equilibrium transport model used here.

Table 6.1. Set of equations used in the equilibrium transport model.

$\dfrac{\partial c^*}{\partial t} = -\dfrac{\partial J}{\partial z} - R_\mathrm{t}$	(2.1)
$c^* = \theta\ c + \rho_\mathrm{b}\ X$	(2.5)
$X = K_\mathrm{F}\ c^{1/n}$	(6.1)
$J = J^V c - (D_\mathrm{dis} + D_\mathrm{dif})\partial c/\partial z$	(2.2)
$D_\mathrm{dis} = L_\mathrm{dis}\ \lvert J^V \rvert$	(2.3)
$D_\mathrm{dif} = \lambda\ \theta\ D_0$	(2.4)
$R_\mathrm{t} = k_\mathrm{t}^*\ c^*$	(3.1)

As described in Section 4.1, the aim of the experiments was to test only the transport term of the model, $\partial J/\partial z$, and not the transformation term, R_t. Thus, for the simulation of the transformation rate in the field a descriptive model was accepted. An attempt was made to derive the model for R_t from the measured decline of areic mass in soil with time, as shown in Figure 4.11. This figure shows that the decline of areic mass, σ^*, could be described well by an exponential equation (Equation 4.1). It was assumed here that the observed decline in σ^* was completely ascribable to transformation. Then the following rate equation can be derived from Equation 4.1:

$$\frac{\mathrm{d}\sigma^*}{\mathrm{d}t} = -k_t^* \, \sigma^* \qquad (6.2)$$

The areic mass in soil, σ^*, is defined as

$$\sigma^* \equiv \int_0^Z c^* \, \mathrm{d}z' \qquad (6.3)$$

Integration of the mass conservation equation (Equation 2.1) with respect to depth gives:

$$\frac{\partial}{\partial t} \int_0^Z c^* \, \mathrm{d}z' = - \int_0^Z \left(\frac{\partial J}{\partial z'}\right) \mathrm{d}z' - \int_0^Z R_t \, \mathrm{d}z' \qquad (6.4)$$

Integration of the first term of the right-hand side of Equation 6.4 gives:

$$\int_0^Z \frac{\partial J}{\partial z'} \, \mathrm{d}z' = J(Z) - J(0) \qquad (6.5)$$

$J(Z)$ can be made negligible for a certain period by taking Z to be large enough. $J(0)$ is only of importance during the period in which the substance dissolves at the soil surface. This period is probably a negligible fraction of the total experimental period. Thus it is reasonable to assume that the integral given in Equation 6.5 vanishes. It then follows from Equations 6.2, 6.3 and 6.4 that R_t can be described by

$$R_t = k_t^* \; c^* \qquad (6.6)$$

In the field experiments the substances were sprayed in a very thin water film (areic volume of water < 1 mm) on a dry soil surface. It is assumed that after spraying, the substances are present in the undissolved state at the soil surface. The initial condition then reads:

$$t = 0 \qquad z > 0 \qquad c^* = 0 \tag{6.7}$$

The boundary condition at the soil surface is based on the assumption that the substance does not move into the soil system until a downward water flux occurs. Furthermore, it is assumed that the concentration at which the substance dissolves, c_{sol} (kg m^{-3}), is constant. After the complete dose has been dissolved, the flux of substance at the soil surface is set to zero. The mathematical formulation of the upper boundary condition thus becomes:

$$\text{if } J^V(0,t) \leqq 0 \qquad : \quad J(0,t) = 0 \tag{6.8}$$

$$\text{if } J^V(0,t) > 0 \text{ and } \int_0^t J(0,t')\,\mathrm{d}t' < d_A \quad : \quad J(0,t) = J^V(0,t)\,c_{\mathrm{sol}} \tag{6.9}$$

$$\text{if } J^V(0,t) > 0 \text{ and } \int_0^t J(0,t')\,\mathrm{d}t' \geqq d_A \quad : \quad J(0,t) = 0 \tag{6.10}$$

in which

d_A is dose (areic mass) of substance (kg m^{-2})

The soil system considered in the model was 0.4 m deep. It was assumed that the flux of substance at that depth was simply equal to the convective part of the flux given by Equation 2.2. Thus the lower boundary condition reads:

$$t \geqq 0 \qquad z = 0.4\ \mathrm{m} \qquad J = J^V c \tag{6.11}$$

The volume flux of liquid, J^V, and the volume fraction of liquid, θ, were simulated with the model of water flow described in Sections 5.2 and 5.6.

6.2 ESTIMATION OF VALUES OF PARAMETERS

It was assumed that the soil bulk density varied with depth. The bulk density profiles were assumed to be equal to the averages of the measured profiles derived from Tables 4.3 and 4.4, as shown in Figure 6.1.

To estimate the value of the dispersion length, L_{dis}, the measurements of L_{dis} available in the literature were compiled. These measurements were done with non-sorbing conservative solutes such as chloride ion or tritiated water. Usually, the volume fraction of liquid, θ, and the volume flux of liquid, J^V, were constant with depth and time in these experiments. Then the mass conservation equation for the substance is given by

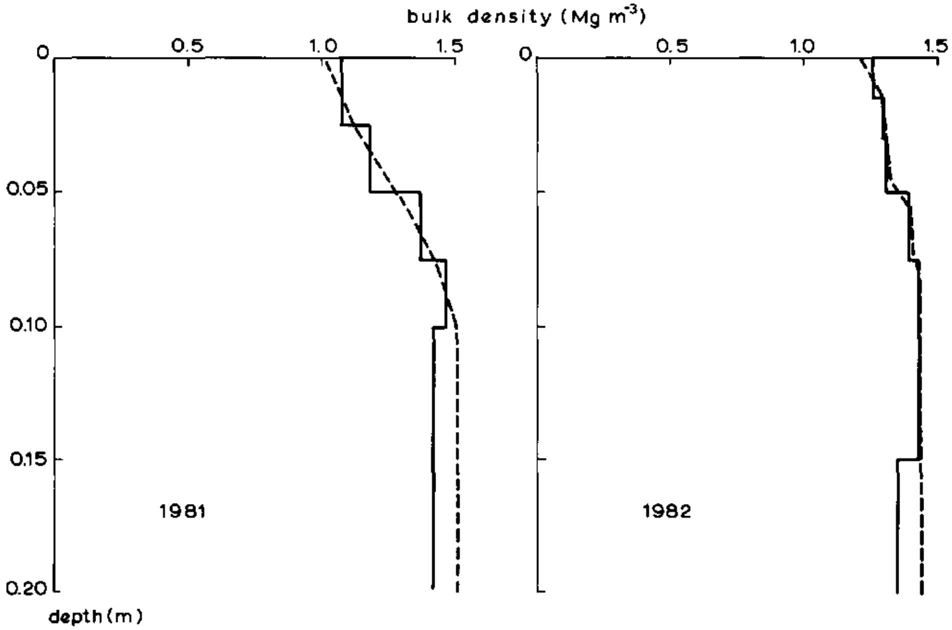


Figure 6.1. The dry soil bulk density, ρ_b, as a function of depth in 1981 and 1982. ———, averages of measured bulk densities; -----, the relationships used in the calculations.

$$\theta \frac{\partial c}{\partial t} = - J^V \frac{\partial c}{\partial z} + D_{dd} \frac{\partial^2 c}{\partial z^2} \tag{6.12}$$

in which D_{dd} (m^2 d^{-1}) is defined by

$$D_{dd} \equiv D_{dis} + D_{dif} \tag{6.13}$$

A dispersion length measurement involves a well defined measurement of e.g. a chloride ion effluent curve or distribution pattern in soil, combined with a fitting procedure. D_{dd} or L_{dis} then result from the best fit of an analytical or numerical solution of Equation 6.12 to the result of the measurements. Often, only the values of D_{dd} were reported in the literature. In those cases, values of the length parameter for the combined effects of diffusion and dispersion, L_{dd} (m), are reported here. L_{dd} is defined by

$$L_{dd} \equiv D_{dd}/|J^V| \tag{6.14}$$

The length parameter for diffusion, L_{dif} (m), is defined by

$$L_{dif} \equiv D_{dif}/|J^V| \tag{6.15}$$

Thus L_{dis} can be written as

$$L_{dis} = L_{dd} - L_{dif} \tag{6.16}$$

Tables 6.2, 6.3 and 6.4 show the results of the literature compilation. In the cases where L_{dd} values are given in the tables, no values of L_{dis} were available from the literature reference. Almost all the L_{dd} values reported were measured using chloride ion. Values of L_{dd} were converted into L_{dis} values with Equations 6.15 and 6.16. The values of D_{dif} for chloride ion was estimated to be 2×10^1 $mm^2\ d^{-1}$ (D_0 was estimated to be 10×10^1 $mm^2\ d^{-1}$ from Weast (1974, p. F-60) and the product of λ and θ was estimated to be 0.2). In the cases where only L_{dis} values are given in Tables 6.2, 6.3 and 6.4, these values were directly available from the literature reference.

Of the 26 L_{dis} values in Table 6.2 only seven are above 10 mm; of these seven, four are in the range from 10 to 20 mm (two clay loams, a clay and a silt). The remaining three L_{dis} values are much higher (60 to 120 mm). These three are the only ones that were found for columns with diameters much greater than 0.1 m. This indicates that L_{dis} is a function of column diameter.

The dispersion length measurements for columns of undisturbed soil (Table 6.3) were all obtained from columns with relatively small diameters. Table 6.3 shows that there is no relationship between L_{dis} values and soil texture for undisturbed soils. In Table 6.3 a larger fraction of the L_{dis} values exceeds 10 mm than in Table 6.2: this indicates that the soil structure influences the value of L_{dis}, and therefore it can be inferred that the measurements given in Table 6.2 are not very useful for estimating L_{dis} in field situations.

Table 6.4 shows information about values of L_{dd} and L_{dis} obtained from field experiments. The L_{dd} values measured by van der Molen (1957) and van Hoorn (1981) may probably be set equal to L_{dis} values, because volume fluxes of liquid in inundation and irrigation situations often exceed 10 mm d^{-1}. The values measured by van der Molen (1957) and van Hoorn (1981) are high vis-à-vis those in Table 6.3. However, in inundation and irrigation situations complications resulting from stagnant phase effects can be more severe than at lower volume fluxes of water. Moreover, if L_{dd} is obtained from some averaged solute pattern, the variability in the areic volume of infiltrating water at a scale of e.g. 100 m^2

Table 6.2. Measurements of L_{dd} or L_{dis} from columns of sieved soil, reported in the literature.

Soil texture	Experimental conditions			L_{dd} (mm)	L_{dis} (mm)	Reference
	column length (m)	column diameter (m)	volume flux of liquid (mm d^{-1})			
Silt loam	0.1	0.04	100	1	1	Elrick & French (1966)
Loam	0.2	0.08	500	5	5	Lai & Jurinak (1972)
Clay loam	0.2	0.08	200	11	11	Lai & Jurinak (1972)
Sandy loam	0.2	0.08	200	3	3	Lai & Jurinak (1972)
Clay loam	0.2	0.03	40	13	12	Smith (1972)
Fine sandy loam	0.2	0.03	40	1	0.5	Smith (1972)
Loam	0.2	0.03	40	2	1	Smith (1972)
Sandy loam	0.2	0.03	40	4	3	Smith (1972)
Silt	0.2	0.03	40	3	2	Smith (1972)
Fine sandy loam	0.2	0.03	40	2	1	Smith (1972)
Silt	0.2	0.03	40	4	3	Smith (1972)
Clay	0.2	0.03	40	20	19	Smith (1972)
Silt	0.2	0.03	40	14	13	Smith (1972)
Silt	0.2	0.03	40	6	5	Smith (1972)
Fine sandy loam	0.2	0.03	40	3	2	Smith (1972)
Loamy sand	0.2	0.03	40	1	0.5	Smith (1972)
Silt	0.2	0.03	40	4	3	Smith (1972)
Silt	0.2	0.03	40	10	9	Smith (1972)
Silt	0.2	0.03	40	7	6	Smith (1972)
Sand	0.5	0.05	10	3	1	Todd & Kemper (1972)
Clay loam	0.5	0.05	10	4	2	Todd & Kemper (1972)
Loam	0.4	0.05	200		2	Bresler & Laufer (1974)
Silty clay loam	1.5	0.7	2-20	70	60-70	Wierenga et al. (1975)
Sandy loam	0.2	0.05	200	1	1	Elprince & Day (1977)
Sandy loam	1.2	1.2-2.4	10-40	60	60	van Hoorn (1981)
Silty clay loam	1.2	1.2-2.4	10-40	120	120	van Hoorn (1981)

Table 6.3. Measurements of L_{dd} or L_{dis} from columns of undisturbed soil, reported in the literature.

Soil texture	Experimental conditions			L_{dd} (mm)	L_{dis} (mm)	Reference
	column length (m)	column diameter (m)	volume flux of liquid (mm d^{-1})			
Silt loam	0.1	0.04	200	9	9	Elrick & French (1966)
Sandy	1.0	0.12	4-60		2	Frissel et al. (1970)
Clay	1.0	0.12	3-30		3	Frissel et al. (1970)
Silt loam	1.0	0.12	6-50		25(8-40)	Frissel et al. (1970)
Clay	1.0	0.12	10		20	Frissel et al. (1974)
Sandy	1.0	0.12	10		11	Frissel et al. (1974)
Sand	0.9	0.12	1-10		20-30	Gerritse et al. (1982)

can induce a greater spread in the solute pattern and thus an additional 'dispersion length'. Biggar & Nielsen (1976) eliminated this variability in their analysis and again found, on average, a low L_{dd} value (30 mm). Thus the information in Table 6.4 does not conflict with the hypothesis that in the field, L_{dis} measured at sampling spots with surface areas of the order of 100 cm^2, is in the range of the values of Table 6.3.

From this literature compilation it is concluded that the L_{dis} value to be expected for solute movement in field soils under natural situations (averaged over a surface area of the order of magnitude of 100 cm^2) is in the range between 2 to 30 mm. In the present study, transport was calculated using L_{dis} = 2 mm as lower limit and L_{dis} = 30 mm as upper limit of the L_{dis} values to be expected. Calculations were also carried out with an intermediate value of 8 mm.

Table 6.4. Measurements of L_{dd} or L_{dis} from field experiments, reported in the literature.

Soil texture	Type of water flow	L_{dd} (mm)	L_{dis} (mm)	Reference
Several textures	natural leaching	20- 40		van der Molen (1956)
Several textures	inundation	50- 70		van der Molen (1957)
Loamy sand	irrigation	50-100		van Hoorn (1981)
Silty clay loam	irrigation	100-200		van Hoorn (1981)
Clay loam	infiltration		10	Bresler (1973)
Loam - clay loam	saturated leaching	30		Biggar & Nielsen (1976)
Silt loam	natural leaching		10	Duynisveld (1981)

The coefficient for diffusion of cyanazine in water, D_0, was estimated to be 36 $mm^2\ d^{-1}$ (at 15 °C) according to the calculation method of Othmer & Thakar as described by Reid & Sherwood (1966, p. 550). Using this method, a value of 39 $mm^2\ d^{-1}$ was calculated for metribuzin. D_0 of bromide ion was estimated to be $1.3 \times 10^2\ mm^2\ d^{-1}$ (Weast, 1974, p. F-60). The tortuosity factor for diffusion in the liquid phase, λ , was introduced as a function of the volume fraction of liquid, θ, (see Figure 6.2). This relationship was derived from a literature compilation by Leistra (1978).

Herbicide/soil sorption characteristics were derived from laboratory experiments with a suspension of soil. Sorption isotherms were measured using the soil sampled before the start of the field experiment in 1982 (see Section 4.2.1). The soil was stored moist in the laboratory (water content: 0.12 kg kg^{-1}). Sorption of both cyanazine and metribuzin was measured at five concentrations using ^{14}C-labelled cyanazine and metribuzin. All experiments were done in triplicate at 19 °C in a suspension of 5 g of soil in 5 cm^3 of water containing the herbicide, plus $CaCl_2$ at a concentration of 10 mol m^{-3}. Initial herbicide concentrations ranged between 0.01 and 7 g m^{-3}. The suspension was continuously mixed on a rotating disc for 24 h. It was assumed that no transformation of herbicides occurred during the sorption experiments. Other details of the experimental procedures of the sorption experiments are described in Section 7.3.2.

Results of the sorption measurements are shown in Figure 6.3. Only the averages of the triplicates are shown, because the individual points almost coincided. Figure 6.3 shows that the sorption isotherms of both cyanazine and metribuzin can be described well with the Freundlich sorption isotherm equation. The lines shown were calculated using a least-squares linear regression approximation. The values found for K_F and $1/n$ are given in Table 6.5.

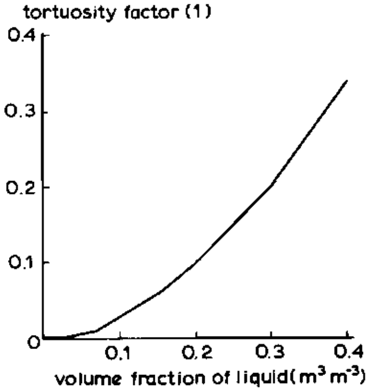


Figure 6.2. Relationship between the tortuosity factor for diffusion in the liquid phase, λ, and the volume fraction of liquid, θ, as taken from Leistra (1978).

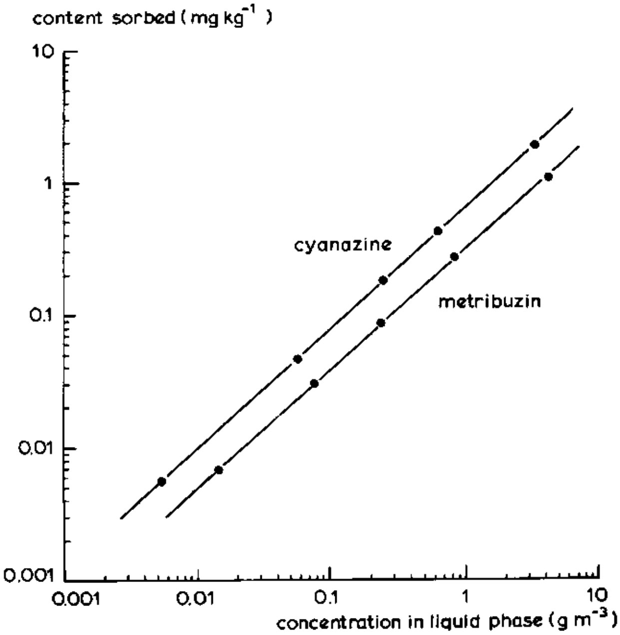


Figure 6.3. Sorption isotherms of cyanazine and metribuzin as measured in a suspension of soil and water after shaking for 24 h. ●, averages of triplicate measurements; ——, linear regression approximation of the Freundlich equation (Equation 6.1).

It was assumed that bromide ion was not sorbed by the soil.

The concentrations at which the substances dissolved in the field were estimated from the values of the solubility in water reported in the literature (see Table 4.1 for these solubilities). A complication is that in the field the concentration in the aqueous solution flowing into soil will be lower than the solubility value, because there is not enough time for complete equilibration. As a rough

Table 6.5. Values of the Freundlich coefficient, K_F, and the Freundlich exponent, $1/n$, as derived from the measured sorption isotherms shown in Figure 6.3.

	K_F ($m^{3/n}$ $kg^{-1/n}$)	$1/n$ (1)
Cyanazine	0.34×10^{-3}	0.91
Metribuzin	0.15×10^{-3}	0.89

approximation it was assumed that the concentrations at which the substances dissolve, c_{sol}, were half the solubility values.

Another complication is that the solubilities of the herbicides probably depend on temperature: Calvet et al. (1975) found that the solubility of three triazine herbicides in water decreased to about one-half if the temperature fell from 30 °C to 10 °C. In 1981, soil temperature in the top centimetres during the first rainfall events was in the range of 15 °C to 25 °C. These temperatures correspond roughly with the temperature used in the measurement of the solubility of cyanazine (25 °C; see Table 4.1). For 1981 the solubility of cyanazine as given in Table 4.1 was used without correction for temperature. In 1982, soil temperature in the top centimetres during the first rainfall events was in the range of 5 °C to 10 °C, which is 10 °C to 20 °C lower than the temperatures used in the measurements of the solubilities of cyanazine and metribuzin (Table 4.1). For 1982 it was assumed that the solubilities at the temperature conditions in the field were half the values reported in the literature. Thus, for cyanazine, c_{sol} values of 0.08 and 0.04 kg m^{-3} were used for the experiments of 1981 and 1982, respectively and for metribuzin a value of 0.3 kg m^{-3} was used.

The solubility of NaBr in water depends little on temperature: from data given by Weast (1974, p. B-136) it was calculated that the solubility of NaBr in water corresponds with a bromide concentration of 900 kg m^{-3} at 50 °C and of 940 kg m^{-3} at 100 °C. Thus for bromide ion a c_{sol} value of 500 kg m^{-3} was used.

Doses of herbicide applied were derived from the least-squares linear regression approximation to the measured decline of areic mass, as shown in Figure 4.11. The values for cyanazine were 48 and 149 mg m^{-2} in 1981 and 1982, respectively. The value for metribuzin was 96 mg m^{-2}. These values correspond reasonably well with the areic masses recovered from the aluminium foils and with those recovered from soil after 1 d (see Table 4.5).

The dose of bromide ion was derived from the areic mass of bromide ion recovered from the 0 to 200 mm layer 1 day after application (9.2 g m^{-2}).

The values of the rate coefficient for transformation of the herbicides, k_{t}^{*}, were assumed to be equal to the k_{dec} values derived from the field measurements given in Figure 4.11. Thus, values of k_{t}^{*} for cyanazine in 1981 and 1982 were 0.040 and 0.033 d^{-1} respectively and for metribuzin in 1982 the k_{t}^{*} value was 0.032 d^{-1}.

It was assumed that bromide ion was not transformed during the field experiment.

6.3 NUMERICAL SOLUTION OF THE MASS CONSERVATION EQUATION

Equation 2.1 was solved in c^* with an explicit finite-difference method. To do this, a rectangular grid of points numbered $i = 1, 2, \ldots$ along the z axis and numbered $j = 0, 1, 2, \ldots$ along the t axis was defined in the (z,t) plane. Downward direction of z is assumed to be positive. Δz_i is defined as the thickness of a compartment around point i (see Figure 6.4). Δt is defined as the time step.

To approximate the flux of the substance, J, in the right-hand side of Equation 2.1, values of c have to be derived from known values of c^*. Combination of Equations 2.5 and 6.1 gives:

$$c^* = \theta \; c + \rho_{\mathrm{b}} \, K_{\mathrm{F}} \, c^{1/n} \tag{6.17}$$

Equation 6.17 shows that it is impossible to derive values of c from values of c^* in an explicit way. Rearranging Equation 6.17 yields an implicit equation in c:

$$c = c^* / \left\{ \theta + \rho_{\mathrm{b}} \, K_{\mathrm{F}} \, c^{(1/n)-1} \right\} \tag{6.18}$$

As the values of $1/n$ for both cyanazine and metribuzin were about 0.9, the value of the right-hand side of Equation 6.18 only changes slightly with a change in c. This is illustrated by Figure 6.5 which shows the right-hand side of Equation 6.18 using values of K_{F} and $1/n$ as measured for cyanazine and metribuzin and using values of c^*, θ and ρ_{b} of 1.0 g m^{-3}, 0.25 m^3 m^{-3} and 1.3 Mg m^{-3} respectively.

Values of c at grid point (i,j), $(c)_i^j$, were calculated with Equation 6.18 by

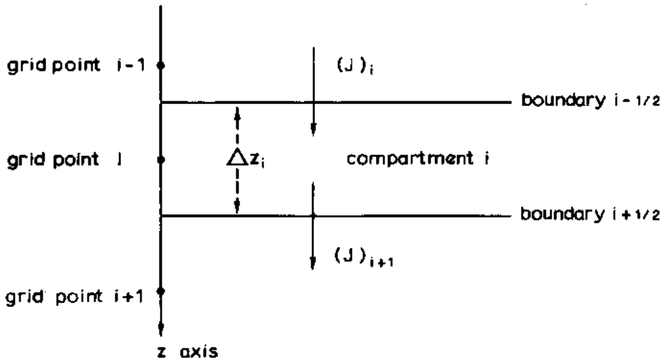


Figure 6.4. Discretization of the z axis for the numerical solution of the mass conservation equation for the substances.

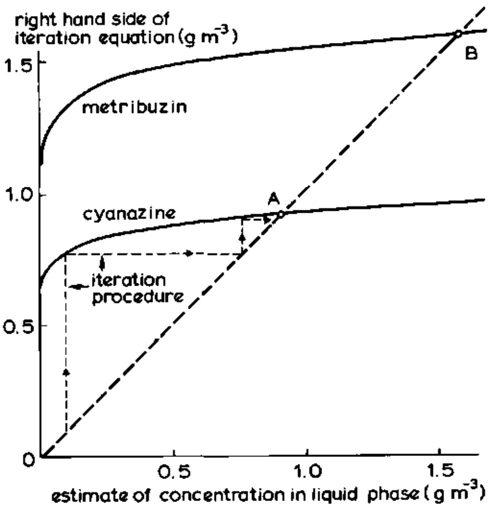


Figure 6.5. Right-hand side of iteration Equation 6.18 as a function of estimate of c. The points of intersection A and B indicate solutions of Equation 6.18.

iteration using known values of the other variables at grid point (i,j) (the iteration procedure is shown graphically for cyanazine in Figure 6.5). At the start $(j = 0)$ no substance was present in the soil system. Thus the initial guess of $(c)_i^0$ was 0. Thereafter, at each moment $j\ \Delta t$ the final value of $(c)_i^{j-1}$ was taken as the initial guess of $(c)_i^j$. The number of iterations at each grid point was regulated with an error criterion: the iteration stopped when successive $(c)_i^j$ values differed from each other by less than 0.1 %. Usually, less than three iterations were required.

It was also attempted to solve Equation 6.18 with the Newton-Raphson iteration procedure (see for instance Froeberg, 1973). This procedure could not be used because no good solution was obtained for initial estimates of c that were for instance 10^{-3} times the actual value.

For the approximation of the right-hand side of Equation 2.1 the following finite-difference equation was used:

$$\left(\frac{\partial c^*}{\partial t}\right)_i^j = \left\{(J)_i^j - (J)_{i+1}^j\right\} / \Delta z_i - k_t^* \, (c^*)_i^j \qquad (6.19)$$

in which $(J)_i^j$ for values of i from 2 to I is given by

$$(J)_i^j = (J^V)_i^j \, (c)_{i-\frac{1}{2}}^j - (D_{dd})_i^j \left\{(c)_i^j - (c)_{i-1}^j\right\} / \tfrac{1}{2}(\Delta z_i + \Delta z_{i-1}) \qquad (6.20)$$

in which

$(c)^j_{i-\frac{1}{2}}$ is value of c at the boundary between compartments i and $i-1$ (kg m^{-3})

The value of c at the boundary between two compartments is calculated via linear interpolation between the values at the adjacent grid points by

$$(c)^j_{i-\frac{1}{2}} = \frac{\Delta z_i \ (c)^j_{i-1} + \Delta z_{i-1} \ (c)^j_i}{\Delta z_i + \Delta z_{i-1}} \tag{6.21}$$

The coefficient D_{dd} is approximated by

$$(D_{\mathrm{dd}})^j_i = L_{\mathrm{dis}} \left| (J^V)^j_i \right| + \tfrac{1}{2} \left\{ (D_{\mathrm{dif}})^j_{i-1} + (D_{\mathrm{dif}})^j_i \right\} \tag{6.22}$$

in which

$$(D_{\mathrm{dif}})^j_i = (\lambda)^j_i \ (\theta)^j_i \ D_0 \tag{6.23}$$

For the approximation of the flux of substance at the soil surface the areic mass still present undissolved at the soil surface, σ_{u} (kg m^{-2}), is calculated using Euler's integration method for $j \geqq 1$ with

$$(\sigma_{\mathrm{u}})^j = d_A - \Delta t \sum_{\zeta=0}^{j-1} (J)^\zeta_1 \tag{6.24}$$

The flux of substance at the soil surface, $(J)^j_1$, is calculated from

$$(J)^j_1 = \min\left[\left\{ (\sigma_{\mathrm{u}})^j / \Delta t \right\} , \ \max\left\{ 0 \ , \ (J^V)^j_1 \ c_{\mathrm{sol}} \right\} \right] \tag{6.25}$$

The flux of substance at the lower boundary of the system was derived from Equation 6.11:

$$(J)^j_{l+1} = (J^V)^j_{l+1} \ (c)^j_l \tag{6.26}$$

Thus, effects of diffusion and dispersion in the last half-compartment were ignored.

Equation 6.19 was integrated with respect to t using Euler's integration method:

$$(c^*)_i^{j+1} = (c^*)_i^j + \Delta t \left(\frac{\partial c^*}{\partial t}\right)_i^j \tag{6.27}$$

Use of Euler's integration method (Equation 6.27) is prescribed by the structure of the infiltration algorithm of the model for water flow (Equations 5.1 and 5.2). However, this method complicates the finite-difference approximation of the derivatives with respect to depth, z. For an accurate numerical solution computations should be done using a corrected coefficient for the spread that results from the combined effects of diffusion and dispersion, $D_{\mathrm{dd}}^{\mathrm{c}}$ ($\mathrm{m}^2\ \mathrm{d}^{-1}$), according to the equation

$$D_{\mathrm{dd}}^{\mathrm{c}} = D_{\mathrm{dd}} + \frac{\Delta t \{J^V\}^2}{2(q' + \theta)} \tag{6.28}$$

in which q' ($\mathrm{m}^3\ \mathrm{m}^{-3}$) is defined by

$$q' \equiv \rho_{\mathrm{b}} K \tag{6.29}$$

Equation 6.28 can be derived from the numerical analysis of van Genuchten & Wierenga (1974, p. 9, Eq. 21) if a system is considered with constant θ, J^V, ρ_{b} and a linear sorption isotherm (see Bolt, 1979, Eq. 9.51). In the analysis of van Genuchten & Wierenga (1974) no transformation was considered. Thus their analysis was extended to a system with a first-order rate equation for transformation. It was found that Equation 6.28 also applies to the computations in the present study (see Appendix D, for details). Thus the flux of substance was calculated from Equation 6.20 with the modification that D_{dd} was replaced with $D_{\mathrm{dd}}^{\mathrm{c}}$:

$$(D_{\mathrm{dd}}^{\mathrm{c}})_i^j = (D_{\mathrm{dd}})_i^j + \frac{\Delta t \{(J^V)_i^j\}^2}{2\{(q')_i^j + (\theta)_i^j\}} \tag{6.30}$$

In the literature, stability criteria have been formulated for the finite-difference approximation of Equations 6.19, 6.20, 6.21 and 6.27 for a system with constant θ, J^V, ρ_{b} and a linear sorption isotherm (Equation 2.6). For constant Δt this finite-difference approximation may be written as

$$(c)_i^{j+1} = G_{i-1}\ (c)_{i-1}^j + G_i\ (c)_i^j + G_{i+1}\ (c)_{i+1}^j \tag{6.31}$$

in which G_{i-1}, G_i and G_{i+1} are given by

$$G_{i-1} = \frac{\Delta t\ J^V}{2\,\Delta z\ (q' + \theta)} + \frac{\Delta t\ D^{c}_{dd}}{\Delta z^2\ (q' + \theta)} \tag{6.32}$$

$$G_i = 1 - \frac{2\,\Delta t\ D^{c}_{dd}}{\Delta z^2\ (q' + \theta)} - \Delta t\ k^*_t \tag{6.33}$$

$$G_{i+1} = -\frac{\Delta t\ J^V}{2\,\Delta z\ (q' + \theta)} + \frac{\Delta t\ D^{c}_{dd}}{\Delta z^2\ (q' + \theta)} \tag{6.34}$$

Lapidus & Pinder (1982, pp. 186-187) carried out a von Neumann stability analysis for Equation 6.31 and found a stability criterion which can be rewritten as

$$\frac{\Delta t\ D^{c}_{dd}}{\Delta z^2\ (q' + \theta)} \leqq \tfrac{1}{2} \tag{6.35}$$

The same result was obtained by Richtmyer & Morton (1967, pp. 195-196). However, as noted by B. Damsté (personal communication, 1986), the derivation of Equation 6.35 by Lapidus & Pinder and Richtmyer & Morton is incorrect. I derived from the amplification factor given by Lapidus & Pinder and Richtmyer & Morton that Equation 6.35 is correct if $k^*_t = 0$. Because k^*_t values are low (0.03-0.04 d^{-1}, see Section 6.2), Equation 6.35 is probably a reasonable approximation of the stability criterion of the system considered.

Combining Equation 6.35 with Equation 6.28 leads to

$$\frac{\{J^V\}^2}{2(q' + \theta)}\Delta t^2 + D_{dd}\ \Delta t - \tfrac{1}{2}\Delta z^2\ (q' + \theta) \leqq 0 \tag{6.36}$$

Equation 6.36 leads to the stability criterion

$$\Delta t \leqq \frac{(q' + \theta)}{\{J^V\}^2}\left\{-D_{dd} + \sqrt{D_{dd}^{\ 2} + \{J^V\}^2\ \Delta z^2}\ \right\} \tag{6.37}$$

The finite-difference approximation described by Equations 6.19 to 6.27 and 6.30, was programmed in the simulation language CSMP III (Speckhart & Green, 1976). The computer program is listed in Appendix E. Thicknesses of the compartments, Δz_i, were equal to those used in the water flow model.

In the computations the stability criterion of Equation 6.37 was always satisfied. For cyanazine the Δt values used were in the range from 0.01 to 0.1 d. For metribuzin and bromide ion the ranges were from 0.006 to 0.02 d and from 0.002 to 0.01 d, respectively.

In the computations with L_{dis} = 2 mm it was found that negative concentrations sometimes occurred, but these were always restricted to compartments with absolute values of concentrations that were less than 1 % of the maximum concentration of the corresponding concentration profile. Thus it was assumed that these artifacts did not influence the interesting part of the computed concentration profile.

It is interesting to know whether the correction of D_{dd} by Equation 6.28 plays an important role in the numerical solution. This can be estimated as follows. Ignoring the spread that results from diffusion, Equation 6.28 may be rewritten as

$$D^{\mathrm{c}}_{\mathrm{dd}} = \left|J^V\right| \{ L_{\mathrm{dis}} + \frac{\left|J^V\right| \Delta t}{2(q' + \theta)} \} \qquad (6.38)$$

Thus a numerical spreading length parameter, L_{num} (m), can be defined as

$$L_{\mathrm{num}} = \frac{\left|J^V\right| \Delta t}{2(q' + \theta)} \qquad (6.39)$$

As can be seen from Equation 6.39, the largest L_{num} is obtained when J^V is highest. The highest daily average of the volume flux of rainfall in the field experiments was about 40 mm d^{-1}. Values of L_{num} for this day were estimated for the computations with the L_{dis} value of 2 mm. Values between 0.7 and 0.9 mm were found for both herbicides and bromide ion. These values are in the same order of magnitude as the L_{dis} value. For the computations with the L_{dis} values of 8 and 30 mm, estimated values of L_{num} were found to be at least one order of magnitude smaller than the corresponding L_{dis} values, and correction for numerical dispersion was of minor importance.

Analytical and numerical solutions for L_{dis} = 2 mm were compared for bromide and cyanazine. In the soil system considered, θ and ρ_{b} were assumed to be constant at values of 0.25 $\mathrm{m}^3\ \mathrm{m}^{-3}$ and 1.3 Mg m^{-3}, respectively. For cyanazine a linear sorption isotherm was assumed with a slope, K, of 0.64 $\mathrm{dm}^3\ \mathrm{kg}^{-1}$. No transformation was assumed to occur. J^V was set constant at the highest daily average that occurred during the field experiments (40 mm d^{-1}). In the numerical solution D_{dd} was corrected according to Equation 6.30. The time steps used were somewhat smaller than prescribed by the stability criterion (Equation 6.37). The boundary condition at the soil surface was:

$$J = J^V c_{sol} \qquad (6.40)$$

The value of c_{sol} used was 1 g m^{-3} for both bromide ion and cyanazine. The analytical solution for this system was taken from Bolt (1979, p. 313). Figure 6.6 shows that numerical and analytical solutions corresponded well for both bromide ion and cyanazine.

In the equation for the flux of substance at the lower boundary of the system (Equations 6.11 or 6.26), the contribution of diffusion and dispersion effects was ignored. The influence of this simplification on calculated concentration profiles was considered. For both herbicides the influence was negligible: cumulative computed herbicide percolation below 0.4 m depth was always lower than 2 % of the areic mass of herbicide computed to be present in the 0 to 0.4 m layer. For bromide ion the lower boundary condition may have influenced results appreciably: using Equation 6.26 it was calculated that 80 %, 74 % and 71 % of the dose applied had leached below 0.4 m depth after 121 d for L_{dis} values of 2, 8 and 30 mm, respectively. Thus, the lower boundary condition for bromide ion was considered in detail.

Van Genuchten & Wierenga (1974, p. 6) described a finite-difference approximation of the flux of substance at the lower boundary, which was based on the correct flux equation (Equation 2.2). In their approximation J^V, θ and Δz are as-

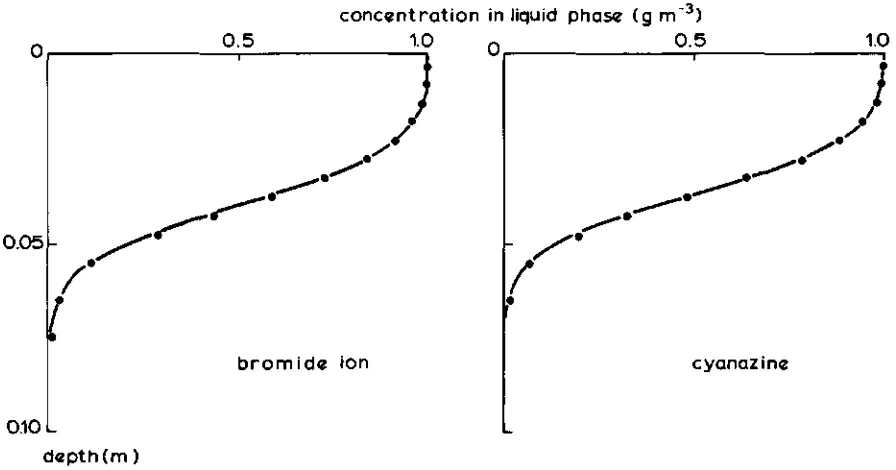


Figure 6.6. Comparison of numerical and analytical solutions for bromide (Δt = 0.016 d, t = 0.25 d) and cyanazine (Δt = 0.05 d, t = 1 d). Properties of soil system were taken to be constant with depth; L_{dis} = 2 mm. ●, numerical solution; ——, analytical solution.

sumed to be constant. The approximation reads:

$$(J)_{l+1}^{i} = J^{V}\ (c)_{l}^{i} - D_{\mathrm{dd}}\{2(c)_{l}^{i} - 3(c)_{l-1}^{i} + (c)_{l-2}^{i}\} / \Delta z \qquad (6.41)$$

However, if used in combination with Equation 6.20 for the approximation of $(J)_{l}^{i}$, this results in a systematically incorrect approximation of $\partial c/\partial z$ at grid point $i = l$. A consistent approximation for this situation reads:

$$(J)_{l+1}^{i} = \tfrac{1}{2}J^{V}\{3(c)_{l}^{i} - (c)_{l-1}^{i}\} - D_{\mathrm{dd}}\{2(c)_{l}^{i} - 3(c)_{l-1}^{i} + (c)_{l-2}^{i}\} / \Delta z \qquad (6.42)$$

In the water flow part of the model it is assumed that no water can flow into the soil system from below. Consequently, computed convective flow of the substance must be downward. Thus Equation 6.42 was used with the modification that only positive values of $\{3(c)_{l}^{i} - (c)_{l-1}^{i}\}$ were allowed. If negative values were found, they were set to zero.

Concentration profiles of bromide ion were calculated with the simplified lower boundary condition (Equation 6.26) and with the physically more correct condition (Equation 6.42). The soil system in these calculations consisted of 20 compartments each 20 mm thick. J^{V} and θ were set constant at values of 10 mm d^{-1} and 0.25 $m^{3}\ m^{-3}$, respectively. L_{dis} was 8 mm and the time step 0.01 d. The results (Figure 6.7) show that the differences between the two calculated concentration profiles were small. Thus Equation 6.26 seems sufficiently accurate to estimate the flux of bromide ion at the lower boundary.

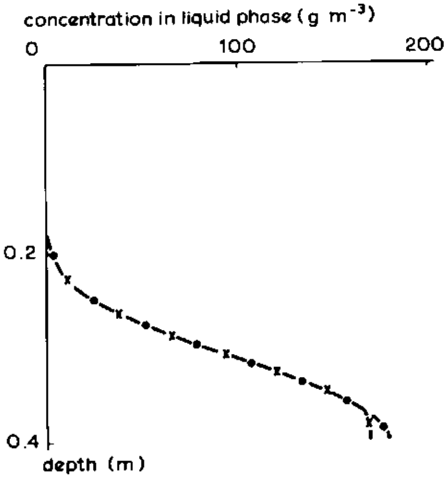


Figure 6.7. Effect of the lower boundary condition on the calculated concentration profile for bromide ion. Properties of soil system were taken to be constant with depth; t = 10 d, L_{dis} = 8 mm; -●-, calculated with Equation 6.26 (standard procedure); -x-, calculated with Equation 6.42.

6.4 RESULTS OF FIELD TEST AND DISCUSSION

Figure 6.8 shows results of the test of the model for bromide ion on a few sampling dates in 1982. The model explains bromide ion movement reasonably well: the measured average concentration is nearly always located between the concentrations as calculated with the upper and lower limits of L_{dis} (30 and 2 mm) estimated from the literature. Figure 6.8 shows that measured concentration profiles spread somewhat wider than those calculated with L_{dis} = 2 mm and somewhat narrower than those calculated with L_{dis} = 30 mm. The measured concentration profiles in Figure 6.8 were described fairly well by the intermediate value of L_{dis} of 8 mm. Figure 6.9 shows that this was also the case for the other sampling dates (days 34 and 121). Thus the value of 8 mm was used as a standard in the calculations for the herbicides and the upper and lower limits of L_{dis} (30 and 2 mm) were considered in sensitivity analyses only.

Figures 6.10 and 6.11 show results of the model tests for cyanazine in 1981 and 1982. In great contrast to the bromide test, the model overestimated cyanazine movement at all sampling dates except after 1 d in 1982. In both years, dif-

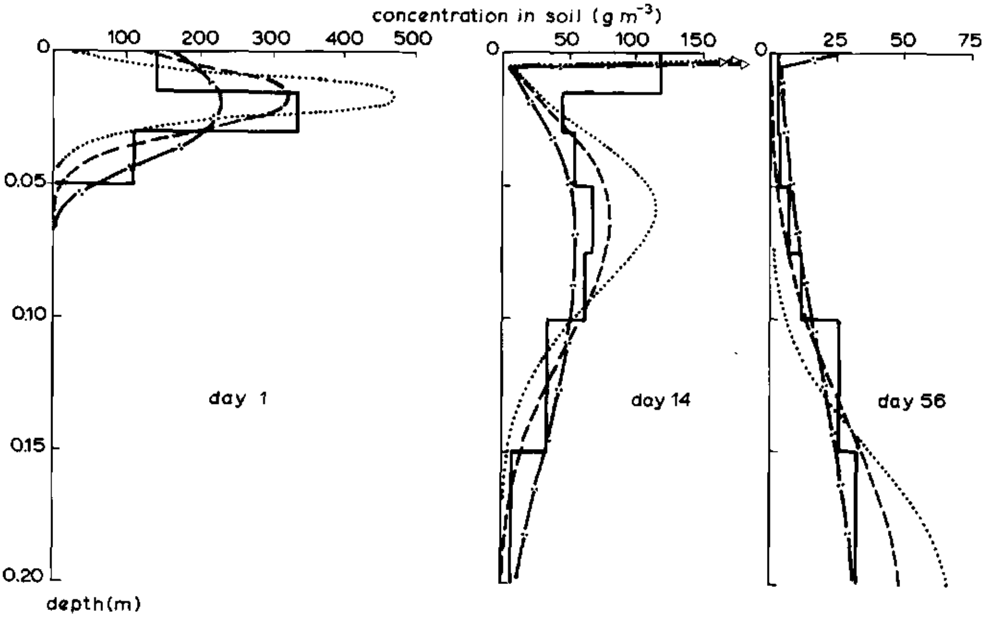


Figure 6.8. Comparison of calculated and measured concentration profiles of bromide ion on three sampling dates in 1982. Vertical solid line segments are averages of measured concentrations; ....., calculated with L_{dis} = 2 mm; ---, calculated with L_{dis} = 8 mm; -:-:-, calculated with L_{dis} = 30 mm.

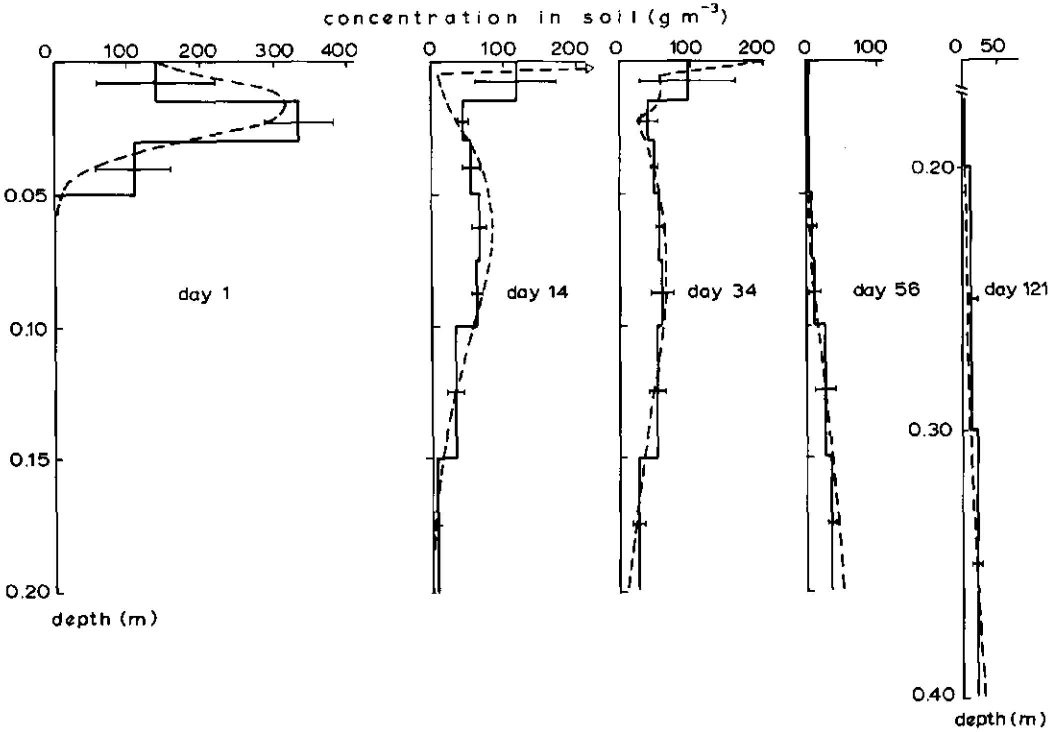


Figure 6.9. Comparison of calculated and measured concentration profiles of bromide ion in 1982. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated with L_{dis} = 8 mm.

ferences between calculated and measured movement increased with time. These differences were especially clear after 64 d in 1981 and after 56 and 121 d in 1982. On these dates the excess of cumulative rainfall over cumulative evaporation was larger than on all other sampling dates (see Figure 5.4). Figure 6.12 shows results of the model test for metribuzin in 1982. The model also overestimated metribuzin movement, especially after 121 d.

In order to avoid possible misunderstanding, it must be pointed out that the concentration profiles of bromide ion and both herbicides in Figures 6.9 to 6.12 have been plotted in such a way that total areic mass of substance in soil corresponded with the same area in each graph, irrespective of the substance and the sampling date. This was done to give the same weight to all sampling dates in the test of the model. If concentration profiles had been plotted with the same concentration axis at all sampling dates (as in Figures 4.8 to 4.10), the most distinct discrepancies between calculated and measured concentration profiles of the herbicides (after 121 d in 1982) would not have been recognized. Another advantage of the way of plotting in Figures 6.9 to 6.12 is that on a given sampling date in 1982 both the calculated and the measured mobilities of the three different sub-

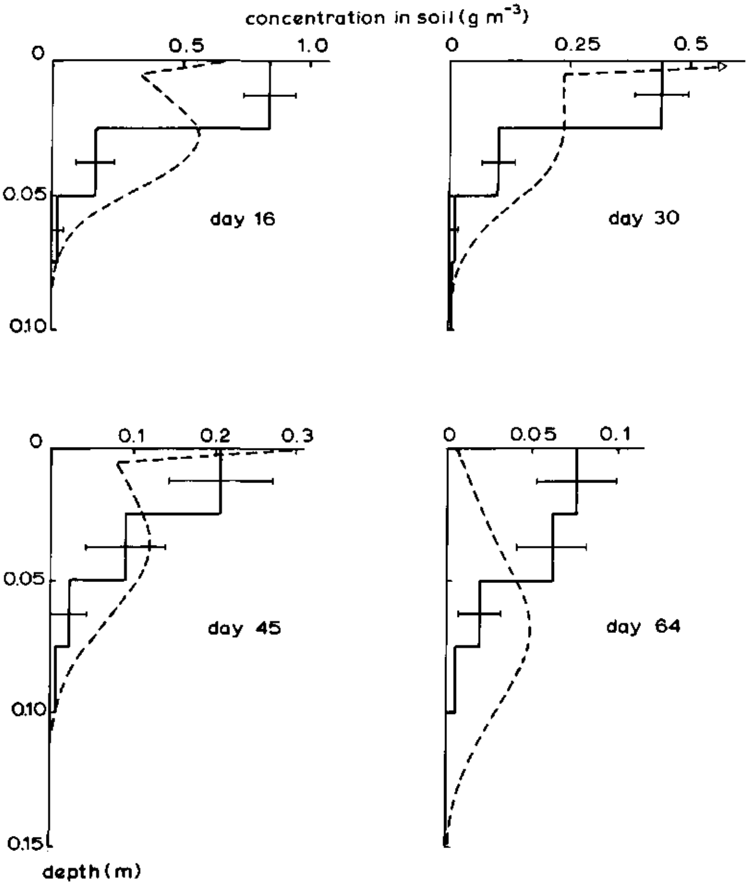


Figure 6.10. Comparison of calculated and measured concentration profiles of cyanazine in 1981. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated with L_{dis} = 8 mm.

stances may be compared with each other.

From Figures 6.10 to 6.12 it may be derived that after two to four months the coefficients of variation of measured concentrations of herbicides range between 20 % and 50 %. The coefficients of variation of total areic masses (shown in Figure 4.12) were between 20 % and 60 % after two to four months. Consequently, an important fraction of the spatial variability results from the variabilities of the deposition and of the transformation process. The spatial variability of the transport process is thus not very large.

Figures 6.9 to 6.12 show that the course of calculated concentration profiles with depth is usually smooth. An exception is the top centimetre, in which steep concentration gradients often occur because substance accumulates in the surface layer as a result of the evaporation of water. An accurate calculation of the con-

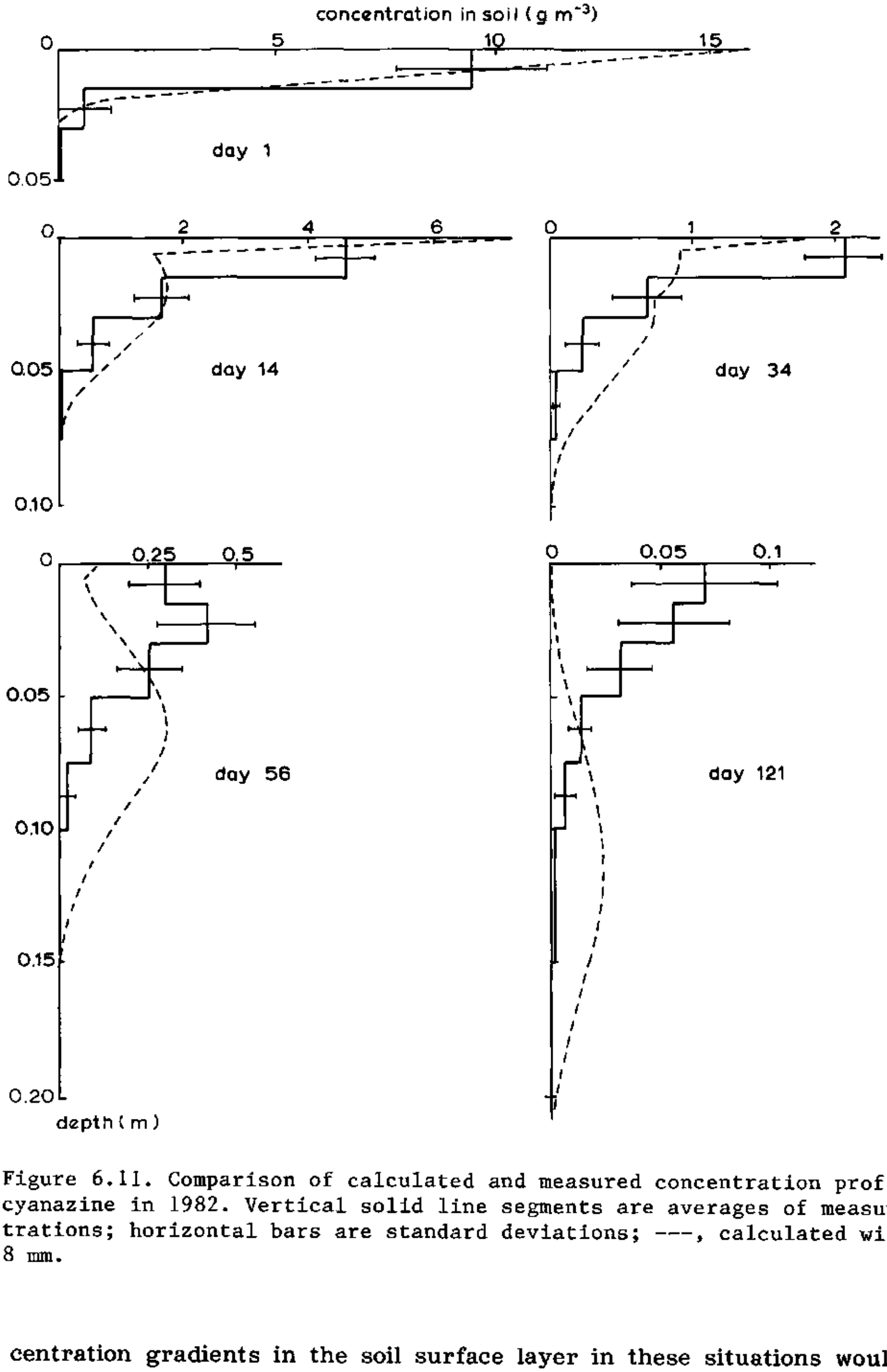


Figure 6.11. Comparison of calculated and measured concentration profiles of cyanazine in 1982. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated with L_{dis} = 8 mm.

centration gradients in the soil surface layer in these situations would probably require a thickness of the compartments, Δz, that is 5 to 10 times smaller than the thickness of 5 mm used here. This would lead to an appreciable increase of

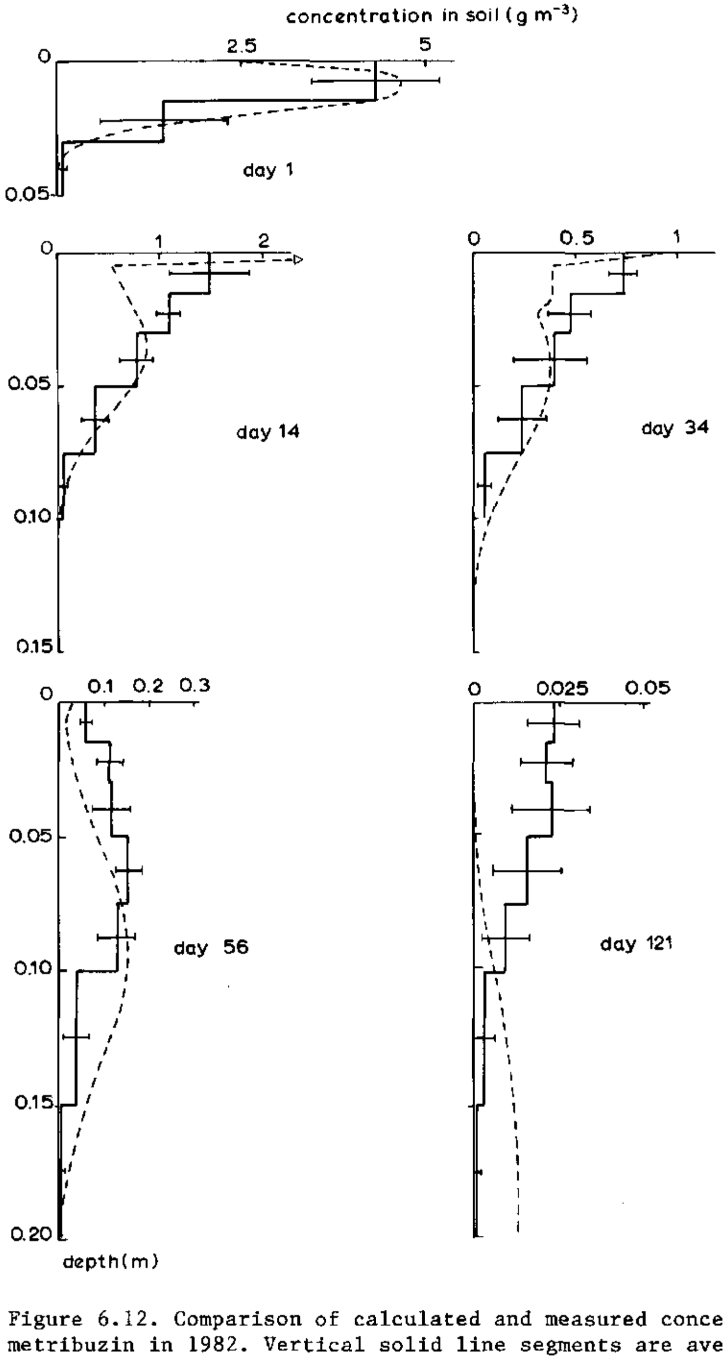


Figure 6.12. Comparison of calculated and measured concentration profiles of metribuzin in 1982. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated with L_{dis} = 8 mm.

computer time (Equation 6.37). Such detailed computations do not seem to be justifiable anyway, because the concentration gradient in the top 10 mm was not measured in detail.

Looking for possible causes of the observed discrepancies in Figures 6.10 to 6.12, the sensitivity of calculated concentration profiles of the herbicides was considered to a number of parameters in the substance part of the model.

Firstly, the sensitivity of calculated profiles of herbicide concentrations to the L_{dis} value was investigated. From results shown in Figure 6.13 it is concluded that the discrepancies between calculated and measured herbicide movement cannot be the result of uncertainties in the L_{dis} value.

Secondly, the sensitivity of calculated profiles to the way of calculation of the rate coefficient for transformation of substance in the soil system, k_t^*, was considered. So far, in all calculations it has been assumed that k_t^* is constant. However, in Chapter 3 k_t^* was described to be a function of soil water content and soil temperature. As described in Chapter 3, k_t^* usually increases continuously with increasing water content (in the range between air-dry and field capacity) and with increasing temperature (in the range 5-35 °C). In the field ex-

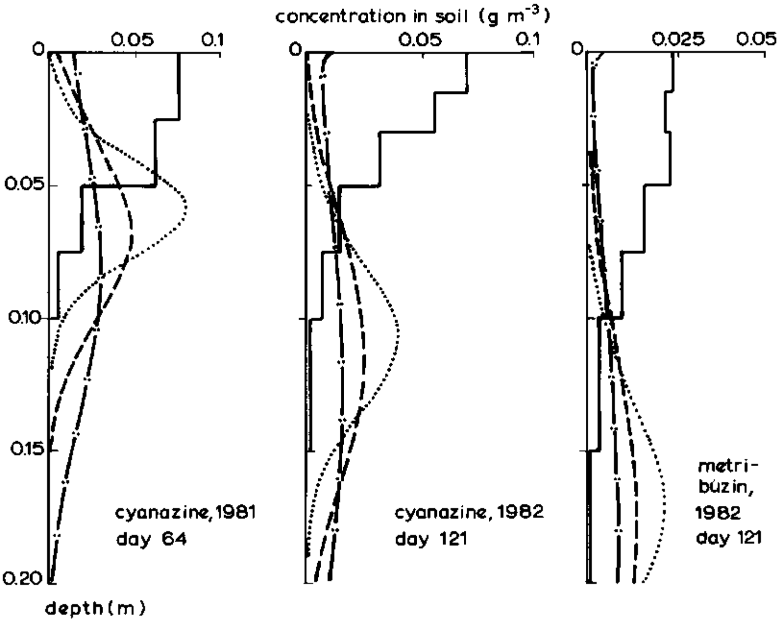


Figure 6.13. Effect of the dispersion length, L_{dis}, on calculated concentration profiles of herbicides on a few sampling dates. ····, calculated with L_{dis} = 2 mm; ---, calculated with L_{dis} = 8 mm; -:-:-, calculated with L_{dis} = 30 mm; ———, averages of measured concentration profiles.

periments of 1981 and 1982 the volume fraction of liquid in the top layer was usually lower than that of deeper layers (see Figures 5.8 and 5.9). As described in Section 4.3, the daily averages of soil temperatures measured at 10 and 50 mm depth were approximately equal in the field experiments. It follows that k_t^* should usually increase with depth in the field experiments. This might also be a factor partly responsible for the discrepancies between calculated and measured concentration profiles in Figures 6.10 to 6.12. Thus the sensitivity of calculated concentration profiles to the relationship between k_t^* and θ had to be investigated. To do this, calculations were done using Equation 3.5 with a B value of 1.0. According to the literature this is a value high in the range of measured values (see Figure 3.2). The value of $C_{t,4}$ in Equation 3.5 was calculated in such a way that during each time step the total areic rate of transformation in the soil system was equal to that calculated with the constant value of k_t^*. This was done with the equation

$$(C_{t,4})^j = k_{dec} \frac{\sum_{i=1}^{I} \Delta z_i \; (c^*)_i^j}{\sum_{i=1}^{I} (\theta)_i^j \; \Delta z_i \; (c^*)_i^j} \tag{6.43}$$

One may expect the highest sensitivity in those calculations in which a large fraction of the herbicide is present in a soil layer with a large gradient in volume fraction of liquid. Thus, in the sensitivity analysis only cyanazine was considered, because in the calculations it penetrated less deeply into soil than metribuzin (compare Figures 6.11 and 6.12). The results (Figure 6.14) show that in the present case calculated concentration profiles of cyanazine were not sensitive to the relationship between k_t^* and θ.

Thirdly, the sensitivity of calculated profiles of herbicide concentration to the concentration at which the herbicides dissolve, c_{sol}, was considered. The values estimated for c_{sol} and for the doses of herbicide implied that in 1981 the complete dose of cyanazine was dissolved after an areic volume of water of 0.6 mm had infiltrated: in 1982 the areic volume of water required was 4 mm. For metribuzin this value amounted to 0.3 mm (the value for bromide was 0.02 mm). These areic volumes are low compared with cumulative rainfall during the field experiments (see Figure 5.4). Thus it cannot be expected that concentration profiles calculated with higher c_{sol} values would differ greatly from the profiles calculated with the standard values. Lower c_{sol} values for the herbicides could, in principle, be responsible for the discrepancies between calculated and measured profiles of Figures 6.10 to 6.12. To test this, the sensitivity to c_{sol} was con-

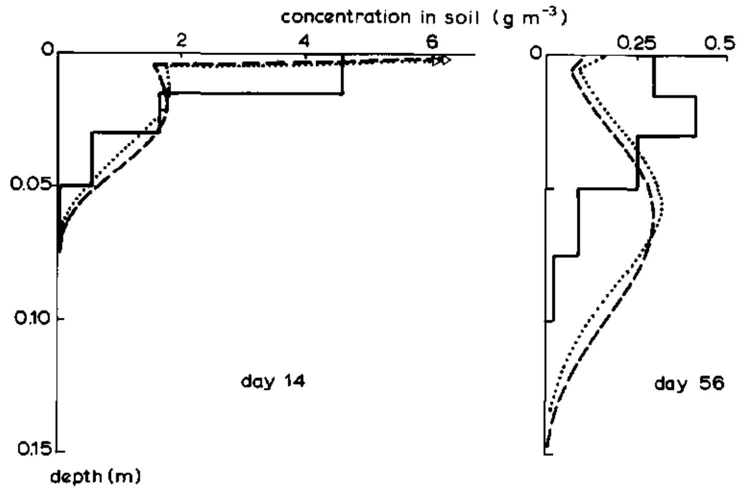


Figure 6.14. Effect of the relationship between the rate coefficient for transformation, k_t^*, and the volume fraction of liquid, θ, on calculated concentration profiles of cyanazine in 1982. ---, calculated with constant k_t^*; ····, calculated with Equations 3.5 and 6.43; ——, averages of measured concentrations.

sidered for cyanazine in 1982: the c_{sol} value used (4 g m^{-3}) was 0.1 times the standard value (40 g m^{-3}). The results (Figure 6.15) show that even such a low c_{sol} value could not have been responsible for the discrepancy between the calculated and the measured concentration profiles for cyanazine after 121 d in 1982.

In the foregoing sensitivity analysis, all the important parameters in the substance part of the model were considered, except those in the sorption part. As, furthermore, the test for bromide ion indicated that the model successfully explained the movement of a non-sorbing substance, it may be concluded with fair certainty that the discrepancies between calculated and measured herbicide movement as shown in Figures 6.10, 6.11 and 6.12 resulted from incorrect assumptions in the sorption part of the herbicide transport model. The assumptions in the sorption part of that model were:

- the herbicide sorbed is continuously in equilibrium with that in the liquid phase
- the sorption equilibrium is described correctly by the isotherm found by shaking a soil suspension at a solid:liquid ratio of about 1 kg kg^{-1} for about 24 h at 19 °C (the solid:liquid ratio of a system is defined here as the ratio of the mass of solid phase divided by the mass of liquid phase).

These assumptions may be wrong, for various reasons. Firstly, the sorption process may not reach equilibrium during rainfall at high fluxes, and as a result,

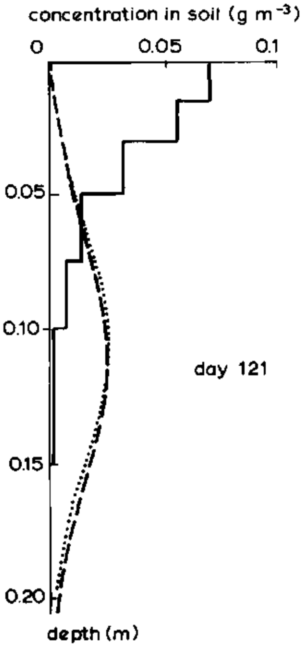


Figure 6.15. Effect of the dissolution concentration, c_{sol}, on the concentration profile calculated for cyanazine after 121 d in 1982. ---, calculated with $c_{sol} = 40$ g m^{-3} (standard value); ·····, calculated with $c_{sol} = 4$ g m^{-3}; ——, averages of measured concentrations.

there may be less movement than expected from the equilibrium isotherm. This can be illustrated by a theoretical study done by Leistra & Dekkers (1977). They calculated the effect of sorption kinetics on movement of a pesticide with a linear sorption isotherm with a slope of 0.8 dm^3 kg^{-1}. If the pesticide was initially at sorption equilibrium in the top layer of soil, sorption kinetics resulted in less calculated movement than sorption equilibrium. Thus the effect of sorption kinetics on herbicide movement in the field experiments has to be estimated.

As discussed in Section 2.3.1, results obtained by Rao et al. (1979) implied that transport of a non-sorbing substance (tritiated water) could be described well by the equilibrium transport model, whereas under the same experimental conditions clear physical non-equilibrium effects were found for sorbing substances (herbicides). Thus the good correspondence between calculated and measured bromide concentration profiles in Figure 6.9, does not exclude the possibility that equilibration between all or some of the sorption sites and the bulk of the liquid phase was only slow.

Secondly, the sorption equilibrium in the field may be different from that measured in the laboratory experiment. Higher sorption (i.e. higher values of the Freundlich coefficient, K_F) also leads to less movement (see calculations by Leistra, 1980, for the sensitivity of the model to K_F if $1/n = 1$). Higher sorption could be caused by, for example, lower temperature or higher salt concentration in the field (Calvet, 1980). Furthermore, hysteresis may occur in the sorption process (van Genuchten & Cleary, 1979). In other words, desorption isotherms may result in higher contents sorbed at a given concentration in the liquid phase than adsorption isotherms. In the field, desorption situations may occur not only because the herbicide leaches from a certain soil layer but also because in the liquid phase the herbicide is transformed. Thus, hysteresis may also be responsible for the discrepancies between calculated and measured movement in Figures 6.10 to 6.12.

There are many possible reasons for making incorrect assumptions in the sorption part of the transport model. To clarify the situation it was decided to systematically study the sorption process of cyanazine and metribuzin in the loamy sand soil in laboratory experiments (i.e. at the explanatory level!, see Figure 1.1).

It is interesting to know whether the calculated concentration profiles of the substances are sensitive to the way in which the volume fraction of liquid, θ, is simulated. This was tested in calculations for cyanazine and bromide ion in 1982 in which it was assumed that θ was constant with time and in each layer equal to θ_{max} (i.e. the value corresponding with field capacity). The results (Figure 6.16) show that concentration profiles were usually very close to the profiles calculated with the standard procedure. Serious discrepancies between calculated profiles occurred only for bromide ion during accumulation in the top five centimetres after 14 d. It is thus concluded that calculated concentration profiles are not very sensitive to the way in which θ is simulated.

Another interesting point is whether calculated concentration profiles are sensitive to a change in the volume flux of evaporation of water. This was tested in calculations for cyanazine and bromide in 1982, again with θ set constant at θ_{max}. Evaporation fluxes were assumed to be 1.25 times the fluxes derived from the evaporation model applied in Section 5.4. The model overestimated movement of the herbicides and therefore only effects of an increase of evaporation fluxes are of interest. The results (Figure 6.16) show that a 25 % increase in evaporation fluxes resulted in more accumulation of the substances near the soil surface after 14 d. The cyanazine profile calculated after 56 d was only moderately sensitive to the evaporation flux. However, the bromide profile calculated after 56 d was sensitive to the evaporation flux: when the flux increased by 25 % there was a clear upward shift of the calculated profile. The concentration profile of bromide ion calculated after 56 d with the increased evaporation flux also differed markedly from the measured concentration profile. As the concentration profile of bromide ion calculated after 56 d is sensitive to the evaporation flux and as the profile calculated with the standard evaporation flux corresponded

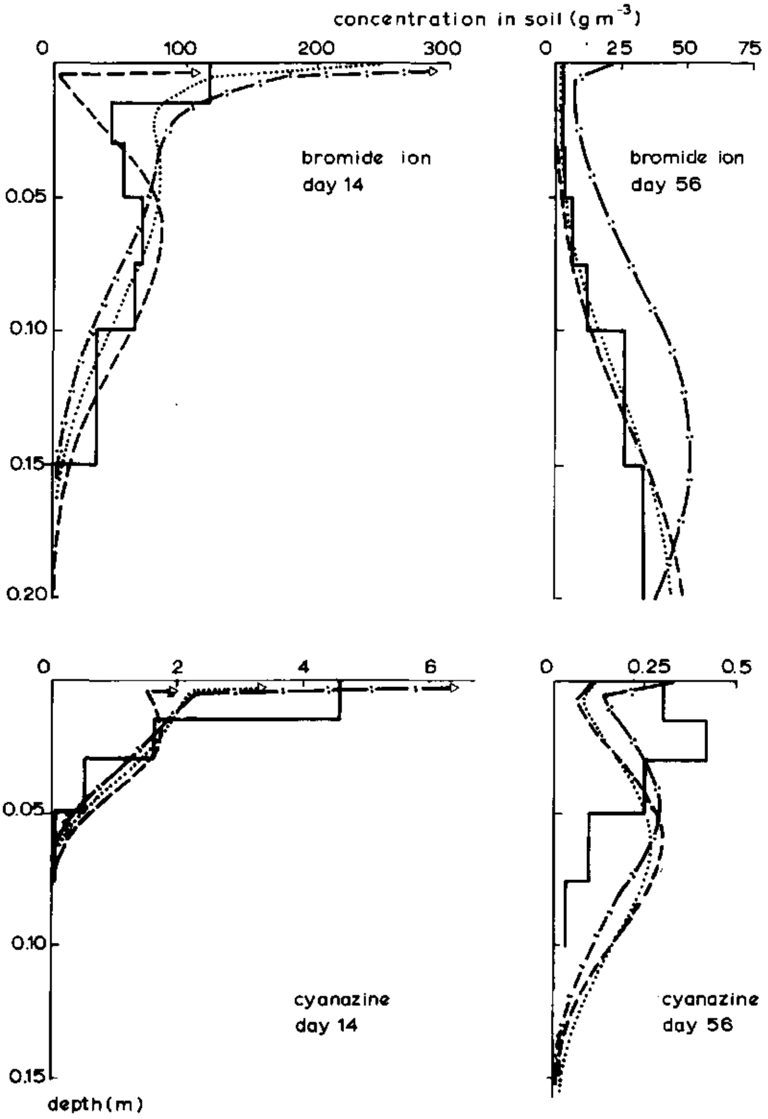


Figure 6.16. Effect of constant volume fraction of liquid, θ, and increased evaporation fluxes on calculated concentration profiles of bromide ion and cyanazine after 14 and 56 d in 1982. ——, averages of measured concentrations; ---, calculated with model of water flow as applied in Section 5.6 (standard run); ····, calculated with θ constant in time and equal to θ_{max} (field capacity); -:-:-, calculated with θ constant in time and equal to θ_{max} (field capacity) and with evaporation fluxes multiplied by a factor of 1.25.

well with the measured profile after 56 d, it is tempting to conclude that this is further endorsement of the sub-model for simulating evaporation, as applied in Section 5.4. However, this is no direct test of the evaporation model, because it cannot be stated a priori that the equilibrium transport model is valid for bromide ion. Calculations of bromide ion transport with, for instance, the non-equilibrium model of Addiscott (1977) would result in bromide ion penetrating the soil more deeply than calculated with the equilibrium model. Thus it is theoretically possible that in the present study an unjustified omission of non-equilibrium effects was compensated for by a too low estimate of the evaporation flux.

In the model for bromide ion, the effect of anion exclusion was not considered. When anion exclusion is incorporated in the transport model it only influences calculated movement if it is also assumed that some or all of the water that is inaccessible to anions is less mobile than the remainder of the water. This is probable, because the inaccessible water is next to the surface of the solid phase. Thus, the transport model used for bromide ion is only jusitified if the volume fraction of liquid from which the anions are excluded, θ_{ex} ($m^3\ m^{-3}$), is small compared with the total volume fraction of liquid in soil, θ. In the literature, for sands θ_{ex} values of 0.02-0.03 $m^3\ m^{-3}$ were found (Smith, 1972; Frissel et al., 1974). These θ_{ex} values are indeed small, compared with the values of θ that occurred during transport in the field (see Figures 5.8 and 5.9).

It was tested whether calculated concentration profiles were sensitive to the coefficient for diffusion in liquid phase in soil, D_{dif}. To do this, calculations in which the diffusion process was omitted (i.e. $D_{dif} = 0$) were done for cyanazine and bromide ion in 1982. The results (Figure 6.17) show that this hardly influenced the concentration profile of cyanazine after 14 d. Figure 6.17 shows that the effect of omitting the diffusion process was fairly small for bromide ion and very small for cyanazine. The less small effect for bromide ion may be because of the value estimated for the coefficient for diffusion in water, D_0, which for bromide ion was about four times the D_0 value estimated for cyanazine.

In the transport model used (Table 6.1), movement of herbicides in the gas phase is ignored. In a simulation study, Leistra (1979) found that the contribution of the flux resulting from diffusion in the gas phase was almost negligible for the nematicide ethoprophos in a sandy loam soil. Sorption of ethoprophos by the soil was comparable with the sorption of cyanazine by the loamy sand soil used here. Leistra (1979) estimated for ethoprophos that the ratio of the concentration in the liquid phase divided by the concentration in the gas phase was about 10^6. This ratio was estimated for cyanazine and metribuzin from their water solubilities and saturated vapour pressures listed in Table 4.1. The ratio was

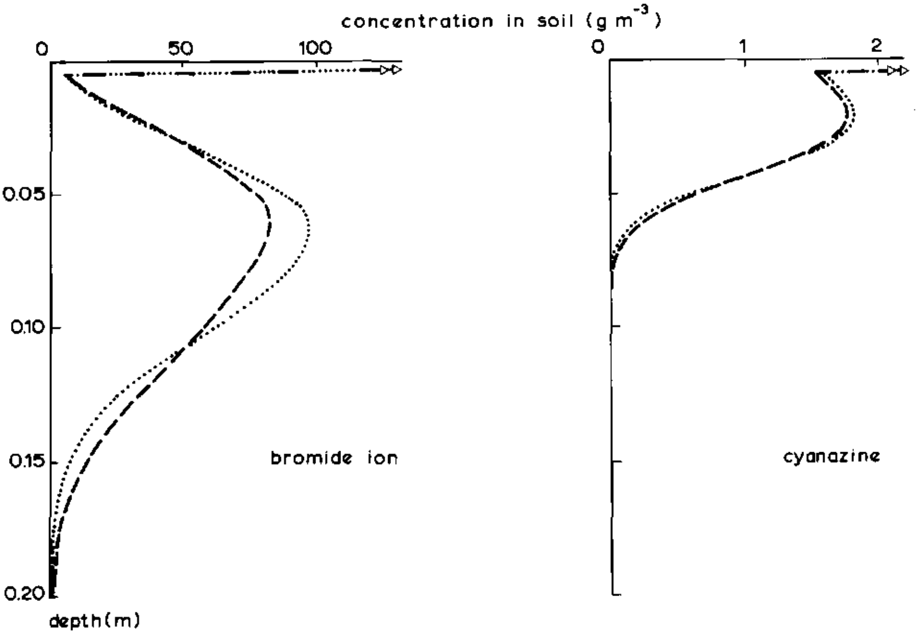


Figure 6.17. Effect of omission of the diffusion process on calculated concentration profiles of bromide ion and cyanazine after 14 d in 1982. ---, calculated with $D_{dif} = \lambda\ \theta\ D_0$ (standard procedure); ·····, calculated with $D_{dif} = 0$.

estimated to be in the order of 10^{10} for cyanazine. For metribuzin the ratio was estimated to be greater than 10^7 (at 20 °C). It was concluded for both herbicides that a significant contribution of the flux in the gas phase was unlikely.

7 SHORT-TERM SORPTION STUDIES WITH HERBICIDES

7.1 INTRODUCTION

As described in Section 6.4, the sorption of both cyanazine and metribuzin had to be studied in detail in laboratory experiments in order to elucidate the cause(s) of the discrepancies between calculated and measured concentration profiles of herbicides shown in Figures 6.10 to 6.12. Both adsorption/desorption kinetics and the influence of various soil/herbicide factors on sorption had to be studied.

In the following sections of Chapter 7, only short-term sorption of herbicides will be considered. This means that measuring periods did not exceed 24 h. Long-term sorption studies are described in Chapter 8.

Section 7.2 describes the mathematical models of sorption kinetics that will be used in attempts to describe or explain experimental results. Section 7.3 describes experiments on short-term adsorption kinetics in soil suspension and in moist soil. Section 7.4 describes experiments on short-term desorption kinetics and equilibria. Section 7.5 describes experiments on the influence of various factors on short-term adsorption equilibria.

7.2 MATHEMATICAL MODELS OF HERBICIDE SORPTION KINETICS

Let us first consider a system in which the assumptions associated with the Langmuir equation are valid. The Langmuir sorption rate equation has been formulated by various researchers, for instance Burchill et al. (1981, p. 246). Rearranging their equation gives

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_{\mathrm{a,L}}\, c\, (p - X) - k_{\mathrm{d}}\, X \qquad (7.1)$$

in which

$k_{\mathrm{a,L}}$	is adsorption rate constant	($\mathrm{m^3\ kg^{-1}\ d^{-1}}$)
p	is maximum content sorbed ('plateau' value)	($\mathrm{kg\ kg^{-1}}$)
k_{d}	is desorption rate constant	($\mathrm{d^{-1}}$)

After introducing the parameter $K_L \equiv k_{a,L}/k_d$ (m^3 kg^{-1}), Equation 7.1 can be rearranged by eliminating $k_{a,L}$ to

$$\frac{dX}{dt} = k_d(1 + K_L\, c)\left(\frac{p\, K_L\, c}{1 + K_L\, c} - X\right) \tag{7.2}$$

If k_d is eliminated instead of $k_{a,L}$ Equation 7.1 becomes

$$\frac{dX}{dt} = k_{a,L}(p - X)\left\{c - \frac{X}{K_L\,(p - X)}\right\} \tag{7.3}$$

At equilibrium, dX/dt is zero. Equations 7.2 and 7.3 then yield the Langmuir isotherm equation:

$$X = \frac{p\, K_L\, c}{1 + K_L\, c} \tag{7.4}$$

Let us now consider a system with a linear sorption isotherm. The corresponding sorption rate equation can be derived from Equation 7.1 by assuming that $p \gg X$:

$$\frac{dX}{dt} = k_{a,L}\, p\, c - k_d\, X \tag{7.5}$$

After introducing the parameter $k_a \equiv k_{a,L}\, p$ (m^3 kg^{-1} d^{-1}), Equation 7.5 can be rewritten as

$$\frac{dX}{dt} = k_a\, c - k_d\, X \tag{7.6}$$

From Equation 7.6 and the equation of the linear sorption isotherm (Equation 2.6) it can be derived that

$$K \equiv k_a/k_d \tag{7.7}$$

Equation 7.6 may be rewritten as

$$\frac{dX}{dt} = k_d(K\, c - X) \tag{7.8}$$

or as

$$\frac{dX}{dt} = k_a(c - X/K) \tag{7.9}$$

Hornsby & Davidson (1973) postulated a sorption rate equation that is different from Equation 7.6. Their equation has been frequently applied (van Genuchten et al., 1974; Cameron & Klute, 1977; Leistra & Dekkers, 1977; Rao et al., 1979). The sorption rate equation of Hornsby & Davidson (1973) reads

$$\frac{dX}{dt} = k_\alpha \frac{V}{M} c - k_d X \tag{7.10}$$

in which

k_α	is adsorption rate constant	(d^{-1})
V	is volume of liquid in the system	(m^3)
M	is mass of solid phase in the system	(kg)

Multiplying all terms in Equation 7.10 by M results in

$$\frac{dx}{dt} = k_\alpha V c - k_d x \tag{7.11}$$

in which

x	is mass sorbed in the system	(kg)

Thus the concept of Hornsby & Davidson (1973) implies that the adsorption rate dx/dt in a system is proportional to its volume of liquid, V. There is no physical basis for such a proportionality (A. de Keizer, personal communication, 1984). Multiplying all terms in Equation 7.6 by M results in:

$$\frac{dx}{dt} = k_a M c - k_d x \tag{7.12}$$

Here the adsorption rate is proportional to the mass of solid phase, M. This is correct, because M is directly proportional to the number of sorption sites available: in a system with a linear sorption isotherm the number of occupied sorption sites is a negligible fraction of the total number of sites.

Finally, let us consider a system with sorption sites exhibiting a distribution of sorption energies. Back in 1950 it was shown (Sips, 1950) that for such a system the equation for the Freundlich sorption isotherm (Equation 6.1) can be derived, provided reasonable assumptions are made about the distribution pattern (cf. also the relevant discussions in Sposito, 1984, p. 120, and van Riemsdijk et al., 1986). It is common for the results of pesticide-sorption experiments to be described well by the Freundlich isotherm equation (Calvet et al., 1980c, p. 240). This equation is often indicated as a strictly empirical expression (Hamaker & Thompson, 1972, p. 64; de Haan & Zwerman, 1976, p. 243; Calvet et al., 1980a, p. 41). However, in pesticide/soil systems, various sorption mechanisms operate and the properties of sorption sites can be expected to be heterogeneous. Therefore, for these systems, the equation for the Freundlich sorption isotherm is to be preferred a priori to the equation for the Langmuir sorption isotherm: the former equation accounts in a certain way for surface heterogeneity whereas the Langmuir sorption isotherm assumes uniform sorption sites.

The following equation is commonly used in literature (for instance: van Genuchten & Cleary, 1979; Rao & Jessup, 1982) to describe pesticide-sorption kinetics in soil:

$$\frac{dX}{dt} = k_d(K_F\, c^{1/n} - X) \tag{7.13}$$

Equation 7.13 is a first-order rate equation that is analogous to Equation 7.8. Another possible equation (analogous to Equation 7.9), reads

$$\frac{dX}{dt} = k_a \left\{ c - \left(\frac{X}{K_F} \right)^n \right\} \tag{7.14}$$

No one has yet derived a Freundlich sorption rate equation in a way analogous to that of the Freundlich isotherm equation. Such a derivation has to start from Equation 7.1 and the surface heterogeneity is then reflected in frequency distributions of both $k_{a,L}$ and k_d. This would be an interesting topic for further theoretical investigation. Equations 7.13 and 7.14 were accepted, even though they imply that the heterogeneity is completely attributable to heterogeneity in either $k_{a,L}$ (Equation 7.13) or in k_d (Equation 7.14). Later it will be shown that this simplification did not lead to errors in calculated concentrations that were of any practical significance in field situations. Note that Equation 7.13 differs from Equation 7.14, whereas the analogous equations for the systems with both Langmuir and linear sorption isotherms (Equations 7.2 and 7.3 and Equations 7.8 and 7.9, respectively) were mathematically identical.

It is known that soil aggregates are porous (Greenland & Mott, 1978). Thus for a soil, as a first approximation, the sorption sites can be divided into two classes: sites of one class are located on the external surface (class-1 sites), those of a second are located within the porous aggregates on the internal surface (class-2 sites). It is assumed as a first approximation that sorption properties of the internal and external sites do not differ at molecular level. It must be stressed that the distinction between the two classes of site is based purely on differences in accessibility: at molecular level, the properties of sites within each class can be expected to be heterogeneous.

If it is assumed that the heterogeneity of the sorption sites at molecular level is negligible, the Langmuir isotherm equations for both classes of site are identical with the understanding that the capacity of the two classes is a freely adjustable parameter:

$$\frac{X_k}{\rho_k} = \frac{K_L\ c}{1 + K_L\ c} \qquad (7.15)$$

in which

X_k	is content sorbed as class-k sites (k = 1,2)	(kg kg^{-1})
ρ_k	is maximum content sorbed at class-k sites	(kg kg^{-1})

The linear sorption isotherms for the two classes of site are:

$$X_1 = K_1\ c \qquad (7.16)$$

$$X_2 = K_2\ c \qquad (7.17)$$

in which

X_1, X_2	are contents sorbed at class-1 and class-2 sites, respectively	(kg kg^{-1})
K_1, K_2	are slopes of linear sorption isotherms for class-1 and class-2 sites, respectively	(m^3 kg^{-1})

The Freundlich sorption isotherms for the two classes of site are

$$X_1 = K_{F,1}\ c^{1/n} \qquad (7.18)$$

$$X_2 = K_{F,2}\ c^{1/n} \qquad (7.19)$$

in which

$K_{F,1}$, $K_{F,2}$	are values of K_F for class-1 and class-2 sites, respectively	($m^{3/n}$ $kg^{-1/n}$)

Sorption rate equations for class-1 sites are analogous to Equations 7.2/7.3, 7.8/7.9 and 7.13/7.14 for systems with Langmuir, linear and Freundlich sorption isotherms, respectively. It is assumed that for sorption at class-2 sites the diffusion process in the internal liquid phase is rate-limiting. As first approximations for such a process the following rate equations are postulated:

$$\frac{dX_2}{dt} = k_{a,2}(c - c_{2,h}) \qquad (7.20)$$

or

$$\frac{dX_2}{dt} = k_{d,2}(X_{2,h} - X_2) \tag{7.21}$$

in which

$k_{a,2}$	is adsorption rate constant for class-2 sites	$(m^3\ kg^{-1}\ d^{-1})$
$c_{2,h}$	is hypothetical value of c in equilibrium with the momentary value of X_2	$(kg\ m^{-3})$
$k_{d,2}$	is desorption rate constant for class-2 sites	(d^{-1})
$X_{2,h}$	is hypothetical value of X_2 in equilibrium with the momentary value of c	$(kg\ kg^{-1})$

Equations 7.20 and 7.21 are first-order rate equations and thus the most simple equations available. For Langmuir and linear sorption isotherms Equations 7.20 and 7.21 are mathematically identical. For a Freundlich isotherm this is not true. However, if $1/n$ is near unity, Equations 7.20 and 7.21 will yield similar descriptions of experimental data.

It is stressed that for class-2 sites a derivation of the sorption rate equation from the kinetics of the surface reaction (for instance, Equation 7.1) is not valid, because the kinetics are not controlled by this reaction.

A mechanistic treatment of the sorption kinetics at class-2 sites would involve solving the diffusion equation for the unknown but probably complex geometry of the internal liquid phase and for an also unknown spatial distribution of the internal sites. This would result in a model whose complexity is not justified in first attempts to describe herbicide/soil sorption kinetics.

Thus, both Equations 7.20 and 7.21 have no thorough theoretical basis. Equation 7.20 is conceptually more attractive than Equation 7.21, because the diffusion in liquid phase is related to a difference in concentrations in liquid phase. However, Equation 7.21 is more simple, because the rate of change in content sorbed is proportional to a difference in two contents sorbed. A further advantage of Equation 7.21 is the more simple dimension of the rate constant. Equation 7.21 was arbitrarily chosen to describe the laboratory measurements. In conformity, the rate equation for class-1 sites for a system with a Freundlich isotherm was based on Equation 7.13 and thus not on Equation 7.14.

The following rate equations for class-1 and class-2 sites for a system with a linear sorption isotherm can be derived from Equations 7.8, 7.16, 7.17 and 7.21:

$$\frac{dX_1}{dt} = k_{d,1}(K_1\ c - X_1) \tag{7.22}$$

$$\frac{dX_2}{dt} = k_{d,2}(K_2\ c - X_2) \tag{7.23}$$

in which

$k_{d,1}$ is desorption rate constant for class-1 sites (d^{-1})

For a system with a Freundlich isotherm the rate equations for class-1 and class-2 sites can be derived from Equations 7.13, 7.18, 7.19 and 7.21:

$$\frac{dX_1}{dt} = k_{d,1}(K_{F,1}\ c^{1/n} - X_1) \tag{7.24}$$

$$\frac{dX_2}{dt} = k_{d,2}(K_{F,2}\ c^{1/n} - X_2) \tag{7.25}$$

The model based on Equations 7.24 and 7.25 will be referred to as the Freundlich model with two-site kinetics.

Theoretically, instead of using $K_{F,1}$ in the Freundlich model with two-site kinetics it is more elegant to use the product of the 'overall' Freundlich coeffiecient, K_F, and F_F. The latter is defined as the fraction of K_F to be attributed to class-1 sites ($F_F = K_{F,1}/K_F$). Similarly, the product of K_F and ($1 - F_F$) could be used instead of $K_{F,2}$. However, (anticipating results to be shown in Chapter 8) at a later stage it will be necessary to add a third class of site to the model and for cross-references it is then easier to use absolute values of $K_{F,1}$ and $K_{F,2}$ in Equations 7.24 and 7.25.

7.3 ADSORPTION OF HERBICIDES IN SOIL SUSPENSION AND IN MOIST SOIL

7.3.1 Introduction

Only a few studies on sorption kinetics of herbicides or other pesticides in soil have been reported. Hance (1967) measured adsorption kinetics of four herbicides in suspensions of a loam and a sandy loam. Adsorption times ranged between 0.5 h and 72 h. He found that the decrease in concentration in liquid phase between 0 and 0.5 h was larger than that in the remainder of the experiment; between 24 h and 72 h, usually no significant decrease was found. Kay & Elrick (1967) measured adsorption kinetics of lindane in suspensions of a loam, a loamy sand and a sandy loam. They used adsorption times between a few minutes and 3 h. They found that during the first few minutes the concentration in liquid phase fell very rapidly before levelling off, becoming almost constant after 1 h. Neither Hance (1967) nor Kay & Elrick (1967) attempted to describe their results with a mathematical model.

One may wonder whether sorption measurements in a soil suspension (as described by e.g. Hance, 1967), may be used to predict sorption in moist soil. There is no reason why sorption sites available in soil suspension would not be available in moist soil. One would thus expect sorption isotherms in both systems to be equal. However, the kinetics of sorption are probably slower in moist soil, because there solid and liquid phases do not move. In the literature, information on the relationship between the sorption of pesticides in soil suspension and that in moist soil is very limited. Green & Obien (1969) found for a few soil types that sorption of atrazine in moist soil after an equilibration period of 24 h was lower than expected from sorption isotherms measured in a suspension after shaking for 2 h. Green & Corey (1971) found for a few soil types that sorption isotherms of atrazine and diuron measured after 2.5 h in moist soil with percolating water, corresponded well with isotherms measured after 2.5 h in soil suspension. Given these findings, plus the recommendation in Calvet's review article (Calvet, 1980, p. 21) that further research be done on the comparison between sorption in moist soil and sorption in soil suspension, it was decided to measure adsorption kinetics in both systems.

There have been indications in the literature (e.g. Grover & Hance, 1970) that herbicide adsorption isotherms depend on the solid:liquid ratio used (the solid:liquid ratio of a system is defined as the mass of solid phase divided by the mass of liquid phase). A literature search yielded around 30 measurements concerning the influence of solid:liquid ratio on pesticide adsorption isotherms (Grover & Hance, 1970; Green & Corey, 1971; Graham-Bryce, 1972; Dao & Lavy, 1978; Davidson et al., 1980b). Solid:liquid ratios of the soil suspensions in these studies were in the range 0.05-4.0 kg kg^{-1}. In some 85 % of the cases the ratio had no influence on measured isotherms, whereas in about 15 % of the cases an increase in the ratio resulted in sorption decreasing considerably. In the publications either an influence was found for all pesticide/soil combinations studied (Grover & Hance, 1970; Graham-Bryce, 1972) or it was not found at all (Dao & Lavy, 1978; Davidson et al., 1980b). Obviously, the experimental conditions rather than the specific pesticide/soil combination determines whether or not an effect is found. A possible explanation is that Grover & Hance (1970) and Graham-Bryce (1972) were the only ones that used a reciprocating shaker. I concluded that the solid:liquid ratio usually has no influence on sorption of pesticides in soil suspensions. However, as a possible influence cannot be excluded, I had to check whether the solid:liquid ratio influenced sorption in the present study.

7.3.2 Procedures for measuring adsorption

7.3.2.1 Purification of radioactive substances

Herbicide concentrations were measured by liquid scintillation counting of ^{14}C-labelled herbicides (henceforth the expression 'labelled' refers to ^{14}C-labelled). This method can only be used if transformation of the herbicides is negligible during the experiments. This requirement was met, because sorption measurements with labelled herbicides lasted no longer than 24 h.

A sample of labelled cyanazine was available in solid state. The sample was dissolved in acetone and was used to obtain a number of samples with a range of massic activities. Non-labelled cyanazine with a purity exceeding 99 % was used to lower the massic activity of the original sample. All samples were purified on silica gel thin-layer plates with a mixture of hexane and acetone (70:30 by volume) as mobile phase. The cyanazine spot was scratched off and extracted with acetone (6 times with 2 cm^3). Massic activities were determined by measuring the concentrations directly with spectrophotometry at a wavelength of 218 nm or after separation via HPLC as described in Section 4.2.3 and by measuring the radioactivities with liquid scintillation counting. The direct measurements differed from the measurements after separation via HPLC by less than 3 %. The massic activities used were in the range from 20 to 1200 GBq kg^{-1}.

A sample of labelled metribuzin was available in acetone. This sample was also used to obtain a number of samples with a range of massic activities. Non-labelled metribuzin with a purity exceeding 99 % was used to lower the massic activity of the original sample. All samples were purified in the same way as described for cyanazine. The massic activities were determined using spectrophotometry at wavelengths of 294 nm and 211 nm and using liquid scintillation counting. The measurement at 294 nm resulted in massic activities that were, on average, 102 % (s = 4 %) of those found at 211 nm. The massic activities used ranged from 10 to 400 GBq kg^{-1}. All purified herbicide samples were stored in acetone at -18 °C.

7.3.2.2 Experimental conditions and measuring techniques

The soil was sampled at the experimental plot before the start of the field experiment in 1982 (see Section 4.2.1 for sampling details and soil properties). After mixing and sieving, the soil was stored in the dark at room temperature. At the start of the sorption experiments, water content was measured by drying a sub-sample overnight at 115 °C. It was found to be 0.12 kg kg^{-1}.

At the start of each experiment a known volume of acetone containing labelled herbicide was evaporated in a conical flask. Then the herbicide was dissolved in distilled water that contained $CaCl_2$ at a concentration of 10 mol m^{-3} (henceforth called $CaCl_2$ solution).

Sorption experiments in soil suspension (all in triplicate) were done in glass-stoppered centrifuge glass tubes (volume: 10 cm^3). 5 g of moist soil and 5 cm^3 of the $CaCl_2$ solution containing the herbicide, were added to the tubes. The solid: liquid ratio in this system was 0.8 kg kg^{-1}. The tubes were shaken on a rotating disk (angle: 1.4 rad) with a rotation frequency of 0.3 s^{-1} at a temperature of 19 °C. If shaking times were shorter than 5 min, shaking was done manually at room temperature. After shaking, the tubes were centrifuged (Heraeus Christ Varifuge GL) for 5 min with a swing-out rotor at a rotation frequency of 50 s^{-1}. A sample of 0.75 cm^3 of the liquid phase was collected.

Sorption experiments in moist soil were done as follows. To 20 g of moist soil 2 cm^3 of a $CaCl_2$ solution containing a herbicide were added. This resulted in the sample having a water content of 0.23 kg kg^{-1}. The soil was mixed with a spatula and stored at 19 °C for the adsorption equilibration period. Then the soil was divided into three portions and the liquid phase in each of the portions was sampled.

A new method was developed for sampling the liquid phase in moist soil. The point of a Pasteur pipette was broken off and the pipette was melted in a flame until a small hole (inner diameter less than 1 mm) was left. This pipette was put in a glass centrifuge tube that contained the soil. The bottom of the pipette was at the bottom of the tube. After centrifuging at a rotation frequency of 75 s^{-1} for 5 min, about 0.2 cm^3 of liquid in the pipette was collected with a syringe and its mass was determined.

The radioactivity in the samples of liquid phase was measured using a Philips PW4540 liquid scintillation analysor with Insta-Gel (Packard) as scintillator. The counting period was 10 min and all samples were counted two or three times. Coefficients of variation between count rates of one sample were about 1 %. Average count rates were converted into herbicide concentrations.

Total initial herbicide mass in the sorption systems was derived from triplicate measurements of concentration in samples of the $CaCl_2$ solution that was added. Coefficients of variation of these triplicate measurements were about 1 %. After the sorption experiment, concentrations in the liquid phase were measured. It was assumed that the difference between herbicide mass added and herbicide mass in liquid phase at the end, was the result of sorption.

It was checked whether the herbicides sorbed onto the glass tubes to a significant extent. 5 cm^3 of $CaCl_2$ solution with a cyanazine concentration of 0.01 g m^{-3} were shaken in the glass tubes for 1 h. The final concentration was found to be 102 % (s = 2 %) of the initial concentration. For metribuzin a similar experiment was done with an initial concentration of 0.02 g m^{-3}. The final concentration was found to be 99 % (s = 1 %) of the initial concentration. Thus, no herbicide sorption onto the glass tubes was detected.

7.3.2.3 Herbicide concentrations and equilibration periods

Herbicide adsorption isotherms were measured in soil suspension by shaking for 24 h. Initial herbicide concentrations in the $CaCl_2$ solutions varied from 0.01 to 7 g m^{-3} for cyanazine and from 0.02 to 6 g m^{-3} for metribuzin.

Adsorption kinetics were measured in soil suspension by shaking for periods of time between 2 min and 24 h. For cyanazine, three experiments were done with initial concentrations in the $CaCl_2$ solution of 0.7, 1 and 7 g m^{-3}. For metribuzin, two experiments were done with initial concentrations in the $CaCl_2$ solution of 1 and 5 g m^{-3}.

Influence of the solid:liquid ratio on herbicide adsorption in soil suspension was measured by shaking for 1 h using ratios of 0.2 and 1.5 kg kg^{-1}. The $CaCl_2$ solution initially contained 1 g m^{-3} cyanazine or metribuzin.

Adsorption kinetics in moist soil were measured by varying the equilibration periods between 10 min and 24 h. For cyanazine, one experiment was done with an initial concentration of 6 g m^{-3} in the $CaCl_2$ solution. One experiment was also done for metribuzin, with an initial concentration of 4 g m^{-3} in the $CaCl_2$ solution.

For both cyanazine and metribuzin, adsorption points were measured in moist soil at five concentrations. The equilibration period was 3 h. Initial cyanazine concentrations in the $CaCl_2$ solution ranged from 0.2 to 20 g m^3 and those for metribuzin ranged from 0.1 to 20 g m^{-3}.

7.3.3 Results and discussion of adsorption measurements

7.3.3.1 Adsorption in soil suspension

The results of sorption isotherm measurements in soil suspension were shown in Figure 6.3. Isotherms of both herbicides could be described well by the Freundlich isotherm equation (Equation 6.1) with values of K_F and $1/n$ as given in Table 6.5.

It was investigated whether the measured isotherms could also be described by the Langmuir isotherm equation (Equation 7.4). For $X \neq p$ this equation may be rewritten as

$$\frac{X}{c} = K_L(p - X) \tag{7.26}$$

The sorption coefficient, S ($m^3\ kg^{-1}$), is defined as

$$S \equiv \frac{X}{c} \tag{7.27}$$

Thus, if the Langmuir isotherm equation holds, plotting the sorption coefficient, S, against content sorbed, X, should give a straight line. Figure 7.1 shows that this was not the case for either of the measured isotherms. Next, it was attempted to describe the measurements with the sum of two Langmuir isotherms covering adsorption at two types of site ('A' and 'B') having different properties at the molecular level. This yields

$$X \equiv X_A + X_B = \frac{p_A\ K_{L,A}\ c}{1 + K_{L,A}\ c} + \frac{p_B\ K_{L,B}\ c}{1 + K_{L,B}\ c} \tag{7.28}$$

in which

X_A, X_B	are contents sorbed at 'A' and 'B' sites, respectively	($kg\ kg^{-1}$)
p_A, p_B	are maximum contents sorbed at 'A' and 'B' sites, respectively	($kg\ kg^{-1}$)
$K_{L,A}$, $K_{L,B}$	are K_L values for 'A' and 'B' sites, respectively	($m^3\ kg^{-1}$)

Note that the distinction between 'A' and 'B' sites differs from that between external and internal sites (class-1 and class-2 sites) in Section 7.2. 'A' and 'B' sites are assumed to be different at the molecular level, resulting in different

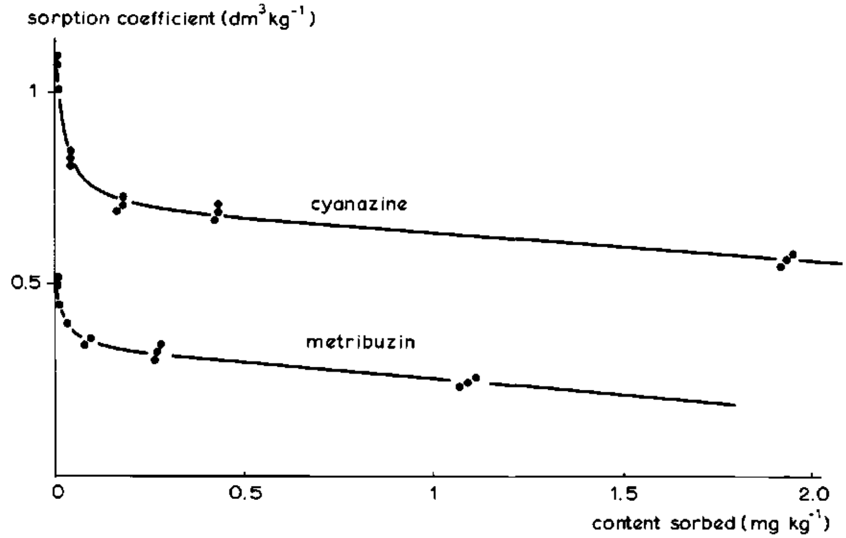


Figure 7.1. Langmuir plot of sorption isotherms of cyanazine and metribuzin as measured in a suspension of soil and water after shaking for 24 h. ●, measured; —, description with sum of two Langmuir sorption isotherms (Equation 7.28).

values for K_L. In Section 7.2 it was assumed that at the molecular level class-1 and class-2 sites were identical but that their accessibility was different.

Measured sorption isotherms were fitted to Equation 7.28 using the non-linear regression model BMDP3R as described by Dixon (1981). Figure 7.1 shows the results. It is concluded that the measured sorption isotherms could be described well by Equation 7.28. The optimized values of the parameters of Equation 7.28 are shown in Table 7.1.

It is interesting to know whether the values for ρ_B in Table 7.1 correspond with the surface of the soil being completely covered with a monolayer of herbicide molecules. This was checked by a rough estimation of the molecular area corresponding with the ρ_B values of Table 7.1. The massic area of the clay fraction of the soil was estimated to be in the order of 10^5 m^2 kg^{-1} (van der Marel, 1966). The mass fraction of clay was estimated to be 0.03 kg kg^{-1} (Table 4.2). Thus the ρ_B values of cyanazine and metribuzin were found to correspond with a molecular area in the order of 100 nm^2 which is two orders of magnitude larger than realistic values of molecular areas to be expected.

Thus, measured isotherms could be described well with only two parameters if the Freundlich isotherm equation was used. In contrast, the two-site Langmuir isotherm equation (Equation 7.28) needs four parameters. From a practical point of view the Freundlich equation is thus more efficient. As stated in Section 7.2,

Table 7.1. Optimized values of parameters in the equation for the sum of two Langmuir sorption isotherms (Equation 7.28) as derived from measured sorption isotherms of cyanazine and metribuzin. (Standard deviations are in parenthesis.)

	Cyanazine	Metribuzin
ρ_A (mg kg^{-1})	0.010 (0.002)	0.007 (0.003)
ρ_B (mg kg^{-1})	10 (1)	4.1 (0.5)
$K_{L,A}$ (m^3 kg^{-1})	40 000 (10 000)	30 000 (10 000)
$K_{L,B}$ (m^3 kg^{-1})	70 (10)	80 (10)

the Freundlich isotherm equation can also be considered to be theoretically superior to the Langmuir isotherm equation for pesticide sorption in soils. That the measured isotherms can be described well by Equation 7.28 is not conclusive evidence for the existence of only two classes of sorption site in the soil: Sposito (1982) showed that any sorption isotherm can be described with Equation 7.28, provided that at equilibrium the sorption coefficient is a finite, decreasing function of content sorbed and extrapolates to zero at a finite value of the content sorbed.

It was attempted to describe the results of measurements of sorption kinetics by the models given in Section 7.2. Thus the rate equations had to be solved for the experimental conditions of these experiments. During the experiments the concentrations in liquid phase decreased to only 30-80 % of the values at the start. One may expect that for such a limited concentration range the Freundlich and Langmuir models for sorption kinetics are similar to models based on linear isotherms. For models based on linear isotherms, the rate equations can be solved analytically; their solutions are given here.

It was assumed that during the experiments total mass of herbicide was constant. The mass conservation equation then reads

$$m = V\,c + M\,X \tag{7.29}$$

in which

m is total mass of herbicide in the system (kg)

If Equation 7.29 applies, a simple analytical solution may be given for a model with one-site kinetics and a linear isotherm (one-site linear model). Using the equation for the linear sorption isotherm (Equation 2.6) and Equation 7.29, Equation 7.8 may be rewritten as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_\mathrm{d} \left(1 + \frac{K\ M}{V}\right) \{X(\infty) - X\} \tag{7.30}$$

in which

$X(\infty)$ is content sorbed after infinite time (sorption-isotherm value) (kg kg^{-1})

The solution of Equation 7.30 becomes (see for instance van Rootselaar, 1970, p. 131)

$$\frac{X - X(\infty)}{X(0) - X(\infty)} = \exp\left\{-k_\mathrm{d}\left(1 + \frac{K\ M}{V}\right)t\right\} \tag{7.31}$$

in which

$X(0)$ is content sorbed at the start (t = 0) (kg kg^{-1})

For c the solution becomes

$$\bar{c} \equiv \frac{c - c(\infty)}{c(0) - c(\infty)} = \exp\left\{-k_\mathrm{d}\left(1 + \frac{K\ M}{V}\right) t\right\} \tag{7.32}$$

in which

$\bar{c}$	is the fractional concentration in liquid phase	(1)
$c(0)$, $c(\infty)$	are concentrations in the liquid phase at t = 0 and t = ∞ , respectively	(kg m^{-3})

Thus if the one-site linear model is correct, lg $\bar{c}$ plotted against time should give a straight line. The time constant τ_so (d) is then given by

$$\tau_\mathrm{so} = \frac{1}{k_\mathrm{d}\left[1 + \frac{K\ M}{V}\right]} \tag{7.33}$$

Equation 7.33 shows that the sorption equilibration proceeds faster in a system with a larger quotient of M and V. Because V is directly proportional to mass of liquid phase, the equilibration proceeds faster in a system with a higher solid: liquid ratio.

For the two-site linear model (Equations 7.22 and 7.23 combined with Equation 7.29), the analytical solution has the general form

$$\bar{c} = a \exp(b_1\ t) + (1 - a) \exp(b_2\ t) \tag{7.34}$$

in which

a is a constant between 0.0 and 1.0 (1)

b_1, b_2 are constants (d^{-1})

For the way the constants a, b_1 and b_2 are calculated, see for instance van Rootselaar (1970, pp. 138-142). The constants b_1 and b_2 are negative for the system of Equations 7.22, 7.23 and 7.29.

At first, I attempted to describe measured sorption kinetics by linear, Freundlich and Langmuir models in which only external sites were considered. For the Langmuir model only 'B' sites were considered. This was justifiable, because calculated values of X_A ranged between only 0.5-4 % of the equilibrium values of total contents sorbed in all measurements of adsorption kinetics.

Sorption rate equations for the models with one-site kinetics and Langmuir and Freundlich sorption isotherms (Equations 7.2 and 7.13 respectively) together with the mass conservation equation (Equation 7.29) were solved numerically using computer programs written in the simulation language CSMP III (Speckhart & Green, 1976). The integrations were performed using the Runge-Kutta method with variable time step.

Only the results of calculations made for the measurement with the highest initial cyanazine concentration will be discussed. The parameters of the Langmuir sorption isotherm equation were those of 'B' sites as given in Table 7.1. For the linear model the slope of the sorption isotherm, K, was calculated from the Freundlich equation by requiring that

$$\int_{c(0)}^{c(\infty)} K\, \eta\, d\eta = \int_{c(0)}^{c(\infty)} K_F\, \eta^{1/n}\, d\eta \qquad (7.35)$$

in which

η is integration dummy (1)

A value of K of 0.54 $dm^3\ kg^{-1}$ was found. For all models, the desorption rate constant k_d was assigned a value of 30 d^{-1}.

The results are shown in Figure 7.2. This figure shows that for the Freundlich and Langmuir models lg $\bar{c}$ was also almost a linear function of time under these experimental conditions. Lines calculated with linear and Freundlich models almost coincided. This was expected, because the Freundlich isotherm can be closely approximated by a linear isotherm for the limited experimental range of c. The line computed for the Langmuir model was below the two other lines. This is

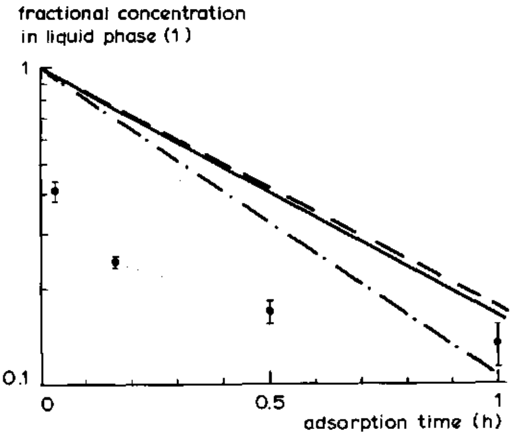


Figure 7.2. Adsorption kinetics of cyanazine simulated by models with one-site kinetics with $k_d = 30\ d^{-1}$ compared with a measurement in soil suspension. Initial concentration of cyanazine was 7 g m^{-3}. ●, average of measured concentrations; vertical bars are standard deviations; ——, – – –, —·—·—, calculated with models based on linear, Freundlich and Langmuir sorption isotherm equations, respectively.

caused by the term $(1 + K_L\ c)$ in Equation 7.2 which leads to a higher 'effective' value of k_d.

Figure 7.2 shows that the measured points cannot be described by a linear function of time. This was also the case in all other measurements of adsorption kinetics. Thus, the measured adsorption kinetics could not be described by any of the three models with one-site kinetics.

I then attempted to describe measured adsorption kinetics by a Freundlich model with external and internal sites as given by the Equations 7.24, 7.25 and 7.29. This model has five adjustable parameters: $k_{d,1}$, $k_{d,2}$, $K_{F,1}$, $K_{F,2}$, $1/n$. Of these parameters, $K_{F,1}$ and $K_{F,2}$ are mutually dependent: their sum is equal to the value of the overall coefficient, K_F. Values of $1/n$ and K_F were taken from Table 6.5. Thus, three adjustable parameters remain: $k_{d,1}$, $k_{d,2}$, and F_F (i.e. the fraction of K_F to be attributed to class-1 sites, as already stated at the end of Section 7.2).

A computer program was written in the simulation language CSMP III to obtain a numerical solution for the Freundlich model with two-site kinetics. The integrations were performed using the Runge-Kutta method with variable time step. The computer program is listed in Appendix F. If $1/n$ equals unity an analytical solution can be obtained for these equations as given by Equation 7.34. Results of the numerical solution were compared with those of the analytical solution for $1/n = 1$, $K_F = 0.64\ dm^3\ kg^{-1}$, $m = 8.4\ \mu g$, $M = 4.5$ g, $V = 5.5\ cm^3$, $F_F = 0.7$, $k_{d,1} = 864\ d^{-1}$ and $k_{d,2} = 17.3\ d^{-1}$. The analytical solution is then given by Equation 7.34 with $a = 0.782$, $b_1 = -1180\ d^{-1}$ and $b_2 = -19.3\ d^{-1}$. It was found that concentrations in the liquid phase computed with the numerical and the analytical solution always differed from each other by less than 0.01 %.

The PODS-module described by Birta (1977) was used to obtain values for the parameters F_F, $k_{d,1}$ and $k_{d,2}$. This module searches iteratively for parameter values that correspond to a minimum of the sum of the squares of the differences between computed and measured c values.

Figures 7.3 and 7.4 show that the Freundlich model with two-site kinetics was able to describe all measurements of adsorption kinetics satisfactorily. The corresponding optimized values of the parameters are given in Table 7.2. Table 7.2 shows that no clear effect of herbicide concentration on parameter values was found. Values of F_F and $k_{d,1}$ found for cyanazine were similar to those found for metribuzin; values of $k_{d,2}$ found for cyanazine were 4 to 9 times higher than those found for metribuzin. The value of $k_{d,2}$ is mainly determined by the slope of the lg $\bar{c}$ line for adsorption times longer than about 10 min. As is shown by Figures 7.3 and 7.4, the uncertainty in the lg $\bar{c}$ values may be considerable for these times. Thus it may be questioned whether the difference found between the $k_{d,2}$ values of cyanazine and metribuzin is significant.

The values of $k_{d,1}$ and $k_{d,2}$ given in Table 7.2 indicate that the fast equilibrating sorption sites reach approximate equilibrium at a time scale of minutes,

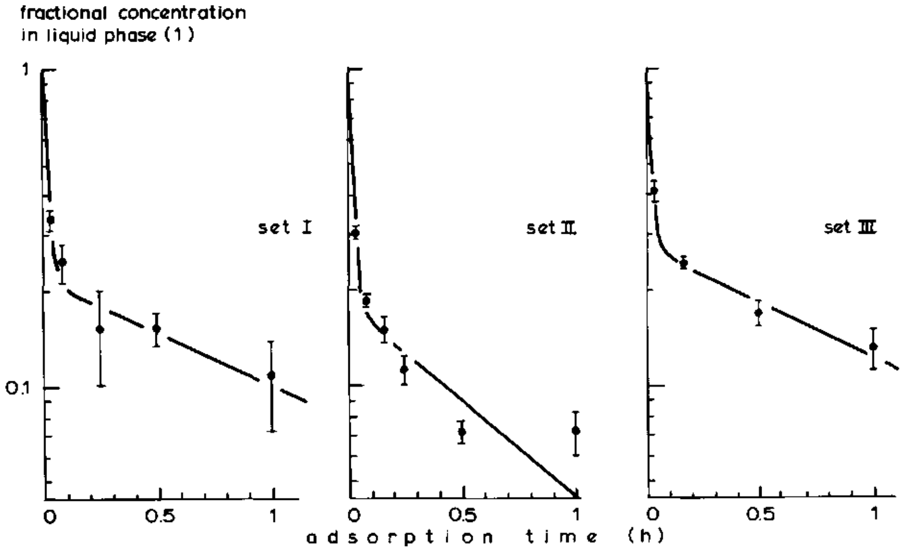


Figure 7.3. Adsorption kinetics of cyanazine simulated by the Freundlich model with two-site kinetics, compared with the measurements in soil suspension. The numbers of the sets of parameter values correspond with those in Table 7.2. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

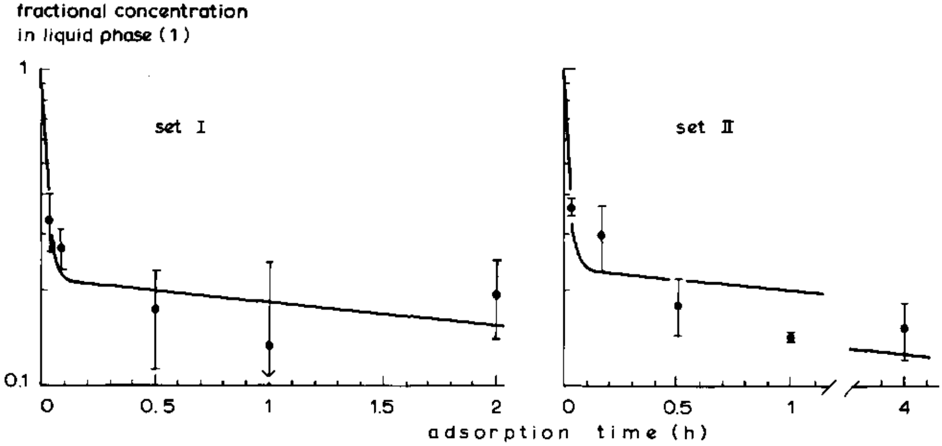


Figure 7.4. Adsorption kinetics of metribuzin simulated by the Freundlich model with two-site kinetics, compared with the measurements in soil suspension. The numbers of the sets of parameter values correspond with those in Table 7.2.
●, average of measured concentrations; vertical bars are standard deviations;
——, calculated.

whereas slowly equilibrating sorption sites reach approximate equilibrium at a time scale of hours. This difference indicates that at least two different rate-controlling sorption processes are operating, and it seems plausible that class-1 and class-2 sites are indeed respectively external and internal sites. It would be interesting to use the $k_{d,2}$ values found to estimate the order of magnitude of the thickness of the internal space. In principle, a first approximation could be made with the equation for diffusion into, for example, a sphere. However, to do so, one needs estimates of the volume fraction of liquid in the internal space, the tortuosity factor in the internal space and of q' in the internal space. As no reliable estimates for all of these quantities could be made, the estimation of the thickness of the internal space was not carried out.

In the first minutes of the experiments, contents sorbed at class-2 sites are very small. Thus, sorption at class-1 sites may then be approximated by a one-site linear model. The time constant of sorption at class-1 was calculated with Equation 7.33 and the $k_{d,1}$ values of Table 7.2 and a value of about 1 min was found for both herbicides. The shortest adsorption time was 2 min. Thus, the values found for $k_{d,1}$ imply that sorption at class-1 sites was almost at equilibrium at the shortest adsorption time. One may expect that higher $k_{d,1}$ values would have been found if the results of shorter adsorption times had been available. The shortest adsorption times that could be applied were a few minutes, because it

Table 7.2. Optimized values of parameters in the Freundlich model with two-site kinetics as derived from measurements of adsorption kinetics with cyanazine and metribuzin in soil suspension.

Herbicide	Initial concentration ($g\ m^{-3}$)	Parameter set	Optimized values of parameters F_F (1)	$k_{d,1}$ (d^{-1})	$k_{d,2}$ (d^{-1})
Cyanazine	0.7	I	0.70	950	16
	1	II	0.75	930	30
	7	III	0.66	930	16
		average	0.70	940	21
Metribuzin	1	I	0.75	1140	3.8
	5	II	0.73	1150	3.5
		average	0.74	1150	3.6

took about 30 s to separate the bulk of the solid phase from the supernatant. The values found for $k_{d,1}$ should therefore be considered as lower limits.

Given the particular difficulty of approximating the kinetics of class-1 sites in experiments, the theoretical problem of the choice of the type of sorption rate equation (Equation 7.13 or Equation 7.14) seems of minor practical importance for this class of site. For class-2 sites this problem is also of minor importance, because for this class of site the sorption process itself is not considered to be rate-determining.

Table 7.3 compares the results of adsorption measurements done at solid: liquid ratios of 0.2 and 1.5 kg kg^{-1} with the results of calculations with the Freundlich model with two-site kinetics. Average values of $k_{d,1}$, $k_{d,2}$ and F_F were taken from Table 7.2. Thus, all parameter values were derived from measurements taken at a solid:liquid ratio of 0.8 kg kg^{-1}. Table 7.3 shows that

Table 7.3. Effect of solid:liquid ratio on herbicide sorption coefficient, S, in soil suspension. The effect is expressed in the ratio of the measured sorption coefficient divided by the sorption coefficient calculated with the Freundlich model with two-site kinetics, which was based on measurements at a solid:liquid ratio of 0.8 kg kg^{-1}. (Standard deviations are in parenthesis.)

Solid:liquid ratio (kg kg^{-1})	Ratio of sorption coefficients (1) cyanazine	metribuzin
0.2	0.98 (0.07)	1.05 (0.26)
1.5	0.98 (0.03)	1.02 (0.02)

results of measurements done at ratios of 0.2 and 1.5 kg kg^{-1} were explained well by the model that was based on measurements at a ratio of 0.8 kg kg^{-1}. Thus it was found that the solid:liquid ratio had no effect on sorption of both herbicides in soil suspension. This corresponds with the usual experience in literature (see Section 7.3.1).

The data on adsorption kinetics obtained by Hance (1967) and Kay & Elrick (1967) were replotted in the form of Figures 7.2 to 7.4 (i.e. as lg $\bar{c}$ against t). It was found that the points for none of the pesticide/soil combinations could be described by a straight line: this corresponds qualitatively with the results shown in Figures 7.3 and 7.4.

Wauchope & Myers (1985) measured the adsorption kinetics of two herbicides in suspensions of a number of sediments, for adsorption times between 0 and 60 min, and found that results for these adsorbents could be described by a model with two-site sorption kinetics. Unfortunately, they did not describe a number of essential quantities in their model, and this makes it impossible to compare the values they found for the rate constants with the values found in Table 7.2. However, qualitatively the correspondence between their measurements and those of Figures 7.3 and 7.4 is good: they too found a very rapid decrease in the concentration in liquid phase in the first minutes and a slow decrease thereafter.

7.3.3.2 Adsorption in moist soil

It was attempted to describe the data obtained on adsorption kinetics in moist soil with the same model as used for the measurements in soil suspension, i.e. the model based on a Freundlich isotherm and two-site kinetics. It was assumed that sorption isotherms as found in soil suspension, were also valid for moist soil, that the two classes of site as given in soil suspension could also be discerned in moist soil, and that F_F (the fraction of K_F to be attributed to class-1 sites) in moist soil was equal to that found in suspension. For F_F the average values were taken as found for both herbicides in Table 7.2. Thus, only two adjustable parameters remain: $k_{d,1}$ and $k_{d,2}$. Via the values to be found for these parameters it can be tested whether sorption kinetics in moist soil do indeed proceed more slowly than in soil suspension. The rate equations of the Freundlich model with two-site kinetics (Equations 7.24 and 7.25) were solved numerically as described before (see Appendix F for a list of the computer program). The two parameters were fitted to the measurements with the Miniquad module (Anonymous, 1980). This module searches iteratively for parameter values that correspond with a minimum of the sum of the squares of the differences between computed and measured concentrations in liquid phase.

Figures 7.5 and 7.6 show that the Freundlich model with two-site kinetics could describe measured adsorption kinetics well. The corresponding values of $k_{d,1}$ and $k_{d,2}$ are shown in Table 7.4. The values found for both herbicides were very similar. As sorption at class-2 sites is negligible during the first hour, sorption at class-1 sites in this period may be approximated by a model based on a linear isotherm and one-site kinetics. Using Equation 7.33 and values of $k_{d,1}$ from Table 7.4, values of 3-6 min for the time constant were found for both herbicides. The shortest experimental adsorption time was 10 min. Thus the values found for $k_{d,1}$ imply that sorption at class-1 sites was almost at equilibrium at the shortest adsorption time. One may expect that higher values of $k_{d,1}$ would have been found if results of shorter adsorption times had been available. Values of $k_{d,1}$ should thus be considered as lower limits.

The values of $k_{d,1}$ and $k_{d,2}$ in Table 7.4 were derived from one experiment only, at only one concentration for both herbicides. It was tested whether the model could simulate adsorption at a range of concentrations: concentration in liquid phase was calculated for the experiments with the five different initial concentrations and an adsorption time of 3 h. Excellent agreement was found between

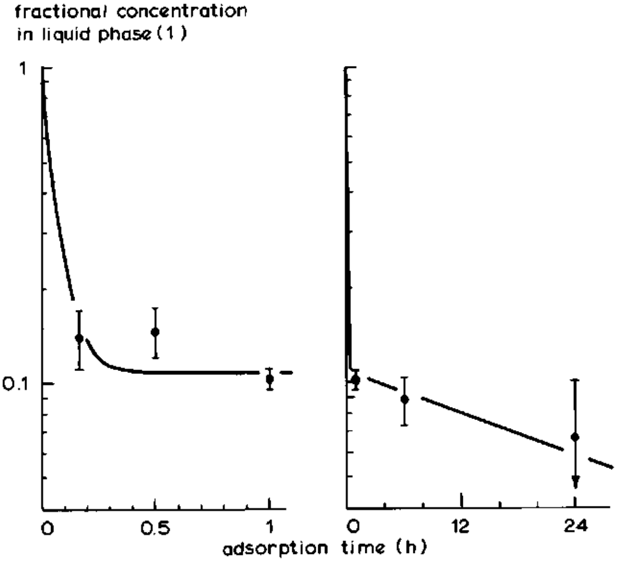


Figure 7.5. Adsorption kinetics of cyanazine simulated by the Freundlich model with two-site kinetics, compared with the measurement in moist soil. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

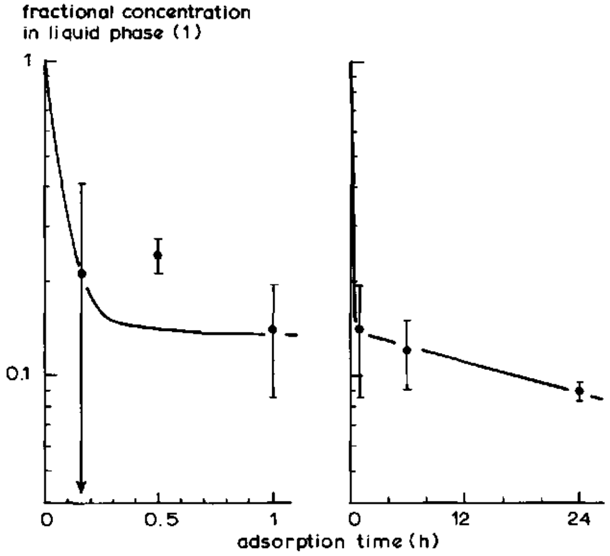


Figure 7.6. Adsorption kinetics of metribuzin simulated by the Freundlich model with two-site kinetics, compared with the measurement in moist soil. •, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

the calculated and measured concentrations: for cyanazine and metribuzin respectively the calculated concentrations were, on average, 100 % (s = 2 %) and 98 % (s = 3 %) of those measured.

The values of $k_{d,1}$ and $k_{d,2}$ for moist soil (Table 7.4) are about one order of magnitude lower than the corresponding values for a suspension of soil (Table 7.2). For $k_{d,1}$ one may question the difference, because both for moist soil and soil suspension the $k_{d,1}$ values found were only lower limits. The lower values for $k_{d,2}$ are, by definition, caused by physical non-equilibrium conditions (see Section 2.4 for the operational definition of physical non-equilibrium). In a first approximation to describe physical non-equilibrium one may divide the external liquid phase into two zones: the first zone is located 'far' from the internal liquid phase, the second zone borders on internal liquid phase. In the first approximation it seems reasonable to assume for a soil system with flowing liquid that the liquid in the first zone is mobile or in equilibrium with the flowing fraction of the liquid and that the liquid in the second zone is stagnant and not in equilibrium with the flowing liquid. Thus, although no flow of liquid took place during the experiments on adsorption kinetics, the terms 'mobile' and 'stagnant' zones used in Chapter 2 will be used here as well, to denote the first and second zones, respectively (note

Table 7.4. Optimized values of desorption rate constants in the Freundlich model with two-site kinetics as derived from measurements of adsorption kinetics with cyanazine and metribuzin in moist soil.

Herbicide	$k_{d,1}$ (d^{-1})	$k_{d,2}$ (d^{-1})
Cyanazine	150	0.5
Metribuzin	180	0.4

that via the sampling procedure (centrifugation) only mobile liquid was sampled). In view of the foregoing it seemed appropriate to analyse the results of the measurements of adsorption kinetics in moist soil with a model of physical non-equilibrium. To do this the model of van Genuchten & Wierenga (1976) was used as described by Equations 2.12 to 2.15. Because in the present system c^* is constant with time, the solution for the concentration in the mobile liquid phase, c_m, is the same as already given for c_s in Equation 2.16:

$$\bar{c}_m \equiv \frac{c_m - c_m(\infty)}{c_m(0) - c_m(\infty)} = \exp(-t/\tau_{m,s}) \qquad (7.36)$$

in which

$\bar{c}_m$	is the fractional concentration in mobile liquid phase	(1)
$c_m(\infty)$	is c_m at $t = \infty$	(kg m^{-3})
$c_m(0)$	is c_m at $t = 0$	(kg m^{-3})

The equation for $\tau_{m,s}$ is given by Equation 2.17.

Measured concentrations in liquid phase were now considered as measured values of c_m. Values of $c_m(\infty)$ were known from the sorption isotherm, and therefore values of $c_m(0)$ and $\tau_{m,s}$ could be estimated via linear regression analysis from a plot of $\ln\{c_m - c_m(\infty)\}$ against t. The plots for both herbicides are shown in Figure 7.7 together with the linear regression approximations. For further calculations with the model, the sorption isotherms of both herbicides had to be linearized: this was done with an equation similar to Equation 7.35. At the start of the experiments c_s and X_s are zero, and therefore from Equations 2.12 and 2.13 it follows that

$$\phi\, \theta + f\, \rho_b\, K = c^*/c_m(0) \qquad (7.37)$$

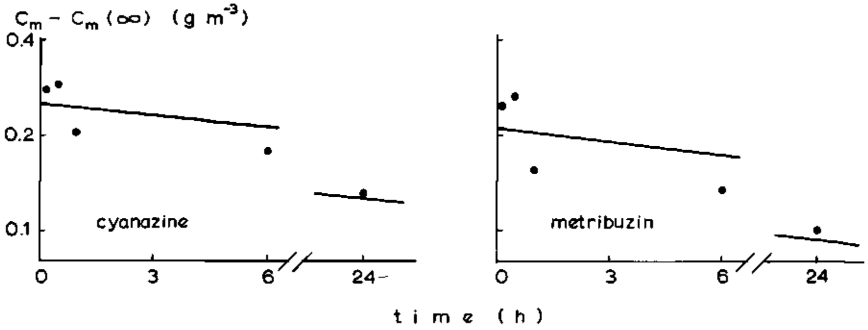


Figure 7.7. Results of the measurements of adsorption kinetics of cyanazine and metribuzin in moist soil plotted as a decrease in concentrations in the mobile liquid phase as a function of time. ●, average of measured concentrations; ——, linear regression approximation.

It seems reasonable to assume that ϕ values for cyanazine and metribuzin are equal and that so are the f values. Then ϕ and f can be calculated from the two sets of measurements shown in Figure 7.7. The values for ϕ and f were found to be 1.00 and 0.66, respectively. Thus, the fraction stagnant liquid was found to be negligible.

Values of $\tau_{m,s}$ were derived from the slopes of the lines in Figure 7.7 and using the ϕ and f values found, the values of $k_{m,s}$ were calculated with Equation 2.17. This resulted in a value of $k_{m,s}$ of 0.1 d^{-1} for both cyanazine and metribuzin.

The results found here correspond well with those obtained for the herbicides 2,4,5-T and 2,4-D by van Genuchten & Cleary (1979, p. 375) and Rao et al. (1979) in column experiments with sieved soils. In these studies ϕ values close to 1.0 were found in combination with f values around 0.5 and $k_{m,s}$ values of about 0.1 d^{-1}. It seems universally valid that physical non-equilibrium effects are significant for sorbing substances in non-structured soils.

Nkedi-Kizza et al. (1984) have shown that the model for chemical non-equilibrium of Cameron & Klute (1977) described by Equations 2.8 and 2.9 results in the same dimensionless transport equations as the model for physical non-equilibrium of van Genuchten & Wierenga (1976) described by Equations 2.11 to 2.15. Below I shall show that this analogy also holds for a system without a downward flux of substance. For such a system, the model of Cameron & Klute (1977) is described by Equations 2.8 and 2.9 together with the mass conservation equation of the system:

$$c^* = \theta\ c + \rho_b(X_1 + X_2) \tag{7.38}$$

Equations 2.8, 2.9 and 7.38 can be rewritten as

$$\frac{d\{c/c(0)\}}{dt} = k_{d,2}\{1 - \frac{c}{c(0)}\left(\frac{\theta + \rho_b K}{\theta + \rho_b F K}\right)\} \tag{7.39}$$

Equations 2.12 to 2.15 of the model of van Genuchten & Wierenga (1976) can be rewritten as

$$\frac{d\{c_m/c_m(0)\}}{dt} = \frac{k_{m,s}}{(1-\phi)\theta + (1-f)\rho_b K}\{1 - \frac{c_m}{c_m(0)}\left(\frac{\theta + \rho_b K}{\phi\theta + f\rho_b K}\right)\} \tag{7.40}$$

A comparison of Equations 7.39 and 7.40 shows that the parameters for the model of Cameron & Klute (1977) can be directly calculated from those found for the model of van Genuchten & Wierenga (1976) via the equations

$$k_{d,2} = \frac{k_{m,s}}{(1-\phi)\theta + (1-f)\rho_b K} \tag{7.41}$$

$$F = \{(\phi - 1)\theta/(\rho_b K)\} + f \tag{7.42}$$

Thus, $k_{d,2}$ values of 0.5 and 0.6 d^{-1} were found for cyanazine and metribuzin, respectively. As ϕ was 1.00, the values found for F were equal to those found for f (i.e. 0.66 for both herbicides). Thus, the values for $k_{d,2}$ and F derived from Equations 7.41 and 7.42 differ only slightly from the values for $k_{d,2}$ and F_F derived from the measurements with the Freundlich model with two-site kinetics (see Table 7.4 for the latter values for $k_{d,2}$ and Table 7.2 for the values for F_F).

The analysis of measured adsorption kinetics in Figures 7.5 and 7.6 with the Freundlich model with two-site kinetics showed that equilibration of class-2 sites proceeds much more slowly in moist soil than in soil suspension. However, the analysis of the same measurements with the model for physical non-equilibrium of van Genuchten & Wierenga (1976) showed that the fraction of the liquid that was stagnant was negligibly small. Obviously, a very small fraction of the liquid phase in close proximity to the internal liquid phase is a considerable barrier to diffusion. The mechanism responsible for this barrier is not clear.

In a first attempt to elucidate the mechanism for the slow equilibration of class-2 sites in moist soil, it was assumed that this slow equilibration was the result of diffusion in spherical aggregates of soil. If a constant concentration in liquid phase at the boundary of these spheres is assumed, the order of magnitude of the radius of the spheres can be roughly estimated from

$$r = O\left(\pi \sqrt{\frac{\lambda\ \theta\ D_0\ \tau_{\mathrm{dif,sp}}}{q' + \theta}}\right) \tag{7.43}$$

in which

r	is radius of the spheres	(m)
O	means 'in the order of magnitude of'	
$\tau_{\mathrm{dif,sp}}$	is time constant for the diffusion process in the spheres	(d)

(see Crank, 1983, p. 91, Eqn 6.20).

From Equation 7.23 it can be seen that the time constant for equilibration of sorption at class-2 sites (if exposed to a constant concentration in liquid phase) equals $k_{\mathrm{d,2}}^{-1}$. Thus, the value of $\tau_{\mathrm{dif,sp}}$ was estimated to be 2 d for both herbicides. Values of r for both herbicides as calculated with Equation 7.43 were found to be in the order of a few millimetres. Such high values are not realistic for a non-structured soil in which ϕ is near 1.0. In such a situation one would expect the actual diffusion distances between the external liquid phase and class-2 sites to be in the order of the diameters of the soil particles (i.e. 0.1 mm or less: see Table 4.2). If an r value of 0.1 mm is inserted in Equation 7.43, it follows that the quotient $\lambda\ \theta/(q' + \theta)$ is in the order of 10^{-5}. The mechanism that could account for such low values of this quotient is not clear.

Because a barrier outside the internal liquid phase is considered to be responsible for the slow equilibration of class-2 sites in moist soil, it seems probable that this barrier also contains external sites. Furthermore, given that $k_{\mathrm{d,1}}$ values found for moist soil are one or two orders of magnitude larger than $k_{\mathrm{d,2}}$ values found in soil suspension, one would expect the F_{F} values derived from measurements in the moist-soil system to be lower than those derived from measurements in the soil-suspension system. However, the data obtained in moist soil (Figures 7.5 and 7.6) were described satisfactorily with F_{F} values derived from the measurements in soil suspension. Thus, F_{F} values for moist soil were found not to differ significantly from those in soil suspension. Given the accuracy of the measurements in Figures 7.5 and 7.6, it seems improbable that a decrease in F_{F} of, say, 10 % could have been detected. It would be worth investigating whether the finding that it are almost exclusively the internal sites that suffer from physical non-equilibrium conditions in moist-soil systems is a general phenomenon for non-structured soils.

As the fraction of stagnant liquid was found to be negligibly small, it seems inappropriate to use a model in which the liquid phase is divided into two zones (e.g. the model of van Genuchten & Wierenga, 1976). Therefore the Freundlich model with two-site kinetics as applied in Figures 7.5 and 7.6 will be used in the remaining chapters to describe the sorption kinetics of both herbicides in moist soil.

7.4 DESORPTION OF HERBICIDES IN SOIL SUSPENSION

7.4.1 Introduction

The Freundlich model with two-site kinetics (and also the other models of Section 7.2) implies that values of the rate constants and of the parameters of the sorption isotherm equation, in desorption situations are equal to those in adsorption situations. These assumptions have been challenged in the literature.

For instance, from measurements with a few herbicides Hance (1967) concluded that desorption processes were generally slower than adsorption processes. In a review, Calvet (1980, p. 6) stated: 'Desorption is generally slower than adsorption, but its kinetic characteristics are less well known'. However, the views of Hance (1967) and Calvet (1980) are obscure: do they imply that values of k_d or k_a during desorption are smaller than during adsorption, or do they mean that the rate of decrease of content sorbed (dX/dt) in desorption experiments is smaller than its rate of increase in adsorption experiments? The former interpretation would be incompatible with the Freundlich model with two-site kinetics, the latter would not necessarily invalidate this model: in desorption experiments initial conditions are different from those in adsorption experiments and thus the behaviour of the system as calculated by the model may be different. No references supporting the former interpretation of the view of Hance (1967) and Calvet (1980) were found. Therefore the assumption of rate constants that are equal in adsorption and desorption situations, was retained.

In a number of studies with soils and herbicides (for instance Wood & Davidson, 1975; Barthélemy, 1981) it has been reported that adsorption/desorption hysteresis occurred. Desorption measurements in these studies were usually carried out as follows. Water containing the radioactively labelled pesticide and a salt was added to the soil to obtain a suspension that could be continuously mixed by shaking or tumbling (solid:liquid ratio between 0.1 and 1 kg kg^{-1}). After equilibration the suspension was centrifuged, the concentration in the supernatant was measured and the adsorption was calculated. Desorption was induced by replacing a fraction of the supernatant by herbicide-free aqueous solution. After equilibration the concentration in the supernatant was measured and the corresponding desorption point was calculated. By repeating this desorption procedure several times, desorption isotherms were measured using one soil sample only.

However, one may wonder whether the measured hysteresis has been caused by artifacts associated with the experimental method. The following factors should be considered:

- transformation of the pesticide during the experiment (into volatile or more strongly sorbed products)
- a change in the properties of the surface of the solid phase during the experiment as a result of e.g. shaking, tumbling, or centrifuging
- a change in the composition of the liquid phase resulting from the repeated replacement of the liquid phase
- incomplete desorption equilibration.

Transformation may have a large influence on the contents sorbed of the desorption points. This can be illustrated by calculating the content sorbed in such an experiment after a certain desorption step:

$$X = \{ m_{\mathrm{i}} - V_{\mathrm{re}} \left(\sum_{\zeta=1}^{\nu} c_{\zeta-1} \right) - V c_{\nu} \} / M \tag{7.44}$$

in which

m_{i}	is total mass of herbicide initially present in the system (i.e. before the first desorption step)	(kg)
V_{re}	is volume of liquid replaced by herbicide-free solution at the start of each desorption step	(m^3)
c_{ζ}	is concentration in the liquid phase after the ζ-th desorption step	(kg m^{-3})
ν	is number of desorption steps	(1)

After a number of desorption steps, X usually becomes small as compared with m_{i}/M and transformation of only a few per cent of m_{i} may lead to a large apparent hysteresis effect. This may be illustrated by the 2,4,5-T adsorption/desorption measurements of van Genuchten et al. (1977). The hysteresis they observed corresponded ultimately with about 5 % of the initial mass in the system. As their experiments lasted for 8 d and as they did not measure the mass of 2,4,5-T in the system at the end, it is probable that they measured an artifact instead of adsorption/desorption hysteresis.

In a few studies with soils and pesticides centrifugation, repeated replacement of supernatant and shaking of the suspension have been shown to result in increased adsorption (Savage & Wauchope, 1974; Rao et al., 1978). In other studies it was shown that ultrasonic disintegration or prolonged tumbling of the soil suspensions did not influence sorption behaviour (Graham-Bryce, 1972; Rao & Davidson, 1980).

Using five hysteresis measurements obtained from the literature (Wood & Davidson, 1975; van Genuchten et al., 1977; Koskinen et al., 1979; Bladel & Moreale, 1980; Barthélemy, 1981) I checked whether the artifacts mentioned above had been considered. In only two of the five studies was the possibility of transformation eliminated, whereas all experiments lasted at least a few days. In none of the studies did the researchers check whether the sorption properties of the suspension changed as a result of handling the suspension. The time periods necessary for desorption equilibration were usually determined from desorption kinetics measured after one desorption step. If a Freundlich model with two-site kinetics applies, the time period to approach the content sorbed at equilibrium within, say 1 %, depends on the initial conditions of the system and may, for instance, be longer for the fourth desorption step than for the first.

Curl & Keoleian (1984) suggested that the observed hysteresis effects resulted from unknown substances ('implicit adsorbates') that compete with the herbicides for the sorption sites. To account for the observed hysteresis effects these unknown substances must have been removed from the sorption system to a significant extent as a result of the repeated replacement of supernatant. Thus, sorption coefficients of the unknown substances should be of the same order of magnitude as those of the herbicides. In general it is improbable that 'implicit adsorbates' play an important role in climates with a yearly excess of rainfall over evaporation as in the Netherlands. In such climates one would expect these 'implicit adsorbates' to be leached out of the plough layer.

It was concluded that the objections in literature to the Freundlich model with two-site kinetics were not convincing. Thus, as a working hypothesis it was assumed that the model with parameters derived from adsorption experiments could be used to explain the results of desorption experiments.

A number of measurements of desorption kinetics and equilibria were done to test the model under desorption conditions. Experimentally it is difficult to perform desorption measurements in a moist-soil system; a soil-suspension system seems much more appropriate. Theoretically, testing the model under desorption conditions in a soil-suspension system only, presents no problems. Differences between sorption kinetics in a soil-suspension system and in a moist-soil system should be attributable to differences in diffusion pathways. One may expect the diffusion process to be equally operative in adsorption and desorption situations. In a soil-suspension system it should be possible to investigate the extent to which desorption would suffer from surface-induced hysteretic phenomena. Therefore the comparison between adsorption and desorption was limited to a soil-suspension system.

7.4.2 Procedures for desorption measurements

All experiments were done with labelled cyanazine or metribuzin (see Section 7.3.2.1 for details). Treatment of the soil sample and procedures for measurements were described in Section 7.3.2.2. All experiments were done in triplicate.

Kinetics of the desorption process were measured as follows. 5 g of moist soil and 5 cm^3 of $CaCl_2$ solution containing a herbicide were shaken for 1 h. After centrifuging, 3.5 cm^3 of the supernatants were replaced by equal volumes of herbicide-free $CaCl_2$ solution. Thus the concentrations in the liquid phase after 1 h were lowered by 63 %. Thereafter the suspensions were shaken for periods of time between 2 min and 24 h. Two experiments on desorption kinetics were done for both cyanazine and metribuzin. Initial concentrations in the $CaCl_2$ solutions were 1 and 7 g m^{-3} for cyanazine and 1 and 5 g m^{-3} for metribuzin.

Experiments were done in which one point of a desorption isotherm was measured after a number of desorption steps had been applied. 5 g of moist soil were shaken for 1 h with 5 cm^3 of $CaCl_2$ solution containing a herbicide. After centrifuging, 3.3 cm^3 of the supernatant was replaced by an equal volume of herbicide-free $CaCl_2$ solution (first desorption step). After shaking for 1 h and centrifuging, 3.3 cm^3 of supernatant was again replaced by 3.3 cm^3 of herbicide-free $CaCl_2$ solution (second desorption step). In these experiments 6 desorption steps were applied with cyanazine and with metribuzin. In all cases, the shaking period after the last desorption step was 18 h. Thereafter 2.5 cm^3 of supernatant were removed and the remainder of the suspension was extracted with 5 cm^3 of ethyl acetate by shaking for 1 h. The ethyl acetate layer was removed and a second extraction was done with 5 cm^3 of ethyl acetate by shaking for 24 h. The ethyl acetate layers were dried over anhydrous Na_2SO_4. The herbicide concentrations in all supernatants and ethyl acetate extracts were measured. Two experiments were done with cyanazine with initial concentrations of 1 and 29 g m^{-3} in the $CaCl_2$ solution. For metribuzin two experiments were also done, with initial concentrations of 1 and 12 g m^{-3}.

In a series of experiments it was checked whether the experimental manipulation as applied during the desorption experiments, changed the sorption properties of the soil suspension used. 5 g of soil and 5 cm^3 of herbicide-free $CaCl_2$ solution were exposed to treatments that were the same as applied in the desorption experiments with 6 desorption steps. After these treatments, herbicide was added to the suspensions and adsorption was measured after shaking for 1 h. For cyanazine and metribuzin the concentrations found in the liquid phase of the manipulated suspensions were, on average, 103 % and 102 % respectively of the values expected from measurements in systems that were not manipulated before the addition of the herbicides. Thus the experimental manipulation of the suspension did not change its sorption properties.

7.4.3 Results and discussion of desorption measurements

7.4.3.1 Desorption kinetics

Measured desorption kinetics and equilibria were compared with results of calculations made with the Freundlich model with two-site kinetics. The parameter values were those derived from the data on adsorption isotherms (Table 6.5) and adsorption kinetics in Table 7.2. In the calculations with the model, the procedure in the experiments was simulated. Thus, initially adsorption was allowed to proceed for 1 h. Thereafter in the calculations 3.5 cm^3 of the liquid phase were replaced by an equal volume of herbicide-free liquid and the concentration in the liquid phase was calculated until an equilibrium value was approximately reached.

Figures 7.8 and 7.9 show results for the two measurements of cyanazine desorption kinetics. From these figures it was concluded that measured desorption kinetics and equilibria were explained well. None of the averaged measured concentrations differed more than 10 % from the three corresponding calculated concentrations. During the first hour, measured concentrations were systematically higher than calculated concentrations. Differences were largest after a desorption time of 2 min. Obviously, the class-1 sites desorb even faster than expected from the adsorption measurements.

Results for metribuzin are shown in Figures 7.10 and 7.11. Calculations were done using the two parameter sets found for metribuzin as given in Table 7.2. It was found that desorption kinetics calculated with the two sets resulted in concentrations that differed from each other by less than 0.5 %. Thus, only one calculated line is given in Figures 7.10 and 7.11. These figures show that the measured metribuzin desorption kinetics were explained well by the model based on adsorption measurements: differences between calculated and averaged measured concentrations were mostly less than 2 % and always less than 5 %.

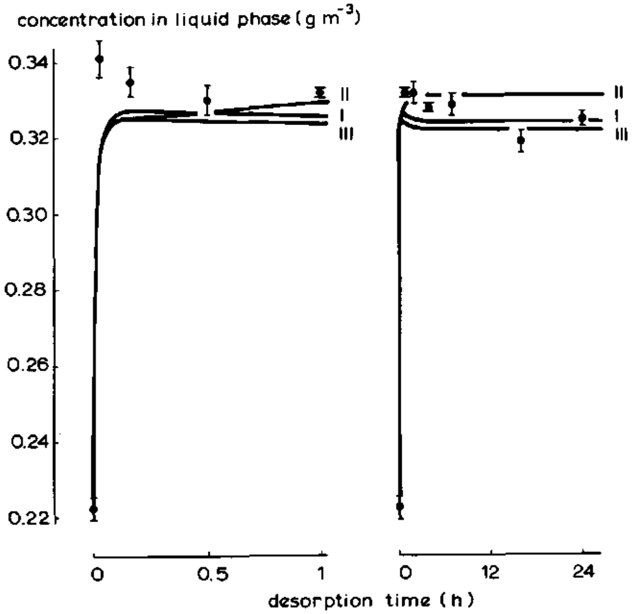


Figure 7.8. Measured cyanazine desorption kinetics compared with calculations from the Freundlich model with two-site kinetics. Initial concentration in the $CaCl_2$ solution added at the start was 1 g m^{-3}. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated; Roman numerals indicate sets of parameter values as given in Table 7.2.

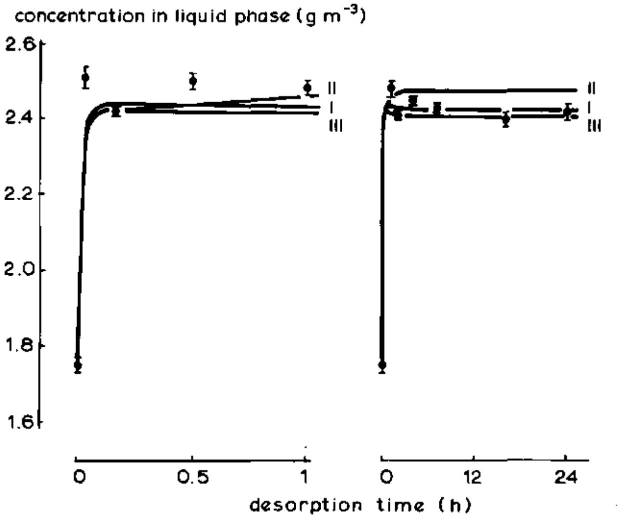


Figure 7.9. Measured cyanazine desorption kinetics compared with calculations from the Freundlich model with two-site kinetics. Initial concentration in the $CaCl_2$ solution added at the start was 7 g m^{-3}. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated; Roman numerals indicate sets of parameter values as given in Table 7.2.

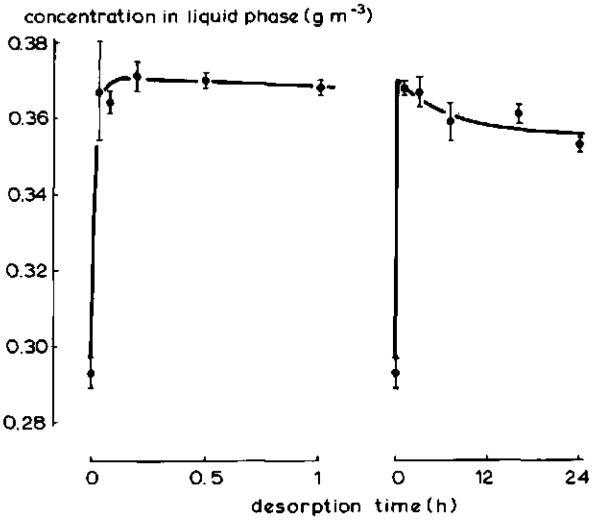


Figure 7.10. Measured metribuzin desorption kinetics compared with calculations from the Freundlich model with two-site kinetics. Initial concentration in the $CaCl_2$ solution added at the start was 1 g m^{-3}. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

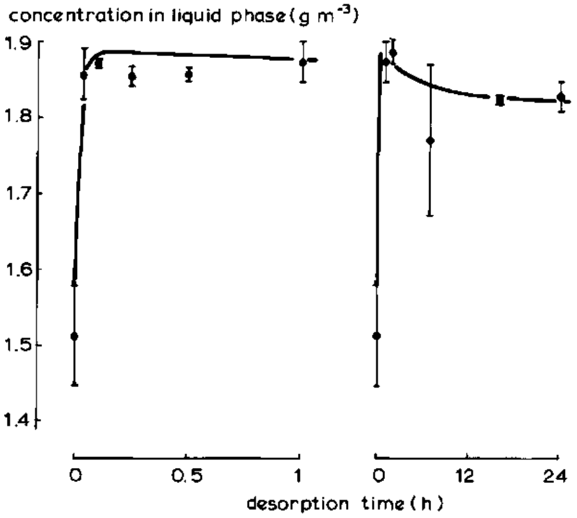


Figure 7.11. Measured metribuzin desorption kinetics compared with calculations from the Freundlich model with two-site kinetics. Initial concentration in the $CaCl_2$ solution added at the start was 7 g m^{-3}. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

Figures 7.8 to 7.11 show that the measured equilibrium concentrations of both herbicides after 1 desorption step were explained well by the model based on adsorption measurements. Equilibrium contents sorbed for both herbicides were about 40 % lower than those just before the desorption step. Thus, no evidence of adsorption/desorption hysteresis was found in these experiments.

7.4.3.2 Desorption points after a series of desorption steps

Contents sorbed after the last of a series of desorption steps were obtained from the sum of the concentrations measured with the two successive extractions with ethyl acetate. For cyanazine and metribuzin the concentrations found in the second extract were, on average, respectively 4.2 % (s = 0.3 %) and 7 % (s = 1 %) of the values found in the first extract. Recoveries of total herbicide masses added to the system were 99.8 % (s = 0.6 %) and 100.3 % (s = 0.1 %) in the two experiments with cyanazine, and 100.5 % (s = 1.1 %) and 100.7 % (s = 0.1 %) in the two experiments with metribuzin.

Table 7.5 shows that contents sorbed for metribuzin after the last desorption step were 50-100 % higher than those calculated from the Freundlich isotherms that were measured in an adsorption experiment. For cyanazine, contents sorbed were about 10 % lower than the values calculated from the sorption isotherms. At first sight the results indicate that hysteresis occurred for metribuzin but not for cyanazine. One may question whether the effect shown for metribuzin in Table 7.5 was actually caused by hysteresis. The differences between measured and calculated contents sorbed of metribuzin in Table 7.5 correspond with only 0.3-0.4 % of the total mass of metribuzin added to the system. Such a difference could be

Table 7.5. Contents sorbed at the end of the experiments with 6 desorption steps compared with contents sorbed calculated from the Freundlich sorption isotherms using the measured concentrations in the liquid phase. (Standard deviations are in parenthesis.)

Herbicide	Initial concentration ($g\ m^{-3}$)	Content sorbed ($\mu g\ kg^{-1}$) after last desorption step	
		measured	calculated
Cyanazine	1	23 (1)	25 (1)
	29	340 (20)	383 (2)
Metribuzin	1	11.6 (0.5)	7.6 (0.1)
	12	111 (2)	55 (1)

explained by transformation of metribuzin into a strongly sorbed product at a rate equal to that observed in the field ($k_t^* = 0.04\ d^{-1}$). A strongly sorbed impurity in the radioactive metribuzin at only about 0.3 % would have the same effect. Thus, from the results given in Table 7.5 it cannot be concluded that hysteresis occurred for metribuzin. Furthermore, it would be strange if hysteresis occurred for metribuzin but not for cyanazine, because the molecular structures of these substances are similar (see Table 4.1). It was concluded that the assumption of a non-hysteretic adsorption/desorption process should not be rejected for the two herbicides.

In the hysteresis measurements reported in literature, content sorbed was usually calculated from concentrations in liquid phase with Equation 7.44 (see Section 7.4.1).This method was also applied to the measurements of cyanazine and metribuzin reported here and the results were compared with those derived from the two extractions with ethyl acetate. The ratio of content sorbed calculated from Equation 7.44 divided by content sorbed derived from the extractions, was, on average, 0.4 for metribuzin (the range was from -0.8 to + 1.3). For cyanazine this ratio was, on average, 0.9 (the range was from 0.6 to 1.4). These ratios show that the calculation method of Equation 7.44 was inaccurate (especially for metribuzin). This is not surprising, because X in Equation 7.44 is calculated from the difference between two numbers that are almost equal after 6 desorption steps.

Because it was checked experimentally (see Section 7.4.2) that repeated replacement of supernatant by herbicide-free $CaCl_2$ solution did not result in a change in the sorption properties of the soil suspension, it is concluded that unknown substances (called 'implicit adsorbates' by Curl & Keoleian, 1984) did not influence sorption of the herbicides to a significant extent. The concept of the 'implicit adsorbates' of Curl & Keoleian (1984) implies that the solid:liquid ratio has an influence on the measured sorption isotherm. As shown earlier (Table 7.3) the observed effect of the solid:liquid ratio could be explained satisfactorily with the Freundlich model with two-site kinetics in which it is assumed that the sorption isotherm equation is independent of the solid:liquid ratio. This is a second argument for the absence of effects of 'implicit adsorbates' on sorption of the herbicides.

7.5 INFLUENCE OF VARIOUS SOIL AND HERBICIDE FACTORS ON SORPTION OF HERBICIDES IN SOIL SUSPENSION

7.5.1 Introduction

A number of soil and herbicide factors may lead to sorption equilibria in the field that are different from those measured in a soil suspension. In a review, Calvet et al. (1980b) reported that pesticide sorption in soil may be higher at a higher salt concentration or at a lower temperature. Hance (1977) found that sorption of herbicides in dry soil was much greater than that in moist soil. The extent of sorption in dry soil does not have much effect on movement of herbicides, because of the low liquid fluxes in dry soil. However, Burchill et al. (1981, p. 314) stated that when dried, humic structures rehydrate with difficulty. It thus may be questioned whether water content at the start of an experiment may influence results. It is also possible that the sorption properties of the top layer of soil in the field change with time. Calvet et al. (1980b, p. 155) stated that no general conclusions can be drawn on how additives in the formulated products influence the sorption of pesticides. Another point is that cyanazine and metribuzin may have mutually influenced their sorption behaviour, because they were sprayed onto the same experimental field in 1982.

The influence on herbicide sorption of the factors mentioned above was checked in a number of experiments with the soil-suspension system.

The effect of pH on sorption was not considered. Because the soil contains $CaCO_3$ (see Table 4.2) fluctuations in pH in the field resulting from, for instance, rainfall were probably fairly small. It can be expected that the pH will have a large influence on sorption if the herbicide molecules become protonated because of a decrease in pH. However, protonation of both cyanazine and metribuzin becomes significant only if the pH decreases to values as low as pH = 1 (Weber, 1980).

7.5.2 Procedures

All experiments were done with labelled cyanazine or metribuzin (see Section 7.3.2.1 for details). Treatment of the soil sample and procedures for measurements were described in Section 7.3.2.2. All experiments were done in triplicate.

All the sorption experiments in soil suspension described so far in this study were done by adding water that contained $CaCl_2$ at a concentration of 10 mol m^{-3}. To measure the influence of salt concentration and salt species on herbicide sorption, 5 g of moist soil was shaken for 24 h with 5 cm^3 of water containing $CaCl_2$ at a concentration of 100 mol m^{-3} or water containing KCl at a concentration of 200 mol m^{-3}. The water initially contained 1 g m^{-3} cyanazine or metribuzin.

Furthermore, all the sorption experiments described so far in this study were done at a temperature of 19 °C. But to check the influence of temperature, adsorption kinetics were measured at 3 °C by shaking 5 g of soil and 5 cm^3 of $CaCl_2$ solution for periods of time between 2 min and 24 h. For both cyanazine and metribuzin one experiment was done with an initial concentration of 1 g m^{-3} in the $CaCl_2$ solution.

The influence of using initially air-dry soil on sorption was measured by drying a sample of the soil to a water content of 0.01 kg kg^{-1}. Herbicide adsorption was measured by shaking 5 g of this soil sample and 5 cm^3 of $CaCl_2$ solution for a period of time between 2 min and 24 h. The $CaCl_2$ solution initially contained 1 g m^{-3} cyanazine or metribuzin.

Instead of using soil sampled before the start of the field experiment in 1982, as was done for all the sorption experiments described so far, cyanazine sorption was measured using soil sampled in the field after 121 d in 1982, so that the influence of time of soil sampling in the field could be ascertained (see Section 4.2.1 for sampling details). Only the soil samples from the 0 to 15 mm and the 30 to 50 mm layers were used. After storage for 7 months at -18 °C the 5 different samples from each layer were mixed. The water content of the mixture from the 0 to 15 mm layer was 0.07 kg kg^{-1} and that of the mixture from the 30 to 50 mm layer was 0.18 kg kg^{-1}. Sorption was measured using 5 g of moist soil and 5 cm^3 of $CaCl_2$ solution with cyanazine concentrations of 0.06 and 1 g m^{-3}. Shaking time was 1 h.

The influence of cyanazine on metribuzin sorption and vice-versa was studied in adsorption experiments with 5 g of soil and 5 cm^3 of $CaCl_2$ solution and with a shaking period of 1 h. The $CaCl_2$ solution initially contained 1 g m^{-3} of the herbicide whose sorption was being measured. The influence of cyanazine on metribuzin sorption was studied in two experiments with initial cyanazine concentrations of 1 and 5 g m^{-3} in the $CaCl_2$ solution. The infuence of metribuzin on cyanazine sorption was studied in three experiments with initial metribuzin concentrations of 1, 5 and 10 g m^{-3} in the $CaCl_2$ solution. In these experiments, pure herbicides were used (purity > 99 % for both herbicides).

The influence of both formulated products (Bladex and Sencor) on sorption of both herbicides was studied. The mass fraction of cyanazine in Bladex is 0.5 and that of metribuzin in Sencor is 0.7. The influence of the use of Bladex on cyanazine sorption was measured using a mixture with a mass fraction of radioactive cyanazine of 0.02 and a mass fraction of Bladex of 0.98. The influence of the use of Sencor on metribuzin sorption was measured using a mixture with a mass fraction of radioactive metribuzin of 0.03 and a mass fraction of Sencor of 0.97. The adsorption experiments (shaking period 1 h) were done with 5 g of soil and 5 cm^3 $CaCl_2$ solution that contained one of the mixtures at a cyanazine or metribuzin concentration of 1 g m^{-3}. For measuring the influence of Bladex on metribuzin sorption a similar adsorption experiment was done, with initial concentrations of metribuzin and Bladex of 1 and 2 g m^{-3}, respectively. For measuring the influence of Sencor on cyanazine sorption, the initial concentrations of cyanazine and Sencor were 1.0 and 1.4 g m^{-3}, respectively.

7.5.3 Results and discussion

The results of the measurements on the influence of salt concentration on sorption of the herbicides are shown in Table 7.6. It was concluded that the influence of salt concentration and salt species on sorption of both herbicides was small.

From the sorption points measured after shaking for 24 h at 3 °C, K_F values were derived for the two herbicides using Equation 6.1 and the values of $1/n$ as given in Table 6.5. It was found that the K_F values for cyanazine and metribuzin at 3 °C, were respectively 1.5 and 1.2 times the values found at 19 °C. These figures correspond with an increase in the K_F values of cyanazine and metribuzin of 3 % and 1 %, respectively, per decrease of 1 °C.

Figure 7.12 shows the results of measurements of adsorption kinetics done at 3 °C, and the results of calculations with the Freundlich model with two-site kinetics. In these calculations it was assumed that temperature influenced the value of K_F only. Thus the averaged values of $k_{d,1}$, $k_{d,2}$ and F_F were taken from Table

Table 7.6. Effect of salt concentration and salt species on herbicide sorption coefficient, S. The effect is expressed in the ratio of the sorption coefficient found, divided by the sorption coefficient derived from measurements at a $CaCl_2$ concentration of 10 mol m^{-3}. (Standard deviations are in parenthesis.)

Salt species	Concentration of the salt (mol m^{-3})	Ratio of sorption coefficients (1)	
		cyanazine	metribuzin
$CaCl_2$	100	0.91 (0.02)	1.01 (0.05)
KCl	200	1.06 (0.01)	1.18 (0.04)

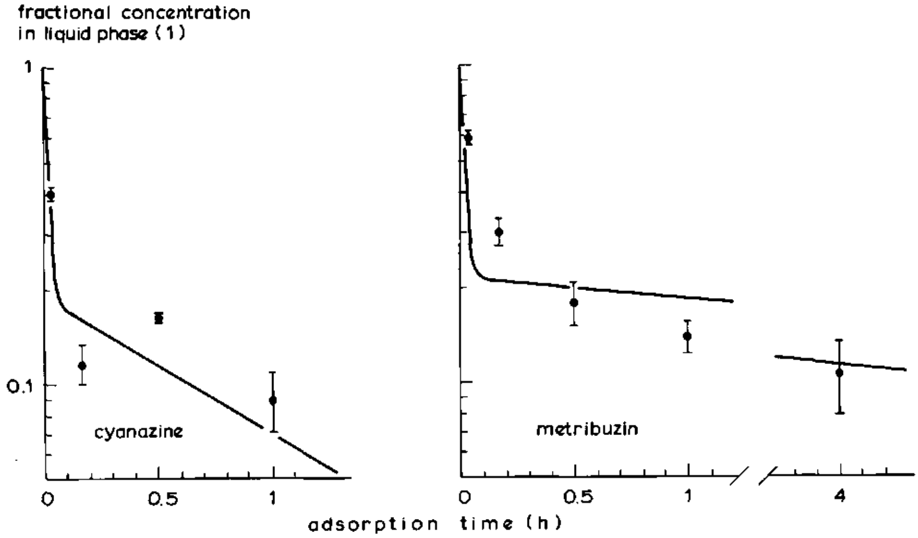


Figure 7.12. Adsorption kinetics simulated by the Freundlich model with two-site kinetics, compared with the measurements in soil suspension at 3 °C. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

7.2 and values of $1/n$ were those of Table 6.5. The values of K_F were derived from the sorption measurements after shaking for 24 h at 3 °C. Figure 7.12 shows that there were no systematic differences between calculations and measurements. Thus temperature did not influence adsorption kinetics strongly.

From the sorption points measured after shaking initially air-dry soil for 24 h, K_F values were derived for the two herbicides using Equation 6.1 and values of $1/n$ as given in Table 6.5. For both herbicides it was found that the resulting K_F values were 1.2 times the values found for initially moist soil (i.e. with a water content of 0.12 kg kg^{-1}). Obviously, the sorption of water by the soil has not yet reached equilibrium after a rewetting period of 24 h.

The results of the measurements in soil suspension of initially air-dry soil for equilibration periods shorter than 24 h are shown in Figure 7.13, together with the results of calculations with the Freundlich model with two-site kinetics. The K_F values in the model were derived from the measurements in soil suspension of initially air-dry soil after shaking for 24 h. The values of $k_{d,1}$ and $k_{d,2}$ were assumed to be equal to the average values found in soil suspension of initially moist soil (see Table 7.2). The values of the fractions of the K_F values to be attributed to class-1 sites (i.e. F_F values) were calculated by using the average F_F values from Table 7.2 as a starting point and by assuming that the sorption sites

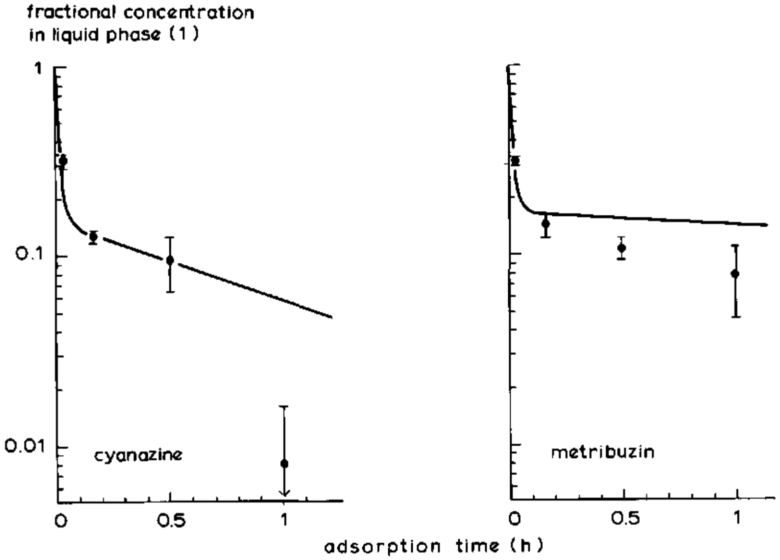


Figure 7.13. Adsorption kinetics simulated by the Freundlich model with two-site kinetics, compared with the measurements in soil suspension of initially dry soil. In the model, values of $K_{F,1}$ as given in Table 7.7 for dry soil were used. ●, average of measured concentrations; vertical bars are standard deviations; ——, calculated.

that are available only in initially air-dry soil, are class-1 sites. Figure 7.13 shows that these assumptions resulted in a reasonable description of measured sorption kinetics in initially air-dry soil. Concentrations measured after 1 h were overestimated for both herbicides. The values of $K_{F,1}$ and $K_{F,2}$ as used for the calculations of Figure 7.13 are shown in Table 7.7 together with the values derived from the experiments with initially moist soil (values of $K_{F,2}$ were assumed to be equal for initially moist and air-dry soil). Sorption kinetics were also calculated

Table 7.7. The Freundlich coefficient, K_F, for class-1 and class-2 sites in initially moist and air-dry soil, as derived from experiments in soil suspensions.

	K_F ($m^{3/n}$ $kg^{-1/n}$)		
	class-1 sites		class-2 sites
	moist soil	air-dry soil	
Cyanazine	0.24×10^{-3}	0.32×10^{-3}	0.10×10^{-3}
Metribuzin	0.11×10^{-3}	0.14×10^{-3}	0.04×10^{-3}

with F_F values equal to the averages found for initially moist soil. This resulted in calculated concentrations that were higher than the concentrations calculated previously. Consequently, the F_F values taken from moist soil resulted in larger differences between measured and calculated concentrations. This indicates that sorption sites that are solely available in a suspension of initially air-dry soil, are probably located on the external surfaces of the soil particles.

The soil sample used in the experiments with air-dry soil was obtained from the 0 to 200 mm layer of the field soil. At the time of sampling the soil had been tilled for about 40 years. Thus a large fraction of the soil sample was occasionally air-dry during these 40 years. Consequently, it is probable that the difference found between dried and undried soil would disappear if the period of rewetting of the soil were long enough. This was tested in an experiment in which soil was first dried and thereafter rewetted for periods of time varying between 0 and 28 d. The water contents of the dried and rewetted soil samples were 0.01 and 0.21 kg kg^{-1}, respectively. Using the soil samples that were rewetted for various periods of time, a cyanazine adsorption experiment in soil suspension was done with a shaking period of 24 h and an initial concentration of 1 g m^{-3} in the $CaCl_2$ solution. The results (Figure 7.14) show that after a rewetting period of about 2 weeks, sorption properties no longer differed from those of the undried soil.

The results of experiments on the influence of time of soil sampling on cyanazine sorption are shown in Table 7.8. The cyanazine sorption coefficient of soil sampled at the end of the field experiment in 1982, differed by about 10 % from the coefficient of soil sampled before the start of the field experiment. This is a small difference, and may be the result of the spatial variability of the sorption properties of the field soil: the soil sampled on day 121 was collected at 5 spots in the field, whereas the soil sampled before the start of the field experiment was collected at 100 spots in the field.

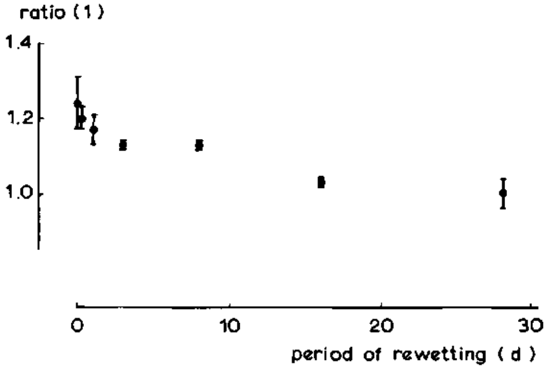


Figure 7.14. Ratio of the sorption coefficient of cyanazine for dried soil divided by that for non-dried soil as a function of period of rewetting. ●, average of measured values; vertical bars are standard deviations.

Table 7.8. Effect of the time of soil sampling in 1982 on cyanazine sorption coefficient, *S*. The effect is expressed in the ratio of sorption coefficient measured with soil sampled after 121 d divided by that measured with soil sampled before the start of the field experiment. (Standard deviations are in parenthesis.)

Initial cyanazine concentration (g m^{-3})	Ratio of sorption coefficients (1) for soil sampled between	
	0 to 15 mm depth	30 to 50 mm depth
0.06	1.06 (0.04)	1.11 (0.02)
1	1.15 (0.02)	1.09 (0.04)

The results of experiments on the influence of pure cyanazine on metribuzin sorption and vice-versa are shown in Tables 7.9 and 7.10. The influence of cyanazine on metribuzin sorption was very small. The influence of metribuzin on cyanazine sorption was also small: adding a mass of metribuzin to a system that was 10 times as large as the mass of cyanazine added, resulted in a cyanazine sorption

Table 7.9. Effect of cyanazine on sorption coefficient, *S*, of metribuzin. The effect is expressed in the ratio of the sorption coefficient measured with cyanazine, divided by that measured without cyanazine. Initial concentration of metribuzin was 1 g m^{-3}. (Standard deviations are in parenthesis.)

Initial concentration of cyanazine (g m^{-3})	Ratio (1) of sorption coefficients of metribuzin
1	0.99 (0.06)
5	1.00 (0.02)

Table 7.10. Effect of metribuzin on sorption coefficient, *S*, of cyanazine. The effect is expressed in the ratio of the sorption coefficient measured with metribuzin, divided by that measured without metribuzin. Initial concentration of cyanazine was 1 g m^{-3}. (Standard deviations are in parenthesis.)

Initial concentration of metribuzin (g m^{-3})	Ratio (1) of sorption coefficients of cyanazine
1	0.97 (0.04)
5	0.90 (0.04)
10	0.89 (0.03)

coefficient that was only about 10 % lower.

Using the formulated product of cyanazine, Bladex, resulted in a cyanazine sorption coefficient that was 89 % (s = 3 %) of the value found for pure cyanazine. Adding the formulated product of metribuzin, Sencor, resulted in a cyanazine sorption coefficient that was 103 % (s = 2 %) of the value found for cyanazine alone.

Using the formulated product of metribuzin, Sencor, resulted in a metribuzin sorption coefficient that was 109 % (s = 3 %) of the value found when using pure metribuzin. Adding the formulated product of cyanazine, Bladex, resulted in a metribuzin sorption coefficient that was 115 % (s = 2 %) of the values found for pure metribuzin.

Thus, the influence of formulation additives on sorption of both herbicides was slight.

8 LONG-TERM SORPTION STUDIES WITH HERBICIDES

8.1 INTRODUCTION

The sorption experiments described in Chapter 7 did not last longer than 1 d. The desorption rate constants for class-1 and class-2 sites found for moist soil were about 150 d^{-1} and 0.5 d^{-1}, respectively (Table 7.4). This implies that sorption at these sites reaches approximate equilibrium within 1 h and 1 week, respectively. However, contact between the herbicides and the top layer of soil in the field lasted for months. The largest discrepancies between calculated and measured concentration profiles of the herbicides, as discussed in Section 6.4, were found a few months after application. Thus, long-term sorption processes, with rate constants in the order of 0.01 d^{-1}, could have played a significant role in the field.

Hamaker & Thompson (1972) reviewed literature on sorption of pesticides onto soils and concluded that there was some experimental evidence for long-term sorption equilibration (resulting in higher sorption than expected from measurements in a soil-suspension system after shaking for 1 d). They noted the general experience that it is more difficult to extract an amount of aged pesticide residue with an organic solvent from soil than an amount of freshly-mixed pesticide. This can be illustrated by measurements obtained by Smith (1981). He found that the content of atrazine extracted from three field soils one year after application varied roughly by a factor of two, depending on the extraction method and organic solvent employed. If used 1 d after application, probably all extraction methods would have resulted in recoveries of 90-100 %. This phenomenon of decreasing extractability is additional evidence for long-term sorption equilibration. Mercer & Hill (1975) measured the sorption coefficients of five herbicides on a peat soil and a sandy loam soil at 1 d and at 6 months after application. In the long term the coefficients were circa 3-12 times as high as those after 1 d. Unfortunately Mercer and Hill did not give details of their measuring method.

There is also evidence in the literature that a single drying treatment after addition of herbicides to soil may appreciably increase sorption coefficients found after rewetting. Both Mercer & Hill (1975) and Hance & Embling (1979) found that sorption coefficients of herbicides measured after a drying and a wetting cycle were circa 2-3 times as high as those found for non-dried soil. Graham-Bryce (1967) found a similar but smaller increase for the insecticide disulfoton.

The reason that drying may influence the sorption coefficient found after rewetting is not difficult to surmise: after drying there is close contact between herbicide molecules and the sorbent surface. It is possible that upon drying, herbicide molecules are 'pressed' onto sorption sites that are not readily accessible in moist soil.

Hance (1977) showed that sorption of atraton and monuron from solutions of these herbicides in an apolar organic solvent (immiscible with water) increased markedly if soil water content decreased below that corresponding with a matric pressure of -2.5 MPa. A similar effect is known for volatile pesticides (Calvet et al., 1980b, p. 157). Thus apparently in dry soil a large number of sorption sites become available by the removal of the water. Hance (1977) found for atraton that the sorption equilibrium in dry soil was approximately reached after only 5 min. This indicates that sorption at the large number of sites available in dry soil, proceeds at a rate comparable with that found for class-1 sites in our experiments. Hance (1977) also found for atraton that desorption equilibria after rewetting the soil corresponded with the adsorption equilibria found for wet soil. Thus, adding water induced complete desorption from the large number of sorption sites that were only available in dry soil.

A search of the literature failed to produce references in which attempts were made to describe mathematically measurements of long-term sorption equilibration in moist soil or measurements of sorption in soil subjected to drying and wetting cycles.

It was concluded that long-term sorption experiments with cyanazine and metribuzin were necessary and that in these experiments the influence of drying and wetting cycles also had to be considered.

Section 8.2 describes sorption experiments carried out in the laboratory with soil sampled in the experimental field in 1982 two and four months after application. These experiments were done as a first test of the hypothesis that the sorption process during the field experiments can be predicted well on the basis of the short-term studies. The results of the experiments showed that the predictions were wrong. Consequently, further systematic laboratory research after long-term sorption processes was deemed appropriate. Section 8.3 describes sorption experiments with soil stored in the laboratory for periods of between 1 d and 300 d after application of herbicides to this soil. Section 8.3 also contains the sorption model used to describe the results, and an account of how the values of the model parameters were determined.

8.2 LONG-TERM SORPTION UNDER FIELD CONDITIONS

8.2.1 Introduction

If a long-term sorption process is operative, it can be expected that desorption points measured with soil taken from the experimental field a long time after application, will result in contents sorbed that are higher than those expected from the short-term experiments. Therefore it was deemed appropriate to carry out such desorption experiments as a first rough test for the significance of a long-term process.

The consequence of a long-term sorption process can be that an aged herbicide residue is more difficult to extract than a freshly-mixed residue (see Section 8.1). In Section 4.2.3 it was found that the single extraction with ethyl acetate resulted in recoveries around 100 % for 1-day-old residues of both cyanazine and metribuzin. If a long-term process is operative, instead of yielding total content of herbicide in soil, this extraction may yield an arbitrary fraction of that content. Therefore, it was necessary to check the extent to which the single extraction with ethyl acetate removed aged herbicide residues from soil.

8.2.2 Procedures

Desorption experiments were done with herbicide residues in soil sampled from the experimental field in 1982 after 56 and 121 days. Only the samples from the 0 to 15 mm and 30 to 50 mm layers were used. To determine the content of herbicide, the samples were extracted once with ethyl acetate. Procedures of extraction and analysis were described in Section 4.2.3. The desorption experiments were done within a few days after sampling and on the same day as the extraction with ethyl acetate. 25 g of moist soil were weighed into a glass-stoppered centrifuge tube (volume: 90 cm^3) and 25 cm^3 of water containing CaCl_2 at a concentration of 10 mol m^{-3} were added. All experiments were done in singular. The samples from day 56 were shaken for 1 h on a rotating disc at 20 °C, those from day 121 were shaken for 17 h. After centrifuging at a rotation frequency of 30 s^{-1} for 10 min, a volume of the water layer was extracted with an equal volume of ethyl acetate. Herbicide concentrations in the ethyl acetate fractions were measured with the GLC method as used for soil samples of the 1982 field experiment (see Section 4.2.3).

To check the efficacy of the single extraction with ethyl acetate for aged residues, extraction experiments were done with soil sampled in the field at 56 d after application in 1982. Composite soil samples were taken from two layers: 0 to 15 mm and 30 to 50 mm, and each of the samples was thoroughly mixed. After sampling, the soil had been stored for 5 or 17 months at -18 °C. In the first test the soil was successively extracted with ethyl acetate. In two other tests two other extraction liquids were used. All experiments were done in triplicate.

In the first test, three successive extractions were made with ethyl acetate: 25 g of soil were weighed into a 250 cm^3 jar after which 12.5 cm^3 of water (containing $CaCl_2$ at a concentration of 10 mol m^{-3}) and 25 cm^3 of ethyl acetate were added. After shaking for 1 h, the soil was separated from the solution by filtering under suction. The soil with the filter paper was shaken in the same jar for a second time with the same volumes of ethyl acetate and water (both herbicide-free), now for 17 h. After filtering, the soil was shaken for a third time with the volumes of ethyl acetate and water, now for 24 h.

In the second test, two successive extractions were made with a mixture of acetonitrile and water (70:30 by volume). Before adding the acetonitrile, the water (distilled) was adjusted to pH = 9 with water containing NH_4OH at a concentration of 500 mol m^{-3}. This mixture was used because Smith (1981) had found it to be the most efficient one for extraction of 1-year-old atrazine soil residues in a series of soil types. 25 g of soil were weighed into a 250 cm^3 jar and 25 cm^3 of the extraction mixture was added. After shaking for 1 h, the soil was separated from the solution by filtering under suction. The soil with the filter paper was shaken in the same jar a second time with a herbicide-free mixture, this time for 17 h, and the filtrate was collected. The filtrates were concentrated at 40 °C until approximately 0.5 cm^3 remained; 12.5 cm^3 of water (containing $CaCl_2$ at a concentration of 10 mol m^{-3}) and 25 cm^3 of ethyl acetate were added and the mixture was shaken by hand. The masses recovered with the second extraction were corrected for the masses still present in the liquid phase of the soil after the first filtering.

In the third test the soil was extracted with methanol using a Soxhlet apparatus. 15 g of soil were weighed into an extraction hull and extracted with 125 cm^3 of methanol. The extraction period was 2 h, which corresponded with about 50 cycli. At the end the methanol was evaporated in a rotavapor. The residue was dissolved in 30 cm^3 of ethyl acetate by shaking manually.

Herbicide concentrations in all ethyl acetate fractions were measured with the GLC method used for the soil samples from the 1982 field experiment (see Section 4.2.3).

8.2.3 Results and discussion

Figure 8.1 shows the results of desorption experiments with soil sampled from the experimental field in 1982. The results are compared with part of the adsorption isotherm as measured in a suspension of initially moist soil after shaking for 24 h (the complete sorption isotherm has already been shown in Figure 6.3). Measured contents sorbed of the desorption points were always higher than the corresponding values obtained in the short-term adsorption experiments. However, the shaking period after 56 d was only 1 h, which is not sufficient for equilibrium, as shown by the short-term experiments in Chapter 7 (for instance, Figure 7.8). The shaking period after 121 d was 17 h, which is comparable with the shaking period for the adsorption isotherm (24 h). Sorption coefficients of the desorption points obtained after 121 d were averaged and values of 5 and 4 $dm^3\ kg^{-1}$ were found for cyanazine and metribuzin, respectively. The values expected from the sorption isotherms were about 1 and 0.5 $dm^3\ kg^{-1}$, respectively. Sorption coefficients after 121 d were thus about 5-10 times higher than those derived from the short-term experiments. Thus, this test clearly showed that a long-term sorption process was operative.

Figure 8.1 shows that at a given cyanazine concentration in the liquid phase,

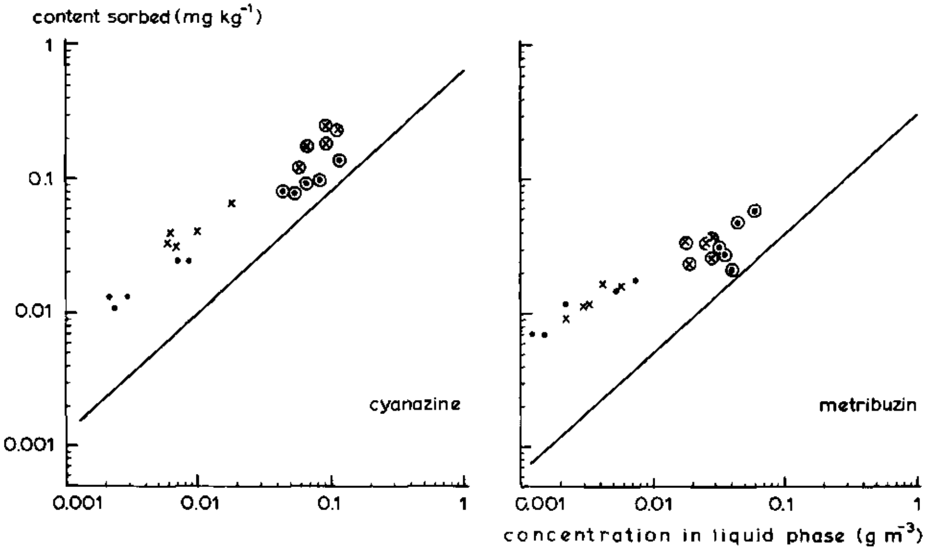


Figure 8.1. Desorption points of field-aged herbicide residues compared with the Freundlich sorption isotherm for class-1 plus class-2 sites as derived from Figure 6.3. ×, layer 0-15 mm; •, layer 30-50 mm; symbols in circles, day 56; symbols without circles, day 121; ——, Freundlich sorption isotherm.

contents sorbed in the 0 to 15 mm layer were always higher than those in the 30 to 50 mm layer . The figure further shows that this effect was not clear in the desorption experiments with metribuzin. The 0 to 15 mm layer was subjected to drying cycles, whereas the lowest volume fraction of liquid in the 30 to 50 mm layer measured in the field was about 0.2 $m^3\ m^{-3}$ (Figure 5.9). Because for metribuzin no clear differences were found between the two layers, the drying cycles probably had no large influence on sorption after rewetting.

Table 8.1 shows the results of the experiments with the three different extraction methods. The results of the three successive extractions with ethyl acetate show that the second extraction yielded an amount of herbicide corresponding to 15-30 % of that recovered by the first extraction (the standard method used in Chapter 4). The third extraction yielded another amount of herbicide, this time corresponding to 5-10 % of that obtained in the first extraction. The first extraction of soil from the 0 to 15 mm layer with the mixture of acetonitrile and water was somewhat more efficient than the first extraction with ethyl acetate. For the 30 to 50 mm layer there was no clear difference between values found with the first extractions with ethyl acetate and the mixture of acetonitrile and water. In all cases the second extraction with acetonitrile and water was less efficient than the second extraction with ethyl acetate. The Soxhlet extraction with methanol was somewhat more efficient than the standard method.

The results in Table 8.1 correspond with the experience reported in the literature that it is more difficult to extract aged pesticide contents than freshly-applied contents. It is almost impossible to determine total content of an aged resi-

Table 8.1. Efficiency of different extraction methods using soil sampled after 56 d in the field in 1982. Figures in parenthesis are standard deviations.

Extraction liquid	Extraction no.	Content recovered from soil (all values in % of average value found with standard method)			
		cyanazine		metribuzin	
		0-15 mm layer	30-50 mm layer	0-15 mm layer	30-50 mm layer
Ethyl acetate	1 (standard)	100 (4)	100 (2)	100 (4)	100 (2)
	2	19 (2)	14 (2)	28 (5)	18 (3)
	3	7 (2)		9 (3)	
Acetonitrile + water	1	117 (4)	101 (6)	111 (9)	101 (1)
	2	7 (3)	2 (2)	11 (4)	5 (5)
Methanol (Soxhlet)		107 (7)		112 (3)	

due in soil unambiguously, but the results suggest that three successive extractions with ethyl acetate give a good estimate of total herbicide content in soil.

Storage of the soil for 17 months at -18 °C may have influenced extractability of the herbicide residues. This was checked in a triplicate desorption experiment with the soil mixture of the 0 to 15 mm layer that was used in the extraction experiments and thus had been stored for 17 months after sampling in the field. Experimental procedures were equal to those in the desorption experiments done with the soil samples of day 56, as described earlier. It was found that for both cyanazine and metribuzin the desorption points measured with the soil sample that had been stored for 17 months were in the range of the desorption points of the corresponding day and layer as given in Figure 8.1. Thus the extractability of the herbicide soil residues probably did not change during storage at -18 °C.

It was concluded from Table 8.1 that the total contents of extractable cyanazine and metribuzin soil residues after 56 d in 1982 were probably 20-40 % higher than the contents extracted with the single extraction with ethyl acetate (the standard method). If this had been taken into account in Figure 8.1, the contents sorbed of the desorption points of day 56 would have been 20-40 % higher; i.e. the discrepancy in Figure 8.1 between the results of short-term and long-term sorption experiments would have been even larger.

8.3 LONG-TERM SORPTION UNDER LABORATORY CONDITIONS

8.3.1 Introduction

The results of the desorption experiments shown in Figure 8.1 revealed that the Freundlich model with two-site kinetics invoked on the basis of the short-term studies was not satisfactory to describe the results of long-term experiments. Therefore a third class of sorption site had to be assumed: class-3 sites. The content sorbed at class-3 sites, X_3 (kg kg^{-1}), is defined as the content sorbed in excess of the content (either measured or calculated) sorbed at class-1 plus class-2 sites. The definition of content sorbed at class-3 sites is purely operational: it implies that X_3 is zero in soil (initially herbicide-free) that was subjected in suspension to an adsorption experiment with a shaking period of 24 h.

The mechanism of sorption at class-3 sites is not yet clear: class-3 sites may be internal sites located 'deep' in a porous solid matrix. However, it is also possible that class-3 sites are external sites with a large activation energy for sorption. Another possibility is that the location of class-3 sites at the sorbent surface is no different from that of class-1 or class-2 sites, and that class-3 'sites' then are formed from class-1 or class-2 'sites' via rearrangement of sorbate molecules (then the terminology of classes of site is inaccurate and it would be better to speak of classes of sorbate).

Note that an important fraction of the molecules sorbed at class-3 sites is already desorbed by a single extraction with ethyl acetate with a shaking period of 1 h (see Figure 8.1 and Table 8.1). One could argue that this refutes the hypothesis that class-3 sites are located 'deep' in a porous matrix. However, it was observed that the ethyl acetate extracts were yellow, which indicates that some organic material was dissolved during the extraction. It is possible that this dissolution removes essential diffusion barriers between class-3 sites and the external liquid phase.

It was decided to measure rates of changes of X_3 in a moist-soil system only. This system is most relevant as it corresponds with the field system. Measurements in a soil-suspension system were not done because they are difficult to interpret, as sorption properties of a soil suspension that is shaken continuously for weeks or months may change with time (see Section 7.4.1).

8.3.2 Mathematical model

Content of herbicide in the soil system, m_r^* (kg kg^{-1}), is defined as mass of herbicide in the system divided by mass of dry soil; m_r^* can be written as

$$m_r^* = (w/\rho_1)c + X_1 + X_2 + X_3 \qquad (8.1)$$

in which

w	is water content of the soil	(kg kg^{-1})
ρ_1	is phase density of liquid phase in soil	(kg m^{-3})

X_1 and X_2 were calculated with the Freundlich model with two-site kinetics as given by Equations 7.24 and 7.25.

As to X_3, measurements of long-term sorption have not yet been described mathematically in literature and the mechanism of sorption at class-3 sites is a priori unknown. Therefore, it was deemed appropriate to begin by using the simplest model available for describing the sorption kinetics of class-3 sites. The simplest model assumes first-order kinetics and a linear sorption isotherm. Furthermore, it was assumed that no transformation took place at class-3 sites. In analogy with Equation 7.8, this leads to the following sorption rate equation:

$$\frac{dX_3}{dt} = k_{d,3}(K_3\ c - X_3) \tag{8.2}$$

in which

$k_{d,3}$	is desorption rate constant for class-3 sites	(d^{-1})
K_3	is slope of linear sorption isotherm for class-3 sites	$(m^3\ kg^{-1})$

At equilibrium, dX_3/dt is zero and Equation 8.2 results in the sorption isotherm equation for class-3 sites:

$$X_3 = K_3\ c \tag{8.3}$$

The model that consists of the sorption rate equations 7.24, 7.25 and 8.2 for class-1, class-2 and class-3 sites respectively, will be referred to as the three-site model.

It is easily shown that Equation 8.2 is reasonable, even if it is assumed that sorption at class-3 sites is caused by rearrangement of sorbate molecules already sorbed at class-1 or class-2 sites. In that case, the corresponding first-order rate equation for X_3 becomes

$$\frac{dX_3}{dt} = k_{12,3}(X_1 + X_2) - k_{d,3}\ X_3 \tag{8.4}$$

in which

$k_{12,3}$ is rate constant for conversion of X_1 and X_2 into X_3 (d^{-1})

If it is assumed that X_1 and X_2 are in equilibrium with c according to Equations 7.18 and 7.19, it follows from Equation 8.4 that

$$\frac{dX_3}{dt} = k_{12,3}(K_{F,1} + K_{F,2})\ c^{1/n} - k_{d,3}\ X_3 \tag{8.5}$$

Via introduction of the Freundlich coefficient for class-3 'sites', $K_{F,3}$ $(m^{3/n}\ kg^{-1/n})$, Equation 8.5 can be rewritten as

$$\frac{dX_3}{dt} = k_{d,3}(K_{F,3}\ c^{1/n} - X_3) \tag{8.6}$$

in which

$$K_{F,3} = \frac{k_{12,3}(K_{F,1} + K_{F,2})}{k_{d,3}} \tag{8.7}$$

Because $1/n$ was 0.9 for both herbicides, Equation 8.6 is similar to Equation 8.2.

Similarly, it may be shown that Equation 8.2 may be used to describe dX_3/dt if transformation (catalytic) of molecules sorbed at class-3 sites occurs. If a first-order transformation process is assumed, Equation 8.2 changes into

$$\frac{dX_3}{dt} = k_{d,3}\ K_3\ c - k_{d,3}\ X_3 - k_{t,3}\ X_3 \qquad (8.8)$$

in which

$k_{t,3}$ is rate coefficient for transformation of molecules sorbed at class-3 sites (d^{-1})

Equation 8.8 can be rewritten as

$$\frac{dX_3}{dt} = k^e_{d,3}(K^e_3\ c - X_3) \qquad (8.9)$$

in which

$k^e_{d,3}$ is 'effective' value of $k_{d,3}$ (d^{-1})

K^e_3 is 'effective' value of K_3 ($m^3\ kg^{-1}$)

The quantities $k^e_{d,3}$ and K^e_3 are defined by

$$k^e_{d,3} \equiv k_{d,3}(1 + k_{t,3}/k_{d,3}) \qquad (8.10)$$

$$K^e_3 \equiv K_3 \frac{1}{1 + k_{t,3}/k_{d,3}} \qquad (8.11)$$

As Equation 8.9 is mathematically analogous to Equation 8.2, the assumption of a first-order transformation process for X_3 does not invalidate the model of Equation 8.2. The analysis above shows that the values for $k_{d,3}$ and K_3 found with Equation 8.2 in the case of a first-order transformation process for X_3 should be interpreted as the effective values of these parameters, as indicated by Equations 8.10 and 8.11.

Because it was the aim to describe measurements in soil subjected to wetting and drying cycles, the influence of volume fraction of liquid on the values of the parameters in the three-site model had to be considered. One may expect the sorption process in dry soil to be different from that in moist soil. The data obtained by Hance (1977) discussed in Section 8.1, indicate that in dry soil there are many sorption sites with kinetic properties similar to those of class-1 sites. It is not surprising that sorption at the external surface proceeds very rapidly in dry soil, because as a result of drying, the sorptive molecules are 'pressed against' the external surface. It seems justified to assume as a first approximation that $k_{d,1}$ does not depend on volume fraction of liquid. Class-2 sites are probably located on the internal surface, and sorption at these sites requires additional diffusion barriers to be taken. From the relationship between diffusion coefficient and volume fraction of liquid as given by Equation 2.4 and Figure 6.2, it can be concluded that diffusion as measured at a macroscopic level becomes almost zero at volume fractions of liquid below about 0.04 $m^3\ m^{-3}$. One can expect exchange between the external and internal liquid phase for $\theta < 0.04\ m^3\ m^{-3}$ to become limited. Consequently, one can expect $k_{d,2}$ to become very low in dry soil.

The desorption rate constant of class-3 sites, $k_{d,3}$, also probably becomes very low in dry soil, irrespective of the actual mechanism of sorption at class-3 sites: if class-3 sites are located 'deep' in a porous matrix, the effect of a low water content is similar to that for class-2 sites; if an energetic barrier is responsible for the slow equilibration at class-3 sites, it is also likely that water is necessary as a medium to overcome this barrier.

Hance (1977) found a sharp increase in sorption from solutions of herbicides in an apolar solvent if water contents decreased below values corresponding with matric pressures of -2.5 MPa. The water content of the soil used in the present study at -2.5 MPa was estimated. Results of a water content measurement were available after equilibration at a pressure of -1.5 MPa using soil collected near the experimental plots. The water content was found to be 0.04 kg kg^{-1}. The water content in equilibrium with a relative humidity of 60 % (corresponding with a pressure of -70 MPa) was found to be 0.01 kg kg^{-1} (see Section 5.6). Thus a value of 0.04 kg kg^{-1} is a reasonable approximation of the water content at -2.5 MPa.

Given that the bulk density of the soil in the uppermost centimetres is near 1 Mg m^{-3} (see Figure 6.1), the volume fraction of liquid below which sorption at class-1 sites increases sharply is roughly equal to that below which $k_{d,2}$ and $k_{d,3}$ become very low. This allows a simplified model to be used, which seems appropriate, given that our knowledge of the processes involved is very limited. The desorption rate constants $k_{d,2}$ and $k_{d,3}$ were assumed to be zero below volume fractions of liquid of 0.04 $m^3\ m^{-3}$ and constant at higher volume fractions of liquid. The sharp increase in $K_{F,1}$ below 0.04 $m^3\ m^{-3}$ was omitted from the model. This does not lead to incorrect calculation of content sorbed at class-1 sites in moist soil, because Hance's (1977) data indicated that rewetting resulted in complete desorption of the large number of sites that were available in dry soil only. Leaving out the sharp increase in $K_{F,1}$ does not lead to incorrect calculations of contents sorbed at class-2 and class-3 sites either, because their desorption rate constants are set at zero in dry soil. For other purposes the actual contents sorbed in dry soil are also of minor importance: the movement of the herbicides is already limited because of low liquid fluxes, and soil water in dry soil is not available for plants.

The relationships between volume fraction of liquid and the values of the parameters in the three-site sorption model can be summarized as follows: $K_{F,2}$, K_3, $1/n$ and $k_{d,1}$ do not depend on volume fraction of liquid, θ. $K_{F,1}$ in the model does not depend on actual volume fraction of liquid, but $K_{F,1}$ does depend on initial moisture condition of the soil (see Table 7.7 and Figure 7.14). $k_{d,2}$ and $k_{d,3}$ have a constant positive value for $\theta > 0.04\ m^3\ m^{-3}$ but are zero for $\theta < 0.04\ m^3\ m^{-3}$.

8.3.3 Procedures

8.3.3.1 Treatments of soil samples

All experiments were done with the soil from the field experimental plot in 1982, which was also used in the short-term sorption experiments (see Section 7.3.2). Three experiments were done with samples of about 1 kg of soil each (water content 0.13 kg kg^{-1}). All samples were wetted to a water content of 0.25 kg kg^{-1} with an aqueous solution. This solution contained $CaCl_2$ at a concentration of 10 mol m^{-3} and concentrations of cyanazine and metribuzin of 100 and 50 g m^{-3},respectively. This resulted in herbicide contents of 12 and 6 mg kg^{-1}, respectively. During the experiment, all samples were placed in a constant-temperature cabinet at 19 °C.

In the first experiment, the sample was kept at a water content of 0.25 kg kg^{-1} for the whole experimental period (see Table 8.2, code M). In the second and the third experiments the samples were dried to a water content of 0.01 kg kg^{-1}, using a gentle current of air: this took about 18 h. Subsequently, in the second experiment (coded M/D in Table 8.2) the sample was subjected to 26 wetting and drying cycles in the first 90 d. Each time, soil was wetted with distilled water to a water content of 0.25 kg kg^{-1}. During drying in the cabinet, the soil was thoroughly mixed and the loss of water was measured regularly. Usually, average water content fell to about 0.10 kg kg^{-1} within 0.5 d and to 0.05

Table 8.2. Course of soil water content in the long-term sorption experiments in the laboratory.

Code of experiment	*Course of water content (kg kg^{-1}) in period*	
	1 - 90 d	91 - 260 d
M	continuously at 0.25	continuously at 0.25
M/D	fluctuating between 0.25 and 0.01 (27 cycli)	continuously at 0.25
D	after first day continuously at 0.01	continuously at 0.25

$kg\ kg^{-1}$ within 0.75 d. Within 2 d the water content reached a final value of about 0.01 $kg\ kg^{-1}$. About 3.5 d after the drying started, the soil was wetted again, and immediately thereafter a new drying cycle started. After 90 d the soil in experiment M/D was wetted again and kept at a water content of 0.25 $kg\ kg^{-1}$ for the remainder of the experimental period.

After the initial drying cycle, in the third experiment (coded D in Table 8.2) the sample was stored air-dry for the first 90 d. Then it was wetted with distilled water to a water content of 0.25 $kg\ kg^{-1}$ and kept at that level for the remainder of the experimental period.

8.3.3.2 Sampling of soil and liquid phase

At 1, 8, 15, 29, 57, 168 and 260 d after the start of the experiments samples were taken in all experiments. After 231 d samples were taken from soil in experiment M only. After 1, 8, 15, 29 and 57 d the soil in experiment M/D was always air-dry. At all sampling dates two quantities were measured:

- herbicide content in soil
- concentration in liquid phase of moist soil.

Herbicide content in soil was measured using three successive extractions with ethyl acetate. This extraction method was used because it was found to be efficient for the extraction of aged residues of cyanazine and metribuzin (Table 8.1). Volumes of 2.5 cm^3 of water containing $CaCl_2$ at a concentration of 10 mol m^{-3} and 5 cm^3 of ethyl acetate were added to each of three samples of 5 g of soil and the mixture was shaken on a reciprocating shaker for 1 h. After centrifugation of the tubes, the ethyl acetate layer was collected. Subsequently, 5 cm^3 of fresh ethyl acetate were added and the mixture was shaken for 24 h. After centrifugation and collection of the ethyl acetate layer a third extraction with 5 cm^3 of ethyl acetate was carried out by shaking for 24 h. All ethyl acetate extracts were dried over anhydrous Na_2SO_4.

The liquid phase in moist soil was sampled using two glass compartments separated by a glass filter, as shown in Figure 8.2. The glass filter was 16 mm in diameter and 3 mm thick. Pore diameters in the filter were between 10 and 16 μm. 25 g of moist soil were put into the upper compartment and after centrifugation for 5 min at a rotation frequency of 40 s^{-1} about 2 cm^3 of the liquid phase was collected from the lower compartment.

Adsorption of the herbicides onto the glass filter could cause losses, so adsorption of cyanazine to the glass filter was studied. A volume of 0.75 cm^3 of water with $CaCl_2$ at a concentration of 10 mol m^{-3} and radioactively labelled cyana-

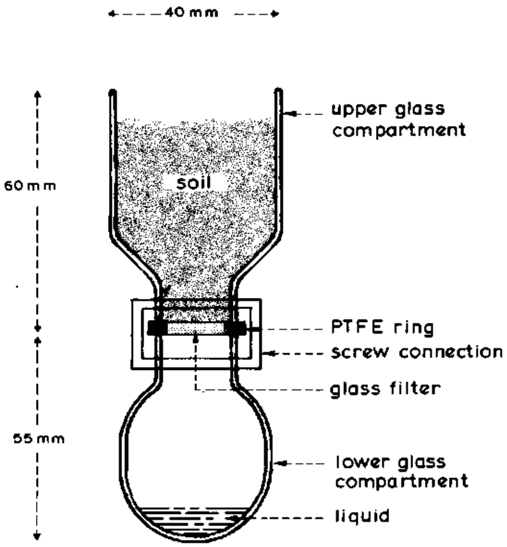


Figure 8.2. The system of two glass compartments with filter used for sampling the liquid phase in moist soil by centrifugation. PTFE, polytetrafluoroethene.

zine at concentrations of 30 and 300 mg m^{-3} were put in the upper compartment. After centrifugation, the average concentration in the filtrates was found to be 96 % of the initial concentration. It was concluded that adsorption onto the glass filter could be ignored.

If soil was moist at the time of sampling, 3 samples of 25 g of soil were taken and a fraction of the liquid phase was collected by centrifugation using the system shown in Figure 8.2. If soil was dry at the time of sampling, 6 samples of 20 g of soil were taken and wetted to a water content of 0.25 kg kg^{-1}. After equilibration periods of 0.5 h (3 samples) and 24 h (3 samples), fractions of the liquid phase were collected by centrifugation.

8.3.3.3 Analysis of the herbicides

Herbicide concentrations in the ethyl acetate extracts from soil samples of days 1 to 57 were measured with a Tracor-550 gas chromatograph equipped with an electron capture detector (^{63}Ni). A Pyrex glass column (0.4 m long; 2 mm inner diameter) packed with 2.8 % Carbowax 20 M on Chromosorb WHP (0.13-0.15 mm) was used. The isothermal operating conditions were: inlet port 225 °C; column oven 180 °C; detector 300 °C. Nitrogen was used as carrier gas at a volume rate of 1 cm^3 s^{-1}. Retention times for cyanazine and metribuzin were 7.8 and 2.4 min, respectively. Standard solutions with concentrations of 50 to 300 mg m^{-3}

cyanazine and 5 to 30 mg m^{-3} metribuzin were made from cyanazine (purity 96 %) and metribuzin (purity 97 %) and were injected regularly. Standard curves were made from peak heights. Limits of detection were 10 and 0.2 mg m^{-3} for cyanazine and metribuzin, respectively.

Herbicide concentration in the liquid phase sampled after 1 to 57 d, was measured using high pressure liquid chromatography. A volume of 100 mm^3 of the liquid phase was injected directly into the chromatograph. The same apparatus and analytical procedures were used as described in Section 4.2.3 for cyanazine analysis in the 0 to 50 mm soil layers of the field experiment in 1981. Metribuzin was detected at the same wavelength (225 nm) as cyanazine. Retention time of metribuzin was 13.0 min. Standard solutions with concentrations of 1 to 10 g m^{-3} cyanazine or metribuzin were made from cyanazine (purity 96 %) and metribuzin (purity 97 %) and they were injected regularly. Standard curves were made from peak areas. The limits of detection were 0.03 and 0.05 g m^{-3} for cyanazine and metribuzin, respectively.

Herbicide concentrations in the samples of the liquid phase and in the ethyl acetate extracts from the soil samples of days 168 to 260 were measured with the same Tracor-550 gas chromatograph. Samples of the liquid phase were extracted with equal volumes of ethyl acetate which were dried over anhydrous Na_2SO_4. The Pyrex glass column (1.55 m long; 2 mm inner diameter) was packed with 1 % SP 2330 on Supelcoport (0.15-0.18 mm). The isothermal operating conditions were: inlet port 230 °C; column oven 185 °C; detector 300 °C. Nitrogen was used as carrier gas at a volume rate of 0.7 cm^3 s^{-1}. Retention times for cyanazine and metribuzin were 8.4 and 2.6 min, respectively. Concentrations of standard solutions and limits of detection were similar to those mentioned before.

As a check, about 30 concentrations of metribuzin in ethyl acetate extracted from soil samples of days 1 to 57 were also measured at the analytical conditions used for the samples of days 168 to 260. It was found that the values measured in the second period were, on average, 100 % (s = 7 %) of the values measured in the first period.

8.3.4 Results and discussion

8.3.4.1 Time series of extractions with ethyl acetate

Figure 8.3 shows the course of time of herbicide content extracted with the successive ethyl acetate extractions. Herbicide contents recovered by the first, second and third extractions are called $m^*_{r,1}$, $m^*_{r,2}$ and $m^*_{r,3}$, respectively.

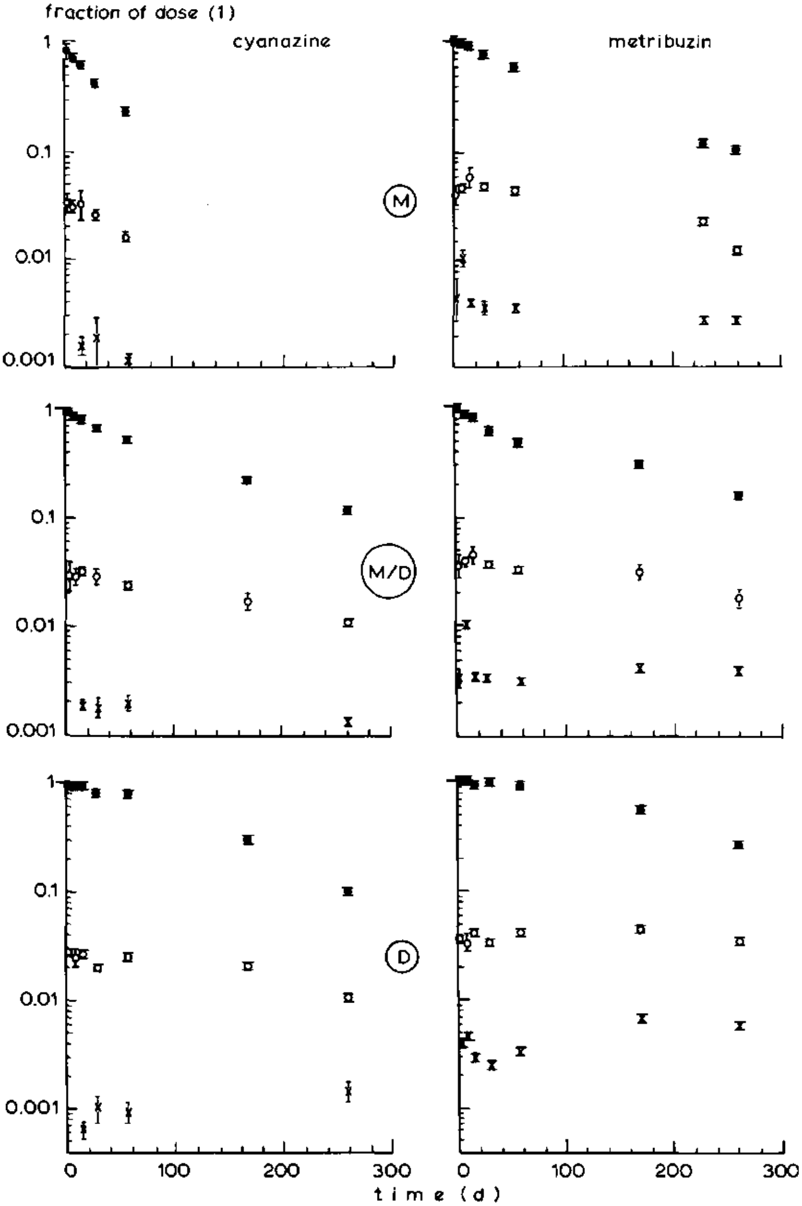


Figure 8.3. Herbicide content found by extraction with ethyl acetate, as a function of time in long-term sorption experiments in the laboratory. ●, o, x, found after first, second and third extraction, respectively. Points are averages of measured contents, bars are standard deviations.

Figure 8.3 shows that values for $m^*_{r,2}$ were one to two orders of magnitude smaller than the values for $m^*_{r,1}$. Values for $m^*_{r,3}$ were two to three orders of magnitude smaller than $m^*_{r,1}$.

Figure 8.3 shows that already after 1 d the values of $m^*_{r,2}$ were 3-4 % of the $m^*_{r,1}$ values. This is probably the result of experimental artifacts: for instance, droplets of ethyl acetate still present in soil. The mass of herbicide in such droplets was already taken into account in the value of $m^*_{r,1}$ because the volume of the ethyl acetate layer after extraction was not ascertained via a measurement but was derived from the added volume of ethyl acetate. Values of $m^*_{r,1}$ after 1 d in all experiments did not differ significantly from 100 % (see Figure 8.3). For the calculation of total content of herbicide in soil it is thus realistic to take only that fraction of $m^*_{r,2}$ into account that is 3-4 % higher than the corresponding $m^*_{r,1}$ value. Figure 8.4 shows that the ratio $m^*_{r,2}/m^*_{r,1}$ increased with time for all experiments and at some time always exceeded the 3-4 % level. The results in Figure 8.4 show that after 100-300 d the ratio $m^*_{r,2}/m^*_{r,1}$ was about 2 to 3 times as high as that at the start of the experiment. These results correspond with the general experience reported in the literature that it is more difficult to extract an amount of aged pesticide residue than an amount of freshly-mixed pesticide (see Section 8.1). Values of the ratio $m^*_{r,2}/m^*_{r,1}$ as determined in soil sampled after 56 d in the field in 1982 were in the range from 0.1 to 0.3 (Table 8.1). Thus, the values found in

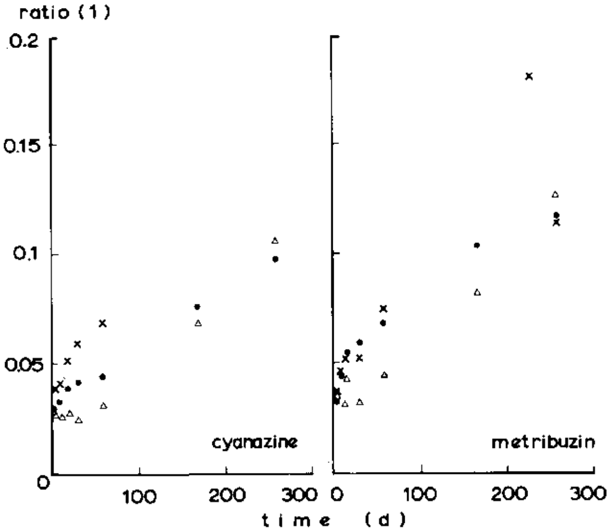


Figure 8.4. Ratio of herbicide content found after the second extraction with ethyl acetate to that found after the first extraction with ethyl acetate ($m^*_{r,2}/ m^*_{r,1}$) as a function of time in long-term sorption experiments in the laboratory. x, •, Δ, found in experiments M, M/D and D respectively.

the field were higher than those found in the laboratory.

Total herbicide content in soil, m_r^*, was calculated from $m_{r,1}^*$ and $m_{r,2}^*$ with the restriction that only that fraction of $m_{r,2}^*$ was taken into account that exceeded 4 % of the corresponding $m_{r,1}^*$ value. $m_{r,3}^*$ was ignored in this calculation, because it was at most a few per cent of the corresponding $m_{r,1}^*$ value. Figure 8.5 shows the results of the calculation.

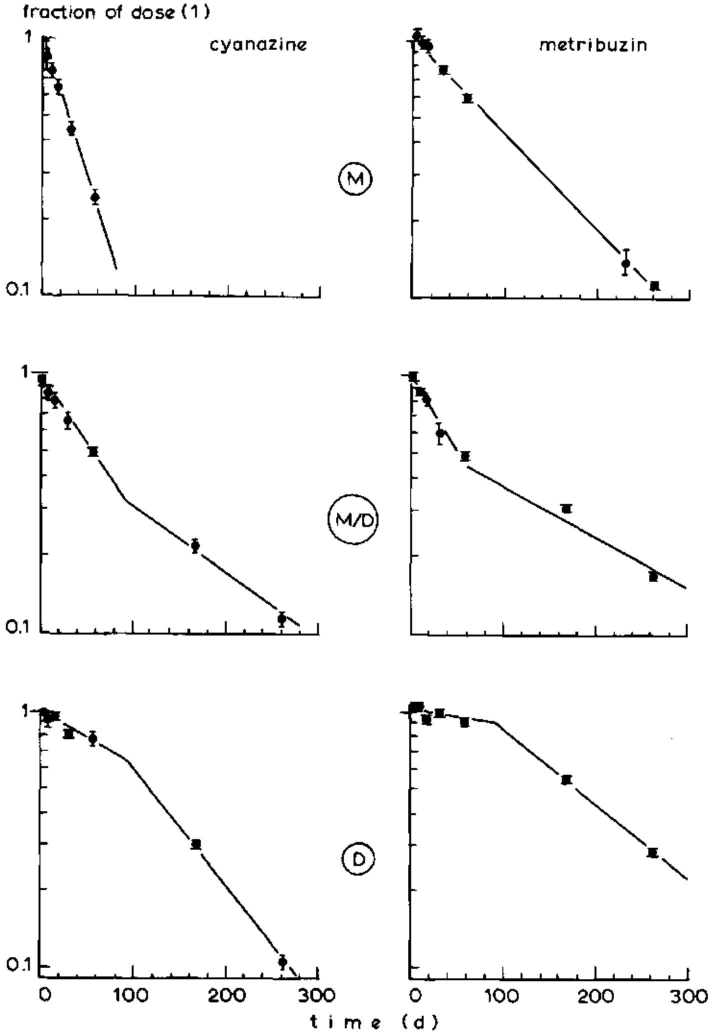


Figure 8.5. Total content of herbicide, m_r^*, found by successive extractions with ethyl acetate as a function of time in long-term sorption experiments in the laboratory. Points are averages of measured contents, bars are standard deviations; ——, calculated with Equation 8.12.

It was attempted to describe the transformation rate in the experiments with a first-order rate equation (Equation 3.1). The analytical solution of such an equation can be written as:

$$m_r^*(t) = m_r^*(0) \exp(-k_t^* t) \qquad (8.12)$$

A linear regression least-squares optimization was used with a fixed initial value, $m_r^*(0)$, calculated from the dose of herbicide. Figure 8.5 shows that the measurements for experiment M could be described reasonably by Equation 8.12. Because moisture conditions in experiments M/D and D changed after 90 d (see Table 8.2), one would expect the transformation rate coefficient also to change at that time. As Figure 8.5 shows, measured m_r^* values for cyanazine in experiments M/D and D could indeed be described well by Equation 8.12 if different rate coefficients were used for the two periods with different conditions. The same applied to metribuzin in experiment D. However, measured m_r^* values for metribuzin in experiment M/D could only be described well if it was assumed that the rate coefficient had already changed after 60 d. The reason for this is not clear. Table 8.3 shows that the transformation rate coefficients found for cyanazine were usually higher than those found for metribuzin. For cyanazine, the highest rate coefficient was found in experiment M. In experiment M/D the rate coefficient in the first few months was higher for both cyanazine and metribuzin than those found after 90 and 60 d, respectively. Thus, keeping the soil permanently moist after 27 wetting and drying cycles lowered the transformation rate coefficient. In experiment D the transformation rate coefficients in the wetted

Table 8.3. The first-order transformation rate coefficient, k_t^*, as derived from the decline of total herbicide content in the long-term sorption experiments in the laboratory.

Code of experiment	Period (d)	Rate coefficient (d^{-1})	
		cyanazine	metribuzin
M	0 - 260	0.026	0.008
M/D	0 - 90	0.012	0.014[1]
	90 - 260	0.006	0.004[2]
D	0 - 90	0.005	0.001
	90 - 260	0.011	0.007

1. period 0 - 60 d
2. period 60 - 260 d

soil (period 90-260 d) were higher than those in the previous period with dry soil (0-90 d).

8.3.4.2 Time series of sorption points

Figure 8.6 shows time series of sorption points as found in moist soil. These points were based on the calculation of total herbicide content as described in Section 8.3.4.1. The points shown for soil samples that were dry at the sampling time, were those measured after a rewetting period of 24 h. The averaged concentrations in liquid phase measured after rewetting periods of $\frac{1}{2}$ h were, for cyanazine and metribuzin respectively, 102 % (s = 4 %) and 99 % (s = 4 %) of those found after 24 h. Given that the changes in concentration between rewetting periods of $\frac{1}{2}$ h and 24 h were so small, it can be assumed that contents sorbed at class-1 plus class-2 sites were approximately at equilibrium after a rewetting period of 24 h. Contents sorbed at class-1 plus class-2 sites were also approximately at equilibrium for the soil samples that were moist at the time of sampling: after an initial equilibration period, changes in concentration result solely from transformation of the herbicides, and the transformation rate coefficients in Table 8.3 are one order of magnitude smaller than the desorption rate constants as given for class-2 sites in Table 7.4.

Because it was concluded that contents sorbed at class-1 plus class-2 sites were approximately at equilibrium for the sorption points in Figure 8.6, the points can be compared with the sum of the sorption isotherms for class-1 and class-2 sites. The Freundlich coefficients for these isotherms were taken from Table 7.7. In Figure 8.6 only those parts of the isotherms that correspond with the moisture conditions of the sorption points are shown.

Figure 8.6 shows that contents sorbed at class-3 sites were usually small compared with the contents sorbed at class-1 plus class-2 sites. An exception are the points found after 168 d for cyanazine: then, content sorbed at class-3 sites was about equal to that sorbed at class-1 plus class-2 sites. It can be derived from Figure 8.6 that for both experiments M/D and D, the contents sorbed at class-3 sites after 260 d were lower than after 168 d. This supports qualitatively the reversibility assumed in the sorption rate equation proposed (Equation 8.2).

Drying and wetting the soil had almost no influence: after 57 d in experiment M/D, contents sorbed for both herbicides hardly exceeded the equilibrium value for class-1 plus class-2 sites. At that time the soil had been dried and wetted 17 times! This contrasts with the large effect of one drying cycle on measured sorption coefficients found by Mercer & Hill (1975) and Hance & Embling (1979)

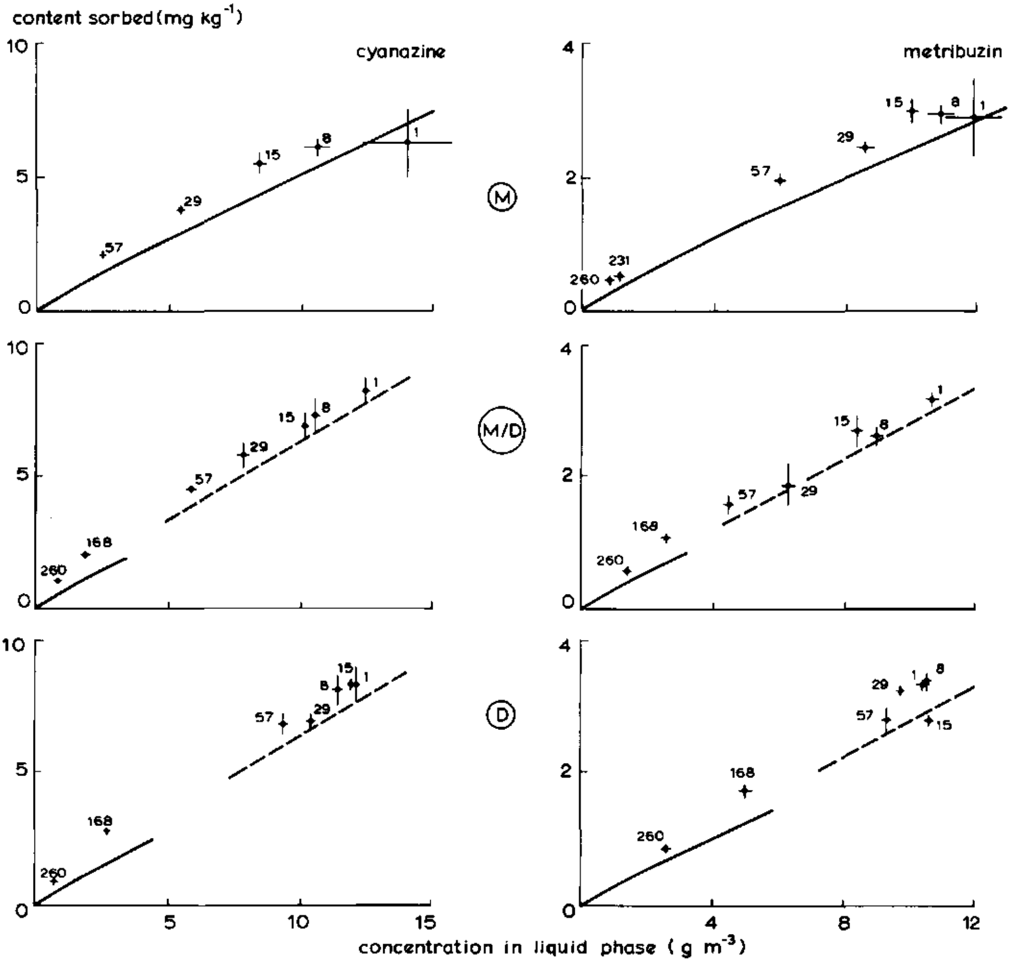


Figure 8.6. Time series of sorption points of herbicide in long-term sorption experiments in the laboratory. Points are averages of measured points, vertical and horizontal bars are standard deviations; the numbers indicate sampling dates in days. The initially dry soil samples were wetted for 24 h. ——, ---, Freundlich sorption isotherms for class-1 plus class-2 sites for initially moist and air-dry soil, respectively.

with a number of soils and herbicides. As Hance & Embling (1979) also used metribuzin, the extent of the effect obviously depends on soil type.

8.3.4.3 Estimation of values for sorption parameters for class-3 sites from experiment M

Figure 8.7 shows the measured decline of herbicide concentration in the liquid phase of the permanently moist soil. It was attempted to describe these declines by an exponential equation:

$$c = c(0)\ \exp(-k_c\ t) \tag{8.13}$$

in which

k_c is rate coefficient for decline of c (d^{-1})

Figure 8.7 shows that description with Equation 8.13 was satisfactory. The values of $c(0)$ and k_c found for cyanazine using a linear regression least-squares optimization were 13.8 g m^{-3} and 0.031 d^{-1}, respectively. In the same way, values of $c(0)$ = 11.6 g m^{-3} and k_c = 0.010 d^{-1} were found for metribuzin.

The fact that the declines of both $m_r^*(t)$ and $c(t)$ could be described by exponential equations, enables $k_{d,3}$ and K_3 to be estimated in a simple way, as will be shown below.

If it is assumed that contents sorbed at class-1 and class-2 sites are contin-

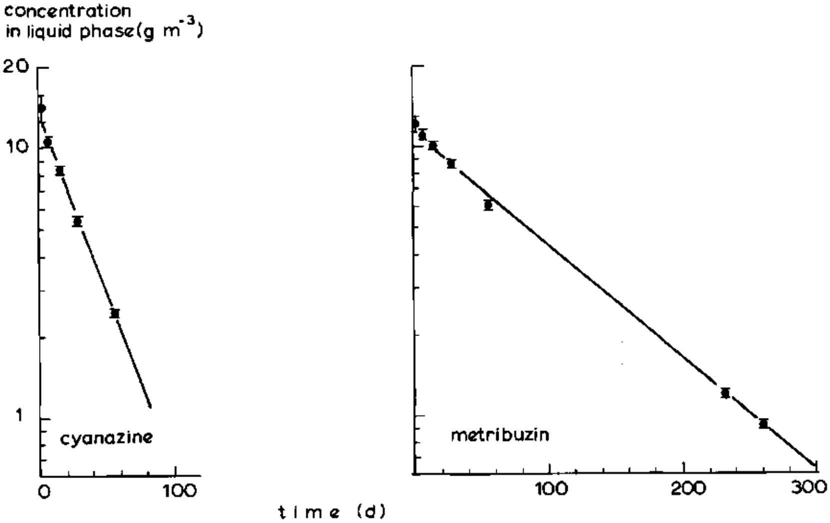


Figure 8.7. Herbicide concentration in liquid phase as a function of time in experiment M. Points are averages of measured concentrations, bars are standard deviations; ——, calculated with Equation 8.13.

uously in equilibrium with c, Equation 8.1 becomes:

$$m_{\mathrm{r}}^{*} = (w/\rho_1)c + (K_{\mathrm{F},1} + K_{\mathrm{F},2})c^{1/n} + X_3 \tag{8.14}$$

Figure 8.7 shows that values of c for both herbicides did not vary more than a factor of 10 during experiment M. The sum of the Freundlich sorption isotherms of class-1 and class-2 sites for both herbicides can then be closely approximated with a linear sorption isotherm:

$$X_1 + X_2 = (K_1 + K_2)c \tag{8.15}$$

The sum of K_1 and K_2 was calculated by assuming that the surface areas below the Freundlich and the linearized isotherms were equal over the experimental range of c:

$$\int_{c_{\mathrm{min}}}^{c_{\mathrm{max}}} (K_{\mathrm{F},1} + K_{\mathrm{F},2})\eta^{1/n} \;\mathrm{d}\eta = \int_{c_{\mathrm{min}}}^{c_{\mathrm{max}}} (K_1 + K_2)\,\eta \;\mathrm{d}\eta \tag{8.16}$$

in which

c_{min}	is minimum value of c during the experiment	(kg m^{-3})
c_{max}	is maximum value of c during the experiment	(kg m^{-3})

Combining Equations 8.1, 8.12, 8.13, and 8.15 gives

$$X_3 = -c(0)\ (w/\rho_1 + K_1 + K_2)\ \exp(-k_c\ t) + m_{\mathrm{r}}^{*}(0)\ \exp(-k_{\mathrm{t}}^{*}\ t) \tag{8.17}$$

At the start X_3 is zero. Thus for $t = 0$ it may be derived from Equations 8.1 and 8.15 that

$$m_{\mathrm{r}}^{*}(0) = c(0)\ (w/\rho_1 + K_1 + K_2) \tag{8.18}$$

Equation 8.17 may then be simplified to

$$X_3 = -c(0)\ (w/\rho_1 + K_1 + K_2)\ \{\exp(-k_c\ t) - \exp(-k_{\mathrm{t}}^{*}\ t)\} \tag{8.19}$$

If it is assumed that c decreases exponentially with time (Equation 8.13), that X_3 is zero at the start and that $k_{\mathrm{d},3}$ and K_3 are constant, the following analytical solution of Equation 8.2 can be derived (see van Rootselaar, 1970,

p. 131):

$$X_3 = \frac{k_{d,3}\ K_3\ c(0)}{k_{d,3} - k_c}\ \{\exp(-k_c\ t) - \exp(-k_{d,3}\ t)\} \tag{8.20}$$

Combination of Equations 8.19 and 8.20 shows that $k_{d,3}$ has to be equal to k_t^* and that

$$K_3 = \frac{k_c - k_{d,3}}{k_{d,3}}\ (w/\rho_1 + K_1 + K_2) \tag{8.21}$$

Remember that there is no causal relationship between $k_{d,3}$ and k_t^*: they are only equal because the declines of both $m_r^*(t)$ and $c(t)$ can be described with first-order rate equations. Note that the validity of the first-order rate equations can only be assessed approximately in experiments.

Values for $K_{F,1}$ and $K_{F,2}$ for initially moist soil were taken from Table 7.7. From these values the sum of K_1 and K_2 was estimated with Equation 8.16 and found to be 0.52 $dm^3\ kg^{-1}$ for cyanazine and 0.25 $dm^3\ kg^{-1}$ for metribuzin. Substituting values measured for cyanazine in experiment *M* in Equation 8.17 gave

$$X_3 = -0.0000106 \exp(-0.031\ t) + 0.0000116 \exp(-0.026\ t) \tag{8.22}$$

Rewriting Equation 8.22 in a form similar to Equation 8.19 gave

$$X_3 = -0.0000106\,\{\exp(-0.031\ t) - 1.09 \exp(-0.026\ t)\} \tag{8.23}$$

Equation 8.23 implies that the value for $c(0)$ as estimated from the linear regression equation was 9 % lower than the value expected from the linearized sorption isotherms of class-1 and class-2 sites. This can be the result of experimental error. To approximate $k_{d,3}$ and K_3, Equation 8.23 has to be set equal to Equation 8.20. This leads to the equation

$$\exp(-k_{d,3}\ t) = 1.09 \exp(-0.026\ t) \tag{8.24}$$

The value of $k_{d,3}$ was approximated by requiring that

$$\int_0^{t_e} \exp(-k_{d,3}\ \eta)\ d\eta = \int_0^{t_e} 1.09 \exp(-0.026\ \eta)\ d\eta \tag{8.25}$$

in which

t_e is time at the end of the experimental period (57 d for cyanazine) (d)

Equation 8.25 leads to an implicit equation in $k_{d,3}$:

$$k_{d,3} = \frac{1 - \exp(-57\ k_{d,3})}{32.5} \tag{8.26}$$

Equation 8.26 was solved numerically and a $k_{d,3}$ value of 0.022 d^{-1} was found. When this value was substituted in Equation 8.21 a K_3 value of 0.3 $dm^3\ kg^{-1}$ was obtained. Experimental results for metribuzin were analysed using the same procedure, and values of $k_{d,3}$ and K_3 were found to be 0.009 d^{-1} and 0.07 $dm^3\ kg^{-1}$, respectively.

In the above procedure $k_{d,3}$ and K_3 were approximated from $m_r^*(t)$ using $c(t)$ as a boundary condition. To check whether the numerical approximations of Equations 8.16 and 8.25 were valid, $m_r^*(t)$ was calculated with Equation 8.14 in which X_3 was calculated with the analytical solution (Equation 8.20). Results for cyanazine (Figure 8.8) show that the K_3 value of 0.3 $dm^3\ kg^{-1}$ systematically overestimated the m_r^* values and that a value of 0.2 $dm^3\ kg^{-1}$ gave a better de-

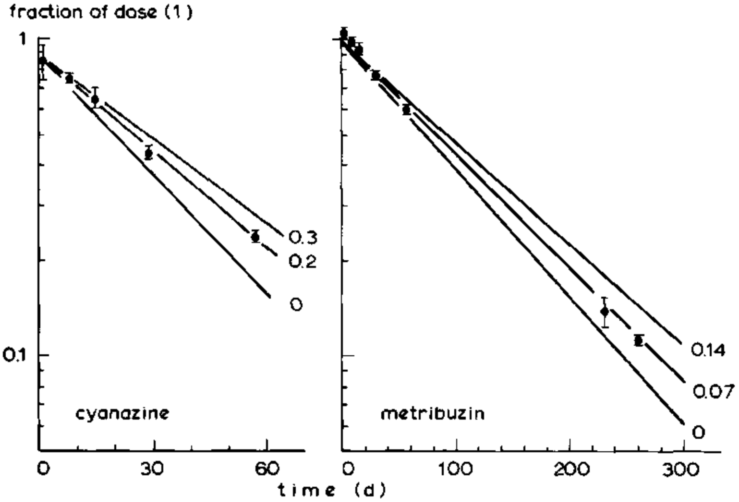


Figure 8.8. Total content of herbicide, m_r^*, found by successive extractions with ethyl acetate in experiment M as a function of time compared with calculations using Equations 8.14 and 8.20. Points are averages of measured contents, bars are standard deviations; ——, calculated with K_3 values ($dm^3\ kg^{-1}$) as indicated.

scription. m_r^* was calculated also with $k_{d,3} = K_3 = 0$ (i.e. class-3 sites are absent). Figure 8.8 shows that this resulted in too low m_r^* values. In another calculation with $K_3 = 0.2$ dm^3 kg^{-1}, $k_{d,3}$ was assumed to be infinitely large, i.e. class-3 sites are continuously at equilibrium. This resulted in m_r^* values (not shown in Figure 8.8) which during the whole experimental period were about 25 % higher than those calculated with $k_{d,3} = K_3 = 0$. This shows that the sensitivity of calculated m_r^* values to $k_{d,3}$ was small. It was concluded that results of cyanazine measurements in experiment M could be described well with $k_{d,3} = 0.02$ d^{-1} and $K_3 = 0.2$ dm^3 kg^{-1}. However, the uncertainty in the $k_{d,3}$ value is large.

Results for metribuzin in Figure 8.8 show that m_r^* values calculated with $k_{d,3} = 0.009$ d^{-1} and $K_3 = 0.07$ dm^3 kg^{-1} described measured values reasonably well. Values of m_r^* calculated with $k_{d,3} = K_3 = 0$ were too low after 231 and 260 d. Values of m_r^* calculated with $k_{d,3} = 0.009$ d^{-1} and $K_3 = 0.14$ dm^3 kg^{-1} were systematically higher than the values measured after 231 and 260 d. A calculation with $k_{d,3} = \infty$, $K_3 = 0.07$ dm^3 kg^{-1} resulted in m_r^* values that were 13-14 % higher during the whole experimental period than those calculated with $k_{d,3} = K_3 = 0$. This shows that the sensitivity to $k_{d,3}$ was again low. It was concluded that results for metribuzin in experiment M could be described well with $k_{d,3} = 0.01$ d^{-1} and $K_3 = 0.07$ dm^3 kg^{-1}. However, the uncertainty in the $k_{d,3}$ value is again large.

In the foregoing analysis it was assumed that contents sorbed at class-1 and class-2 sites were continuously at equilibrium. As discussed in Section 8.3.4.2, this assumption can be roughly based on the fact that rate coefficients for the decline of m_r^* in experiment M were at least one order of magnitude smaller than the desorption rate constants for class-1 and class-2 sites (see Tables 7.4 and 8.3). Figure 8.7 showed that concentration in liquid phase decreased exponentially with time, and therefore the deviations from the contents sorbed at equilibrium can be considered in detail with an analytical solution. The values of $k_{d,1}$ were two orders of magnitude larger than values of $k_{d,2}$, and so this was done for class-2 sites only. Assuming a linear sorption isotherm for class-2 sites with slope K_2 and assuming an exponentially decreasing $c(t)$-function, the solution for X_2 (if initially zero) reads (by analogy with Equation 8.20):

$$X_2 = \frac{k_{d,2}\ K_2\ c(0)}{k_{d,2} - k_c} \{ \exp(-k_c\ t) - \exp(-k_{d,2}\ t) \} \qquad (8.27)$$

To estimate the deviation of X_2 from its equilibrium value, the reduced content sorbed at class-2 sites, $\overline{X}_2$, is considered. $\overline{X}_2$ is defined as the ratio of the actual value of X_2 divided by the value of X_2 in equilibrium with the concentration in liquid phase, c. The value of X_2 in equilibrium with c can be derived from Equation 8.27 by assuming that $k_{\mathrm{d},2}$ approaches infinity. It then follows that $\overline{X}_2$ is given by

$$\overline{X}_2 = \frac{k_{\mathrm{d},2}}{k_{\mathrm{d},2} - k_c} \quad \frac{\exp(-k_c\ t) - \exp(-k_{\mathrm{d},2}\ t)}{\exp(-k_c\ t)} \tag{8.28}$$

Values of $k_{\mathrm{d},2}$ in moist soil were found to be 0.5 and 0.4 d^{-1} for cyanazine and metribuzin, respectively (Table 7.4). The values of k_c in experiment M were found to be 0.031 and 0.010 d^{-1} for cyanazine and metribuzin, respectively. Figure 8.9 shows reduced content sorbed at class-2 sites as a function of time for $k_{\mathrm{d},2} = 0.5\ \mathrm{d}^{-1}$ and for $k_c = 0$ and $k_c = 0.03\ \mathrm{d}^{-1}$. It was concluded that even by the second sampling date (after 8 d) X_2 is very close to its equilibrium value. For $k_c = 0.03\ \mathrm{d}^{-1}$, from about 10 d onwards, X_2 lags continuously behind its equilibrium value by 6 %. If, for cyanazine, a $K_{\mathrm{F},2}$ value that is 6 % higher than its actual value is substituted in Equation 8.14, this results in a value of m_{r}^* that is only 1 % higher, or a value of c that is only 1 % lower. For metribuzin, the deviations were even smaller than 1 %, because its k_c value was only 0.01 d^{-1}. Thus it seems justified to assume that class-1 and class-2 sites were at equilibrium in experiment M for both herbicides after only 8 d. According to Figure 8.9, X_2 had only reached about half its equilibrium value after 1 d (the first sampling date). Consequently, the values of c measured after 1 d should not have been taken into account in the foregoing analysis. To estimate the error made, the values of $c(0)$ and k_c were recalculated but now the value of c found after 1 d was not taken into account. The resulting values differed by only 1-4 % from the old ones.

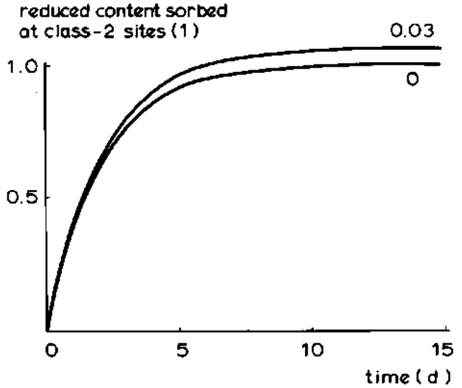


Figure 8.9. Reduced content sorbed at class-2 sites ($\overline{X}_2$) in moist soil as a function of time, as calculated with Equation 8.28 with $k_{\mathrm{d},2} = 0.5\ \mathrm{d}^{-1}$. Values of k_c (d^{-1}) are indicated.

In the foregoing analysis it was assumed via Equation 8.12 that the transformation rate of the herbicides is proportional to the total content of herbicide, m_r^*. This assumption was inductively based on the observed decline of m_r^*. Because content sorbed at class-3 sites, X_3, is part of m_r^*, it was conceptually inconsistent to assume via Equation 8.2 that X_3 is not transformed. One way of trying to overcome this problem is to state that incorporation of a first-order transformation rate of X_3 with a $k_{t,3}$ value equal to k_t^* does not change the mathematical analysis, as is shown by the analogy between Equations 8.2 and 8.9. The consequence is that the $k_{d,3}$ values found should be interpreted as values of $k_{d,3}^e$ as given by Equation 8.10. However, it is improbable that the mechanism for a possible transformation of molecules sorbed at class-3 sites is the same as that for transformation in the remainder of the soil system. Thus there is no a-priori reason why $k_{t,3}$ should equal the 'overall' transformation rate coefficient, k_t^*. An alternative model was considered in which transformation takes place in liquid phase only. If a first-order transformation process is assumed, the rate equation for transformation is given by

$$\frac{dm_r^*}{dt} = -k_{t,1}(w/\rho_1)c \tag{8.29}$$

in which

$k_{t,1}$ is rate coefficient for transformation in liquid phase (d^{-1})

It is assumed that X_1 and X_2 are in equilibrium with c and can be described with linear sorption isotherm equations (Equations 7.16 and 7.17) over the experimental range of c. After substituting Equation 8.1 for m_r^*, Equation 8.29 can be rearranged to

$$(w/\rho_1 + K_1 + K_2)\frac{dc}{dt} = -k_{t,1}(w/\rho_1)c - \frac{dX_3}{dt} \tag{8.30}$$

Substituting the sorption rate equation (Equation 8.2) for dX_3/dt in Equation 8.30 and rearranging, results in

$$\frac{dc}{dt} = \frac{1}{(w/\rho_1 + K_1 + K_2)}\left[c\{-k_{t,1}(w/\rho_1) - k_{d,3}K_3\} + k_{d,3}X_3\right] \tag{8.31}$$

The system of Equations 8.2 and 8.31 can be solved as described by van Rootselaar (1970, pp. 137-139). The solutions for m_r^* and c are given by equations of the form of

$$m_r^*(t) = m_r^*(0)\,\{ g \exp(\Lambda_1 t) + (1 - g) \exp(\Lambda_2 t)\} \tag{8.32}$$

$$c(t) = c(0)\,\{ h \exp(\Lambda_1 t) + (1 - h) \exp(\Lambda_2 t)\} \tag{8.33}$$

in which

g, h are constants with values between 0 and 1 (1)
Λ_1, Λ_2 are constants (d^{-1})

To describe the constants Λ_1, Λ_2, g and h the constants κ_3 (d^{-1}) and κ_t (d^{-1}) are defined as follows:

$$\kappa_3 \equiv \frac{k_{d,3}\, K_3}{(w/\rho_1 + K_1 + K_2)} \tag{8.34}$$

$$\kappa_t \equiv \frac{k_{t,1}\, w/\rho_1}{(w/\rho_1 + K_1 + K_2)} \tag{8.35}$$

The equations for Λ_1, Λ_2, g and h are then given by

$$\Lambda_1 = -\tfrac{1}{2}(k_{d,3} + \kappa_3 + \kappa_t) + \tfrac{1}{2}\sqrt{(k_{d,3} + \kappa_3 + \kappa_t)^2 - 4k_{d,3}\, \kappa_t} \tag{8.36}$$

$$\Lambda_2 = -\tfrac{1}{2}(k_{d,3} + \kappa_3 + \kappa_t) - \tfrac{1}{2}\sqrt{(k_{d,3} + \kappa_3 + \kappa_t)^2 - 4k_{d,3}\, \kappa_t} \tag{8.37}$$

$$g = \frac{\Lambda_2(\Lambda_2 + \kappa_3 + \kappa_t)}{k_{d,3}(\Lambda_1 - \Lambda_2)} \tag{8.38}$$

$$h = \frac{\Lambda_2 + \kappa_3 + \kappa_t}{\Lambda_2 - \Lambda_1} \tag{8.39}$$

Thus the model based on Equation 8.29 implies that measured declines of c and m_r^* are to be described with the sum of two exponential functions, whereas Equations 8.12 and 8.13 assume single exponential functions only.

It was checked to what extent the more simple descriptions of $m_r^*(t)$ and $c(t)$ with Equations 8.12 and 8.13 differed from the descriptions with Equations 8.32 and 8.33. The only parameter yet unknown in the system of Equations 8.2 and 8.31 is $k_{t,1}$. The values of $k_{t,1}$ for both herbicides were estimated by trial and error from the measured declines of m_r^*. The resulting values were 0.089 d^{-1} for

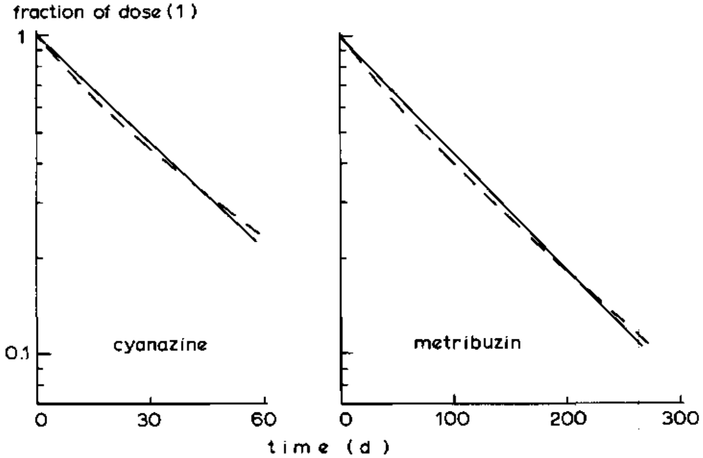


Figure 8.10. Total content of herbicide, m_r^*, in experiment M as a function of time as calculated with Equation 8.12 (——) and with Equation 8.32 (---).

cyanazine and 0.019 d^{-1} for metribuzin. Figure 8.10 compares $m_r^*(t)$ as calculated with Equations 8.12 and 8.32. Figure 8.10 shows that the values of the sum of the two exponential functions as calculated with Equation 8.32 are very close to the values calculated with the single exponential function assumed before. Correspondence between the decline of c as calculated with Equation 8.13 and that calculated with Equation 8.33 was similar to that shown for m_r^* in Figure 8.10. This shows that the values as estimated for $k_{d,3}$ and K_3 are not in conflict with the model based on Equation 8.29.

8.3.4.4 Evaluation of experiments M/D and D with three-site model

It was attempted to explain the results of experiments M/D and D with the three-site model as derived from experiment M. There are two possibilities: $c(t)$ is derived as output with $m_r^*(t)$ as input and vice-versa. The first possibility was applied, because it gives the best link to the test of the model in the field: there total areic mass recovered by a single extraction with ethyl acetate is known as a function of time and is used to calculate c values in each soil layer.

For the calculation of $c(t)$ the three-site model was used as described in Section 8.3.2. In the model, m_r^* was described with the analytical solution of the first-order rate equation for transformation (Equation 8.12) with k_t^* values as given in Table 8.3.

The course of time of the water content during drying cycles was described with the equation

$$w = 0.01 + 0.24 \exp\{-k_w (t - t_{dr})\} \tag{8.40}$$

in which

k_w	is the rate coefficient for decrease in w	(d^{-1})
t_{dr}	is time at start of the corresponding drying cycle	(d)

The decrease in w during the first drying cycle could be described reasonably well with $k_w = 7\ d^{-1}$ for experiment M/D and $k_w = 5\ d^{-1}$ for experiment D. The decrease in the 26 remaining cycles in experiment M/D could be described fairly well with $k_w = 2\ d^{-1}$.

Values for the desorption rate constants $k_{d,1}$ and $k_{d,2}$ were taken from Table 7.4. Values for $K_{F,1}$ and $K_{F,2}$ were taken from Table 7.7 and values for $1/n$ were taken from Table 6.5. The $K_{F,1}$ value for initially air-dry soil was used for the period 0-90 d in both experiments M/D and D. Because the soil was continuously moist thereafter, $K_{F,1}$ was then calculated from the equation

$$K_{F,1} = K_{F,1}^{m} + (K_{F,1}^{d} - K_{F,1}^{m})\exp\{-(t - 90)/\tau^{d,m}\} \tag{8.41}$$

in which

$K_{F,1}^{m}$	is $K_{F,1}$ of moist soil	($m^{3/n}\ kg^{-1/n}$)
$K_{F,1}^{d}$	is $K_{F,1}$ of dry soil	($m^{3/n}\ kg^{-1/n}$)
$\tau^{d,m}$	is time constant for decline of $K_{F,1}$ from $K_{F,1}^{d}$ to $K_{F,1}^{m}$ after initially dry soil is rewetted	(d)

The value of $\tau^{d,m}$ was estimated to be 7 d from the course of time of the ratio of sorption coefficients shown in Figure 7.14. Values of $k_{d,3}$ and K_3 were taken from experiment M.

It was assumed that contents sorbed at class-1 sites were continuously at equilibrium. The most rapid changes in the system occur at the moment dried soil is rewetted. However, no detailed measurements were made of desorption kinetics after rewetting: the first sampling time was ½ h after rewetting. As $k_{d,1}$ values are 6 to 8 h^{-1}, it is justifiable to assume that content sorbed at class-1 sites was near equilibrium after ½ h (see Equation 7.33). During the subsequent drying cycle, deviations from the equilibrium value were small, because values of rate coefficients for decline in water content, k_w, were one or two orders of magnitude lower than $k_{\mathrm{d},1}$ values. Equation 8.1 can then be rewritten as

$$m_{\mathrm{r}}^* = (w/\rho_1)c + K_{\mathrm{F},1}\, c^{1/n} + X_2 + X_3 \tag{8.42}$$

In the model, values of m_{r}^*, X_2 and X_3 were at each moment explicitly calculated from Equation 8.12 and (via integration) from Equations 7.25 and 8.2, respectively. Thus, in the model Equation 8.42 was an implicit equation in c, which was solved numerically by the iteration algorithm

$$c_{\iota+1} = (m_{\mathrm{r}}^* - X_2 - X_3)/\{w/\rho_1 + K_{\mathrm{F},1}\, c_\iota^{(1/n)-1}\} \tag{8.43}$$

in which

ι is index of iteration number (1)

The number of iterations was regulated with an error criterion which implied that the iteration stopped when two successive c values differed from each other by less than 0.1 %.

The model described above was translated into a computer program using the simulation language CSMP III (Speckhart & Green, 1976). X_2 and X_3 were integrated with Euler's method. The time step was 0.02 d in the first drying cycle and 0.04 d in subsequent drying cycles. In the period 90-260 d, the time step was 0.25 d.

Figure 8.11 shows results for experiment M/D for both herbicides. In the period 0-90 d, c values as measured ½ h after rewetting are shown and compared with c values calculated immediately after rewetting the soil. Figure 8.11 shows that measured c values were explained reasonably well with $K_3 = 0.2$ for cyanazine and $K_3 = 0.07\ \mathrm{dm}^3\ \mathrm{kg}^{-1}$ for metribuzin: differences between measured and calculated values were usually less than 1 %.

At all sampling dates in the period 0-90 d, c was also measured 24 h after rewetting the soil (during these 24 h water content was kept constant at 0.25 $\mathrm{kg\ kg}^{-1}$). The course of time of c in these 24 h was calculated in separate runs. For cyanazine and metribuzin respectively, the calculated values of c for a rewetting period of 24 h after the first drying cycle were 92 % and 95 % of those calculated for a period of ½ h. The measured figures were 97 % and 102 %, respectively. For all other sampling dates, calculated values of c for a rewetting period of 24 h were, for both herbicides, in the range from 98 % to 102 % of those calculated for a period of ½ h. Figures of 102 % (s = 2 %) and 104 % (s = 3 %) were

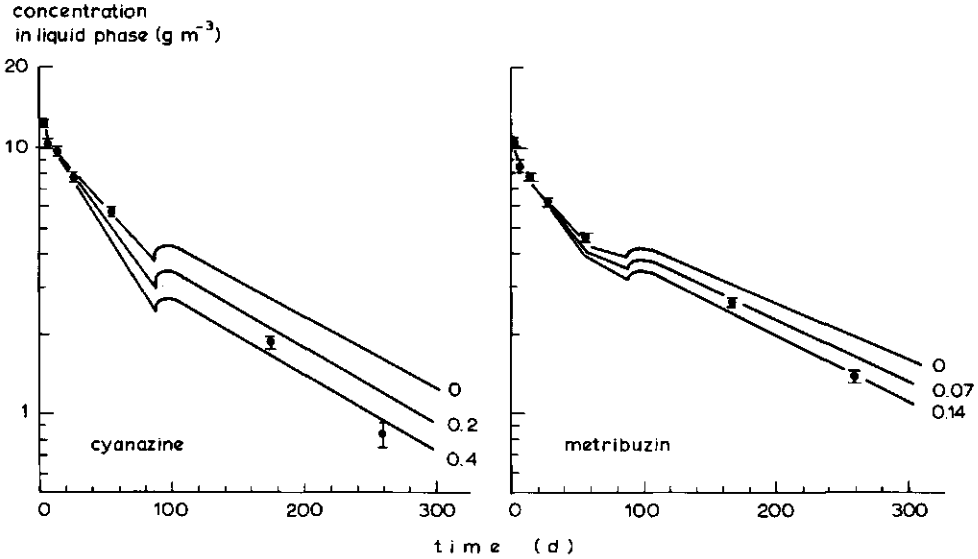


Figure 8.11. Herbicide concentration as a function of time in liquid phase in soil ½ h after rewetting (in period 0-90 d) and in continuously moist soil (in period after 90 d) in experiment M/D. Points are averages of measured concentrations, bars are standard deviations; ——, calculated with K_3 values (dm^3 kg^{-1}) as indicated.

measured for cyanazine and metribuzin, respectively. It was concluded that the model accurately simulated the sorption kinetics in the soil that had been rewetted.

The sensitivity of the calculated c values to K_3 was investigated: calculations were done with $K_3 = 0$ (i.e. class-3 sites are absent) and with double the values as derived from experiment M. The results shown in Figure 8.11 show that $K_3 = 0$ for cyanazine resulted in a clear overestimate of c values measured after 168 and 260 d. For metribuzin $K_3 = 0$ also resulted in overestimated c values on these sampling dates. Taking double the standard K_3 value for both herbicides resulted in underestimated c values after 57 and 168 d, but results after 260 d were described reasonably.

The sensitivity to $k_{d,3}$ was checked by carrying out calculations with double the values as derived from experiment M. It was found for both herbicides that c values usually differed by only a few per cent and always differed by less than 10 % from the values calculated with the standard values. Thus, sensitivity to $k_{d,3}$ was again small.

Figure 8.12 shows results for experiment D for both herbicides. For the period 0-90 d, c values as measured ½ h after wetting are compared with c values calculated immediately after wetting. Figure 8.12 shows that measured c values

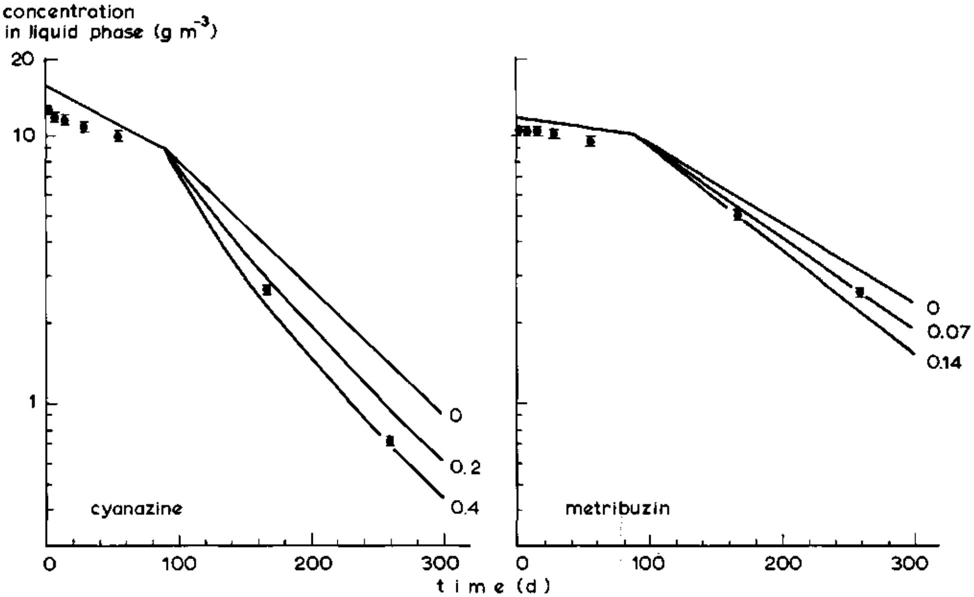


Figure 8.12. Herbicide concentration as a function of time in liquid phase in soil ½ h after rewetting (in period 0-90 d) and in continuously moist soil (in period after 90 d) in experiment D. Points are averages of measured concentrations, bars are standard deviations; ——, calculated with K_3 values (dm^3 kg^{-1}) as indicated.

were explained reasonably well with the K_3 values as derived from experiment M (0.2 and 0.07 dm^3 kg^{-1} for cyanazine and metribuzin, respectively): differences between measured and calculated values were usually between 10-20 %. However, differences were systematic: calculated values were nearly always higher than measured ones. Possibly, the model underestimates content sorbed at class-2 sites after the single drying cycle.

At all sampling dates in the period 0-90 d, c was measured also 24 h after rewetting the soil. The course of time of c in these 24 h was calculated in separate runs. For all sampling dates, calculated c values for a rewetting period of 24 h were, for cyanazine and metribuzin respectively, 92 % and 96-97 % of those calculated for a period of ½ h. Figures of 95 % (s = 3 %) for cyanazine and 99 % (s = 3 %) for metribuzin were measured. Again, the model accurately simulated the sorption kinetics in the soil that had been rewetted.

The sensitivity of calculated c values to K_3 was investigated: calculations were done with K_3 = 0 and with double the values derived from experiment M. Figures 8.11 and 8.12 show that using K_3 = 0 for both herbicides resulted in too high c values after 168 and 260 d. Taking double the standard K_3 value resulted in calculated c values that corresponded equally well with the measurements as those calculated with the standard values. It was concluded that the course of time of concentrations in liquid phase in experiments M/D and D was explained reasonably well by the three-site model based on previous measurements.

8.3.4.5 Description of contents still sorbed after the first extraction with ethyl acetate

In the field experiments, the herbicide contents in soil were derived from a single extraction with ethyl acetate (see Section 4.2.3). Thus, as a rule only $m^*_{r,1}$ values were measured. In view of the results shown in Table 8.1 and Figure 8.4, one may expect that, with the exception of those measured 1 d after application, these contents did not represent the total contents in soil. Consequently, total contents in soil during the field experiments were not known. Because the calculation of the concentration of herbicide in liquid phase in field soil could only be based on the content released by a single extraction, it was necessary to estimate that part of X_3 that is still sorbed after the first extraction with ethyl acetate, i.e. $X_{3,sf}$ (kg kg^{-1}). It was assumed as a first approximation that $X_{3,sf}$ is a constant fraction of X_3:

$$X_{3,sf} = \Phi \; X_3 \tag{8.44}$$

in which

Φ is fraction of X_3 still sorbed after first extraction with ethyl acetate (1)

Thus, the content sorbed at class-3 sites that is released by the first extraction with ethyl acetate, $X_{3,f}$ (kg kg^{-1}), is given by

$$X_{3,f} = (1 - \Phi) \; X_3 \tag{8.45}$$

An attempt was made to derive estimates for Φ from the three-fold extractions with ethyl acetate shown in Figure 8.3. $X_{3,sf}$ was assumed to be equal to that fraction of $m^*_{r,2}$ that exceeded 4 % of the corresponding $m^*_{r,1}$ value (see Section 8.3.4.1; $m^*_{r,3}$ was not taken into account as it was still an order of magnitude lower than $m^*_{r,2}$). The resulting $X_{3,sf}$ values shown in Figure 8.13 are only rough estimates: the correction of 4 % of the $m^*_{r,1}$ value was usually larger than the $X_{3,sf}$ value found (see Figure 8.4).

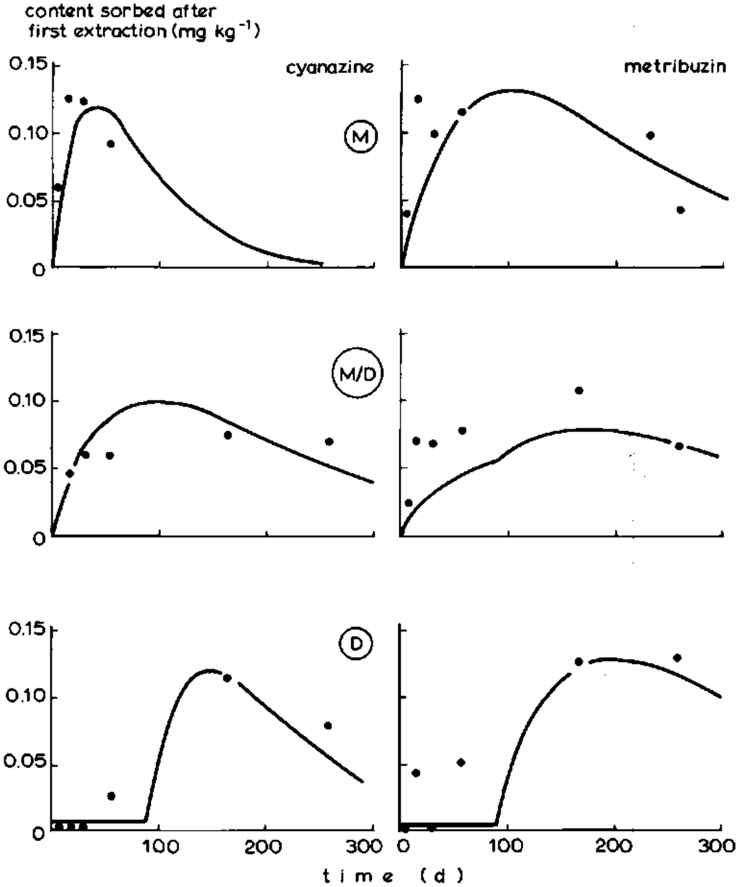


Figure 8.13. Content still sorbed after the first extraction with ethyl acetate, $X_{3,sf}$, as a function of time in long-term sorption experiments in the laboratory. Points are averages of measured contents; ——, calculated with Equations 8.2 and 8.44.

For experiment M, course of time of $X_{3,sf}$ can be calculated from the analytical solution of the sorption rate equation as given by Equations 8.20 and 8.44. In this solution, $X_{3,sf}$ is directly proportional to Φ. Thus, Φ can be easily estimated. Figure 8.13 shows $X_{3,sf}$ as calculated with $\Phi = 0.15$ for cyanazine and $\Phi = 0.4$ for metribuzin: using this value, measured $X_{3,sf}$ values were described well.

For experiments M/D and D, course of time of c was calculated with the three-site model as described in Section 8.3.4.4, using K_3 values of 0.2 and 0.07 dm^3 kg^{-1} for cyanazine and metribuzin, respectively. $X_{3,sf}$ was calculated from calculated X_3 values with Equation 8.44 using the Φ values derived from experiment M. Figure 8.13 shows that this resulted in an acceptable description of the measured $X_{3,sf}$ values. Only the $X_{3,sf}$ values for metribuzin in experiment M/D were systematically underestimated. A Φ value of about 0.6 would have given a good description.

It was concluded that measured $X_{3,sf}$ values in all experiments were described reasonably well with Φ values of 0.15 for cyanazine and 0.4 for metribuzin. As the Φ value found for cyanazine is smaller than that found for metribuzin, the extraction with ethyl acetate of herbicide sorbed at class-3 sites is obviously more efficient for cyanazine than for metribuzin.

8.4 GENERAL DISCUSSION

Because sorption kinetics at class-3 sites were measured in a moist-soil system only, it cannot be derived directly from the measurements whether physical or chemical non-equilibrium processes were rate-determining for the rate of change in X_3. As described in Section 7.3.3.2, the values of $k_{d,2}$ in moist soil are probably determined by a diffusion barrier in the external liquid phase. Because the $k_{d,3}$ values found are still an order of magnitude smaller than the $k_{d,2}$ values found for moist soil, it is improbable that diffusion in the external liquid phase is rate-limiting for sorption at class-3 sites. Thus it can be expected that $k_{d,3}$ values for a moist-soil system and a soil-suspension system are equal. Consequently, it can be expected that the value of $k_{d,3}$ is mainly determined by a chemical non-equilibrium process. In further research it would be interesting to check whether $k_{d,3}$ values in moist-soil systems are equal to those in soil-suspension systems.

The values of K_3 of both herbicides were compared with the K_1 and K_2 values as estimated for the range of c in experiment M with an approximation similar to Equation 8.16. For cyanazine, K_1 was estimated to be 0.37 dm^3 kg^{-1} and K_2 0.16 dm^3 kg^{-1}; the corresponding figures for metribuzin were 0.18 and 0.07 dm^3 kg^{-1}. Thus, for both cyanazine and metribuzin the K_3 value found was roughly equal to the K_2 value and to half the K_1 value. Because K_3 values roughly equalled the K_2 values it is possible that the location of class-2 sites at the sorbent surface is identical to that of class-3 sites. The concept for X_3 is then that class-3 sorbate molecules are formed out of class-2 sorbate molecules via rearrangement in situ. The experiments in Chapter 7 have not proved unambiguously that class-2 sites are internal sites: it remains possible that it is not diffusion into the internal liquid phase that is rate-determining for sorption at class-2 sites, but an energetic barrier. However, it is speculative to base the hypothesis of formation of class-3 sorbate out of class-2 sorbate inductively on the fact that K_3

values roughly equal K_2 values.

As shown by the calculation in Section 7.3.3.1, in all experiments the contents sorbed were orders of magnitude smaller than those corresponding to the sorbent surface being completely occupied by a monolayer of herbicide molecules. This low degree of occupancy prevents any conclusion about where the class-3 sorbate is actually located.

In the three-site model the sorption sites are divided into three types of sites with different kinetic properties. Such a division is, perforce, schematic: in real life one would expect the distribution of the kinetic properties of sorption sites in soil to be more or less continuous. However, use of a model with a continuous distribution of kinetic properties of sorption sites would lead to a degree of refinement (coupled with a number of additional parameters!) that does not seem justified in view of our limited knowledge of the processes involved.

As described in Walker's review (1980), the activity of soil-applied herbicides against weeds is often insufficient if cumulative rainfall in the first weeks after application is low. A number of data obtained by Mercer & Hill (1975) and by Hance & Embling (1979) indicated that a single drying cycle of the soil may result in a large increase of sorption coefficients being found after dry soil is rewetted (see Section 8.1). Their results suggest that low herbicide concentrations in the liquid phase of rewetted soil could be the main cause of poor weed control after a low cumulative rainfall in the first weeks after application. However, results from the present study indicate that a drying cycle has almost no influence on the sorption coefficients found after rewetting (see Figure 8.6), so this phenomenon does not always contribute to the low efficacy under low-rainfall conditions.

9 FIELD TEST OF A NON-EQUILIBRIUM TRANSPORT MODEL

9.1 MATHEMATICAL DESCRIPTION OF NON-EQUILIBRIUM TRANSPORT MODEL

In this chapter a new transport model based on the results of the studies reported in Chapters 7 and 8 is formulated. This model is used in an attempt to explain the results of the field experiments on herbicide transport described in Chapter 4.

Only the sorption part of the new model is different from the equilibrium transport model used in Chapter 6. Therefore, transport of bromide ion (which is not sorbed) will be ignored here.

The new model may be classified as a non-equilibrium transport model. Its basis is the mass conservation equation for the substance (Equation 2.1; see Table 9.1). In the model, the mass concentration of substance in the soil system,

Table 9.1. Set of equations used in transport model with three-site sorption sub-model.

$\frac{\partial c^*}{\partial t} = - \frac{\partial J}{\partial z} - R_t$	(2.1)
$c^* = \theta\ c + \rho_b(X_1 + X_2 + X_3)$	(9.1)
$X_1 = K_{F,1}\ c^{1/n}$	(7.18)
$\frac{\partial X_2}{\partial t} = k_{d,2}(K_{F,2}\ c^{1/n} - X_2)$	(7.25)
$\frac{\partial X_3}{\partial t} = k_{d,3}(K_3\ c - X_3)$	(8.2)
$c_f^* = c^* - \rho_b\ \Phi\ X_3$	(9.2)
$J = J^V c - (D_{dis} + D_{dif}) \partial c / \partial z$	(2.2)
$D_{dis} = L_{dis}\ \lvert J^V \rvert$	(2.3)
$D_{dif} = \lambda\ \theta\ D_0$	(2.4)
$R_t = k_{t,1}\ \theta\ c$	(9.3)

c^*, is described by

$$c^* = \theta\ c + \rho_b(X_1 + X_2 + X_3) \tag{9.1}$$

Content sorbed at class-1 sites, X_1, is assumed to be in equilibrium with the concentration in liquid phase, c (Equation 7.18). Contents sorbed at class-2 and class-3 sites (X_2 and X_3) are calculated from their sorption rate equations (Equations 7.25 and 8.2).

Because concentrations in the field were measured after single extraction with ethyl acetate (see Section 4.2.3), results of calculations could not be compared with measured values of c^* but only with measured values of c_f^*, the concentration (kg m^{-3}) released by single (first) extraction with ethyl acetate. The latter can be calculated from c^* with help of the fraction Φ defined in Section 8.3.4.5:

$$c_f^* = c^* - \rho_b\ \Phi\ X_3 \tag{9.2}$$

In the model, the mass flux of substance, J, was described with the same set of equations as in the equilibrium model (Equations 2.2 to 2.4).

It is assumed in the model that the volumic mass rate of transformation, R_t, is proportional to that fraction of c^* that is present in the liquid phase in soil, i.e. $\theta\ c$:

$$R_t = k_{t,l}\ \theta\ c \tag{9.3}$$

This assumption is consistent with the sorption rate equations for class-2 and class-3 sites (Equations 7.25 and 8.2) which imply that no transformation takes place at the sorption sites.

The initial condition and the boundary conditions at the soil surface and at 0.4 m depth are equal to those used in Chapter 6 (Equations 6.7 to 6.11).

The volume flux of liquid, J^V, and the volume fraction of liquid, θ, were simulated with the model for water flow as described in Sections 5.2 and 5.6.

9.2 ESTIMATION OF VALUES OF PARAMETERS

It was assumed that the soil bulk density varied with depth as in Chapter 6. The bulk density profiles were derived from the averages of the profiles measured for both years, as shown in Figure 6.1.

Values for $K_{F,1}$ and $K_{F,2}$ were assumed to be equal to the values given in Table 7.7 for initially moist soil. Values for $1/n$ were taken from Table 6.5. It was assumed, as in Section 8.3.2, that $k_{d,2}$ and $k_{d,3}$ have a constant positive value for $\theta \geqq 0.04$ m^3 m^{-3} and that they are zero for $\theta < 0.04$ m^3 m^{-3}. The values for $k_{d,2}$ for $\theta \geqq 0.04$ m^3 m^{-3} were taken from Table 7.4. Values for $k_{d,3}$ for $\theta \geqq 0.04$ m^3 m^{-3} and for K_3 were taken from Section 8.3.4.3: for cyanazine $k_{d,3} = 0.02$ d^{-1}, $K_3 = 0.2$ dm^3 kg^{-1}; for metribuzin $k_{d,3} = 0.01$ d^{-1}, $K_3 = 0.07$ dm^3 kg^{-1}. Values for Φ were taken from Section 8.3.4.5 (0.15 for cyanazine and 0.4 for metribuzin).

The value for the dispersion length, L_{dis}, was taken to be 8 mm, as derived from the measurements of bromide ion (Figure 6.8).

Values for the diffusion coefficient of cyanazine and metribuzin in the liquid phase in soil, D_{dif}, were estimated as described in Section 6.2.

As in Chapter 6, a descriptive model was used for the simulation of the transformation rate, R_t. As in Section 6.1, this model was based on the acceptable description of the measurements shown in Figure 4.11 by exponential equations. A complication is that the areic masses shown in Figure 4.11 were measured after single extraction with ethyl acetate. Thus, in the context of the non-equilibrium model the measurements shown in Figure 4.11 have to be re-interpreted as measurements of the quantity σ_f^* (kg m^{-2}), i.e. the areic mass of substance in the soil system released by the first extraction with ethyl acetate. The definition of σ_f^* reads

$$\sigma_f^* \equiv \int_0^Z c_f^* \, dz' \qquad (9.4)$$

Figure 4.11 shows that measured declines of σ_f^* approximately satisfy a first-order rate equation:

$$\frac{d\sigma_f^*}{dt} = - k_{dec} \, \sigma_f^* \qquad (9.5)$$

The rate coefficient for transformation in the liquid phase, $k_{t,l}$, can then be estimated as follows. Equations 2.1, 9.2 and 9.3 can be rearranged to

$$k_{t,l} \; \theta \; c = - \frac{\partial \, (c_f^* + \rho_b \, \Phi \, X_3)}{\partial t} - \frac{\partial J}{\partial z} \qquad (9.6)$$

It was assumed that $k_{t,l}$ was constant with depth. Integration of Equation 9.6 with respect to depth in soil, z, then results in

$$k_{t,1} \int_0^Z \theta \;\; c \; dz' = - \int_0^Z \frac{\partial(c_f^* + \rho_b \;\Phi\;\; X_3)}{\partial t} \; dz' - \int_0^Z \frac{\partial J}{\partial z'} \; dz' \qquad (9.7)$$

Integration of the second term on the right-hand side of Equation 9.7 yields

$$\int_0^Z \frac{\partial J}{\partial z'} \; dz' = J(Z) - J(0) \qquad (9.8)$$

$J(Z)$ can be made negligible for a certain period by taking Z large enough. The influx at the surface, $J(0)$, is only important during the period in which the substance dissolves at the soil surface. As this period is probably a negligible fraction of the total period, it is assumed that the integral given in Equation 9.8 vanishes; thus it can be derived from Equations 9.4, 9.5, and 9.7 that $k_{t,1}$ can be estimated from

$$k_{t,1} = \int_0^Z \{k_{dec} \; c_f^* - \frac{\partial(\rho_b \;\Phi\;\; X_3)}{\partial t}\} \; dz' \Big/ \int_0^Z \theta \;\; c \; dz' \qquad (9.9)$$

Values of k_{dec} were derived from Figure 4.11 with a least-squares linear regression approximation as described in Section 4.3. The values obtained for cyanazine in 1981 and 1982 were 0.040 and 0.033 d^{-1}, respectively; for metribuzin a value of 0.032 d^{-1} was obtained.

The calculation method for $k_{t,1}$ (Equation 9.9) is artificial: its only justification is that it describes the data well. The right-hand side of Equation 9.9 is a function of time and therefore the estimated values of $k_{t,1}$ are also a function of time. Values of $k_{t,1}$ for cyanazine, as estimated from Equation 9.9, usually ranged between 0.1 and 1 d^{-1}. Values for metribuzin usually ranged between 0.1 and 0.2 d^{-1}.

For cyanazine, values of the concentration at which the substance dissolves, c_{sol}, were estimated to be 0.08 kg m^{-3} in 1981 and 0.04 kg m^{-3} in 1982; for metribuzin a value of 0.3 kg m^{-3} was estimated (see Section 6.2).

The doses of cyanazine were estimated to be 0.048 g m^{-2} in 1981 and 0.149 g m^{-2} in 1982; for metribuzin a value of 0.096 g m^{-2} was estimated (see Section 6.2).

9.3 NUMERICAL SOLUTION OF THE MASS CONSERVATION EQUATION

The mass conservation equation of the non-equilibrium transport model (Equation 2.1 in Table 9.1) was solved in c^* with an explicit finite-difference method.

To do this a rectangular grid of points numbered $i = 1, 2, 3, \ldots$ along the z axis and numbered $j = 0, 1, 2, \ldots$ along the t axis is defined in the (z,t) plane. Downward direction of z is assumed to be positive. Δz_i is defined as the thickness of a compartment around point i (see Figure 6.4). Δt is defined as the time step.

To be able to approximate the right-hand side of Equation 2.1, values of c have to be derived from known values of c^*. Rearranging Equations 9.1 and 7.18 yields an implicit equation in c similar to Equation 6.18:

$$c = \{c^* - \rho_b(X_2 + X_3)\} / \{\theta + \rho_b\, K_{F,1}\, c^{(1/n)-1}\} \tag{9.10}$$

Values of c at grid point (i,j), $(c)_i^j$, were calculated from Equation 9.10 by iteration, using known values of the remaining variables at grid point (i,j). The procedure to estimate initial guesses of $(c)_i$ and the regulation of the number of iterations were the same as described in Section 6.3.

The sorption rate equations in the model (Equations 7.25 and 8.2) were approximated by

$$\left(\frac{\partial X_2}{\partial t}\right)_i^j = k_{d,2}\left[K_{F,2}\ \{(c)_i^j\}^{1/n} - (X_2)_i^j\right] \tag{9.11}$$

$$\left(\frac{\partial X_3}{\partial t}\right)_i^j = k_{d,3}\{K_3\ (c)_i^j - (X_3)_i^j\} \tag{9.12}$$

The approximation of the concentration in soil released by the first extraction with ethyl acetate, c_f^*, was based on Equation 9.2:

$$(c_f^*)_i^j = (c^*)_i^j - (\rho_b)_i\ \Phi\ (X_3)_i^j \tag{9.13}$$

The mass flux of the substance, J, was approximated as described by Equations 6.20 to 6.23. For calculation of J at the boundaries of the system ($i = 1$ and $i = I$) Equations 6.25 and 6.26 were used.

Starting from Equation 9.3, the volumic mass rate of transformation, R_t, was approximated by

$$(R_t)_i^j = (k_{t,1})^j\ (\theta)_i^j\ (c)_i^j \tag{9.14}$$

The right-hand side of the mass conservation equation (Equation 2.1) was approximated as follows:

$$\left(\frac{\partial c^*}{\partial t}\right)_i^j = \{(J)_i^j - (J)_{i+1}^j\} / \Delta z_i - (R_t)_i^j \tag{9.15}$$

Equations 9.11, 9.12, and 9.15 were integrated with respect to time, t, using Euler's integration method as described for c^* by Equation 6.27.

The finite-difference approximations described, were programmed in the simulation language CSMP III (Speckhart & Green, 1976). Thicknesses of the compartments, Δz_i, were equal to those in the water flow model. The computer program is listed in Appendix G.

A numerical analysis of the finite-difference equations similar to that carried out in Chapter 6 (Appendix D) was not possible, because X_2 and X_3 cannot be eliminated from the set of equations in Table 9.1. The main difference between the set of equations in Table 6.1 and the set in Table 9.1 is that in Table 9.1 X_2 and X_3 are calculated by sorption rate equations. The numerical analysis in Chapter 6 showed that correction for numerical dispersion becomes only important at high liquid fluxes (Equation 6.39). However, at high liquid fluxes the time available for exchange of substance between the percolating liquid phase in soil and class-2 and class-3 sites is short. Then the model described in Table 9.1 behaves approximately as an equilibrium model with sorption at class-1 sites only. Values of the numerical dispersion length, L_{num}, for the model of Table 9.1 can thus probably be estimated from the following equation, which is analogous to Equation 6.39 and which takes into account equilibrium sorption at class-1 sites only:

$$L_{\text{num}} = \frac{|J^V| \, \Delta t}{2(\rho_b K_1 + \theta)} \tag{9.16}$$

If the sorption isotherm at class-1 sites is assumed to be linear, the finite-difference approximations described for the set of equations in Table 9.1 can be considered as a system with three dependent variables (c, X_2, X_3). Lapidus & Pinder (1982, pp. 176-177) described the general procedure for a von Neumann stability analysis of systems with more than one dependent variable. The stability requirement in such an analysis is derived from the condition that all eigenvalues of the so-called amplification matrix must have moduli less than or equal to 1. To be able to calculate the matrix, it had to be assumed that all soil properties are constant with depth and that sorption isotherms of class-1 and class-2 sites are linear (Equations 7.16 and 7.17). The amplification matrix found contains one complex element and only 2 of the 9 elements are zero. It is thus probably impossible to obtain an explicit analytical expression for the stability criterion. However, when numeric values of $k_{t,1}$, $k_{d,2}$, $k_{d,3}$, K_1, K_2, K_3, D_{dd}, θ, ρ_b, Δz, and J^V were substituted in the elements of the matrix, it could be shown numerically (using Gerschgorin's theorem; see e.g. Smith, 1969, p. 65) for both herbicides that the stability criterion reads

$$\frac{\Delta t \; D_{dd}}{(\Delta z)^2 \; (\rho_b \; K_1 + \theta)} < 0.50 \qquad (9.17)$$

Equation 9.17 is similar to the criterion found for the finite-difference approximation of Section 6.3 (Equation 6.35).

Time steps for periods in 1982 with J^V values below 10 mm d^{-1} were 0.1 d for cyanazine and 0.06 d for metribuzin. Time steps for periods in 1982 with J^V values above 10 mm d^{-1} were 0.025 d for cyanazine and 0.016 d for metribuzin. In 1981, the maximum J^V value was 15 mm d^{-1} and for the whole period a time step of 0.06 d was used.

Values of L_{num} were estimated from Equation 9.16 for the maximum J^V value (40 mm d^{-1}) and the time steps used. For both cyanazine and metribuzin a value of 0.8 mm was found. As the value for L_{dis} was 8 mm, correction for numerical dispersion was considered to be unnecessary.

The effect of the time step, Δt, on calculated concentrations was checked. Concentration profiles of cyanazine after infiltration of 20 mm of rain within 1 d were calculated with Δt = 0.025 d (the standard value) and with Δt = 0.0025 d. Calculated values of c^* for depths between 0 and 50 mm differed by only 0 to 3 %.

The way that J at the lower boundary of the soil system was calculated (Equation 6.26) was not important, because cumulative areic mass of substance calculated to be leached below 0.4 m depth was always smaller than 10^{-6} times the dose for both herbicides.

In the numerical solution a complication occurred with respect to Equation 9.11 for values of c^* that were many orders of magnitude smaller than values of practical significance. In compartments with such low c^* values, negative values of c occurred. This can be understood by calculating the time constant for an isolated soil compartment as given by Equation 7.33. If c approaches zero, the slope of the Freundlich sorption isotherm for class-2 sites goes to infinity. Thus, τ_{so} as calculated with Equation 7.33, goes to zero. For values of c between 1 and 10^{-3} g m^{-3}, values of τ_{so} were estimated to be in the range of 0.6 to 2 d for cyanazine and metribuzin. Thus, the time steps used in the computations were always smaller than those required for Equation 9.11 in compartments with c values of practical significance. To prevent negative c values, it was assumed that the sorption isotherm of class-2 sites was linear at c values below 10^{-4} g m^{-3}.

In the transport model summarized in Table 9.1 it is assumed that class-1 sites are continuously at sorption equilibrium (Equation 7.18). As described in Section 7.3.3.2, sorption kinetics at class-1 sites in moist soil could be described by a sorption rate equation (Equation 7.24) with values of $k_{d,1}$ of 150 to 180 d^{-1} (Table 7.4). One can consider Equation 7.18 in Table 9.1 as a numerical approximation of X_1 as calculated with the sorption rate equation. In a series of calculations it was tested whether the assumption of sorption equilibrium at class-1 sites was approximately valid. The calculations were based on the set of equations described in Table 9.2. It was assumed that bulk density and volume fraction of liquid were constant with depth and equal to 1.3 Mg m^{-3} and 0.25 m^3 m^{-3}, respectively. Calculations were carried out for cyanazine only, and values for $K_{F,1}$ and $k_{d,1}$ were taken from Tables 7.7 and 7.4 (0.24 $m^{3/n}$ $kg^{-1/n}$ and 150 d^{-1}, respectively). At the start of the calculations the dose of cyanazine (149 mg m^{-2}) was assumed to be present in the top compartment, which also initially had sorption equilibrium. Calculations were stopped after a water layer of 40 mm had infiltrated. The volume flux of liquid, J^V, was varied: in one run the value for J^V was 150 mm d^{-1} and in another it was 750 mm d^{-1}. In a third run with a J^V value of 750 mm d^{-1} it was assumed that X_1 was in equilibrium with c (Equation 7.18). The numerical solutions for the three runs were obtained with the computer program developed to solve the set of equations of Table 9.1 (see Appendix G). The soil system in the calculations consisted of 35 compartments with a constant value of Δz of 5 mm. The time step used was 0.0001 d.

If, in the model of Table 9.2 it is assumed that diffusion is negligible ($D_{dif} = 0$), only the parameters J^V and $k_{d,1}$ have time in their dimension. Consequent-

Table 9.2. Set of equations used in transport model with one-site sorption kinetics.

$$\frac{\partial c^*}{\partial t} = -\frac{\partial J}{\partial z}$$

$$c^* = \theta \; c + \rho_b \; X_1$$

$$\frac{\partial X_1}{\partial t} = k_{d,1}(K_{F,1} \; c^{1/n} - X_1) \tag{7.24}$$

$$J = J^V c - (D_{dis} + D_{dif}) \, \partial c/\partial z \tag{2.2}$$

$$D_{dis} = L_{dis} \; |J^V| \tag{2.3}$$

$$D_{dif} = \lambda \; \theta \; D_0 \tag{2.4}$$

ly, a calculation is characterized by the quotient $J^V/k_{d,1}$, which has the dimension of length. The results (Figure 9.1) show that the concentration profile calculated with values of $J^V/k_{d,1}$ of 1 mm or 5 mm differed only slightly from that calculated with the assumption of sorption equilibrium ($J^V/k_{d,1} = 0$). Figure 4.3 showed that hourly averages of the volume flux of rainfall were always smaller than 300 mm d^{-1}, which corresponds with a quotient of $J^V/k_{d,1}$ of 2 mm. Furthermore, the value used for $k_{d,1}$ was a lower limit (see Section 7.3.3.2), so it was concluded that the assumption of sorption equilibrium at class-1 sites was justified.

9.4 RESULTS OF FIELD TEST AND DISCUSSION

9.4.1 Comparison between measured and calculated results

Usually only measurements of concentrations released by the first extraction with ethyl acetate, c_f^*, were available from the field experiments. Consequently, results of calculations to be shown are always expressed in c_f^* values as derived from Equation 9.2.

Figure 9.2 compares measured and calculated concentration profiles for cyanazine in 1981. The model slightly overestimated the transport at all sampling dates. The results for cyanazine in 1982 (Figure 9.3) show that the model again slightly overestimated transport after 14, 34 and 56 d. After 121 d, measured and calculated concentration profiles corresponded reasonably. Figure 9.4 shows

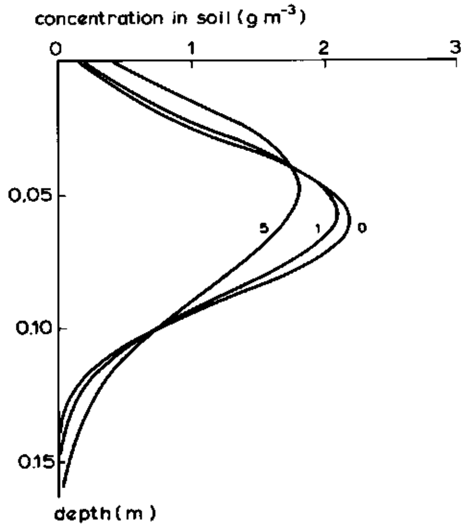


Figure 9.1. Effect of the quotient of $J^V/k_{d,1}$ on the concentration profile of cyanazine as calculated with a transport model with one-site sorption kinetics. Values of $J^V/k_{d,1}$ are indicated in mm.

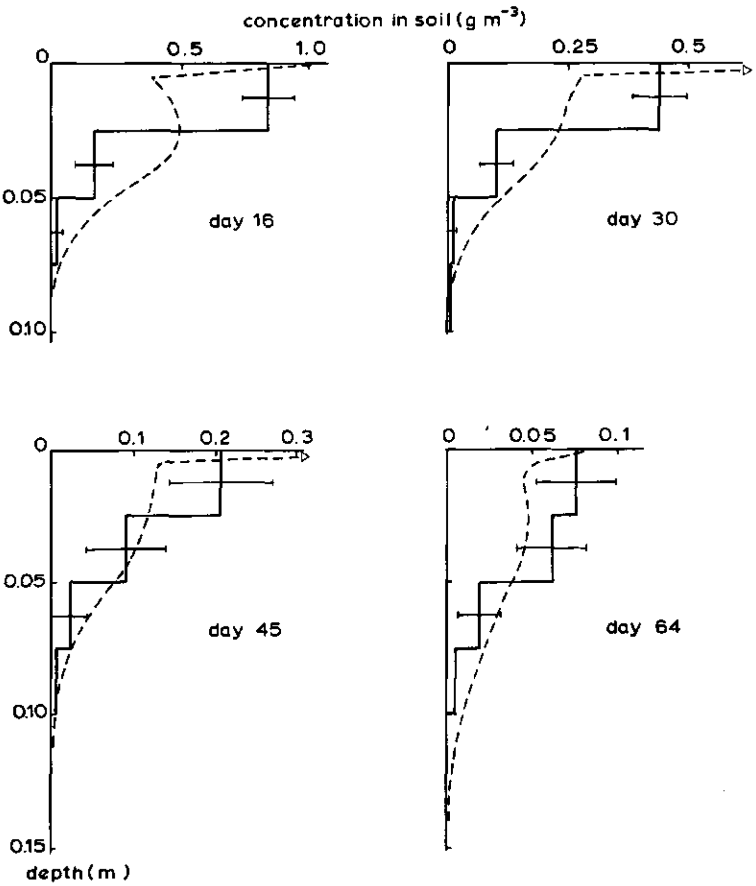


Figure 9.2. Comparison of calculated and measured cyanazine concentration profiles in 1981. Vertical solid line segments indicate averages of measured concentrations, horizontal bars standard deviations; ---, calculated.

the results for metribuzin: at all sampling days (except after 1 d) the model slightly overestimated the transport.

The model was also tested against the results of desorption measurements shown in Figure 8.1. Measured values of $X_{3,f}$ (i.e. the content sorbed at class-3 sites released by first extraction with ethyl acetate; see Section 8.3.4.5) after 121 d were derived from the desorption points by assuming that contents sorbed at class-1 and class-2 sites were at equilibrium with the concentration in liquid phase. This was justified in view of the equilibration period of 17 h used in the desorption experiments with soil sampled after 121 d (the equilibration period in the experiments with soil sampled after 56 d was 1 h, and therefore these were

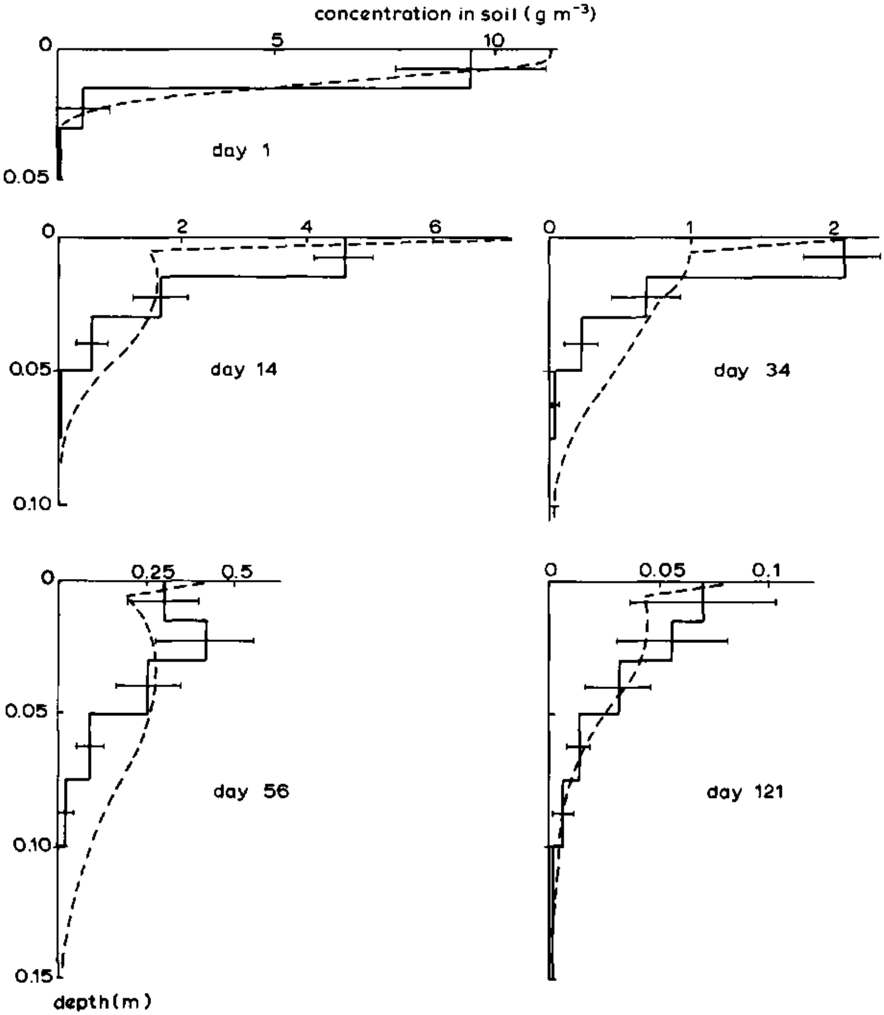


Figure 9.3. Comparison of calculated and measured cyanazine concentration profiles in 1982. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated.

ignored). Calculated values of $X_{3,f}$ were derived from calculated X_3 values, using Equation 8.45. The results in Table 9.3 show that calculated and measured values of $X_{3,f}$ corresponded reasonably. Only for cyanazine in the 30 to 50 mm layer was the discrepancy much larger than the standard deviation of the measured value. In view of the inaccurate determination of the values of $k_{d,3}$, K_3 and Φ from the laboratory experiments, the correspondence between measured and calculated values was considered to be satisfactory.

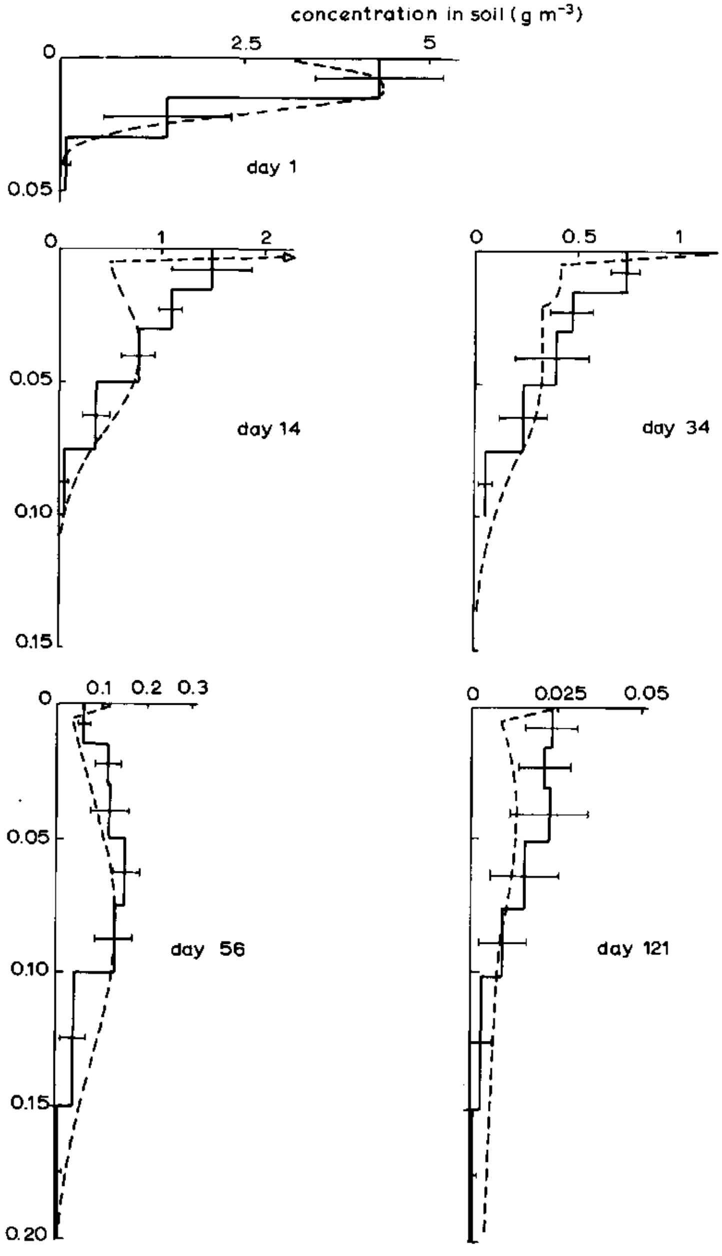


Figure 9.4. Comparison of calculated and measured metribuzin concentration profiles in 1982. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations; ---, calculated.

Table 9.3. Comparison of calculated and measured values of content sorbed ($\mu g\ kg^{-1}$) at class-3 sites released by the first extraction with ethyl acetate, $X_{3,f}$, after 121 d in the field experiment in 1982. Figures in parenthesis are standard deviations.

Layer between depths (mm)	Cyanazine		Metribuzin	
	calculated	measured	calculated	measured
0 - 15	35	32 (9)	7	11 (3)
30 - 50	23	12 (4)	7	10 (4)

The model could also be tested using the results of the measurements with successive extractions, presented in Table 8.1. The content still sorbed at class-3 sites after the first extraction with ethyl acetate ($X_{3,sf}$) after 56 d was estimated from the results in Table 8.1. For this purpose it was assumed that the content recovered by the threefold extraction with ethyl acetate represented total content of herbicide in soil for the 0 to 15 mm layer. For the estimation of total content in the 30 to 50 mm layer it was assumed that the ratio between contents released by the second and third extractions was equal to that of the 0 to 15 mm layer. Calculated values of $X_{3,sf}$ were derived from calculated X_3 values, using Equation 8.44. The results in Table 9.4 show that for cyanazine and metribuzin the calculated values of $X_{3,sf}$ were about 30 % and 50 % of the measured values, respectively. However, the measurements were not very accurate: standard deviations were estimated to be 50-70 % of the averaged measured values.

It was concluded that both the transport of the two herbicides in field soil and the distribution of the herbicides over solid and liquid phase in field soil were simulated adequately by the new model. Obviously, the three-site sorption sub-model developed is a major improvement over the sorption sub-model of the equilibrium transport model as applied in Chapter 6.

Table 9.4. Comparison of calculated and measured values of content sorbed ($\mu g\ kg^{-1}$) at class-3 sites still sorbed after the first extraction with ethyl acetate, $X_{3,sf}$, after 56 d in the field experiment in 1982. Figures in parenthesis are standard deviations.

Layer between depths (mm)	Cyanazine		Metribuzin	
	calculated	measured	calculated	measured
0 - 15	17	60 (30)	9	17 (8)
30 - 50	13	30 (20)	10	19 (10)

9.4.2 Sensitivity analysis of the model

Next, it seemed appropriate to consider the sensitivity of the calculated concentration profiles to the most important parameters in the model, bearing in mind the uncertainty in the estimations of these parameters. It is to be hoped that the sensitivity to most of the parameters will be small, as this makes it more attractive to use the model in future studies!

The sensitivity to the slope of the sorption isotherm of class-3 sites, K_3, was considered. For that purpose, additional calculations were made with $K_3 = 0$ and with twice the standard value for both herbicides (the same values as used in the calculations for Figures 8.11 and 8.12). Concentration profiles for cyanazine calculated with the three K_3 values practically coincided for sampling dates up to 45 d after application for both years. Concentration profiles for metribuzin calculated with the three K_3 values practically coincided for the sampling dates up to 56 d after application. Figure 9.5 shows the results of calculations with the various K_3 values for the remaining dates. Calculated concentration profiles at these dates were influenced strongly by the value of K_3 used. Figure 9.5 shows that,

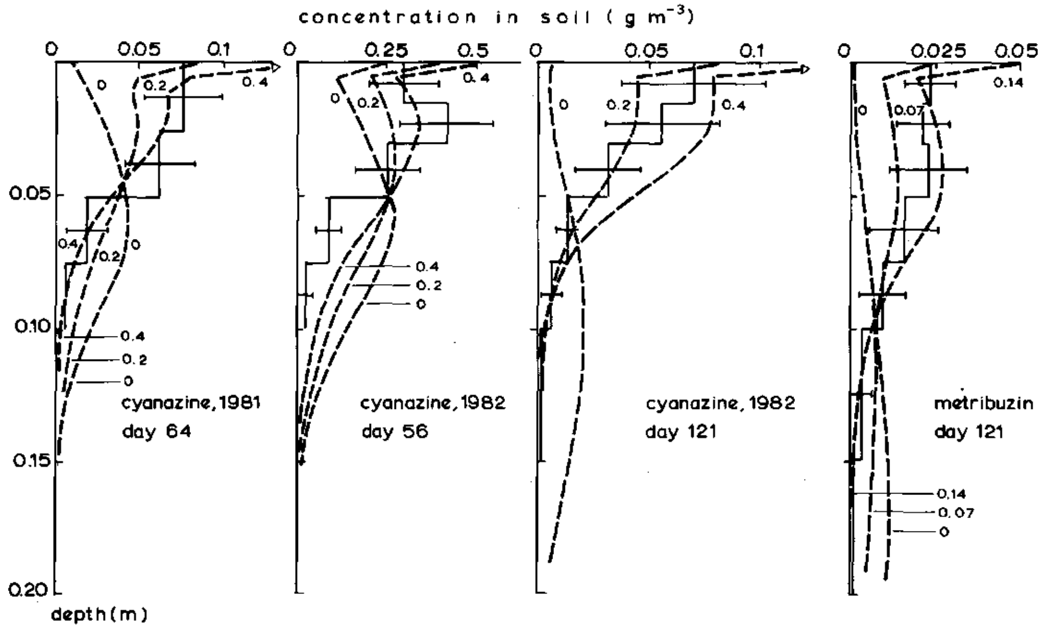


Figure 9.5. Sensitivity of calculated concentration profiles to the slope of the sorption isotherm of class-3 sites, K_3. Vertical solid line segments are averages of measured concentrations; horizontal bars are standard deviations. ---, calculated with K_3 values ($dm^3\ kg^{-1}$) as indicated.

for the sampling dates considered, the small discrepancies between the measured profiles and those calculated with the standard K_3 values, may be almost completely attributed to the uncertainty about the value of K_3.

For the calculations with twice the standard value of K_3 there was a complication in the simulation of the transformation rate. The complication arose because a high fraction of total areic mass of herbicide released by the first extraction with ethyl acetate was sorbed at class-3 sites at the end of the simulation period. For instance, for cyanazine after 100 d this fraction was 0.8. This made it impossible to require that each day about 3 % of total areic mass released by the first extraction with ethyl acetate is transformed because it was assumed that no transformation occurred at the sorption sites. The difficulty was overcome by limiting the rate coefficient for transformation in the liquid phase, $k_{t,1}$, to a maximum value of 1 d^{-1}. After 121 d this resulted in simulated areic masses of 150 % and 115 % of the averaged measured values for cyanazine and metribuzin, respectively. These deviations were accepted in view of the coefficients of variation of the measured areic masses of around 50 % (Figure 4.12).

Next, the sensitivity to the desorption rate constant of class-3 sites, $k_{d,3}$, was considered (values of $k_{d,3}$ refer to non-dry soil, i.e. $\theta > 0.04$ m^3 m^{-3}). Calculations were made for cyanazine in 1982 only. Results of calculated concentration profiles are shown in Figure 9.6 for 121 d only, because at that time the influence of sorption at class-3 sites was most pronounced. Figure 9.6 shows that there was only a small difference between concentration profiles calculated with zero $k_{d,3}$ and infinite $k_{d,3}$. This is not surprising, because in the calculations with infinite $k_{d,3}$, X_3 was only about 30 % of the sum of X_1 and X_2. The profiles calculated with zero and infinite $k_{d,3}$ differed largely from those calculated with the standard

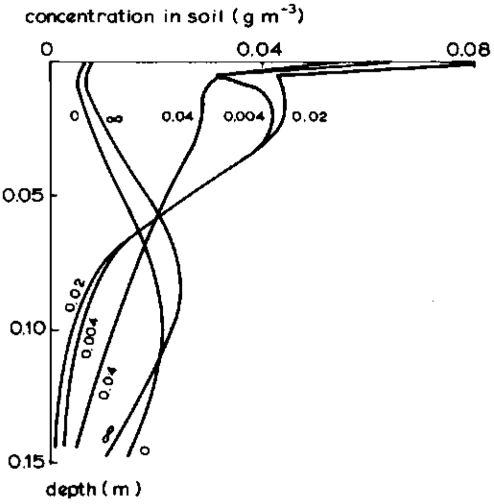


Figure 9.6. Effect of the desorption rate constant for class-3 sites, $k_{d,3}$, on the concentration profile of cyanazine calculated after 121 d in 1982. Values of $k_{d,3}$ are indicated in d^{-1}.

$k_{d,3}$ value (0.02 d^{-1}). The profile calculated with $k_{d,3} = 0.004\ d^{-1}$ differed only slightly from that calculated with $k_{d,3} = 0.02\ d^{-1}$. The profile calculated with $k_{d,3} = 0.04\ d^{-1}$ spread much wider than that calculated with $k_{d,3} = 0.02\ d^{-1}$.

The results in Figure 9.6 indicate that the non-equilibrium effect of sorption at class-3 sites is the main cause for the large discrepancy between measured concentration profiles and the profiles calculated with the equilibrium model of Chapter 6. This is further illustrated by Figure 9.7, which shows the effect of $k_{d,3}$ on the calculated course of time of areic mass in the soil system sorbed at class-3 sites, σ_3 (kg m^{-2}), which is defined by

$$\sigma_3 \equiv \int_0^Z \rho_b \, X_3 \, dz' \qquad (9.18)$$

Values of σ_3 as calculated after 120 d with $k_{d,3}$ values of 0.004 and 0.02 d^{-1} were almost equal to the total areic mass, σ^*, and were about an order of magnitude higher than σ_3 as calculated with infinite $k_{d,3}$.

The discovery (from Figures 9.6 and 9.7) that the non-equilibrium effect for X_3 had a large influence on calculated concentration profiles of cyanazine, raises the question of which factors determine this effect. In a first rough approach to assess these factors, a soil layer was considered in which the concentration in liquid phase decreases exponentially with time according to Equation 8.13 (this

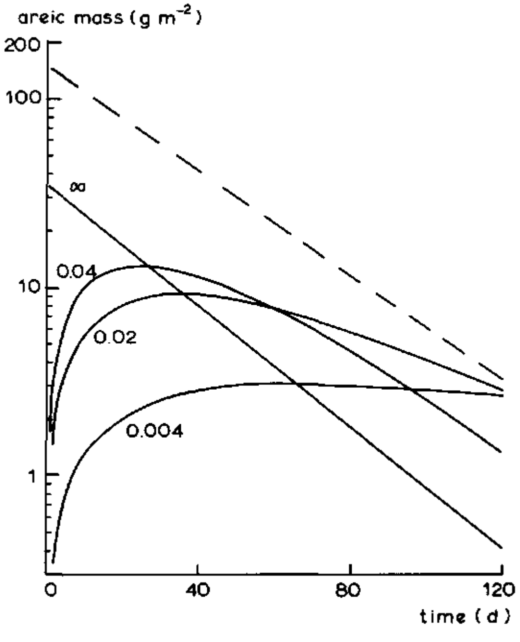


Figure 9.7. Effect of the desorption rate constant for class-3 sites, $k_{d,3}$, on areic mass of cyanazine in soil system calculated to be sorbed on class-3 sites as a function of time in 1982. ——, areic mass sorbed at class-3 sites for $k_{d,3}$ values (d^{-1}) as indicated; ---, total areic mass in soil system (calculated with $k_{d,2} = 0.02\ d^{-1}$).

exponential decrease could be, for instance, caused by transformation in the liquid phase and by leaching). The analytical solution of the sorption rate equation of X_3 (if initially zero) was already given as Equation 8.20. To describe the deviation of X_3 from its equilibrium value, the reduced content sorbed at class-3 sites, $\overline{X}_3$, is considered. $\overline{X}_3$ is defined as the ratio of the actual value of X_3 divided by the value of X_3 that is in equilibrium with the concentration in liquid phase, c. By analogy with Equation 8.28, the equation for $\overline{X}_3$ reads:

$$\overline{X}_3 = \frac{k_{d,3}}{k_{d,3} - k_c} \left[1 - \exp\{(k_c - k_{d,3})\ t\}\right] \tag{9.19}$$

Equation 9.19 shows that the course of time of $\overline{X}_3$ is mainly determined by the difference between k_c and $k_{d,3}$: if k_c is higher than $k_{d,3}$, $\overline{X}_3$ increases exponentially with time and has no limit. If k_c is smaller than $k_{d,3}$, $\overline{X}_3$ approaches the steady state value of $\{k_{d,3}/(k_{d,3} - k_c)\}$. Figure 9.8 shows $\overline{X}_3$ as calculated from Equation 9.19 for $k_{d,3} = 0.02\ d^{-1}$ and for a number of k_c values. An attempt was made to apply Equation 9.19 to the top compartment in the calculations with the transport model for cyanazine in 1982. The simulated decline of c in this compartment (i.e. $(c)_1$) could be described fairly well with Equation 8.13 with a k_c value of $0.057\ d^{-1}$. For this k_c value, $\overline{X}_3$ as calculated with Equation 9.19 with $k_{d,3} = 0.02\ d^{-1}$ was found to be 44 after 120 d, which corresponded well with the $\overline{X}_3$ value of 42 derived from the values of $(X_3)_1$ and $(c)_1$ simulated by the transport model after 120 d.

In the model, $k_{d,2}$ and $k_{d,3}$ are set at zero if the volume fraction of liquid, θ, decreases below $0.04\ m^3\ m^{-3}$ (see Section 8.3.2). To check the sensitivity to this assumption a calculation was carried out for cyanazine in 1982, in which it was assumed that $k_{d,2}$ and $k_{d,3}$ in dry soil were equal to the values found for

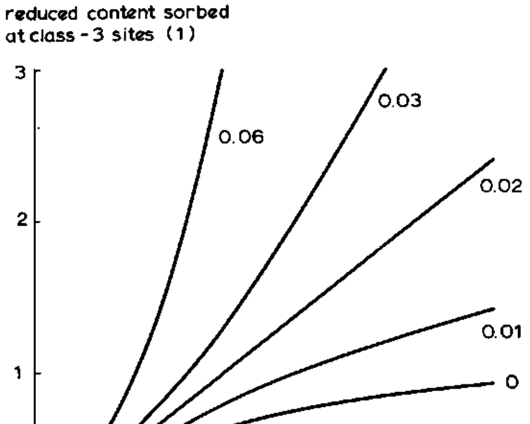


Figure 9.8. Reduced content sorbed at class-3 sites, $\overline{X}_3$, as a function of time as calculated with Equation 9.19 for $k_{d,3} = 0.02\ d^{-1}$ and for the k_c values (d^{-1}) as indicated.

moist soil. From the literature it is known that sorption (at fast-equilibrating sites) increases sharply if the soil becomes dry (see Section 8.1). Consequently, the concentration in liquid phase, c, becomes very low in dry soil. This was roughly approximated by setting c at zero in the calculations of the sorption rates at class-2 and class-3 sites (Equations 7.25 and 8.2 in Table 9.1) for $\theta < 0.04$ m^3 m^{-3}. Results for cyanazine (see Figure 9.9) show that the calculated concentration profile after 121 d differed only slightly from that calculated with the standard model.

The small discrepancy between calculated and measured concentration profiles in Figures 9.2, 9.3 and 9.4 could have been caused by a too high value for the dispersion length, L_{dis}. Therefore, calculations were made with a lower limit of 2 mm for the value of L_{dis}, as compiled from literature (Section 6.2). Results for both cyanazine and metribuzin (Figure 9.10) show that L_{dis} had only a moderate influence on calculated concentration profiles. Even with the low L_{dis} value, some discrepancy remained between calculated and measured profiles after 34 d.

As shown in Figures 9.2, 9.3 and 9.4, the model slightly overestimated movement at almost all sampling dates. This may be caused by too low values for the Freundlich sorption coefficients for class-1 and class-2 sites, $K_{F,1}$ and $K_{F,2}$. From results of experiments of Section 7.5 it can be derived that additives in the formulated products and concentration of salt had almost no influence on sorption in short-term experiments. On the other hand, in Section 7.5 it was shown that temperature had a distinct effect on the sum of $K_{F,1}$ and $K_{F,2}$. The results ob-

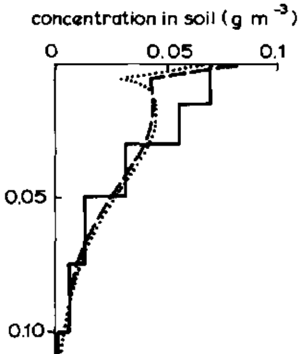


Figure 9.9. Effect of setting $k_{d,2}$ and $k_{d,3}$ to zero in dry soil on the concentration profile calculated for cyanazine after 121 d in 1982. ---, calculated with $k_{d,2} = k_{d,3} = 0$ for $\theta < 0.04$ m^3 m^{-3} (standard); ···, calculated with values of $k_{d,2}$ and $k_{d,3}$ that are constant with θ; ——, averages of measured concentrations.

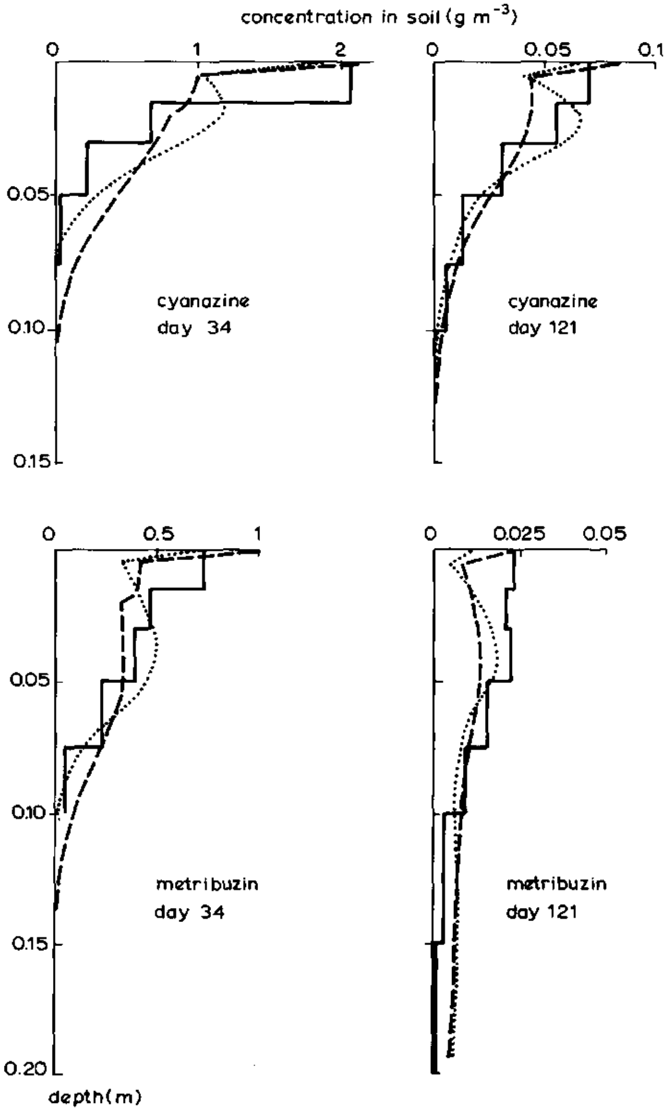


Figure 9.10. Effect of dispersion length, L_{dis}, on calculated concentration profiles in 1982. ---, calculated with L_{dis} = 8 mm (standard value); ·····, calculated with L_{dis} = 2 mm; ——, averages of measured concentrations.

tained implied that the sum of $K_{F,1}$ and $K_{F,2}$ increased by 3 % and 1 % per decrease of 1 °C, for cyanazine and metribuzin, respectively. It was also shown in Section 7.5 that the values of $K_{F,1}$ found for initially dry soil were about 30 % higher than the values found for initially moist soil (Figure 7.13 and Table 7.7).

To test the sensitivity to realistic changes in the $K_{\mathrm{F},1}$ and $K_{\mathrm{F},2}$ values, calculations were made with a model in which $K_{\mathrm{F},1}$ and $K_{\mathrm{F},2}$ were calculated by

$$K_{\mathrm{F},1} = (K^{\mathrm{d,r}}_{\mathrm{F},1} - K^{\mathrm{m,r}}_{\mathrm{F},1}) \exp\{-(t - t_{\mathrm{lw}})/\tau^{\mathrm{d,m}}\} + K^{\mathrm{m,r}}_{\mathrm{F},1}\{1 + C_T(T - 292)\} \tag{9.20}$$

$$K_{\mathrm{F},2} = K^{\mathrm{r}}_{\mathrm{F},2}\ \{1 + C_T(T - 292)\} \tag{9.21}$$

in which

$K^{\mathrm{m,r}}_{\mathrm{F},1}$, $K^{\mathrm{d,r}}_{\mathrm{F},1}$	are values of $K^{\mathrm{m}}_{\mathrm{F},1}$ and $K^{\mathrm{d}}_{\mathrm{F},1}$ at a temperature of 292 K	($\mathrm{m}^{3/n}$ $\mathrm{kg}^{-1/n}$)
t_{lw}	is time at last wetting event	(d)
C_T	is temperature coefficient of $K_{\mathrm{F},1}$	(K^{-1})
T	is soil temperature	(K)
$K^{\mathrm{r}}_{\mathrm{F},2}$	is value of $K_{\mathrm{F},2}$ found at a temperature of 292 K	($\mathrm{m}^{3/n}$ $\mathrm{kg}^{-1/n}$)

The exponential decline of the difference between $K^{\mathrm{m}}_{\mathrm{F},1}$ and $K^{\mathrm{d}}_{\mathrm{F},1}$ was taken from Equation 8.41. As in Equation 8.41, the value used for $\tau^{\mathrm{d,m}}$ was 7 d, which was derived from the decline shown in Figure 7.14. In the calculation procedure it was assumed that a soil layer became dry if its volume fraction of liquid decreased below 0.04 m^3 m^{-3}. In Equations 9.20 and 9.21 it is assumed that $K^{\mathrm{m}}_{\mathrm{F},1}$ and $K_{\mathrm{F},2}$ vary linearly with temperature.

Calculations were done for cyanazine and metribuzin in 1982 with values of the temperature coefficient C_T of -0.03 and -0.01 K^{-1}, respectively. In Equations 9.20 and 9.21 a reference temperature of 292 K was chosen, because this was the standard temperature (19 °C) of the sorption experiments. Soil temperature, T, was estimated as follows. As evaporation takes place mainly during the warmest hours (Figure 5.5), soil temperature was assumed to be equal to the daily maximum as measured at 50 mm depth on days on which evaporation exceeded rainfall. In 1982, only 20 % of the rain fell between 9.00 and 18.00 h. Thus it was reasonable to assume that on days on which rainfall exceeded evaporation, soil temperature was equal to the minimum temperature measured at 50 mm depth.

Results of calculations for cyanazine (Figure 9.11) show that using Equations 9.20 and 9.21 had a moderate effect on calculated profiles. Figure 9.11 shows that the more realistic estimation of $K_{\mathrm{F},1}$ and $K_{\mathrm{F},2}$ via Equations 9.20 and 9.21 removed almost completely the discrepancy between the measured profiles and

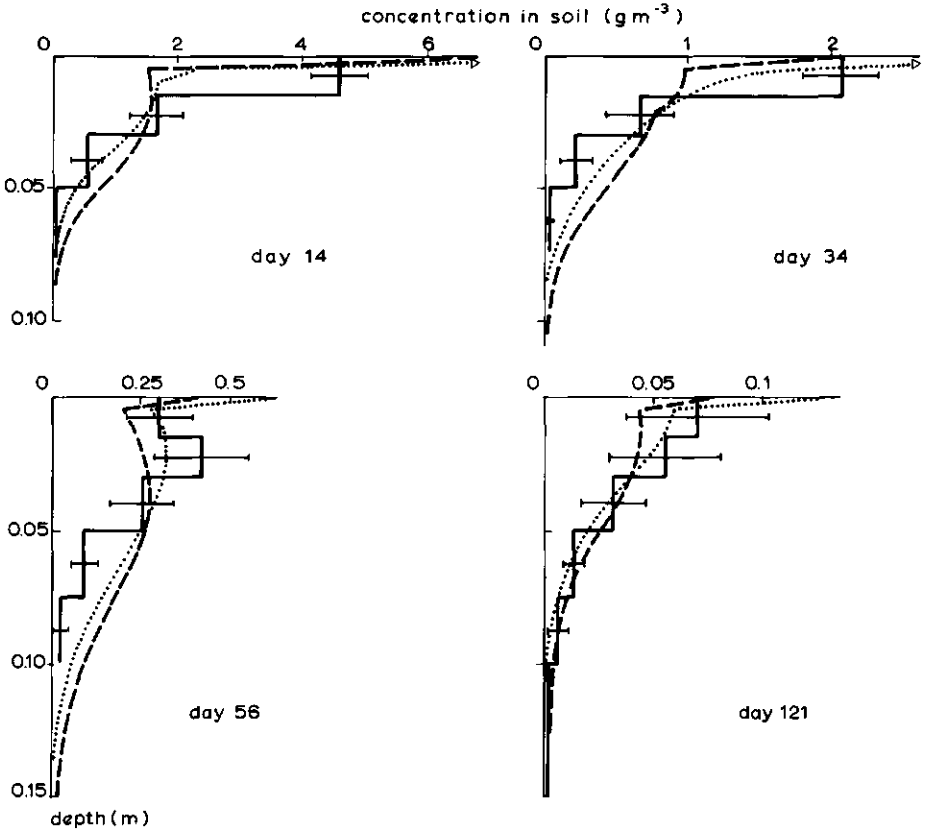


Figure 9.11. Calculated effect of soil temperature and volume fraction of liquid, via $K_{F,1}$ and $K_{F,2}$, on concentration profiles of cyanazine in 1982. ---- , calculated with standard values for $K_{F,1}$ and $K_{F,2}$; ·····, calculated with $K_{F,1}$ and $K_{F,2}$ as estimated from Equations 9.20 and 9.21; vertical solid line segments are averages of measured concentrations, horizontal bars are standard deviations.

those calculated with constant $K_{F,1}$ and $K_{F,2}$ (the standard procedure). Results for metribuzin (Figure 9.12) show that use of Equations 9.20 and 9.21 had only a small influence on calculated profiles.

In the model, daily averages of the volume fluxes of rainfall and evaporation were used. Actual rainfall fluxes were, of course, much higher than the daily averages. Consequently, volume fluxes of liquid in the uppermost centimetres in soil may have been much higher than calculated with the model. The sensitivity to a more detailed input for the volume flux of liquid at the soil surface was investigated in calculations in which 3 h-averages of rainfall were used and in which potential evaporation flux was calculated with Equation 5.22. Actual evaporation

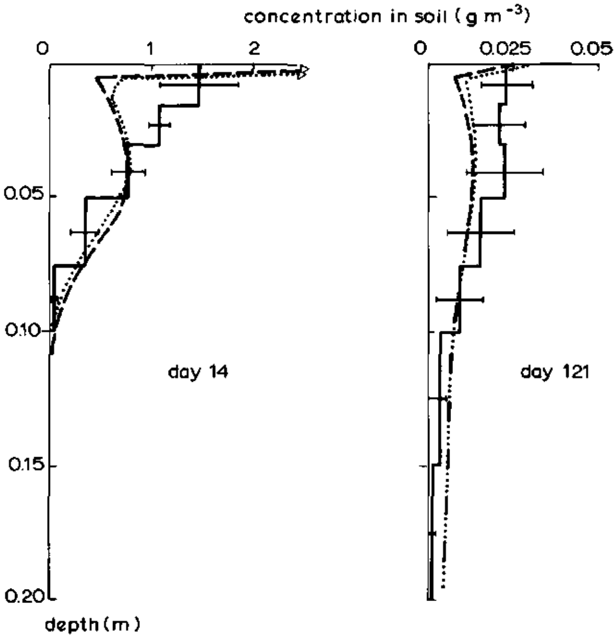


Figure 9.12. Calculated effect of soil temperature and volume fraction of liquid, via $K_{F,1}$ and $K_{F,2}$, on concentration profiles of metribuzin in 1982. ---, calculated with standard values for $K_{F,1}$ and $K_{F,2}$; ·····, calculated with $K_{F,1}$ and $K_{F,2}$ as estimated from Equations 9.20 and 9.21; vertical solid line segments are averages of measured concentrations, horizontal bars are standard deviations.

flux was calculated with the evaporation model described in Section 5.5 and Appendix C. Calculations were made for cyanazine in 1982 only. Results (Figure 9.13) show that concentration profiles calculated with the more detailed (and more realistic) volume flux of liquid at the soil surface almost coincided with profiles calculated with daily averages of the flux: the former profiles were somewhat more spread than the latter.

One may speculate whether the use of a sorption rate equation for class-2 sites had a large influence on calculated movement. This was checked as follows: concentration profiles calculated with a model with only class-1 and class-2 sites (i.e. the three-site model with $K_3 = k_{d,3} = 0$ and with $k_{d,2} = 0.4\text{-}0.5\ d^{-1}$) were compared with profiles calculated with the equilibrium model of Chapter 6. In the equilibrium model no distinction is made between the two classes of site , and the sum of the sorption isotherms of the two classes of site is used ($k_{d,2} = \infty$). Results for cyanazine in 1982 (Figure 9.14) show that the differences in calculated concentration profiles were small: the model with $k_{d,2} = 0.5\ d^{-1}$ resulted in a con-

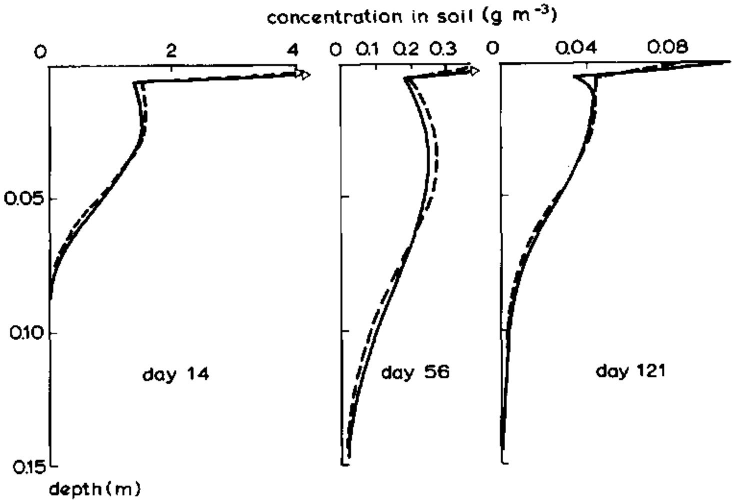


Figure 9.13. Concentration profiles calculated for cyanazine in 1982 with daily averages of the volume flux of liquid at the soil surface (dashed lines) compared with profiles calculated with 3 h-averages of the volume flux of rainfall and with volume fluxes of evaporation as derived from the model in Appendix C (solid lines).

centration profile exhibiting more spread. For metribuzin (not shown) a similar result was found.

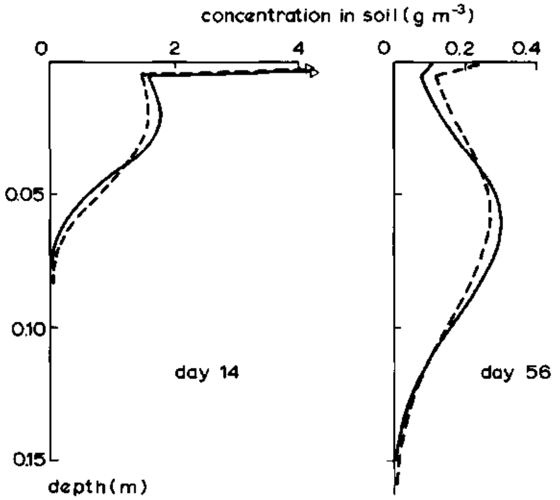


Figure 9.14. Concentration profiles calculated for cyanazine in 1982 with a model with class-1 and class-2 sites ($k_{d,2}$ = 0.5 d^{-1}; dashed lines) compared with profiles calculated with the equilibrium model described in Chapter 6 ($k_{d,2} = \infty$, solid lines).

The three-site sorption model as applied in this chapter accounts for herbicide molecules still sorbed after the first extraction with ethyl acetate. It was checked whether this had a large influence on calculated concentration profiles. This was done for metribuzin only, because the fraction of X_3 still sorbed after the first extraction with ethyl acetate, Φ, was larger for metribuzin than for cyanazine (0.4 as compared with 0.15; see Section 8.3.4.5). If in the experiments of Section 8.3 the soil had been extracted only once with ethyl acetate, a value of K_3 of 0.04 $dm^3\ kg^{-1}$ would have been found for metribuzin. Thus, calculations were done with $K_3 = 0.04\ dm^3\ kg^{-1}$, $\Phi = 0$ and the results were compared with those calculated with the standard values ($K_3 = 0.07\ dm^3\ kg^{-1}$, $\Phi = 0.4$). Figure 9.15 shows that ignoring the content still sorbed at class-3 sites after the first extraction with ethyl acetate hardly influenced the concentration profile calculated for metribuzin after 121 d.

The sensitivity to a relationship between the rate coefficient for transformation in the liquid phase, $k_{t,l}$, and the volume fraction of liquid, θ, was considered (a relationship between $k_{t,l}$ and soil temperature was disregarded, because it had been found (see Section 4.3) that daily averages of soil temperature at depths of 10 mm and 50 mm were about equal). No measurements of the relationship between $k_{t,l}$ and θ were available from the literature (all the data cited in the review in Chapter 3 concerned the rate coefficient for transformation in the

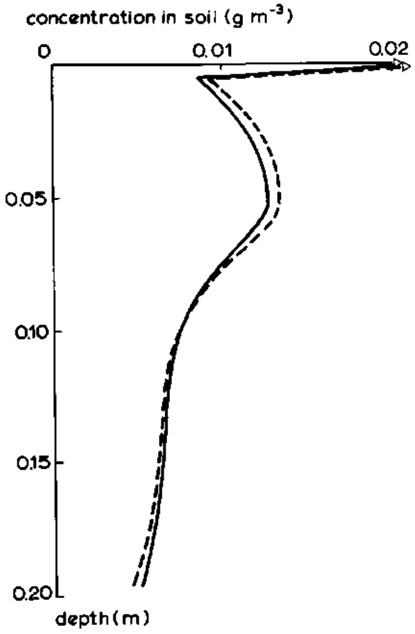


Figure 9.15. Effect of ignoring the content still sorbed at class-3 sites after the first extraction with ethyl acetate, on concentration profiles calculated for metribuzin after 121 d in 1982. ——, calculated with $K_3 = 0.04\ dm^3\ kg^{-1}$ and $\Phi = 0$; --- , calculated with $K_3 = 0.07\ dm^3\ kg^{-1}$ and $\Phi = 0.4$.

whole soil system, k_t^*). In the calculation it was assumed that $k_{t,1}$ was directly proportional to θ :

$$k_{t,1} = C_{t,5}\ \theta \tag{9.22}$$

in which

$C_{t,5}$ is a coefficient (d^{-1})

The coefficient $C_{t,5}$ was estimated by the formula

$$(C_{t,5})^j = (k_{t,1}^{ca})^j \frac{\sum_{i=1}^{I} (\theta)_i^j\ (c)_i^j\ \Delta z_i}{\sum_{i=1}^{I} (\theta^2)_i^j\ (c)_i^j\ \Delta z_i} \tag{9.23}$$

in which

$k_{t,1}^{ca}$ is the value of $k_{t,1}$ as calculated from Equation 9.9 (d^{-1})

Using Equation 9.23 results in the same areic mass rate of transformation as the standard model. Results of calculations with Equations 9.22 and 9.23 (Figure 9.16) show that calculated profiles of both cyanazine and metribuzin were not sensitive to the relationship between $k_{t,1}$ and θ.

The foregoing sensitivity analysis has shown that the sensitivity of calculated concentration profiles to most of the parameters considered was small. Only the sensitivity to the parameters describing sorption at class-3 sites (K_3 and $k_{d,3}$) was considerable. This indicates that the incorporation of sorption at class-3 sites (i.e. a reversible long-term sorption process) in the transport model was mainly responsible for the successful explanation of the field-measured transport of the two herbicides. Further work should be done to determine the values for K_3 and $k_{d,3}$ more accurately: in this study, these parameters could not be estimated accurately (see Section 8.3).

The small sensitivity to most of the parameters in the model is fortuitous because it justifies using approximate values for these parameters (e.g. the daily average of the volume flux of liquid instead of the 3 h-average). Furthermore, the small sensitivity to the $k_{d,2}$ value (as shown in Figure 9.14) suggests that in future studies the model could be simplified by assuming equilibrium sorption for class-2 sites also.

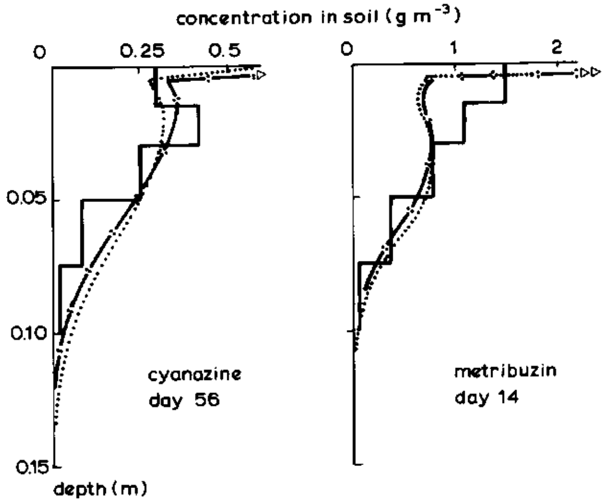


Figure 9.16. Effect of the relationship between the rate coefficient for transformation in the liquid phase, $k_{t,l}$, and the volume fraction of liquid, θ, on a few calculated concentration profiles in 1982. ·····, calculated with constant $k_{t,l}$; -:-:-, calculated with $k_{t,l}$ from Equation 9.22; ——, averages of measured concentrations. Both calculations were done with Equations 9.20 and 9.21.

9.4.3 Concluding remarks

By persevering in the application of the research method associated with explanatory models (see Figure 1.1), this research finally produced a satisfactory explanation of the field-measured transport of the two herbicides. Much effort had to be devoted to eliminating nearly all the possible causes for the discrepancy between calculated and measured herbicide transport as found in Chapter 6. The causes that were successfully eliminated (see Chapters 7 and 8) included: adsorption/desorption hysteresis; effects of concentration of salts, formulation additives, and drying treatments on sorption; and short-term sorption kinetics). Finally, a long-term sorption process remained as almost the only possible explanation to account for the discrepancy.

Given that there are a number of indications in the literature for sorption at class-3 sites (see Section 8.1), it is to be expected that the occurrence of a significant number of class-3 sites is a general phenomenon for pesticide/soil systems. It would be worth checking this in future research, by measuring the parameters describing sorption at class-3 sites for the range of pesticide/soil combinations.

Another interesting topic for future research is the mechanism of sorption at class-3 sites.

It is still not clear whether the effect of sorption at class-3 sites on pesticide transport is always as large as was found in the present study. This should be tested in the future by calculations with the model under a wider range of climatic conditions.

Calculating herbicide transport with the non-equilibrium model developed in this chapter resulted in the transport rate of the main fraction of the amount of herbicide a few months after application being much lower than the rate calculated with the equilibrium model (compare e.g. Figures 6.11 and 9.3). Thus, the fraction of the herbicide dose calculated to be leached eventually to the ground water can be expected to be much smaller for the non-equilibrium model than for the equilibrium model. However, there are indications in the literature that very small fractions of the dose may move even faster than expected from the equilibrium model (Leistra, 1980, pp. 40-41). An interesting point for further research would be to develop and validate models that accurately simulate the fraction of the dose leaching out of the root zone.

The increase of the sorption coefficient with time at a time scale of months (as implied by the model developed in this chapter) may result in a decrease in herbicide availability to micro-organisms that is more than proportional to the decrease of c^* with time. Thus, this increase of the sorption coefficient may be the cause of the deviation from transformation rates first-order in c^* that has been observed in a number of cases in the literature (see review by Hurle & Walker, 1980, p. 85).

The present study indicates that sorption at class-3 sites has a large effect on sorption coefficients of herbicides as found a few months after application (see Figure 8.1). As a consequence, in the field there is no more or less unique relationship between the concentration of herbicide in the soil system, c^*, and the concentration of herbicide in liquid phase, c. The effects of herbicides on plants can be expected to be related to c and not to c^*. Thus the model developed in this chapter contributes to a better understanding of those situations (combinations of herbicides, soils and weather conditions) in which damage to crops may occur.

The occurrence of effects of herbicides on plants (such as damage to subsequent crops, the failure to control weeds after low rainfall, or the failure of depth-protection after much rainfall) can only be explained quantitatively if the whole soil-plant system is simulated. The processes that should be included in such simulations are: the uptake of herbicides by the plants, the translocation of the herbicides in the plants up to the sites of action and the transformation in the plants. For this, simulation models of herbicide behaviour in the whole soil-plant system will have to be developed (and validated!). This requires a multidisciplinary approach.

SUMMARY

Soil-applied herbicides are widely used in agriculture and therefore their behaviour in soil merits study. This behaviour is important both for agricultural aspects (such as the efficacy against weeds and the phytotoxicity for crops) and for environmental aspects (such as leaching to ground water).

The aim of the present study was to assess the possibilities for simulating the transport and the transformation rate of soil-applied herbicides in field soil, using mathematical models. The study was restricted to non-ionic herbicides with low saturated vapour pressures and to natural weather conditions in a maritime temperate climate.

The simulation models considered were of explanatory character. Knowledge gained from well-defined laboratory experiments with herbicides and soils constituted the research level used for explanation. The level to be explained was the behaviour of herbicides in field soils under varying weather conditions (Chapter 1).

In Chapter 2 a review is given of available models of the transport of herbicides in soil and of the laboratory and field tests of these models as described in the literature. The available transport models may be divided into on the one hand the equilibrium model and on the other non-equilibrium models. In the equilibrium transport model it is assumed that the concentration in the liquid phase in soil in a plane perpendicular to the direction of water flow is uniform and that the substance in the liquid phase is always in equilibrium with that sorbed by the solid phase. In non-equilibrium transport models it is assumed that the substance in the liquid phase is not in equilibrium with that sorbed by the solid phase (chemical non-equilibrium) or that, as a result of so-called stagnant-phase effects the concentration in liquid phase is not uniform (physical non-equilibrium). It has been shown in the literature that the dimensionless transport equations of the main physical and chemical non-equilibrium models are mathematically identical. A new operational definition for the distinction between physical and chemical non-equilibrium processes in soil systems is proposed: the rate of the chemical process is measured in a suspension of soil that is continuously being mixed. Consequently, by definition, physical equilibrium exists in such a suspension of soil.

The laboratory tests of the available transport models were usually carried out

at volume fluxes of liquid in the order of 100 mm d^{-1}. The general conclusion from these tests was that at the volume fluxes of liquid used, there was a large deviation from results calculated with the equilibrium model.

Only two of the models described in the literature have been tested under field conditions: the equilibrium transport model and the physical non-equilibrium transport model developed by Nicholls et al. (1982a,b). The field tests in autumn and winter showed that both models tend to everestimate the transport of the main fraction of the amount of pesticide. For the field tests in spring and summer described in the literature, there may be large uncertainties in the estimated values of the flux of evaporation of water from soil. Thus, until the present study there were no reports of field tests in spring and summer in which the model for the pesticide transport had been tested accurately.

From the literature it was derived that concentration profiles of sorbing herbicides as calculated with the equilibrium transport model for a given set of weather conditions were almost equal to those calculated with the non-equilibrium transport model described by Nicholls et al. (1982a,b). As, furthermore, the theoretical basis of the model of Nicholls et al. (1982a,b) is considered to be weak, the equilibrium model is to be preferred for the simulation of herbicide transport under field conditions.

In Chapter 3 the available models of the transformation rate of herbicides in soil and the laboratory and field tests of these models as described in the literature are reviewed. Only two models (that described by Walker, 1974, and a revised version of this model described by Walker & Barnes, 1981) have been developed to explain transformation rates in the field from laboratory data and from weather conditions in the field. In these models the transformation rate is described by a first-order rate equation. It is assumed that the transformation rate coefficient is a function of only the soil temperature and the water content in soil. The vast majority of the laboratory measurements on the effect of temperature and water content on the transformation rate coefficient could be described reasonably well with equations proposed by Walker (1974) which imply that the coefficient continuously increases with both water content and temperature.

In the models developed by Walker (1974) and by Walker & Barnes (1981) it is assumed that only the transformation process is responsible for the decline of the amount of herbicide present in field soil. In the literature, some 100 field test of these models are described. The majority of these tests showed that the models explained the observed decline of the amount of herbicide in field soil reasonably well. In most of the remaining tests the models underestimated the rate of decline in the field.

Chapter 4 describes the experimental procedures and results of field experiments that were conducted to test the equilibrium transport model under spring and summer conditions. The field experiments were conducted in two consecutive years on a bare loamy sand soil. In the first year the transport of the herbicide cyanazine was measured during six weeks in spring and summer. In the second year the transport of the herbicides cyanazine and metribuzin and that of bromide ion was measured during four months in spring and summer. In both years only small fractions of the herbicide doses leached below 100 mm depth. In contrast with the herbicides, a considerable fraction of the bromide dose had even leached below 400 mm depth at the end of the experimental period in the second year.

A prerequisite for testing a model of the transport of substances in soil, is a description of the flow of water in soil. The model used to simulate flow of water in soil during the field experiments is described in Chapter 5. A simple model of flow of water was used because more sophisticated models require input data that are not readily available for field soils and because the validity of the more sophisticated models is questionable. In this model it is assumed that while rain falls the infiltrating water fills up the soil to field capacity and that thereafter no further redistribution of water takes place. During evaporation, water withdrawal from a certain depth in soil is assumed to be proportional to the evaporation flux at the soil surface, the volume fraction of liquid at that depth and a withdrawal factor that decreases with increasing depth in soil.

The model for water flow in soil requires as input the fluxes of rainfall and evaporation at the soil surface. Rainfall was measured continuously at the experimental field, and evaporation was estimated with a new simulation model. In this model the potential evaporation flux is estimated with help of the Penman equation. The new model contains only one soil parameter, which determines the extent of the reduction of evaporation as a result of drying of the soil surface. The soil parameter was measured at the experimental field during a drying cycle. The evaporation model was tested against evaporation as measured at the experimental field in a few periods. Measured and calculated evaporation were found to correspond reasonably well.

The model for flow of water in soil (coupled with the evaporation model) satisfactorily described moisture profiles as measured in the field.

Chapter 6 describes the test of the equilibrium transport model against the concentration profiles of the herbicides cyanazine and metribuzin and of bromide ion as measured in the field. In the model the sorption isotherm was described by the Freundlich equation. The parameters in this equation were derived from sorption measurements in a soil suspension with an equilibration period of 24 h. Results of the test showed that the model explained the measured concentration profiles of bromide ion (a non-sorbing substance) reasonably well. However, the model overestimated the transport of the herbicides cyanazine and metribuzin (both sorbing substances). The discrepancy between measured and calculated concentration profiles of the herbicides was especially large at a few months after application. The reason for the discrepancy was investigated via a sensitivity analysis to the most relevant parameters and it was concluded that it had to be caused by incorrect assumptions in the sorption part of the model. This prompted a systematic laboratory study of sorption of cyanazine and metribuzin in the loamy sand soil.

Chapter 7 describes short-term sorption studies with both herbicides ('short-term' in this context means 'not longer than 1 d').

Adsorption kinetics of the herbicides were studied in a soil-suspension system and in a moist-soil system. It was impossible to describe the results satisfactorily with a model in which it was assumed that at equilibrium the Freundlich sorption isotherm equation is valid and that sorption kinetics of all sites can be described by a single sorption rate equation. To obtain a satisfactory description, it was necessary to use a model based on a Freundlich sorption isotherm equation in which the sorption sites are divided into two classes ('class 1' and 'class 2'), each with their own sorption rate equation (this model is called 'Freundlich model with two-site kinetics'). In the soil-suspension system, sorption at class-1 and class-2 sites equilibrated at time scales of minutes and hours, respectively. In the moist-soil system, sorption at class-1 sites equilibrated at a time scale comparable to that in soil suspension, and sorption at class-2 sites equilibrated at a time scale of days. For the range of contents sorbed considered, about two-thirds of the sites occupied at sorption equilibrium were class-1 sites, and one-third class-2 sites.

Desorption kinetics and equilibria of both herbicides were studied in the soil-suspension system. Results of desorption measurements were explained well by the Freundlich model with two-site kinetics using values of the parameters as determined from adsorption measurements.

Desorption points were measured in the soil-suspension system using soil sampled in the field at 56 and 121 d after the start of the field experiment in the second year (Chapter 8). Contents sorbed of these points were found to be much higher (up to tenfold) than expected from short-term sorption experiments. Thus a third class of sorption sites had to be assumed ('class-3' sites), which equilibrated at a time scale of months.

In the laboratory, long-term sorption experiments were carried out with permanently moist soil and with soil repeatedly subjected to drying and wetting cycles. To describe sorption at class-3 sites a first-order reversible sorption rate equation was used. From the long-term experiments with permanently moist soil, values of the parameters in the sorption rate equation for class-3 sites were estimated. It was found that for the range of contents sorbed considered, the number of class-3 sites occupied at sorption equilibrium was about equal to the corresponding number of class-2 sites. Results of long-term sorption experiments with soil subjected to drying and wetting cycles could be explained reasonably by a sorption model in which class-1, class-2 and class-3 sites were considered using parameter values as estimated from experiments with permanently moist soil. Drying and wetting the soil repeatedly thus had no influence on the properties of the sorption complex.

Based on the results of the short-term and long-term sorption studies (as described in Chapters 7 and 8), a new transport model was formulated (Chapter 9). Only the sorption part of the new model differs from the equilibrium transport model tested in Chapter 6. In the sorption part of the new model it is assumed that class-1 sites are in equilibrium with the concentration in liquid phase at any moment and at any location. Contents sorbed at class-2 and class-3 sites are calculated from their sorption rate equations. The values of the parameters in the sorption part of the model were derived from the experiments described in Chapters 7 and 8.

The new transport model explained reasonably well the concentration profiles of both cyanazine and metribuzin as measured in the field. A sensitivity analysis indicated that the sensitivity to most of the parameters was small, except for the parameters of the sorption rate equation of class-3 sites. The incorporation of class-3 sites into the transport model was mainly responsible for the successful explanation of the field-measured transport of the two herbicides.

SAMENVATTING

Aangezien bodemherbiciden in de hedendaagse landbouw veelvuldig gebruikt worden, is het nodig hun gedrag in de bodem te bestuderen. Dit gedrag is zowel van belang vanuit landbouwkundig oogpunt (b.v. een goede doding van onkruiden en mogelijke schadelijke effecten op gewassen) als vanuit het oogpunt van het milieu (b.v. uitspoeling naar het grondwater).

Het doel van het onderzoek was na te gaan in hoeverre het mogelijk is het transport en de transformatiesnelheid van bodemherbiciden onder veldomstandigheden te simuleren met behulp van wiskundige modellen. Het onderzoek was beperkt tot het gedrag van ongeladen herbiciden met lage verzadigde dampdrukken onder natuurlijke weersomstandigheden in een maritiem gematigd klimaat.

In dit onderzoek zijn verklarende simulatiemodellen gebruikt. Het verklarend onderzoeksniveau bestond uit het gedrag van herbiciden in goed-gedefinieerde laboratoriumproeven met grond. Het te verklaren onderzoeksniveau was het gedrag van herbiciden in de bodem in het veld onder wisselende weersomstandigheden (Hoofdstuk 1).

Hoofdstuk 2 handelt over een literatuuroverzicht van beschikbare modellen van het transport van herbiciden in de bodem en van de veld- en laboratoriumtoetsen van deze modellen. De beschikbare transportmodellen kunnen verdeeld worden in enerzijds het evenwichtsmodel en anderzijds een aantal niet-evenwichtsmodellen. Het evenwichtsmodel is gebaseerd op de veronderstellingen dat de concentratie van de stof in de vloeibare fase van de bodem uniform is in een vlak loodrecht op de stromingsrichting van het water en dat de stof in de vloeibare fase altijd in evenwicht is met de stof gesorbeerd door de vaste fase. Niet-evenwichtsmodellen zijn gebaseerd op de veronderstelling dat de stof in de vloeibare fase niet in evenwicht is met de stof gesorbeerd door de vaste fase (chemisch niet-evenwicht) of dat de concentratie van de stof in de vloeibare fase niet uniform is ten gevolge van zogenaamde stagnante-fase effecten (fysisch niet-evenwicht). In de literatuur is aangetoond dat de dimensieloze transportvergelijkingen van de belangrijkste fysische en chemische niet-evenwichtsmodellen wiskundig identiek zijn. Ik stel een nieuwe operationele definitie voor voor het onderscheid tussen fysische en chemische niet-evenwichtsprocessen: de snelheid van het chemische proces wordt gemeten in een suspensie van grond die voortdurend gemengd wordt. Dit houdt in dat er per definitie fysisch evenwicht heerst in zo'n suspensie.

De laboratoriumtoetsen van de beschikbare transportmodellen werden normaliter uitgevoerd bij volumefluxen van het bodemvocht van de ordegrootte van 100 mm d^{-1}. Uit deze toetsen kwam naar voren dat de meetresultaten sterk afweken van de resultaten berekend met het evenwichtsmodel.

Slechts twee van de transportmodellen zijn getest onder veldomstandigheden: het evenwichtsmodel en het fysisch niet-evenwichtsmodel van Nicholls et al. (1982a,b). Uit de veldtoetsen uitgevoerd in de herfst en de winter bleek dat beide modellen de tendens vertonen het transport van het overgrote deel van de bestrijdingsmiddelhoeveelheid te overschatten. In de veldtoetsen in lente en zomer was de onzekerheid in de schatting van de flux van de verdamping van water vanaf het bodemoppervlak groot. Zodoende waren er bij het begin van het huidige onderzoek nog geen veldtoetsen beschikbaar waarin een model voor het transport van bestrijdingsmiddelen nauwkeurig getoetst was in de lente en de zomer.

Uit de literatuur bleek dat concentratieprofielen van sorberende herbiciden berekend met het evenwichtsmodel vrijwel identiek waren aan profielen berekend voor eenzelfde reeks weersgegevens met het niet-evenwichtsmodel ontwikkeld door Nicholls et al. (1982a,b). Omdat ik de theoretische basis van het model van Nicholls et al. (1982a,b) zwak acht, geef ik voor simulatie van het transport van herbiciden in het veld de voorkeur aan het evenwichtsmodel.

Hoofdstuk 3 beschrijft een literatuuroverzicht van beschikbare modellen van de transformatiesnelheid van herbiciden in de bodem en van de laboratorium- en veldtoetsen van deze modellen. In slechts twee modellen (dat ontwikkeld door Walker, 1974, en een herziene versie van dit model ontwikkeld door Walker & Barnes, 1981) wordt getracht transformatiesnelheden in het veld te verklaren uit laboratoriummetingen en uit weersgegevens van het betreffende veld. In deze modellen wordt de transformatiesnelheid beschreven door een eerste-orde vergelijking. De evenredigheidscoëfficiënt in deze vergelijking is slechts een functie van de temperatuur en het vochtgehalte van de bodem. Walker (1974) formuleerde vergelijkingen voor de verbanden tussen de evenredigheidscoëfficiënt en de temperatuur en het vochtgehalte. Deze vergelijkingen houden in dat de coëfficiënt een voortdurend stijgende functie is van zowel de temperatuur als het vochtgehalte. Het overgrote deel van de laboratoriummetingen over de invloed van de temperatuur en het vochtgehalte op de genoemde evenredigheidscoëfficiënt kon goed beschreven worden met de door Walker geformuleerde vergelijkingen.

Walker (1974) en Walker & Barnes (1981) nemen in hun modellen aan dat de afname van de hoeveelheid herbicide die in de bodem in het veld aanwezig is uitsluitend veroorzaakt wordt door het transformatieproces. In de literatuur zijn er ongeveer 100 veldtoetsen van deze modellen beschreven. In meer dan de helft van de gevallen bleken de modellen de gemeten afname van de hoeveelheid herbicide in de bodem goed te verklaren. In de meeste andere gevallen werd de afnamesnelheid in het veld onderschat.

Hoofdstuk 4 beschrijft twee veldproeven (zowel de daarbij gebruikte meetmethoden als de resultaten) die werden uitgevoerd om het evenwichtsmodel in de lente en de zomer te toetsen. Deze veldproeven werden uitgevoerd in twee opeenvolgende jaren op een onbegroeide grond (grondsoort: matig humusarm, kleiarm tot kleiig zand). In het eerste jaar werd het transport van het herbicide cyanazin gemeten gedurende zes weken. In het tweede jaar werd het transport van de herbiciden cyanazin en meteribuzin en van het bromide-ion gemeten gedurende vier maanden. In beide jaren spoelden slechts kleine fracties van de toegepaste herbicidehoeveelheden uit tot beneden een diepte van 100 mm, terwijl een belangrijk deel van de toegepaste bromidehoeveelheid aan het eind van de proef in het tweede jaar was uitgespoeld tot beneden een diepte van 400 mm.

Een model van de waterstroming in de bodem is een noodzakelijk onderdeel van een model van stoftransport in de bodem. Hoofdstuk 5 beschrijft het model dat gebruikt werd om de waterstroming in de bodem tijdens de veldproeven te simuleren. Het betreft hier een eenvoudig waterstromingsmodel omdat de voor ingewikkelde modellen benodigde invoergegevens niet eenvoudig te verkrijgen zijn en omdat de geldigheid van beschikbare ingewikkelde modellen dubieus is. In het gebruikte eenvoudige model wordt aangenomen dat tijdens regenval het infiltrerende water de bodem opvult tot veldcapaciteit en dat daarna geen verdere herverdeling plaatsvindt. Tijdens verdamping is de wateronttrekking op een bepaalde diepte in de bodem recht evenredig met de verdampingsflux aan het bodemoppervlak, de volumefractie vloeistof op die diepte en een onttrekkingsfactor die afneemt met toenemende diepte in de bodem.

De fluxen van regenval en verdamping aan het bodemoppervlak zijn noodzakelijk als invoergegevens voor het waterstromingsmodel. Regenval werd voortdurend gemeten in het veld en verdamping werd geschat met een nieuwe simulatiemodel. In dit model wordt de potentiële verdampingsflux geschat met behulp van de Penman-vergelijking. Het model bevat slechts één bodemparameter. Deze parameter bepaalt de mate van verdampingsreductie ten gevolge van het uitdrogen van het bodemoppervlak. De bodemparameter werd gemeten op het proefveld tijdens een uitdroogcyclus. Het verdampingsmodel werd getoetst aan verdamping gemeten op het proefveld in enkele perioden. De gemeten en de berekende verdamping bleken redelijk goed met elkaar overeen te komen.

Hoofdstuk 6 beschrijft de toets van het evenwichtstransportmodel aan de in het veld gemeten concentratieprofielen van de herbiciden cyanazin en metribuzin en van het bromide-ion. In het model werd de sorptie-isotherm beschreven met de Freundlich-vergelijking. De parameters in deze vergelijking werden afgeleid uit sorptie-metingen in een grond-suspensie die 24 h geschud werd. Uit de toets bleek dat het model de gemeten concentratieprofielen van het bromide-ion (een niet-sorberende stof) redelijk goed verklaarde. Het model overschatte daarentegen het transport van de herbiciden cyanazin en metribuzin (beide sorberende stoffen). Het verschil tussen de gemeten en de berekende concentratieprofielen van de herbiciden was bijzonder groot enkele maanden na de toepassing. Een gevoeligheidsanalyse van het model wees uit dat het verschil geweten moest worden aan foutieve aannames in het sorptie-onderdeel van het model. Dit was een aanleiding om de sorptie van cyanazin en metribuzin aan de betreffende zandgrond systematisch te onderzoeken in het laboratorium.

Hoofdstuk 7 beschrijft het korte-termijn onderzoek naar de sorptie van beide herbiciden ('korte-termijn' betekent in dit verband 'niet langer dan 1 d').

De adsorptiekinetiek van de herbiciden werd bestudeerd in een grond-suspensie systeem en een vochtige-grond systeem. De resultaten konden niet bevredigd beschreven worden met een model waarin wordt aangenomen dat bij evenwicht de Freundlich-vergelijking geldt en dat alle sorptie-plekken kinetisch bezien homogeen zijn. Een bevredigende beschrijving kon slechts worden verkregen met een model (gebaseerd op de Freundlich-vergelijking voor de sorptie-isotherm) waarin de sorptie-plekken in twee klassen zijn verdeeld ('klasse 1' en 'klasse 2') elk met hun eigen snelheidsvergelijking voor de sorptie (dit model wordt 'het Freundlich-model met twee-plek kinetiek' genoemd). In het grond-suspensie systeem stelde het sorptie-evenwicht van klasse-1 plekken zich in op een tijdschaal van minuten en dat van klasse-2 plekken op een tijdschaal van uren. In het vochtige-grond systeem stelde het sorptie-evenwicht van klasse-1 plekken zich in op een tijdschaal die ongeveer gelijk was aan die in de grond-suspensie. Het sorptie-evenwicht van klasse-2 plekken stelde zich in het vochtige-grond systeem in op een tijdschaal van dagen. Ongeveer tweederde van de sorptieplekken die bezet waren bij evenwicht, was van klasse 1 en dus ongeveer éénderde van klasse 2.

De desorptie-kinetiek en desorptie-evenwichten van beide herbiciden werd onderzocht in het grond-suspensie systeem. De proeven werden nagerekend met het Freundlich-model met twee-plek kinetiek met waarden van de parameters bepaald in de adsorptie-proeven. Dit model verklaarde de resultaten van de desorptie-proeven goed.

In het grond-suspensie systeem werden desorptie-punten gemeten aan grond bemonsterd in het veld 56 en 121 d na de start van de veldproef in het tweede jaar (Hoofdstuk 8). Het bleek dat de gehaltes aan gesorbeerd herbicide van deze punten veel hoger waren dan verwacht werd op basis van de korte-termijn proeven. Zodoende was het noodzakelijk een derde klasse van sorptie-plekken aan te nemen ('klasse 3') met een insteltijd van het sorptie-evenwicht van de ordegrootte van maanden.

Er werden lange-termijn sorptie-proeven uitgevoerd in het laboratorium met grond die voortdurend vochtig gehouden werd en met grond die herhaaldelijk uitgedroogd werd en weer bevochtigd. De sorptie op klasse-3 plekken werd beschreven met een eerste-orde snelheidsvergelijking gebaseerd op een reversibel sorptieproces. De waarden van de parameters in de snelheidsvergelijking werden geschat uit de resultaten van de lange-termijn proeven met grond die voortdurend vochtig gehouden werd. Het aantal klasse-3 plekken bezet bij sorptie-evenwicht was ongeveer gelijk aan het overeenkomstige aantal klasse-2 plekken. De lange-termijn sorptie-proeven met grond die herhaaldelijk werd uitgedroogd en weer bevochtigd, werden nagerekend met een sorptie-model gebaseerd op de drie genoemde klassen aan plekken. In deze berekeningen werden waarden van de parameters gebruikt gebaseerd op de resultaten van proeven met grond die voortdurend vochtig gehouden werd. Het bleek dat dit model een goede verklaring gaf van de resultaten van deze lange-termijn proeven. Het herhaaldelijk uitdrogen en weer bevochtigen van de grond had dus geen invloed op de eigenschappen van het sorptiecomplex.

Hoofdstuk 9 beschrijft een nieuw transportmodel dat gebaseerd is op de resultaten van het korte- en lange-termijn sorptie-onderzoek beschreven in de Hoofdstukken 7 en 8. Uitsluitend het sorptie-onderdeel van het nieuwe model verschilt van het evenwichtstransportmodel dat getoetst werd in Hoofdstuk 6. In het sorptie-onderdeel van het nieuwe model wordt aangenomen dat klasse-1 plekken op elk tijdstip en op elke diepte in de bodem in evenwicht zijn met de concentratie in de vloeibare fase. De gehaltes aan herbicide gesorbeerd op klasse-2 en klasse-3 plekken worden berekend met de twee snelheidsvergelijkingen voor de sorptie op deze plekken. De waarden van de parameters in het sorptie-onderdeel van het model waren gebaseerd op het onderzoek beschreven in de Hoofdstukken 7 en 8.

Het nieuwe transportmodel leverde een redelijk goede verklaring op van de in het veld gemeten concentratieprofielen van beide herbiciden. Uit een gevoeligheidsanalyse bleek dat de gevoeligheid voor de meeste parameters klein was. Een uitzondering hierop vormden de parameters van de snelheidsvergelijking voor de sorptie op klasse-3 plekken. Dit geeft aan dat de goede verklaring van de veldmetingen van beide herbiciden veroorzaakt wordt door het opnemen van klasse-3 plekken in het transportmodel.

APPENDIX A

```
TITLE MODEL OF FLOW OF WATER IN SOIL
************************************

STORAGE TCOM(35),DEPTH(35),DIST(36),WDFA(35),VFLMAX(35),VFLMIN(35)
STORAGE MOWWF(35),RDVFL(35),PRIVFL(35),FLIQ(36),RAINT(121),REVAT(121)
FIXED NCOM,NCOMP,I,NDAY
INITIAL
NOSORT
*
**
***   definition of soil system geometry : one-dimensional,vertical
**
*
* TCOM=thickness of the compartments (m)
TABLE TCOM(1-35)=10*0.005,15*0.01,10*0.02
* NCOM=number of compartments
PARAM NCOM=35
      NCOMP=NCOM+1
* DEPTH=depths of the centres of the compartments (m)
* DIST=distance between compartment centres (m)
      DEPTH(1)=0.5*TCOM(1)
      DO 10 I=2,NCOM
      DIST(I)=0.5*(TCOM(I-1)+TCOM(I))
   10 DEPTH(I)=DEPTH(I-1)+DIST(I)
*
**
***   rainfall and evaporation
**
*
* RAINT=volume flux of rainfall (mm/d),daily values,measured at
*       1.2 m height
TABLE RAINT(1-121)=19.5,3.0,1.5,8*0.0,0.1,2*0.0,11.6,0.0,9.1,0.4, ...
* FCRMHL=factor for conversion from rainfall measured at 1.2 m height
*        to rainfall measured flush with the soil surface (1)
PARAM FCRMHL=1.07
* REVAT=volume flux of actual evaporation (mm/d),daily values,
*       calculated with evaporation model
TABLE REVAT(1-121)=1.50,2.16,2.04,3.10,1.24,0.98,0.92,0.91,0.85,0.74,...
*
**
***  hydraulic properties of the soil
**
*
* WDFA=factor for withdrawal of water resulting from evaporation (1)
*      as a f(depth)
FUNCTION WDFAF=0.0,1.0,0.01,0.4,0.02,0.2,0.03,0.1,0.05,0.03,0.4,0.0
```

```
      DO 11 I=1,NCOM
   11 WDFA(I)=AFGEN(WDFAF,DEPTH(I))
* VFLMAX=maximal volume fraction of liquid (m3/m3)
TABLE VFLMAX(1-35)=2*0.2,2*0.22,2*0.24,4*0.27,5*0.28,20*0.3
* VFLMIN=minimal volume fraction of liquid (m3/m3)
TABLE VFLMIN(1-35)=35*0.01
*
**
***   initial conditions
**
*
* SVFL=starting volume fraction of liquid (m3/m3)
TABLE SVFL(1-35)=3*0.057,3*0.191,4*0.21,2*0.262,3*0.28,20*0.3

DYNAMIC
NOSORT
      NDAY=TIME+1
*
**
***   flow of water in soil
**
*
* VFL=volume fraction of liquid (m3/m3)
* RVFL=rate of change in VFL (m3/(m3 d))
      VFL=INTGRL(SVFL,RVFL,35)
* RAIN=volume flux of rainfall (m/d)
      RAIN=0.001*FCRMHL*RAINT(NDAY)
* CRAIN=cumulative areic volume of rainfall (m)
      CRAIN=INTGRL(0.0,RAIN)
* REVA=volume flux of actual evaporation from the soil surface (m/d)
      REVA=0.001*REVAT(NDAY)
* CEVA=cumulative areic volume of actual evaporation from the soil
*       surface (m)
      CEVA=INTGRL(0.0,REVA)
* FLIQ=volume flux of liquid through the soil (m/d)
      FLIQ(1)=RAIN-REVA
      IF (FLIQ(1).GE.0.0) GO TO 40
*
**  calculation of liquid fluxes if net upward flux at surface
*
* MOWWF=moisture weighed withdrawal factor (m3/m3)
* SUM=compartment thickness weighed sum of MOWWF-factors (m)
      SUM=0.0
      DO 30 I=1,NCOM
      MOWWF(I)=AMAX1(0.0,VFL(I)-VFLMIN(I))*WDFA(I)
   30 SUM=SUM+MOWWF(I)*TCOM(I)
* RDVFL=rate of decrease in VFL resulting from evaporation (m3/(m3 d))
      DO 31 I=1,NCOM
   31 RDVFL(I)=(MOWWF(I)/SUM)*FLIQ(1)
      DO 32 I=2,NCOMP
   32 FLIQ(I)=FLIQ(I-1)-RDVFL(I-1)*TCOM(I-1)
      GO TO 50
   40 CONTINUE
*
**  calculation of liquid fluxes if net downward flux at surface
*
```

```
* PRIVFL=potential rate of increase in VFL resulting from rainfall
*        (m3/(m3 d))
      DO 41 I=1,NCOM
   41 PRIVFL(I)=(VFLMAX(I)-VFL(I))/DELT
      DO 42 I=2,NCOMP
   42 FLIQ(I)=AMAX1(0.0,FLIQ(I-1)-PRIVFL(I-1)*TCOM(I-1))
   50 CONTINUE
* CLPER=cumulative areic volume of liquid percolated (m)
      CLPER=INTGRL(0.0,FLIQ(NCOMP))
*
**  conservation equation for water in soil
*
      DO 51 I=1,NCOM
   51 RVFL(I)=(FLIQ(I)-FLIQ(I+1))/TCOM(I)
*
**
***   output section
**
*
* TVOL=total areic volume of liquid in soil system (m)
      TVOL=0.0
      DO 80 I=1,NCOM
   80 TVOL=TVOL+VFL(I)*TCOM(I)
PRINT TVOL,CRAIN,CEVA,CLPER,FLIQ(1),VFL(1-25)
METHOD RECT
TIMER DELT=0.05,PRDEL=1.0,FINTIM=121.0
END
```

APPENDIX B

```
TITLE EVAPORATION MODEL WITH DAILY AVERAGES OF FLUXES OF RAINFALL...
      AND EVAPORATION
*******************************************************************

STORAGE RAINT(121),REVOBT(121),REVOET(121),REVOKT(121)
FIXED NDAY
INITIAL
NOSORT
* BETA=parameter in relationship between cumulative potential and
*      cumulative actual evaporation during a drying cycle (m1/2)
PARAM BETA=0.0547
* RAINT=volume flux of rainfall (mm/d),daily values,measured at
*       1.2 m height
TABLE RAINT(1-121)=19.5,3.0,1.5,8*0.0,0.1,2*0.0,11.6,0.0,9.1,0.4, ...
* FCRMHL=factor for conversion from rainfall measured at 1.2 m height
*        to rainfall measured flush with the soil surface (1)
PARAM FCRMHL=1.07
* REVOBT=volume flux of evaporation from a hypothetical open water
*        surface at weather station 'de Bilt' (mm/d),daily values
* REVOET=idem as REVOBT but now at weather station 'Eelde'
* REVOKT=idem as REVOBT but now at weather station 'de Kooy'
TABLE REVOBT(1-121)=1.2,2.2,2.7,4.8,4.3,4.4,4.3,5.7,6.2,5.8,4.9,5.5,...
TABLE REVOET(1-121)=2.5,1.7,1.8,4.0,3.7,3.6,4.2,4.3,4.2,5.2,5.0,3.1,...
TABLE REVOKT(1-121)=1.3,3.3,2.3,3.7,3.5,3.5,4.2,4.5,4.7,3.6,4.3,4.5, ...
```

```
PARAM DEBILT=1.0,EELDE=1.0,DEKOOY=1.0
* FCEWWS=factor for conversion from evaporation from a hypothetical open
*        water surface to potential evaporation from soil (1)
PARAM FCEWWS=0.9
* SIGEP=cumulative areic volume of potential evaporation from soil
*       during a drying cycle (m)
* SIGEA=cumulative areic volume of actual evaporation from soil
*       during a drying cycle (m)
INCON SIGEP=0.0,SIGEA=0.0
DYNAMIC
NOSORT
      NDAY=TIME+1
* RAIN=volume flux of rainfall (m/d)
      RAIN=0.001*FCRMHL*RAINT(NDAY)
* CRAIN=cumulative areic volume of rainfall (m)
      CRAIN=INTGRL(0.0,RAIN)
* REVP=volume flux of potential evaporation from soil (m/d)
      REVP=0.001*FCEWWS*(DEBILT*REVOBT(NDAY)+EELDE*REVOET(NDAY)+ ...
           DEKOOY*REVOKT(NDAY))/(DEBILT+EELDE+DEKOOY)
* CEVP=cumulative areic volume of potential evaporation from soil (m)
      CEVP=INTGRL(0.0,REVP)
      IF (KEEP.NE.1) GO TO 21
      IF (RAIN.LE.REVP) GO TO 20
* REVA=volume flux of actual evaporation from soil (m/d)
      REVA=REVP
      SIGEA=AMAX1(0.0,SIGEA-(RAIN-REVA)*DELT)
      SIGEP=AMAX1(SIGEA,SIGEA**2/BETA**2)
      GO TO 21
   20 CONTINUE
      SIGEP=SIGEP+(REVP-RAIN)*DELT
      REVA=RAIN+(AMIN1(SIGEP,BETA*SQRT(SIGEP))-SIGEA)/DELT
      SIGEA=AMIN1(SIGEP,BETA*SQRT(SIGEP))
   21 CONTINUE
* CEVA=cumulative areic volume of actual evaporation from soil (m)
      CEVA=INTGRL(0.0,REVA)
PRINT RAIN,CRAIN,REVP,CEVP,REVA,CEVA
METHOD RECT
TIMER DELT=1.0,PRDEL=20.0,FINTIM=120.0
END
```

APPENDIX C

```
TITLE EVAPORATION MODEL WITH DIURNALLY FLUCTUATING FLUXES OF RAINFALL...
      AND EVAPORATION
************************************************************************

STORAGE RAINT(968),REVOBT(121),REVOET(121),REVOKT(121)
FIXED NDAY,NOCTD
INITIAL
* BETA=parameter in relationship between cumulative potential and
*      cumulative actual evaporation during a drying cycle (m1/2)
PARAM BETA=0.0547
* RAINT=volume flux of rainfall (mm/(0.125 d)), 3 h-averages, measured
*       at 1.2 m height
```

```
TABLE RAINT(1-968)=2*0.0,0.9,0.4,3.3,0.7,4.5,9.7,1.1,3*0.0,1.2,...
* FCRMHL=factor for conversion from rainfall measured at 1.2 m height
*       to rainfall measured flush with the soil surface (1)
PARAM FCRMHL=1.07
* REVOBT=volume flux of evaporation from a hypothetical open water
*       surface at weather station 'de Bilt' (mm/d),daily values
* REVOET=idem as REVOBT but now at weather station 'Eelde'
* REVOKT=idem as REVOBT but now at weather station 'de Kooy'
TABLE REVOBT(1-121)=1.2,2.2,2.7,4.8,4.3,4.4,4.3,5.7,6.2,5.8,4.9,5.5,...
TABLE REVOET(1-121)=2.5,1.7,1.8,4.0,3.7,3.6,4.2,4.3,4.2,5.2,5.0,3.1,...
TABLE REVOKT(1-121)=1.3,3.3,2.3,3.7,3.5,3.5,4.2,4.5,4.7,3.6,4.3,4.5, ...
* FCEWWS=factor for conversion from evaporation from a hypothetical open
*       water surface to potential evaporation from soil (1)
PARAM FCEWWS=0.9,PI=3.141593
* SIGEP=cumulative areic volume of potential evaporation from soil
*      during a drying cycle (m)
* SIGEA=cumulative areic volume of actual evaporation from soil
*      during a drying cycle (m)
* STER=stock of excess in areic volume of rain fallen after 18.00 h the
*     previous day (m)
INCON SIGEP=0.0,SIGEA=0.0,STER=0.0
DYNAMIC
NOSORT
      NDAY=TIME+1
      NOCTD=8.0*TIME+1
* RAIN=volume flux of rainfall (m/d)
      RAIN=0.008*FCRMHL*RAINT(NOCTD)
* CRAIN=cumulative areic volume of rainfall (m)
      CRAIN=INTGRL(0.0,RAIN)
* DAREVP=daily average of volume flux of potential evaporation from
*       soil (m/d)
      DAREVP=0.001*FCEWWS*(REVOBT(NDAY)+REVOET(NDAY)+REVOKT(NDAY))/3.0
* REVP=volume flux of potential evaporation from soil (m/d)
      REVP=-PI*DAREVP*AMIN1(0.0,COS(2.0*PI*TIME))
* CEVP=cumulative areic volume of potential evaporation from soil (m)
      CEVP=INTGRL(0.0,REVP)
      IF (KEEP.NE.1) GO TO 23
      IF (RAIN.LE.REVP) GO TO 20
* REVA=volume flux of actual evaporation from soil (m/d)
      REVA=REVP
      STER=STER+(RAIN-REVP)*DELT
      GO TO 22
   20 CONTINUE
      IF (STER.LT.(REVP-RAIN)*DELT) GO TO 21
      REVA=REVP
      STER=STER-(REVP-RAIN)*DELT
      GO TO 22
   21 CONTINUE
      SIGEP=SIGEP+(REVP-RAIN)*DELT-STER
      REVA=RAIN+STER/DELT+(AMIN1(SIGEP,BETA*SQRT(SIGEP))-SIGEA)/DELT
      STER=0.0
      SIGEA=AMIN1(SIGEP,BETA*SQRT(SIGEP))
   22 CONTINUE
      IF (SAMPLE(0.75,121.0,1.0).EQ.0.0) GO TO 23
      SIGEA=AMAX1(0.0,SIGEA-STER)
      STER=0.0
      SIGEP=AMAX1(SIGEA,SIGEA**2/BETA**2)
```

```
   23 CONTINUE
* CEVA=cumulative areic volume of actual evaporation from soil (m)
      CEVA=INTGRL(0.0,REVA)
PRINT DAREVP,REVP,REVA,RAIN,STER
METHOD RECT
TIMER DELT=0.005,PRDEL=1.0,FINTIM=121.0
END
```

APPENDIX D

Numerical analysis of mass conservation equation including transport and transformation

It is assumed that θ, J^V and ρ_b are constant with depth and time and that the sorption isotherm is linear (Equation 2.6). Equations 2.1, 2.2 and 3.1 may then be simplified to

$$\frac{\partial c^*}{\partial t} = -k_t^* c^* - J^V \frac{\partial c}{\partial z} + D_{dd} \frac{\partial^2 c}{\partial z^2} \tag{D.1}$$

From Equations 2.5, 2.6 and 6.29 it follows:

$$\frac{\partial c}{\partial t} = \frac{1}{q' + \theta} \frac{\partial c^*}{\partial t} \tag{D.2}$$

Rearranging a Taylor-series expansion of $\partial c^*/\partial t$ yields:

$$\frac{\Delta c^*}{\Delta t} = \frac{(c^*)^{j+1} - (c^*)^j}{\Delta t} = \frac{\partial c^*}{\partial t} + \frac{\Delta t}{2} \frac{\partial^2 c^*}{\partial t^2} + \frac{\Delta t^2}{6} \frac{\partial^3 c^*}{\partial t^3} + \cdots\cdots \tag{D.3}$$

Substitution of Equation D.1 in Equation D.3 results in

$$\frac{\Delta c^*}{\Delta t} = -k_t^* c^* - J^V \frac{\partial c}{\partial z} + D_{dd} \frac{\partial^2 c}{\partial z^2} + \frac{\Delta t}{2} \frac{\partial}{\partial t} \left(-k_t^* c^* - J^V \frac{\partial c}{\partial z} + D_{dd} \frac{\partial^2 c}{\partial z^2} \right) + \cdots\cdots \tag{D.4}$$

Reversing the sequence of differentiation and repeatedly using Equations D.1 and D.2 results in

$$\frac{\Delta c^*}{\Delta t} = -k_{\mathrm{t}}^*(1 - \tfrac{1}{2}k_{\mathrm{t}}^*\,\Delta t)c^* - J^V(1 - k_{\mathrm{t}}^*\,\Delta t)\,\frac{\partial c}{\partial z} +$$

$$D_{\mathrm{dd}}\left[1 - k_{\mathrm{t}}^*\Delta t + \frac{\Delta t\ \{J^V\}^2}{2(q' + \theta)D_{\mathrm{dd}}}\right]\frac{\partial^2 c}{\partial z^2} + \ldots\ldots \qquad \text{(D.5)}$$

In Equation D.5 the contributions of terms that comprehend Δt^2, Δt^3, etc. are ignored. In the computations for cyanazine and metribuzin k_{t}^* is lower than or equal to 0.04 d^{-1} and the time step, Δt, is smaller than or equal to 0.1 d. The product of these quantities is so small that Equation D.5 may be simplified to

$$\frac{\Delta c^*}{\Delta t} = -k_{\mathrm{t}}^*\,c^* - J^V\,\frac{\partial c}{\partial z} + \left[D_{\mathrm{dd}} + \frac{\Delta t\ \{J^V\}^2}{2(q' + \theta\,)}\right]\frac{\partial^2 c}{\partial z^2} + \ldots\ldots \qquad \text{(D.6)}$$

For constant J^V, θ and Δz_i the finite-difference approximations described by Equations 6.19, 6.20 and 6.21 are equivalent to the following approximations for $\partial c/\partial z$ and $\partial^2 c/\partial z^2$:

$$\frac{\Delta c}{\Delta z} \equiv \frac{(c)_{i+1} - (c)_{i-1}}{2\Delta z} = \frac{\partial c}{\partial z} + \frac{\Delta z^2}{6}\,\frac{\partial^3 c}{\partial z^3} + \ldots\ldots \qquad \text{(D.7)}$$

$$\frac{\Delta^2 c}{\Delta z^2} \equiv \frac{(c)_{i+1} - 2(c)_i + (c)_{i-1}}{\Delta z^2} = \frac{\partial^2 c}{\partial z^2} + \frac{\Delta z^2}{12}\,\frac{\partial^4 c}{\partial z^4} + \ldots\ldots \qquad \text{(D.8)}$$

Incorporating Equations D.7 and D.8 in Equation D.6 results in

$$\frac{\Delta c^*}{\Delta t} = -k_{\mathrm{t}}^*\,c^* - J^V\,\frac{\Delta c}{\Delta z} + \left[D_{\mathrm{dd}} + \frac{\Delta t\,\{J^V\}^2}{2(q' + \theta\,)}\right]\frac{\Delta^2 c}{\Delta z^2} + \ldots\ldots \qquad \text{(D.9)}$$

Equation D.9 suggests use of a spreading coefficient corrected according to Equation 6.28 (the same as derived from van Genuchten & Wierenga, 1974). Thus here, adding the term $-k_{\mathrm{t}}^*\,c^*$ to the right-hand side of the conservation equation did not influence the ultimate result of the numerical analysis.

APPENDIX E

```
TITLE EQUILIBRIUM TRANSPORT MODEL
*********************************

TITLE TRANSPORT OF METRIBUZIN AT EXPERIMENTAL FIELD 'DE WAAG' IN 1982
STORAGE TCOM(35),DEPTH(35),DIST(36),WDFA(35),VFLMAX(35),VFLMIN(35)
STORAGE MOWWF(35),RDVFL(35),PRIVFL(35),FLIQ(36),RAINT(121),REVAT(121)
STORAGE CL(35),DDIF(35),FSUB(36),DSPR(36),CLAV(35),RTR(35)
STORAGE BD(35),SCO(35),DNUM(36),OLDCL(35)
FIXED NCOM,NCOMP,I,NDAY
INITIAL
NOSORT
*
**
***   definition of soil system geometry : one-dimensional,vertical
**
*
* TCOM=thickness of the compartments (m)
TABLE TCOM(1-35)=10*0.005,15*0.01,10*0.02
* NCOM=number of compartments
PARAM NCOM=35
      NCOMP=NCOM+1
* DEPTH=depths of the centres of the compartments (m)
* DIST=distance between compartment centres (m)
      DEPTH(1)=0.5*TCOM(1)
      DO 10 I=2,NCOM
      DIST(I)=0.5*(TCOM(I-1)+TCOM(I))
   10 DEPTH(I)=DEPTH(I-1)+DIST(I)
*
**
***   rainfall and evaporation
**
*
* RAINT=volume flux of rainfall (mm/d),daily values,measured at
*       1.2 m height
TABLE RAINT(1-121)=19.5,3.0,1.5,8*0.0,0.1,2*0.0,11.6,0.0,9.1,0.4, ...
* FCRMHL=factor for conversion from rainfall measured at 1.2 m height
*        to rainfall measured flush with the soil surface (1)
PARAM FCRMHL=1.07
* REVAT=volume flux of actual evaporation (mm/d),daily values,
*       calculated with evaporation model
TABLE REVAT(1-121)=1.50,2.16,2.04,3.10,1.24,0.98,0.92,0.91,0.85,0.74,...
*
**
*** parameters and relationships
**
*
**  hydraulic properties of the soil
*
* WDFA=factor for withdrawal of water resulting from evaporation (1)
*      as a f(depth)
FUNCTION WDFAF=0.0,1.0,0.01,0.4,0.02,0.2,0.03,0.1,0.05,0.03,0.4,0.0
      DO 11 I=1,NCOM
   11 WDFA(I)=AFGEN(WDFAF,DEPTH(I))
* VFLMAX=maximal volume fraction of liquid (m3/m3)
```

```
TABLE VFLMAX(1-35)=2*0.2,2*0.22,2*0.24,4*0.27,5*0.28,20*0.3
* VFLMIN=minimal volume fraction of liquid (m3/m3)
TABLE VFLMIN(1-35)=35*0.01
*
**  further soil characteristics and interactions between substance
**  and soil system
*
* BD=dry soil bulk density (kg/m3) as f(depth)
FUNCTION BDF=0.0,1.21E3,0.015,1.29E3,0.045,1.31E3,0.055,1.39E3, ...
  0.07,1.39E3,0.08,1.42E3,0.4,1.42E3
      DO 13 I=1,NCOM
   13 BD(I)=AFGEN(BDF,DEPTH(I))
* LDIS=dispersion length (m)
* DO=diffusion coefficient of substance in water (m2/d)
PARAM LDIS=0.008,DO=0.39E-4
* LABDA=tortuosity factor for diffusion through liquid phase (1)
*       as f(vol fr liq)
FUNCTION LABDAF=0.0,0.0,0.035,2.0E-4,0.07,0.01,0.1,0.03,0.15,0.06, ...
      0.2,0.1,0.3,0.2,0.4,0.34,0.5,0.5,0.6,0.6
* INVN=Freundlich exponent (1)
* KF  =Freundlich coefficient (m**(3*INVN) kg**(-INVN))
PARAM KF=0.1467E-3,INVN=0.894
* RER=relative error accepted in iteration procedure (1)
PARAM RER=.001
* CSOL=concentration at which the substance dissolves (kg/m3)
PARAM CSOL=0.3
* KTR=transformation rate coefficient (1/d)
PARAM KTR=0.0322
*
**
***   initial conditions
**
*
* SVFL=starting volume fraction of liquid (m3/m3)
TABLE SVFL(1-35)=3*0.057,3*0.191,4*0.21,2*0.262,3*0.28,20*0.3
* DOSE=areic mass of substance applied (kg/m2)
PARAM DOSE=0.0964E-3
* SCSY=starting concentration of substance in the soil system (kg/m3)
TABLE SCSY(1-35)=35*0.0
* CL=concentration of substance in the liquid phase (kg/m3)
      DO 19 I=1,NCOM
   19 CL(I)=0.0

      WRITE(6,16)(DEPTH(I),I=1,NCOM)
   16 FORMAT(1H0,5X,'DEPTH=',10F10.4/(12X,10F10.4))

DYNAMIC
NOSORT
      NDAY=TIME+1
*
**
***   flow of water in soil
**
*
* VFL=volume fraction of liquid (m3/m3)
* RVFL=rate of change in VFL (m3/(m3 d))
      VFL=INTGRL(SVFL,RVFL,35)
```

```
* RAIN=volume flux of rainfall (m/d)
      RAIN=0.001*FCRMHL*RAINT(NDAY)
* CRAIN=cumulative areic volume of rainfall (m)
      CRAIN=INTGRL(0.0,RAIN)
* REVA=volume flux of actual evaporation from the soil surface (m/d)
      REVA=0.001*REVAT(NDAY)
* CEVA=cumulative areic volume of actual evaporation from the soil
*       surface (m)
      CEVA=INTGRL(0.0,REVA)
* FLIQ=volume flux of liquid through the soil (m/d)
      FLIQ(1)=RAIN-REVA
      IF (FLIQ(1).GE.0.0) GO TO 40
*
**  calculation of liquid fluxes if net upward flux at surface
*
* MOWWF=moisture weighed withdrawal factor (m3/m3)
* SUM=compartment thickness weighed sum of MOWWF-factors (m)
      SUM=0.0
      DO 30 I=1,NCOM
      MOWWF(I)=AMAX1(0.0,VFL(I)-VFLMIN(I))*WDFA(I)
   30 SUM=SUM+MOWWF(I)*TCOM(I)
* RDVFL=rate of decrease in VFL resulting from evaporation (m3/(m3 d))
      DO 31 I=1,NCOM
   31 RDVFL(I)=(MOWWF(I)/SUM)*FLIQ(1)
      DO 32 I=2,NCOMP
   32 FLIQ(I)=FLIQ(I-1)-RDVFL(I-1)*TCOM(I-1)
      GO TO 50
   40 CONTINUE
*
**  calculation of liquid fluxes if net downward flux at surface
*
* PRIVFL=potential rate of increase in VFL resulting from rainfall
*         (m3/(m3 d))
      DO 41 I=1,NCOM
   41 PRIVFL(I)=(VFLMAX(I)-VFL(I))/DELT
      DO 42 I=2,NCOMP
   42 FLIQ(I)=AMAX1(0.0,FLIQ(I-1)-PRIVFL(I-1)*TCOM(I-1))
   50 CONTINUE
* CLPER=cumulative areic volume of liquid percolated (m)
      CLPER=INTGRL(0.0,FLIQ(NCOMP))
*
**  conservation equation for water in soil
*
      DO 51 I=1,NCOM
   51 RVFL(I)=(FLIQ(I)-FLIQ(I+1))/TCOM(I)
*
**
***   behaviour of the substance
**
*
* CSY=concentration of substance in the soil system (kg/m3)
* RCSY=rate of change in CSY (kg/(m3 d))
      CSY=INTGRL(SCSY,RCSY,35)
*
**  iteration procedure for calculation of CL
*
```

```
* TNUMIT=total number of iterations per time step
* OLDCL=old value of CL
* SCO=sorption coefficient (m3/kg)
      TNUMIT=0.0
      DO 52 I=1,NCOM
   53 CONTINUE
      TNUMIT=TNUMIT+1.0
      OLDCL(I)=CL(I)
      SCO(I)=KF*(CL(I)+NOT(CL(I)))**(INVN-1.0)
      CL(I)=CSY(I)/(VFL(I)+BD(I)*SCO(I))
      IF(ABS(CL(I)-OLDCL(I)).GT.(RER*ABS(CL(I)+NOT(CL(I))))) GO TO 53
   52 CONTINUE
*
**  calculation of the fluxes of substance
*
* FSUB=mass flux of substance (kg/(m2 d))
* MASUNS=areic mass of substance undissolved at soil surface (kg/m2)
      FSUB(1)=AMIN1(AMAX1(0.0,CSOL*FLIQ(1)),MASUNS/DELT)
      MASUNS=INTGRL(DOSE,-FSUB(1))
* DDIF=diffusion coefficient for substance in liquid phase (m2/d)
      DO 60 I=1,NCOM
      DDIF(I)=D0*VFL(I)*AFGEN(LABDAF,VFL(I))
   60 CONTINUE
* DNUM=coefficient for numerical dispersion (m2/d)
* DSPR=spreading coefficient (m2/d)
* CLAV=averaged CL used for convective flow
      DO 61 I=2,NCOM
      DNUM(I)=0.5*DELT*FLIQ(I)**2/(VFL(I)+BD(I)*INVN*SCO(I))
      DSPR(I)=LDIS*ABS(FLIQ(I))+0.5*(DDIF(I-1)+DDIF(I))+DNUM(I)
      CLAV(I)=(TCOM(I)*CL(I-1)+TCOM(I-1)*CL(I))/(TCOM(I-1)+TCOM(I))
      FSUB(I)=FLIQ(I)*CLAV(I)-DSPR(I)*(CL(I)-CL(I-1))/DIST(I)
   61 CONTINUE
      IF (FLIQ(2).GE.0.0.OR.CL(1).LE.CL(2)) GO TO 62
      FSUB(2)=FLIQ(2)*CL(2)-0.5*(DDIF(1)+DDIF(2))*(CL(2)-CL(1))/DIST(2)
   62 CONTINUE
      FSUB(NCOMP)=AMAX1(FLIQ(NCOMP)*CL(NCOM),0.0)
      DO 65 I=1,NCOM
      IF (FLIQ(I+1).GT.0.0.AND.CL(I).LT.0.0) FSUB(I+1)=0.0
   65 CONTINUE
* CSPER=cumulative areic mass of substance percolated (kg/m2)
      CSPER=INTGRL(0.0,FSUB(NCOMP))
*
**  transformation of the substance
*
* RTR=volumic mass rate of transformation (kg/(m3 d))
* TRTR=total areic mass rate of transformation (kg/(m2 d))
      TRTR=0.0
      DO 63 I=1,NCOM
      RTR(I)=KTR*CSY(I)
   63 TRTR=TRTR+RTR(I)*TCOM(I)
* CTRAN=cumulative areic mass of substance transformed (kg/m2)
      CTRAN=INTGRL(0.0,TRTR)
*
**  conservation equation for the substance
*
      DO 70 I=1,NCOM
   70 RCSY(I)=(FSUB(I)-FSUB(I+1))/TCOM(I)-RTR(I)
```

```
*
**
***   output section
**
*
* TVOL=total areic volume of liquid in soil system (m)
      TVOL=0.0
      DO 80 I=1,NCOM
   80 TVOL=TVOL+VFL(I)*TCOM(I)
* TMAS=total areic mass of substance in soil system (kg/m2)
      TMAS=0.0
      DO 90 I=1,NCOM
   90 TMAS=TMAS+CSY(I)*TCOM(I)
      CL1=CL(1)
      CL20=CL(20)
PRINT TVOL,CRAIN,CEVA,CLPER,FSUB(1),MASUNS,TMAS,CTRAN,CSPER,DNUM(2),...
  DSPR(2),TNUMIT,CSY(1-35),OLDCL(1),CL(1),SCO(1),VFL(1-2)
METHOD RECT
TIMER DELT=0.015625,PRDEL=1.0,FINTIM=121.0
FINISH CL1=-0.01E-3,CL20=-0.01E-3
END
TITLE MOVEMENT OF CYANAZINE AT EXPERIMENTAL FIELD 'DE WAAG' IN 1982
PARAM DIFL=0.36E-4,KF=0.336E-3,INVN=0.907,CSOL=0.04
PARAM KTR=0.0331,DOSE=0.149E-3
TIMER DELT=0.025,PRDEL=1.0,FINTIM=121.0
END
```

APPENDIX F

```
TITLE FREUNDLICH SORPTION MODEL WITH TWO-SITE KINETICS
******************************************************

* M=mass of solid phase (kg)
* V=volume of liquid (m3)
PARAM M=17.83E-3,V=4.17E-6
* TMSU=total mass of substance (kg)
PARAM TMSU=8.13E-9
* INVN=Freundlich exponent (1)
* KF=Freundlich coefficient (m**(3*INVN) kg**(-INVN))
* FF=fraction of KF to be attributed to class-1 sites (1)
PARAM INVN=0.894,KF=0.147E-3,FF=0.739
* KD1=desorption rate constant of class-1 sites (1/d)
* KD2=desorption rate constant of class-2 sites (1/d)
PARAM KD1=180.0,KD2=0.4
* SX1=starting content of substance sorbed at class-1 sites (kg/kg)
* SX2=starting content of substance sorbed at class-2 sites (kg/kg)
PARAM SX1=0.0,SX2=0.0
* CL=concentration of substance in the liquid phase (kg/m3)
* X1=content of substance sorbed at class-1 sites (kg/kg)
* X2=content of substance sorbed at class-2 sites (kg/kg)
      CL=(TMSU-M*(X1+X2))/V
* RX1=rate of change in X1 (kg/(kg d))
* RX2=rate of change in X2 (kg/(kg d))
      RX1=KD1*(FF*KF*CL**INVN-X1)
```

```
      RX2=KD2*((1.0-FF)*KF*CL**INVN-X2)
      X1=INTGRL(SX1,RX1)
      X2=INTGRL(SX2,RX2)
* X=total content of substance sorbed (kg/kg)
      X=X1+X2
PRINT CL,X,X1,X2
TIMER PRDEL=0.6944E-3,FINTIM=6.944E-3
METHOD RKS
END
```

APPENDIX C

```
TITLE NON-EQUILIBRIUM TRANSPORT MODEL BASED ON THREE-SITE SORPTION MODEL
**************************************************************************

TITLE TRANSPORT OF CYANAZINE AT EXPERIMENTAL FIELD 'DE WAAG' IN 1982
STORAGE TCOM(35),DEPTH(35),DIST(36),WDFA(35),VFLMAX(35),VFLMIN(35)
STORAGE MOWWF(35),RDVFL(35),PRIVFL(35),FLIQ(36),RAINT(121),REVAT(121)
STORAGE CL(35),DDIF(35),FSUB(36),DSPR(36),CLAV(35),RTR(35),CSYRF(35)
STORAGE BD(35),SCO1(35),OLDCL(35),FRED(35),KD2(35),KD3(35)
FIXED NCOM,NCOMP,I,NDAY
INITIAL
NOSORT
*
**
***   definition of soil system geometry : one-dimensional,vertical
**
*
* TCOM=thickness of the compartments (m)
TABLE TCOM(1-35)=10*0.005,15*0.01,10*0.02
* NCOM=number of compartments
PARAM NCOM=35
      NCOMP=NCOM+1
* DEPTH=depths of the centres of the compartments (m)
* DIST=distance between compartment centres (m)
      DEPTH(1)=0.5*TCOM(1)
      DO 10 I=2,NCOM
      DIST(I)=0.5*(TCOM(I-1)+TCOM(I))
   10 DEPTH(I)=DEPTH(I-1)+DIST(I)
*
**
***   rainfall and evaporation
**
*
* RAINT=volume flux of rainfall (mm/d),daily values,measured at
*       1.2 m height
TABLE RAINT(1-121)=19.5,3.0,1.5,8*0.0,0.1,2*0.0,11.6,0.0,9.1,0.4, ...
* FCRMHL=factor for conversion from rainfall measured at 1.2 m height
*        to rainfall measured flush with the soil surface (1)
PARAM FCRMHL=1.07
* REVAT=volume flux of actual evaporation (mm/d),daily values,
*       calculated with evaporation model
TABLE REVAT(1-121)=1.50,2.16,2.04,3.10,1.24,0.98,0.92,0.91,0.85,0.74,...
*
```

```
**
***   parameters and relationships
**
*
**  hydraulic properties of the soil
*
* WDFA=factor for withdrawal of water resulting from evaporation (1)
*      as a f(depth)
FUNCTION WDFAF=0.0,1.0,0.01,0.4,0.02,0.2,0.03,0.1,0.05,0.03,0.4,0.0
      DO 11 I=1,NCOM
   11 WDFA(I)=AFGEN(WDFAF,DEPTH(I))
* VFLMAX=maximal volume fraction of liquid (m3/m3)
TABLE VFLMAX(1-35)=2*0.2,2*0.22,2*0.24,4*0.27,5*0.28,20*0.3
* VFLMIN=minimal volume fraction of liquid (m3/m3)
TABLE VFLMIN(1-35)=35*0.01
*
**  further soil characteristics and interactions between substance
**  and soil system
*
* BD=dry soil bulk density (kg/m3) as f(depth)
FUNCTION BDF=0.0,1.21E3,0.015,1.29E3,0.045,1.31E3,0.055,1.39E3, ...
  0.07,1.39E3,0.08,1.42E3,0.4,1.42E3
      DO 13 I=1,NCOM
   13 BD(I)=AFGEN(BDF,DEPTH(I))
* LDIS=dispersion length (m)
* DO=diffusion coefficient of substance in water (m2/d)
PARAM LDIS=0.008,DO=0.36E-4
* LABDA=tortuosity factor for diffusion through liquid phase (1)
*       as f(vol fr liq)
FUNCTION LABDAF=0.0,0.0,0.035,2.0E-4,0.07,0.01,0.1,0.03,0.15,0.06, ...
      0.2,0.1,0.3,0.2,0.4,0.34,0.5,0.5,0.6,0.6
* INVN=Freundlich exponent (1)
* KF1,KF2=Freundlich coefficients (m**(3*INVN) kg**(-INVN)) for class-1
*          and class-2 sites, respectively
PARAM KF1=0.2353E-3,KF2=0.1008E-3,INVN=0.907
* K2MAX=maximal slope of sorption isotherm of class-2 sites (m3/kg)
PARAM K2MAX=0.4E-3
* K3=slope of sorption isotherm of class-3 sites (m3/kg)
* X3=content of substance sorbed at class-3 sites (kg/kg)
* FI=fraction of X3 still sorbed after first extraction with
*    ethyl acetate (1)
PARAM K3=0.2E-3,FI=0.15
* RER=relative error accepted in iteration procedure (1)
PARAM RER=0.001
* KD2M,KD3M=desorption rate constants for class-2 and class-3 sites,
*            respectively in moist soil (1/d)
PARAM KD2M=0.5,KD3M=0.02
* FRED=factor (1) for reduction of desorption rate constants as a
*      f(vol fr liq)
FUNCTION FREDF=0.0,0.0,0.039,0.0,0.04,1.0,0.5,1.0
* CSOL=concentration at which the substance dissolves (kg/m3)
PARAM CSOL=0.04
* KDEC=rate coefficient for decline of concentration of substance
*      released by first extraction with ethyl acetate (1/d)
PARAM KDEC=0.0331
*
**
```

```
***   initial conditions
**
*
* SVFL=starting volume fraction of liquid (m3/m3)
TABLE SVFL(1-35)=3*0.057,3*0.191,4*0.21,2*0.262,3*0.28,20*0.3
* DOSE=areic mass of substance applied (kg/m2)
PARAM DOSE=0.149E-3
* SCSY=starting concentration of substance in the soil system (kg/m3)
TABLE SCSY(1-35)=35*0.0
* SX2=starting content of substance sorbed at class-2 sites (kg/kg)
TABLE SX2(1-35)=35*0.0
* SX3=starting content of substance sorbed at class-3 sites (kg/kg)
TABLE SX3(1-35)=35*0.0
* CL=concentration of substance in the liquid phase (kg/m3)
      DO 19 I=1,NCOM
   19 CL(I)=0.0

      WRITE(6,16)(DEPTH(I),I=1,NCOM)
   16 FORMAT(1H0,5X,'DEPTH=',10F10.4/(12X,10F10.4))

DYNAMIC
NOSORT
      NDAY=TIME+1
*
**
***   flow of water in soil
**
*
* VFL=volume fraction of liquid (m3/m3)
* RVFL=rate of change in VFL (m3/(m3 d))
      VFL=INTGRL(SVFL,RVFL,35)
* RAIN=volume flux of rainfall (m/d)
      RAIN=0.001*FCRMHL*RAINT(NDAY)
* CRAIN=cumulative areic volume of rainfall (m)
      CRAIN=INTGRL(0.0,RAIN)
* REVA=volume flux of actual evaporation from the soil surface (m/d)
      REVA=0.001*REVAT(NDAY)
* CEVA=cumulative areic volume of actual evaporation from the soil
*      surface (m)
      CEVA=INTGRL(0.0,REVA)
* FLIQ=volume flux of liquid through the soil (m/d)
      FLIQ(1)=RAIN-REVA
      IF (FLIQ(1).GE.0.0) GO TO 40
*
**  calculation of liquid fluxes if net upward flux at surface
*
* MOWWF=moisture weighed withdrawal factor (m3/m3)
* SUM=compartment thickness weighed sum of MOWWF-factors (m)
      SUM=0.0
      DO 30 I=1,NCOM
      MOWWF(I)=AMAX1(0.0,VFL(I)-VFLMIN(I))*WDFA(I)
   30 SUM=SUM+MOWWF(I)*TCOM(I)
* RDVFL=rate of decrease in VFL resulting from evaporation (m3/(m3 d))
      DO 31 I=1,NCOM
   31 RDVFL(I)=(MOWWF(I)/SUM)*FLIQ(1)
      DO 32 I=2,NCOMP
   32 FLIQ(I)=FLIQ(I-1)-RDVFL(I-1)*TCOM(I-1)
```

```
      GO TO 50
   40 CONTINUE
*
**  calculation of liquid fluxes if net downward flux at surface
*
* PRIVFL=potential rate of increase in VFL resulting from rainfall
*         (m3/(m3 d))
      DO 41 I=1,NCOM
   41 PRIVFL(I)=(VFLMAX(I)-VFL(I))/DELT
      DO 42 I=2,NCOMP
   42 FLIQ(I)=AMAX1(0.0,FLIQ(I-1)-PRIVFL(I-1)*TCOM(I-1))
   50 CONTINUE
* CLPER=cumulative areic volume of liquid percolated (m)
      CLPER=INTGRL(0.0,FLIQ(NCOMP))
*
**  conservation equation for water in soil
*
      DO 51 I=1,NCOM
   51 RVFL(I)=(FLIQ(I)-FLIQ(I+1))/TCOM(I)
*
**
***   behaviour of the substance
**
*
* CSY=concentration of substance in the soil system (kg/m3)
* RCSY=rate of change in CSY (kg/(m3 d))
      CSY=INTGRL(SCSY,RCSY,35)
* X2=content of substance sorbed at class-2 sites (kg/kg)
* RX2=rate of change in X2 (kg/(kg d))
      X2=INTGRL(SX2,RX2,35)
* X3=content of substance sorbed at class-3 sites (kg/kg)
* RX3=rate of change in X3 (kg/(kg d))
      X3=INTGRL(SX3,RX3,35)
*
**  iteration procedure for calculation of CL
*
* TNUMIT=total number of iterations per time step
* OLDCL=old value of CL
* SCO1=sorption coefficient of class-1 sites (m3/kg)
      TNUMIT=0.0
      DO 52 I=1,NCOM
   53 CONTINUE
      TNUMIT=TNUMIT+1.0
      OLDCL(I)=CL(I)
      SCO1(I)=KF1*(CL(I)+NOT(CL(I)))**(INVN-1.0)
      CL(I)=(CSY(I)-BD(I)*(X2(I)+X3(I)))/(VFL(I)+BD(I)*SCO1(I))
      IF(ABS(CL(I)-OLDCL(I)).GT.(RER*ABS(CL(I)+NOT(CL(I))))) GO TO 53
   52 CONTINUE
*
**  sorption rate equations
*
      DO 55 I=1,NCOM
      FRED(I)=AFGEN(FREDF,VFL(I))
      KD2(I)=FRED(I)*KD2M
      KD3(I)=FRED(I)*KD3M
      RX2(I)=KD2(I)*(AMIN1(K2MAX*CL(I),KF2*CL(I)**INVN)-X2(I))
   55 RX3(I)=KD3(I)*(K3*CL(I)-X3(I))
```

```
*
**  calculation of the substance fluxes
*
* FSUB=mass flux of substance (kg/(m2 d))
* MASUNS=areic mass of substance undissolved at soil surface (kg/m2)
      FSUB(1)=AMIN1(AMAX1(0.0,CSOL*FLIQ(1)),MASUNS/DELT)
      MASUNS=INTGRL(DOSE,-FSUB(1))
* DDIF=diffusion coefficient for substance in liquid phase (m2/d)
      DO 60 I=1,NCOM
      DDIF(I)=DO*VFL(I)*AFGEN(LABDAF,VFL(I))
   60 CONTINUE
* DSPR=spreading coefficient (m2/d)
* CLAV=averaged CL used for convective flow
      DO 61 I=2,NCOM
      DSPR(I)=LDIS*ABS(FLIQ(I))+0.5*(DDIF(I-1)+DDIF(I))
      CLAV(I)=(TCOM(I)*CL(I-1)+TCOM(I-1)*CL(I))/(TCOM(I-1)+TCOM(I))
      FSUB(I)=FLIQ(I)*CLAV(I)-DSPR(I)*(CL(I)-CL(I-1))/DIST(I)
   61 CONTINUE
      IF (FLIQ(2).GE.0.0.OR.CL(1).LE.CL(2)) GO TO 62
      FSUB(2)=FLIQ(2)*CL(2)-0.5*(DDIF(1)+DDIF(2))*(CL(2)-CL(1))/DIST(2)
   62 CONTINUE
      FSUB(NCOMP)=AMAX1(FLIQ(NCOMP)*CL(NCOM),0.0)
      DO 65 I=1,NCOM
      IF (FLIQ(I+1).GT.0.0.AND.CL(I).LT.0.0) FSUB(I+1)=0.0
   65 CONTINUE
* CSPER=cumulative areic mass of substance percolated (kg/m2)
      CSPER=INTGRL(0.0,FSUB(NCOMP))
*
**  transformation of the substance
*
* TMA=total areic mass of substance in soil system (kg/m2)
* TMAL=total areic mass of substance in liquid phase (kg/m2)
* TMA3=total areic mass of substance sorbed at class-3 sites (kg/m2)
      TMA=0.0
      TMAL=0.0
      TMA3=0.0
      DO 64 I=1,NCOM
      TMA=TMA+TCOM(I)*CSY(I)
      TMAL=TMAL+TCOM(I)*VFL(I)*CL(I)
   64 TMA3=TMA3+TCOM(I)*BD(I)*X3(I)
* TMA3S=fraction of TMA3 still sorbed after first extraction with
*       ethyl acetate (kg/m2)
      TMA3S=FI*TMA3
* TMARF=total areic mass of substance released by first extraction with
*       ethyl acetate (kg/m2)
      TMARF=TMA-TMA3S
* KTL=rate coefficient for transformation in the liquid phase (1/d)
      KTL=(TMARF*KDEC-DERIV(0.0,TMA3S))/(TMAL+NOT(TMAL))
* RTR=volumic mass rate of transformation (kg/(m3 d))
* TRTR=total areic mass rate of transformation (kg/(m2 d))
      TRTR=0.0
      DO 63 I=1,NCOM
      RTR(I)=KTL*VFL(I)*CL(I)
   63 TRTR=TRTR+RTR(I)*TCOM(I)
* CTRAN=cumulative areic mass of substance transformed (kg/m2)
      CTRAN=INTGRL(0.0,TRTR)
*
```

```
**  conservation equation for the substance
*
      DO 70 I=1,NCOM
   70 RCSY(I)=(FSUB(I)-FSUB(I+1))/TCOM(I)-RTR(I)
*
**
***   output section
**
*
* TVOL=total areic volume of liquid in soil system (m)
      TVOL=0.0
      DO 80 I=1,NCOM
   80 TVOL=TVOL+VFL(I)*TCOM(I)
* TMA1=total areic mass of substance sorbed at class-1 sites (kg/m2)
* TMA2=total areic mass of substance sorbed at class-2 sites (kg/m2)
      TMA1=0.0
      TMA2=0.0
      DO 90 I=1,NCOM
      TMA1=TMA1+TCOM(I)*BD(I)*KF1*CL(I)**INVN
   90 TMA2=TMA2+TCOM(I)*BD(I)*X2(I)
* CSYRF=concentration of substance in soil system released
*        by first extraction with ethyl acetate (kg/m3)
      DO 91 I=1,NCOM
   91 CSYRF(I)=CSY(I)-BD(I)*FI*X3(I)
* QCMB=quantity to check the material balance (kg/m2)
      QCMB=TMA-TMAL-TMA1-TMA2-TMA3
      CL1=CL(1)
      CL20=CL(20)
PRINT TVOL,CRAIN,CEVA,CLPER,FLIQ(1),FSUB(1),MASUNS,TMA,CTRAN,CSPER,...
  TNUMIT,CSYRF(1-27),OLDCL(1),CL(1),SC01(1),KD2(1)
OUTPUT QCMB,TMA,TMAL,TMA1,TMA2,TMA3,TMARF,KTL,X2(1),X3(1-10)
LABEL CONTENTS SORBED AT CLASS-2 AND CLASS-3 SITES
METHOD RECT
      IF (SAMPLE(0.0,121.0,1.0).EQ.1.0) CALL PRINT
      IF (SAMPLE(0.0,121.0,1.0).EQ.1.0) CALL OUTPUT
TIMER DELT=0.025,PRDEL=1000.0,OUTDEL=1000.0,FINTIM=1.0
FINISH CL1=-0.01E-3,CL20=-0.01E-3
END CONTINUE
TIMER DELT=0.1,FINTIM=14.0
END CONTINUE
TIMER DELT=0.025,FINTIM=15.0
END CONTINUE
TIMER DELT=0.1,FINTIM=38.0
END CONTINUE
TIMER DELT=0.025,FINTIM=39.0
END CONTINUE
TIMER DELT=0.1,FINTIM=47.0
END CONTINUE
TIMER DELT=0.025,FINTIM=48.0
END CONTINUE
TIMER DELT=0.1,FINTIM=103.0
END CONTINUE
TIMER DELT=0.025,FINTIM=105.0
END CONTINUE
TIMER DELT=0.1,FINTIM=121.0
END
```

LIST OF SYMBOLS

Symbol	Description	Unit
a	a constant	(1)
b_1	a constant	(d^{-1})
b_2	a constant	(d^{-1})
c	mass concentration of substance in liquid phase	(kg m^{-3})
$\bar{c}$	fractional c	(1)
$c(0)$	c at the start ($t = 0$)	(kg m^{-3})
$c(\infty)$	c at equilibrium ($t = \infty$)	(kg m^{-3})
$c_{2,h}$	hypothetical value of c in equilibrium with momentary value of X_2	(kg m^{-3})
c_m	c in mobile region in soil	(kg m^{-3})
$\bar{c}_m$	fractional c_m	(1)
$c_m(0)$	c_m at the start ($t = 0$)	(kg m^{-3})
$c_m(\infty)$	c_m at equilibrium ($t = \infty$)	(kg m^{-3})
c_{max}	maximum of c in experiment	(kg m^{-3})
c_{min}	minimum of c in experiment	(kg m^{-3})
c_s	c in stagnant zone in soil	(kg m^{-3})
$\bar{c}_s$	fractional c_s	(1)
$c_s(0)$	c_s at the start ($t = 0$)	(kg m^{-3})
$c_s(\infty)$	c_s at equilibrium ($t = \infty$)	(kg m^{-3})
c_{sol}	mass concentration in liquid phase at which the substance dissolves	(kg m^{-3})
c_ζ	c after ζ-th desorption step	(kg m^{-3})
c^*	mass concentration of substance in the soil system	(kg m^{-3})
c^*_f	c^* released by first extraction with ethyl acetate	(kg m^{-3})
d_A	dose (areic mass) of substance	(kg m^{-2})
f	mass fraction of solid phase assigned to mobile zone	(1)
g	a constant	(1)
h	a constant	(1)
i	index of grid points (compartments) in space	(1)
j	index of grid points in time	(1)

$k_{12,3}$	rate constant for conversion of X_1 and X_2 into X_3	(d^{-1})
k_{a}	adsorption rate constant	($\mathrm{m}^3\ \mathrm{kg}^{-1}\ \mathrm{d}^{-1}$)
$k_{\mathrm{a},2}$	k_{a} for class-2 sites	($\mathrm{m}^3\ \mathrm{kg}^{-1}\ \mathrm{d}^{-1}$)
$k_{\mathrm{a,L}}$	adsorption rate constant	($\mathrm{m}^3\ \mathrm{kg}^{-1}\ \mathrm{d}^{-1}$)
k_{α}	adsorption rate constant	(d^{-1})
k_c	rate coefficient for decline of c	(d^{-1})
k_{d}	desorption rate constant	(d^{-1})
$k_{\mathrm{d},1}$	k_{d} for class-1 sites	(d^{-1})
$k_{\mathrm{d},2}$	k_{d} for class-2 sites	(d^{-1})
$k_{\mathrm{d},3}$	k_{d} for class-3 sites	(d^{-1})
$k^{\mathrm{e}}_{\mathrm{d},3}$	'effective' $k_{\mathrm{d},3}$	(d^{-1})
k_{dec}	rate coefficient for decline of σ^* or σ^*_{f}	(d^{-1})
$k_{\mathrm{m,s}}$	rate coefficient for transfer of substance between mobile and stagnant zones	(d^{-1})
k^*_{t}	rate coefficient for transformation of substance in the soil system	(d^{-1})
$k_{\mathrm{t},3}$	rate coefficient for transformation of X_3	(d^{-1})
$k_{\mathrm{t,l}}$	rate coefficient for transformation of substance in liquid phase in soil	(d^{-1})
$k^{\mathrm{ca}}_{\mathrm{t,l}}$	value of $k_{\mathrm{t,l}}$ as calculated from Equation 9.9	(d^{-1})
k_w	rate coefficient for decline of w	(d^{-1})
m	mass of substance in sorption system	(kg)
m_{i}	initial m	(kg)
m^*_{r}	content of substance in soil system: mass of substance divided by mass of dry soil	($\mathrm{kg\ kg}^{-1}$)
$m^*_{\mathrm{r},1}$	content of substance in soil system recovered by first extraction with ethyl acetate	($\mathrm{kg\ kg}^{-1}$)
$m^*_{\mathrm{r},2}$	content of substance in soil system recovered by second extraction with ethyl acetate	($\mathrm{kg\ kg}^{-1}$)
$m^*_{\mathrm{r},3}$	content of substance in soil system recovered by third extraction with ethyl acetate	($\mathrm{kg\ kg}^{-1}$)
max	maximum of	
min	minimum of	
n	inverse of Freundlich exponent	(1)
p	maximum (plateau value) of X	($\mathrm{kg\ kg}^{-1}$)
p_{k}	p at class-k sites (k = 1 or 2)	($\mathrm{kg\ kg}^{-1}$)
p_{A}	p at 'A' sites	($\mathrm{kg\ kg}^{-1}$)

ρ_B	ρ at 'B' sites	$(\mathrm{kg\ kg^{-1}})$
q	mass concentration of substance sorbed in soil system	$(\mathrm{kg\ m^{-3}})$
q'	$\equiv \mathrm{d}q/\mathrm{d}c$	$(\mathrm{m^3\ m^{-3}})$
r	radius of sphere	(m)
s	standard deviation	
t	time	(d)
t'	integration dummy for time	(1)
t_1	t at the end of stage 1	(d)
t_{dr}	t at start of a drying cycle	(d)
t_e	t at end of experimental period	(d)
t_{st}	t at which integration of $(P - E_p)$ starts	(d)
t_{lw}	t at last wetting event	(d)
w	water content of soil: mass of water divided by mass of dry soil	$(\mathrm{kg\ kg^{-1}})$
x	mass sorbed in sorption system	(kg)
z	depth in soil	(m)
z'	integration dummy for z	(1)
z_w	characteristic depth for withdrawal of water resulting from evaporation	(m)
B	exponent reflecting the effect of water content on the transformation rate coefficient	(1)
$C_{t,1}$	a coefficient in a transformation rate equation	$(\mathrm{d^{-1}})$
$C_{t,2}$	a coefficient in a transformation rate equation	$(\mathrm{d^{-1}})$
$C_{t,3}$	a coefficient in a transformation rate equation	$(\mathrm{d^{-1}})$
$C_{t,4}$	a coefficient in a transformation rate equation	$(\mathrm{d^{-1}})$
$C_{t,5}$	a coefficient in a transformation rate equation	$(\mathrm{d^{-1}})$
C_T	temperature coefficient of $K_{F,1}$	$(\mathrm{K^{-1}})$
D_0	coefficient for diffusion of substance in water	$(\mathrm{m^2\ d^{-1}})$
D_{dd}	coefficient for spreading of substance in liquid phase as a result of diffusion plus dispersion	$(\mathrm{m^2\ d^{-1}})$
D_{dd}^c	corrected value of D_{dd} in numerical solution	$(\mathrm{m^2\ d^{-1}})$
$D_{dd,m}$	D_{dd} in mobile zone	$(\mathrm{m^2\ d^{-1}})$
D_{dif}	coefficient for diffusion of substance in liquid phase	$(\mathrm{m^2\ d^{-1}})$
D_{dis}	coefficient for dispersion of substance in liquid phase	$(\mathrm{m^2\ d^{-1}})$

E_ac	actual volume flux of evaporation of water from soil	$(\mathrm{m\ d^{-1}})$
E_o	volume flux of evaporation of water from an open water surface	$(\mathrm{m\ d^{-1}})$
E_p	potential volume flux of evaporation of water from soil	$(\mathrm{m\ d^{-1}})$
$E_\mathrm{p,av}$	daily average of E_p	$(\mathrm{m\ d^{-1}})$
F	fraction of K to be attributed to class-1 sites	(1)
F_F	fraction of K_F to be attributed to class-1 sites	(1)
C_i	a coefficient	(1)
I	number of bottom grid point	(1)
J	mass flux of substance in soil	$(\mathrm{kg\ m^{-2}\ d^{-1}})$
J^V	volume flux of liquid in soil	$(\mathrm{m\ d^{-1}})$
K	slope of linear sorption isotherm	$(\mathrm{m^3\ kg^{-1}})$
K_1	K for class-1 sites	$(\mathrm{m^3\ kg^{-1}})$
K_2	K for class-2 sites	$(\mathrm{m^3\ kg^{-1}})$
K_3	K for class-3 sites	$(\mathrm{m^3\ kg^{-1}})$
K_3^e	'effective' value of K_3	$(\mathrm{m^3\ kg^{-1}})$
K_F	Freundlich coefficient	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,1}$	K_F for class-1 sites	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,1}^\mathrm{d}$	$K_\mathrm{F,1}$ of initially dry soil	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,1}^\mathrm{d,r}$	$K_\mathrm{F,1}^\mathrm{d}$ at a temperature of 19 °C	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,1}^\mathrm{m}$	$K_\mathrm{F,1}$ of initially moist soil	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,1}^\mathrm{m,r}$	$K_\mathrm{F,1}^\mathrm{m}$ at a temperature of 19 °C	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,2}$	K_F for class-2 sites	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,2}^\mathrm{r}$	$K_\mathrm{F,2}$ at a temperature of 19 °C	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
$K_\mathrm{F,3}$	K_F for class-3 sites	$(\mathrm{m}^{3/n}\ \mathrm{kg}^{-1/n})$
K_L	parameter in Langmuir sorption isotherm equation	$(\mathrm{m^3\ kg^{-1}})$
$K_\mathrm{L,A}$	K_L for 'A' sites	$(\mathrm{m^3\ kg^{-1}})$
$K_\mathrm{L,B}$	K_L for 'B' sites	$(\mathrm{m^3\ kg^{-1}})$
L_dd	length parameter for diffusion plus dispersion	(m)
L_dif	diffusion length parameter	(m)
L_dis	dispersion length parameter	(m)
L_num	length parameter for numerical spread	(m)
M	mass of solid phase in sorption system	(kg)
P	volume flux of rainfall (precipitation)	$(\mathrm{m\ d^{-1}})$

Q	excess (in areic volume) of cumulative rainfall over cumulative potential evaporation within a day	(m)
R	gas constant	(J mol^{-1} K^{-1})
R_1	rate of change in volume fraction of liquid	(m^3 m^{-3} d^{-1})
$R_{1,p}$	potential R_1	(m^3 m^{-3} d^{-1})
R_t	volumic mass rate of transformation of substance in soil	(kg m^{-3} d^{-1})
S	sorption coefficient (i.e. X/c)	(m^3 kg^{-1})
T	soil temperature	(K)
T_0	reference T	(K)
U	molar energy of activation in Arrhenius equation	(J mol^{-1})
V	volume of liquid in sorption system	(m^3)
V_{re}	V replaced by herbicide-free $CaCl_2$ solution in desorption step	(m^3)
X	content of substance sorbed: mass of substance sorbed divided by mass of dry soil	(kg kg^{-1})
$X(0)$	X at the start ($t = 0$)	(kg kg^{-1})
$X(\infty)$	X at equilibrium ($t = \infty$)	(kg kg^{-1})
X_1	X at class-1 sites	(kg kg^{-1})
X_2	X at class-2 sites	(kg kg^{-1})
$\overline{X}_2$	reduced X_2: actual X_2 divided by $X_{2,h}$	(1)
$X_{2,h}$	hypothetical X_2 in equilibrium with the momentary c	(kg kg^{-1})
X_3	X at class-3 sites	(kg kg^{-1})
$\overline{X}_3$	reduced X_3: actual X_3 divided by hypothetical X_3 in equilibrium with the momentary c	(1)
$X_{3,f}$	content sorbed at class-3 sites released by first extraction with ethyl acetate	(kg kg^{-1})
$X_{3,sf}$	content still sorbed at class-3 sites after first extraction with ethyl acetate	(kg kg^{-1})
X_m	X in equilibrium with c_m	(kg kg^{-1})
X_s	X in equilibrium with c_s	(kg kg^{-1})
X_A	X at 'A' sites	(kg kg^{-1})
X_B	X at 'B' sites	(kg kg^{-1})
Z	z at the lower boundary of the soil system	(m)

α_1	a parameter	$(\mathrm{m\ d^{-\frac{1}{2}}})$
α_2	a parameter	$(\mathrm{m\ d^{-\frac{1}{2}}})$
α_3	a parameter	$(\mathrm{m\ d^{-\frac{1}{2}}})$
β	a parameter	$(\mathrm{m^{\frac{1}{2}}})$
γ	a parameter	$(\mathrm{K^{-1}})$
ζ	dummy in sum	(1)
η	integration dummy	(1)
θ	volume fraction of liquid	$(\mathrm{m^3\ m^{-3}})$
θ_{ex}	the volume fraction of liquid from which anions are excluded	$(\mathrm{m^3\ m^{-3}})$
θ_{max}	maximum θ (field capacity value)	$(\mathrm{m^3\ m^{-3}})$
θ_{min}	minimum θ (air-dry value)	$(\mathrm{m^3\ m^{-3}})$
θ_s	θ located in stagnant zone	$(\mathrm{m^3\ m^{-3}})$
ι	index of iteration number	(1)
κ_3	a constant	$(\mathrm{d^{-1}})$
κ_t	a constant	$(\mathrm{d^{-1}})$
λ	tortuosity factor	(1)
ν	number of desorption steps	(1)
ξ	factor for withdrawal of water as a result of evaporation	(1)
π	circumference of a circle divided by its diameter	(1)
ρ_b	dry soil bulk density: volumic mass of dry soil	$(\mathrm{kg\ m^{-3}})$
ρ_l	phase density of liquid phase in soil:mass of liquid phase divided by volume of liquid phase	$(\mathrm{kg\ m^{-3}})$
σ_3	areic mass of substance in soil system sorbed at class-3 sites	$(\mathrm{kg\ m^{-2}})$
σ_u	areic mass of substance still present undissolved at soil surface	$(\mathrm{kg\ m^{-2}})$
σ^*	areic mass of substance in soil system	$(\mathrm{kg\ m^{-2}})$
σ^*_f	areic mass of substance in soil system released by first extraction with ethyl acetate	$(\mathrm{kg\ m^{-2}})$
$\tau_{dif,sp}$	time constant for diffusion process in spheres	(d)
$\tau_{m,s}$	time constant for exchange of substance between mobile and stagnant zones	(d)
τ_{so}	time constant for sorption process in a system with one class of site	(d)

$\tau^{d,m}$	time constant for decline of $K_{F,1}$ from $K_{F,1}^{d}$ to $K_{F,1}^{m}$ after initially dry soil is rewetted	(d)
ϕ	fraction of θ located in mobile zone	(1)
Δt	time step	(d)
Δz	thickness of compartment	(m)
Λ_1	a constant	(d^{-1})
Λ_2	a constant	(d^{-1})
Ξ	a coefficient	(d^{-1})
Σ or $\sum$	sum	
ΣE_1	cumulative evaporation in a drying cycle at the end of stage 1	(m)
ΣE_{ac}	cumulative actual evaporation during a drying cycle	(m)
ΣE_p	cumulative potential evaporation during a drying cycle	(m)
Φ	fraction of X_3 still sorbed after first extraction with ethyl acetate	(1)

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CURRICULUM VITAE

Jos Boesten werd geboren op 31 juli 1955 te Brunssum (Limburg). In 1973 behaalde hij het Gymnasium B diploma aan het St. Janscollege te Hoensbroek en in hetzelfde jaar begon hij met de studie aan de Landbouwhogeschool te Wageningen in de studierichting Bodemkunde en Bemestingsleer. Het eerste halfjaar van 1976 was hij bestuurslid van de K.S.V. 'St. Franciscus Xaverius'. Zijn praktijktijd bracht hij in 1978 door op het toenmalige Laboratorium voor Insekticidenonderzoek in Wageningen (thans I.O.B.) en op het 'Rothamsted Experimental Station' in Harpenden (Engeland). In 1980 slaagde hij (met lof) voor het doctoraalexamen met als vakken Bodemscheikunde en -natuurkunde (hoofdvak), Natuurkunde (hoofdvak), Wiskunde (bijvak) en Kolloïdchemie (extra bijvak).

Sedert 1980 werkt hij op het Instituut voor Onderzoek van Bestrijdingsmiddelen (I.O.B.) te Wageningen waar hij het gedrag van herbiciden in de bodem onderzoekt. Hij is secretaris van de NRLO-werkgroep 'Herbiciden in het bodem-plant systeem' en van de NRLO-contactgroep 'Milieuvreemde stoffen in de bodem'. Hij maakt deel uit van een commissie die belast is met de organisatie van een in 1988 in Wageningen te houden internationaal symposium over de werking en selectiviteit van herbiciden.