TRANSPORT FROM DIFFUSE SOURCES OF CONTAMINATION AND ITS APPLICATION TO A COUPLED UNSATURATED-SATURATED SYSTEM

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Proefschrift
ter verkrijging van de graad van
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op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
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STELLINGEN

1 De karakteristieke tijd voor het transport van een inerte stof vanaf een diffuse bron van verontreiniging, is gelijk aan de pakketdikte, althans voor Nederlandse omstandigheden.
Dit proefschrift.

2 In practice, the dispersion coefficient is used as an empirical parameter. Besides diffusion and dispersion it incorporates all other solute spreading mechanisms not directly included in the convection-dispersion equation, such as non-linear adsorption or exchange, non-linear decay, or various physical and chemical non-equilibrium conditions.
Nielsen et al., 1986. Water Resour. Res., 22(9):898-1088.

3 Het 'mixing-cell' concept kan eenvoudig worden toegepast op het transport van reactieve componenten in een grondwaterstromingsstelsel. Er dient dan wel aandacht geschonken te worden aan de grootte van de numerieke dispersie, die in de orde van grootte van de fysische dispersie moet liggen.
H.C. van Ommen. The 'mixing-cell' concept applied to transport of reactive components in soil and groundwater. J. of Hydrology 78(1985):201-213.

4 If spatial variation in solute leaching velocity and retardation factor is prominent, the moment of first breakthrough at a particular reference level will considerably be underestimated if average parameters are used.
S.E.A.T.M. van der Zee and W.H. van Riemsdijk. Transport of reactive solute in spatially variable soil systems. Water Resour. Res., 23, 2059-2069, 1987.

5 Bij het bepalen van betrouwbaarheidsintervallen betreffende het verband tussen concentratie en diepte verdient het meer aanbeveling deze gebaseerd te doen zijn op de empirische distributiefunctie zelf, dan op een veronderstelde kansdichtheidsfunctie.

6 Gemeten neerslagen vormen hoogstens een benadering van de gevallen neerslag, een benadering die vrijwel altijd aan de lage kant is.
J.W. de Zeeuw. Over de werkelijkheidsbenadering van gemeten neerslagen. Landbouwkundig Tijdschrift 75(1963), nr. 14:815-832.

7 Een algemene strategie voor integraal waterbeheer op uitvoeringsniveau is niet te realiseren wegens de verscheidenheid aan specifieke belangen die per beheersprobleem optreden.

8 Het onderwijs in de cultuurtechniek dient verzorgd te worden door een associatie van vakgroepen, die ieder vanuit hun eigen discipline een bijdrage hieraan leveren. Om een optimale samenwerking te bewerkstelligen moeten deze vakgroepen zoveel mogelijk in één gebouw worden ondergebracht.

9 Het construeren van bouwwerken, die niet passen in het Nederlandse landschap, kan - afgezien van de estetische beleving van het object - gevaar opleveren voor de verkeersveiligheid.

10 Het gebruik van het voorvoegsel 'turbo' wekt vaak een opgeblazen indruk.

11 Om vergissingen tot een minimum te beperken is het beter dat de cijfervolgorde op toetsenborden van telefoontoestellen en rekenmachines gelijk is.

12 Indien mogelijk, is het aan te bevelen een aantal wetenschappelijke verhandelingen als proefschrift te laten dienen.

13 Diffuse bronnen vereisen concrete maatregelen.

H.C. van Ommen
Transport from diffuse sources of contamination and its application to a coupled unsaturated-saturated system, 21 oktober 1988.

Aan mijn ouders

ABSTRACT

Van Ommen, H.C. 1988. Transport from diffuse sources of contamination and its application to a coupled unsaturated-saturated system. Doctoral thesis. Agricultural University Wageningen, Wageningen, The Netherlands.

A simple theory to predict groundwater quality upon contamination from diffuse sources was developed. It appeared that an analogy exists between the predominant transport phenomena and the reaction of a reservoir, in which perfect mixing takes place. Such an analogy enables a simple incorporation of physico-chemical processes (decomposition, adsorption), as was shown by an illustrative response of the quality of groundwater to an input of a radio-active decaying solute (and its decay components) in its recharge area.

Before solute migration in the saturated zone occurs, transport takes place in the unsaturated zone. The above mentioned analogy allows the derivation of analytical expressions for the response of a coupled unsaturated-saturated transport system. The unsaturated soil is then represented by a series of "perfectly mixed" reservoirs. Each reservoir can be defined in terms of its thickness, water content, in- and outflow rate, decomposition rate or retardation factor. Moreover, the process of bypass flow can be accounted for in a simple way.

To study the practical application of the presented theory, a field experiment was carried out. An amount of tracer was applied to the catchment area of a drain, followed by soil sampling and monitoring of tracer concentrations in the drainage water. From both soil and drainage water sampling it appeared, that transport velocities in the subsoil could impossibly correspond with the observed water content profiles. Therefore it was concluded that preferential flow paths in the subsoil caused this accelerated breakthrough, and transport was confined to these zones only.

To visualize these zones of preferential flow, we used a coloring technique that was developed during this study. This method was applied to ten plots in the same experimental field, where the tracer had been applied before. Preferential flow paths were shown to occur at some plots, but the variation of penetration depth of the solute front could be adequately described by the convection-dispersion equation, using dispersivities of the order of centimetres. The accelerated breakthrough that was measured in our former experiment, could not be explained.

At the same experimental field, a study of the spatial variability of soil physical parameters had been completed recently. From the measured variability, expressed in the distribution of the scaling parameter, the solute breakthrough curve was predicted, and compared with our measured curve. The variation of travel times, based on the soil variability, was estimated too large. It is concluded that this large variation of travel times might have been present under different experimental conditions, such as ponded infiltration.

Additional index words: groundwater quality, travel time distribution, convection-dispersion equation, transfer-function model, preferential flow paths, spatial variability.

WOORD VOORAF

Dit proefschrift is het resultaat van een onderzoek waarop ik met veel voldoening terug kijk en ik dank allen die op enigerlei wijze een bijdrage hebben geleverd aan de totstandkoming hiervan.

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Roel Dijksma en Jan Hulshof, zonder jullie inventiviteit en inzet was het experimentele gedeelte van het onderzoek niet tot een goed einde gekomen. Ik denk met veel plezier terug aan de tijd die we in het veld hebben doorgebracht en merk hierbij op dat perioden met hoge drainafvoer meestal samenvallen met slechte weersomstandigheden. Tijdens de veldexperimenten was de aanwezigheid van een aantal collega's van de STIBOKA een voortdurende bron van inspiratie. In dit kader wil ik in het bijzonder Jan Hendrickx en Louis Dekker noemen.

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CONTENTS

1. GENERAL INTRODUCTION

The major source of water supply, both for domestic and industrial use, is provided by groundwater. Despite the ability to dispose of surface water in an easier way under some circumstances, preference is given to the abstraction of groundwater. This is primarily caused by its common good quality from a chemical and bacteriological point of view, therefore requiring only minimal treatment.

The good quality of groundwater results from the puryfying influence of physico-chemical and biological processes during its passage through soils and transport in aquifers. Examples of such processes are precipitation, adsorption, decomposition, and attenuation of toxic or undesirable components during its prolonged residence in the subsurface environment. The occurrence of these processes and their influence on the quality of abstracted or outcropping groundwater depends on the local geohydrological and geochemical situation. Factors as hydraulic conductivity, temperature, organic matter content and anaerobic conditions can severely affect the behaviour of a pollutant in aquifers. Upon the growing exploitation of natural resources due to the expansion and intensification of human activities, the exhaustibility of the puryfying properties of aquifers has come to light by the occurrence of numerous cases of groundwater pollution. Most of these were caused by point sources such as waste refusal sites, industrial waste dumps, etc. These point sources of pollution are characterized by a burden of groundwater quality imposed on a small part of the entire recharge area. The spread of contaminants by groundwater flow, starting at the location of emission, is often described by the solution of the convection-dispersion equation, given the appropriate boundary and initial conditions. Although doubts have arisen concerning the general applicability of this equation to describe solute transport in aquifers, a practical methodology to model transport in a better way is still lacking.

Recently, consciousness has grown that diffuse sources of contamination might even have a larger impact on the quality of groundwater than point sources. This non-point source pollution is characterized by a wide-spread emission of solutes to the groundwater, operative in the total recharge area of an aquifer. The most striking examples of this kind of pollution are the emission of nutrients to the groundwater by agriculture (especially nitrate and phosphate) and the deposition of 'acid' rain.

Aquifers can be classified on the basis of their accessibility for solutes to penetrate into them. We can schematically distinguish three kinds of aquifers, based on their hydrogeological setting: 1) confined aquifers, which are covered by an impervious layer that prevents the penetration of solutes originating from the soil surface, 2) semi-confined aquifers, which are covered by a semi-pervious layer that forms a barrier to direct infiltration of solutes leached from the soil, and 3) phreatic aquifers, in which solutes originating from the soil surface can directly penetrate into the waterbearing layer. As a matter of fact, the last category of aquifers is most vulnerable to pollution originating from the soil surface. In the following, we therefore restrict ourselves to the description of transport in aquifers of this origin.

To assess the susceptability of groundwater quality in phreatic aquifers upon contamination from non-point sources, a general theory is presented (Chapter 2). This describes the reaction of a phreatic aquifer upon a diffuse input in terms of its intrinsic characteristics such as thickness, porosity, and net recharge. Processes of adsorption and decomposition can easily be incorporated, as is illustrated by the application of the theory to a diffuse input of a radio-active decaying solute (Chapter 3). Based on this theory, the reaction of an aquifer upon a diffuse input of contamination can be expressed in terms of a characteristic time. For Dutch circumstances this turn-over time, expressed in years, is of the order of magnitude of the aquifer thickness in metres. So the quality of groundwater, that is abstracted from a thick aquifer, reacts slowly upon changes of the concentration in the recharge water. On the other hand, groundwater quality from thin aquifers reacts quickly upon changes of the concentration in the recharge water.

A solute that is applied at the soil surface, will be transported through the unsaturated soil before it reaches the groundwater table. As travel times in the unsaturated zone may not always be neglected with respect to residence times in the aquifer, expressions for the reaction of a coupled unsaturated-saturated transport system will be developed in Chapter 4 and 5. On the basis of the theory of Chapter 2, analytical expressions for the reaction of a coupled unsaturated-saturated transport system can easily be derived for time-dependent input concentrations (Chapter 4). In this derivation, the unsaturated soil profile is schematized as a series of identical reservoirs, in which mixing occurs. In Chapter 5, however, an analytical solution is given for the reaction of a coupled unsaturated-saturated transport system, in which the unsaturated soil is schematized as a series of layers, that each may have its own properties such as thickness, moisture content, adsorption isotherm, and decomposition rate.

To verify the theory and apply the presented approach to a field situation, we are faced with a discrepancy between the representativeness and the duration of a validation experiment: the realization of an experiment, involving the migration of a tracer from a diffuse source of contamination, would cost tens of years for an aquifer, that has a representative thickness for Dutch conditions. Thin phreatic aquifers, although not representative for Dutch circumstances, that allow to verify the theory within a period of a few years, are located in the 'Hupsel' catchment area in the Eastern part of the Netherlands.

The experimental validation of the theory, that is described in detail in Chapter 6, involved a uniform application of an amount of tracer solution to the catchment area of a drain, followed by sampling of the soil, groundwater, and the drain water. After analyzing the samples upon the presence of the applied tracer, conclusions could be drawn concerning the transport mechanisms occurring in the soil and the aquifer. From the soil sampling we were able to describe the transport of the tracer in the unsaturated zone, and based on this, drain water concentrations could be predicted using the theory, that was developed in Chapter 2. Comparison of the predicted concentrations with the measured concentrations yielded very good results. However, the samples that were taken from the saturated zone, showed such an irregular pattern of concentrations, that the transport mechanism in the saturated zone could not be checked directly.

The results of the soil sampling indicated an accelerated transport in the subsoil: once the tracer had moved into it, leaching of the solute occurred at such elevated velocities, that only part of the soil matrix could be active in transporting solutes to the groundwater. Transport would then be confined to regions where preferential flow occurred. To visualize these zones of preferential flow, an iodide-coloring technique was developed (Chapter 7) that was successfully applied to ten plots in the same field

(Chapter 8). Results indicated the existence of preferential flow paths, although these could not be responsible for the accelerated transport, that was observed in the former experiment.

At the same field, a study to the spatial variability of soil hydraulic properties had been carried out recently. Based on this, it was possible to predict the transport of a tracer in the unsaturated soil (Chapter 9). Besides, the drain water concentrations could be predicted from data of this study, and compared with the measured tracer concentrations of the former experiment.

2. INFLUENCE OF DIFFUSE SOURCES OF CONTAMINATION ON THE QUALITY OF OUTFLOWING GROUNDWATER INCLUDING NON-EQUILIBRIUM ADSORPTION AND DECOMPOSITION

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INFLUENCE OF DIFFUSE SOURCES OF CONTAMINATION ON THE QUALITY OF OUTFLOWING GROUNDWATER INCLUDING NON-EQUILIBRIUM ADSORPTION AND DECOMPOSITION

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ABSTRACT

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When certain conditions are met, groundwater transport of solutes stemming from a diffuse source can be described by considering the aquifer as a reservoir in which perfect mixing takes place. This theory is illustrated with three groundwater flow regimes of frequent occurrence. Besides, by deriving the mass balance for such a linear — or linearised — system, the influences of several physico-chemical processes such as non-equilibrium adsorption and first-order decomposition or decay can be determined. Special attention is given to the importance of the time scale at which the processes play a role.

INTRODUCTION

In the last few decades, there has been considerable interest in the transport of solutes in groundwater. Much of the emphasis in studies to date has focused on point-source problems with considerably less attention given to diffuse sources. The goal of this paper is to develop a mixing model capable of modeling transport away from diffuse sources.

A diffuse source of contamination is defined as a more-or-less uniformly distributed source of pollution in the area of groundwater recharge. Contaminants from diffuse sources could include, for example, nitrogen or phosphorus compounds leached from agricultural lands, acid rain and irrigation water of poor quality. For problems like this, it is possible to develop a theoretical relation between the concentration of a solute in recharge water and the concentration in outflowing groundwater. As special cases of the general theory, three groundwater flow regimes, commonly encountered in practice, are discussed.

Furthermore, an extension of the generally applicable theory, developed for transport of inert solutes will be worked out, in order to describe physico-chemical processes such as non-equilibrium adsorption and decomposition.

NOTATION

List of symbols used

a	recharge area outside the isochrone under consideration	$[L^2]$
A	total recharge area of the aquifer	$[L^2]$
$a_{1,2}$	eigenvalues of the linear system	$[T^{-1}]$
c	concentration of the solute in the reservoir in which perfect mixing takes place	$[ML^{-3}]$
$\bar{c}$	the average concentration in outflowing groundwater	$[ML^{-3}]$
c^*	dimensionless concentration	
c_{input}	concentration of solute in the recharge water	$[ML^{-3}]$
$c_{\mathrm{orig.}}$	uniformly distributed, original concentration of solute in the aquifer	$[ML^{-3}]$
$c_{0,\mathrm{nl}}$	uniform initial concentration at time t_0 in the non-linear adsorption case	$[ML^{-3}]$
H	thickness of the aquifer	$[L]$
k	slope of the adsorption isotherm or the slope of the chord-envelope of the isotherm	$[L^3M^{-1}]$
l	spacing of the parallel canals (illustration 1)	$[L]$
N	groundwater recharge rate	$[LT^{-1}]$
q_x	flow at distance x from the water divide per unit length of canal	$[L^2T^{-1}]$
$Q(r)$	amount of water flowing to the well from a distance greater than r	$[L^3T^{-1}]$
Q_w	extraction rate of groundwater	$[L^3T^{-1}]$
r	cylindrical coordinate, used in illustration 2	$[L]$
r_e	radius of influence of the extraction well in illustration 2	$[L]$
r_0	radius of the circle around the well from which the displacements are calculated (illustration 3)	$[L]$
S	quantity adsorbed at the solid phase in the perfectly mixed reservoir	$[MM^{-1}]$
$S_{0,\mathrm{nl}}$	uniformly adsorbed quantity at time t_0, corresponding with $c_{0,\mathrm{nl}}$	$[MM^{-1}]$
t	time	$[T]$
t_0	initial time	$[T]$
T	time constant of the migration of a solute in the equilibrium adsorption case	$[T]$
T_r	residence time at point $r = r$ from the well (illustration 2)	$[T]$
T_x	residence time of a water drop starting from a distance x from the water divide to the canal (illustration 1)	$[T]$
u_x	the x-component of the velocity vector in illustration 3	$[LT^{-1}]$
u_y	the y-component of the velocity vector in illustration 3	$[LT^{-1}]$
$u_{x,\mathrm{bf}}$	velocity vector in the x-direction, due to the baseflow	$[LT^{-1}]$
$u_{x,w}$	velocity component in the x-direction due to the groundwater extraction (illustration 3)	$[LT^{-1}]$
$u_{y,w}$	velocity component in the y-direction due to the groundwater extraction (illustration 3)	$[LT^{-1}]$
$\boldsymbol{u}_1$	horizontal velocity vector at the starting location of the displacement (illustration 3)	
$\boldsymbol{u}_2$	horizontal velocity vector at the estimated location of the displacement (illustration 3)	
x	horizontal coordinate in illustrations 1 and 3	$[L]$
$x_{s1,s2}$	locations of the stagnation points in illustration 3	$[L]$
y	horizontal coordinate in illustration 3	$[L]$
$\boldsymbol{z}$	location vector of the displacement points in illustration 3	
α	first-order decomposition constant in the liquid phase	$[T^{-1}]$
β	rate coefficient of the adsorption reaction	$[T^{-1}]$
γ	first-order decomposition constant at the solid phase	$[T^{-1}]$

Δt	time step to calculate the displacement in the horizontal direction (illustration 3)	[T]
ε	porosity of the aquifer	[-]
ϱ	dry bulk density of the aquifer	$[\mathrm{ML}^{-3}]$

This extension is illustrated by two examples. At the end, some conclusions are drawn from the discussed theory.

THE TRANSPORT OF INERT SOLUTES

Following in this section is the development of a relation linking the concentration of an inert solute in recharge water with its concentration in outflowing groundwater. This development requires the following assumptions:

(1) Steady groundwater flow, i.e. the recharge rate multiplied by the total recharge area is equal to the discharge of groundwater from the system.

(2) Changes in thickness of the saturated zone are small compared to the total thickness of the aquifer.

(3) The thickness of the aquifer and its porosity are constant (see also assumption (2)).

(4) Groundwater flow is horizontal, making the Dupuit–Forchheimer assumptions valid.

A transport model is developed for an aquifer (porosity ε, thickness H) with a recharge area A $[\mathrm{L}^2]$ and a well located arbitrarily at location P, where groundwater extraction takes place with a rate Q_w $[\mathrm{L}^3\mathrm{T}^{-1}]$ (Fig. 1).

Supposing the discharge of groundwater Q_w $[\mathrm{L}^3\mathrm{T}^{-1}]$ equal to the recharge rate N $[\mathrm{LT}^{-1}]$ multiplied by the recharge area A $[\mathrm{L}^2]$ (assumption (1)), it follows:

$$Q_w = NA \quad [\mathrm{L}^3\mathrm{T}^{-1}] \tag{1}$$

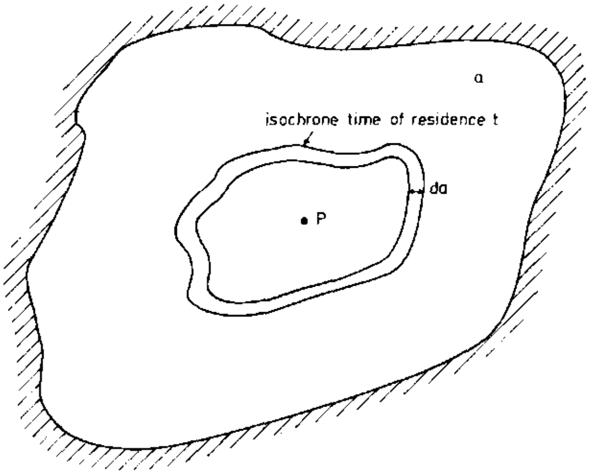

Fig. 1. Recharge area of the aquifer with the groundwater extraction at location P.

Within the recharge area A, a closed line connecting the points having the same residence or travel time to extraction point P can be found. This line represents an isochrone. The recharge area outside this isochrone equals a [L^2]; the area within amounts to $A - a$ [L^2]. The isochrone of residence time t, as a function of a is determined in the following way:

For an increase of the residence time of an amount dt, the following relationship holds:

$$-\mathrm{d}t = \frac{\text{volume}}{\text{flux}} = \frac{\varepsilon H \mathrm{d}a}{Na} \quad [\mathrm{T}] \tag{2}$$

The negative sign indicates a decrease of the residence time with an increasing area a. In eqn. (2) Na represents the amount of water recharging the aquifer outside the isochrone, while $\varepsilon H\mathrm{d}a$ equals the quantity of water present between the isochrone of time t and the isochrone of time $t - \mathrm{d}t$.

The following relation can be developed between the residence time t and the recharge area a:

$$\int_0^t \mathrm{d}t = \int_a^A \frac{\varepsilon H \mathrm{d}a}{Na} \quad [\mathrm{T}] \tag{3}$$

hence:

$$t(\mathrm{a}) = \frac{\varepsilon H}{N} \ln(A/a) \quad [\mathrm{T}] \tag{4}$$

The concentration of the outflowing groundwater is composed of water of a concentration equal to the concentration of the recharge water (c_{input}) originating from the area $A - a$, and water originally present in the aquifer ($c_{\text{orig.}}$) originating from the area a. The average concentration of the outflowing groundwater, formed by mixing waters from these two sources, is calculated with this equation:

$$\bar{c} = \frac{((A - a)\, c_{\text{input}} + a c_{\text{orig.}})N}{NA} \quad [\mathrm{ML}^{-3}] \tag{5a}$$

or:

$$\bar{c} = \left(1 - \frac{a}{A}\right) c_{\text{input}} + \frac{a}{A}\, c_{\text{orig.}} \quad [\mathrm{ML}^{-3}] \tag{5b}$$

In effect, this result simply represents the average concentration as the weighted contribution from the two sources.

Combined with eqn. (3), it follows:

$$\bar{c}(t) = c_{\text{input}} + (c_{\text{orig.}} - c_{\text{input}}) \exp(-Nt/(\varepsilon H)) \quad [\mathrm{ML}^{-3}] \tag{6}$$

which is the equation for the outflow concentration of a reservoir in which perfect mixing takes place (Bird et al., 1960), although the mixing mechanism in these two cases is entirely different.

Following are results for three different problems of practical interest to illustrate the generality of the approach I have just described. In all three cases, it has been possible to develop very simple expressions characterizing the chemistry of groundwater outflow.

Illustration 1. The flow to parallel canals

This case is the one-dimensional analogue of the preceding theory and has been described extensively in the literature (Eldor and Dagan, 1972; Ernst, 1973; Gelhar and Wilson, 1974; Van Ommen, 1985a,b). The recharge N [LT^{-1}] is drained through an aquifer of thickness H towards parallel canals, having a spacing l. Using the coordinate system given in Fig. 2, the flow at distance x from the water divide per unit length of canal (q_x) can be written as:

$$q_x = Nx \quad [L^2T^{-1}] \tag{7}$$

The residence time of a water drop starting at distance x from the divide is:

$$T_x = \frac{\varepsilon H}{N} \ln(l/(2x)) \quad [T] \tag{8}$$

The average solute concentration equals:

$$\bar{c} = \frac{c_{\text{orig.}} Nx + N(l/2 - x)\, c_{\text{input}}}{Nl/2} \quad [ML^{-3}] \tag{9a}$$

or:

$$\bar{c} = c_{\text{input}} + (c_{\text{orig.}} - c_{\text{input}})\, 2x/l \quad [ML^{-3}] \tag{9b}$$

Combining eqns. (8) and (9b) gives:

$$\bar{c}(t) = c_{\text{input}} + (c_{\text{orig.}} - c_{\text{input}}) \exp(-Nt/(\varepsilon H)) \quad [ML^{-3}]$$

which is the same as eqn. (6).

Illustration 2. The flow to a fully penetrating well in a phreatic aquifer

In the framework of the development of a coupled unsaturated/saturated

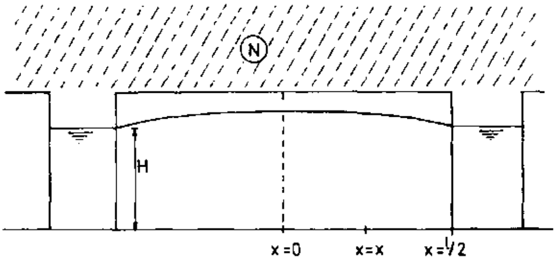

Fig. 2. Flow to parallel canals, having a spacing l.

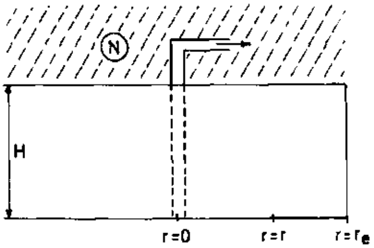

Fig. 3. Flow to a well in a phreatic aquifer.

groundwater quality model, the solution for this case has also been presented elsewhere (Van Ommen, 1985b).

In the cylindrical coordinate system, as given in Fig. 3, the amount of water $Q(r)$ flowing to the well from a distance greater than r equals:

$$Q(r) = \pi N(r_e^2 - r^2) \quad [L^3T^{-1}] \tag{10}$$

where r_e is the radius of influence of the well ($r_e = \sqrt{Q_w/(\pi N)}$). The average concentration of the extracted groundwater is then:

$$\bar{c} = \frac{c_{\text{input}}r^2 + c_{\text{orig.}}(r_e^2 - r^2)}{r_e^2} \quad [ML^{-3}] \tag{11a}$$

or:

$$\bar{c} = c_{\text{orig.}} + (c_{\text{input}} - c_{\text{orig.}})r^2/r_e^2 \quad [ML^{-3}] \tag{11b}$$

The pore water velocity $u(r)$ at a distance r from the well is determined by dividing $Q(r)$ by the effective cross-sectional area at that distance:

$$u(r) = \frac{(r_e^2 - r^2)N}{2r\varepsilon H} \quad [LT^{-1}] \tag{12}$$

From this pore flow velocity, the residence time T_r at a circle $r = r$ from the well becomes:

$$T_r = -\frac{\varepsilon H}{N}\ln\left(1 - \frac{r^2}{r_e^2}\right) \quad [T] \tag{13}$$

The combination of eqns. (13) and (11b) results again in eqn. (6).

Illustration 3. The flow to a fully penetrating well in a phreatic aquifer with a space-dependent baseflow

The original situation is given in Fig. 4a,b: a groundwater divide on the left hand of which a baseflow is developing due to the natural recharge by rain or irrigation water. Such a situation may occur when the natural recharge causes an increasing baseflow to develop in the direction of a valley.

The coordinate of the water divide is indicated as x_{wd}. The pore flow velocity

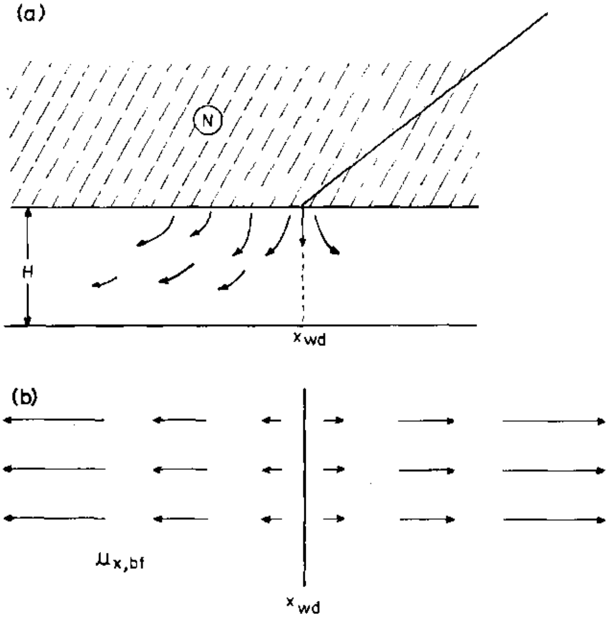

Fig. 4. a. Original situation of illustration 3. Vertical cross-section of the aquifer; b. plane view of the developing baseflow.

($u_{x,\mathrm{bf}}$) at an arbitrary coordinate x on the left of the water divide, is equal to (compare the analogy with illustration 1):

$$u_{x,\mathrm{bf}} = -\frac{N(x_{\mathrm{wd}} - x)}{\varepsilon H} \quad [\mathrm{LT}^{-1}] \tag{14}$$

In this situation, a groundwater production well is installed at the left of the water divide. Provided that the drawdown, caused by the groundwater extraction, is small compared to the thickness of the aquifer (see assumption (2)), this drawdown equals the drawdown in a confined aquifer having the same hydrological properties (see e.g. Bear, 1979, p. 308). In that case the horizontal components of the pore flow velocity in the x- and y-directions, caused by an extraction at $x = 0$ and $y = 0$, are equal to (Bear, 1979; Van den Akker, 1983):

$$u_{x,\mathrm{w}} = -\frac{Q_{\mathrm{w}}x}{2\pi\varepsilon H(x^2 + y^2)} \quad [\mathrm{LT}^{-1}] \tag{15a}$$

$$u_{y,\mathrm{w}} = -\frac{Q_{\mathrm{w}}y}{2\pi\varepsilon H(x^2 + y^2)} \quad [\mathrm{LT}^{-1}] \tag{15b}$$

If the extraction well is located at $x = 0$ and $y = 0$ on the "left" of the water divide, the horizontal pore flow velocity components including the baseflow (in the negative x-direction) are given by:

$$u_x = -\frac{N(x_{wd} - x)}{\varepsilon H} - \frac{Q_w x}{2\pi\varepsilon H(x^2 + y^2)} \quad [\mathrm{LT}^{-1}] \tag{16a}$$

$$u_y = -\frac{Q_w y}{2\pi\varepsilon H(x^2 + y^2)} \quad [\mathrm{LT}^{-1}] \tag{16b}$$

To assess the area of recharge of the flow system for e.g. groundwater protection zones, the stagnation points on the x-axis are located at:

$$x_{s1,s2} = \frac{2\pi x_{wd} \pm \sqrt{4\pi^2 x_{wd}^2 + 8\pi Q_w/N}}{4\pi} \quad [\mathrm{L}] \tag{17}$$

In order to obtain streamlines and residence times to the well, the displacements of a number of discrete particles, located at a circle of r_0 around the well, are followed in time, moving upstream along the streamlines. Remark that in this case, the displacement velocities of the particles are opposite to the velocity vectors composed of u_x and u_y, as defined by eqn. (16). Due to the mutual dependence of the velocity components, a stepwise integration method is applied, as has been described by Olsthoorn (1982). As a criterion of integration the value of the inner product of the velocities at different locations, divided by the squared length of the velocity vector at the "start-location" is used:

$$0.8 < \frac{\boldsymbol{u}_1 \cdot \boldsymbol{u}_2}{|u_1|\,|u_1|} < 1.2 \tag{18}$$

where $\boldsymbol{u}_1$ stands for the velocity at the "start-location" z_t at time t, and $\boldsymbol{u}_2$ represents the velocity at the "estimated-location" $z_{t+\Delta t}$ at time $t + \Delta t$. If the criterion is met, the new location is calculated according to:

$$z_{t+\Delta t} = z_t + \tfrac{1}{2}(\boldsymbol{u}_1 + \boldsymbol{u}_2)\Delta t \tag{19}$$

where Δt is the timestep at which criterion (18) is met. If this is not the case, the timestep is halved and the procedure repeated, and so on.

Figure 5 shows an example of the discussed groundwater flow regime with streamlines and residence times. Because of the symmetry of the flow pattern — the x-axis is an axis of symmetry — only one half of the flow net has been constructed.

The following data are used in this case: 11 streamlines starting from 11 points located at $r_0 = 5\,\mathrm{m}$, $x_{wd} = 5000\,\mathrm{m}$, $\varepsilon = 0.30$, $H = 60\,\mathrm{m}$, $N = 0.30\,\mathrm{m\,yr^{-1}}$ and $Q_w = 5 \cdot 10^6\,\mathrm{m^3\,yr^{-1}}$. From these data the stagnation points on the x-axis are located at:

$$x_{s1} = -484\,\mathrm{m} \qquad x_{s2} = 5484\,\mathrm{m}$$

Streamlines and residence times have been calculated up to 100 yr by applying the discussed integration procedure (a program for HP41CV is available upon request).

The concentration at different times can be derived from Fig. 5. For this purpose the area within the isochrone of the time at hand needs to be known.

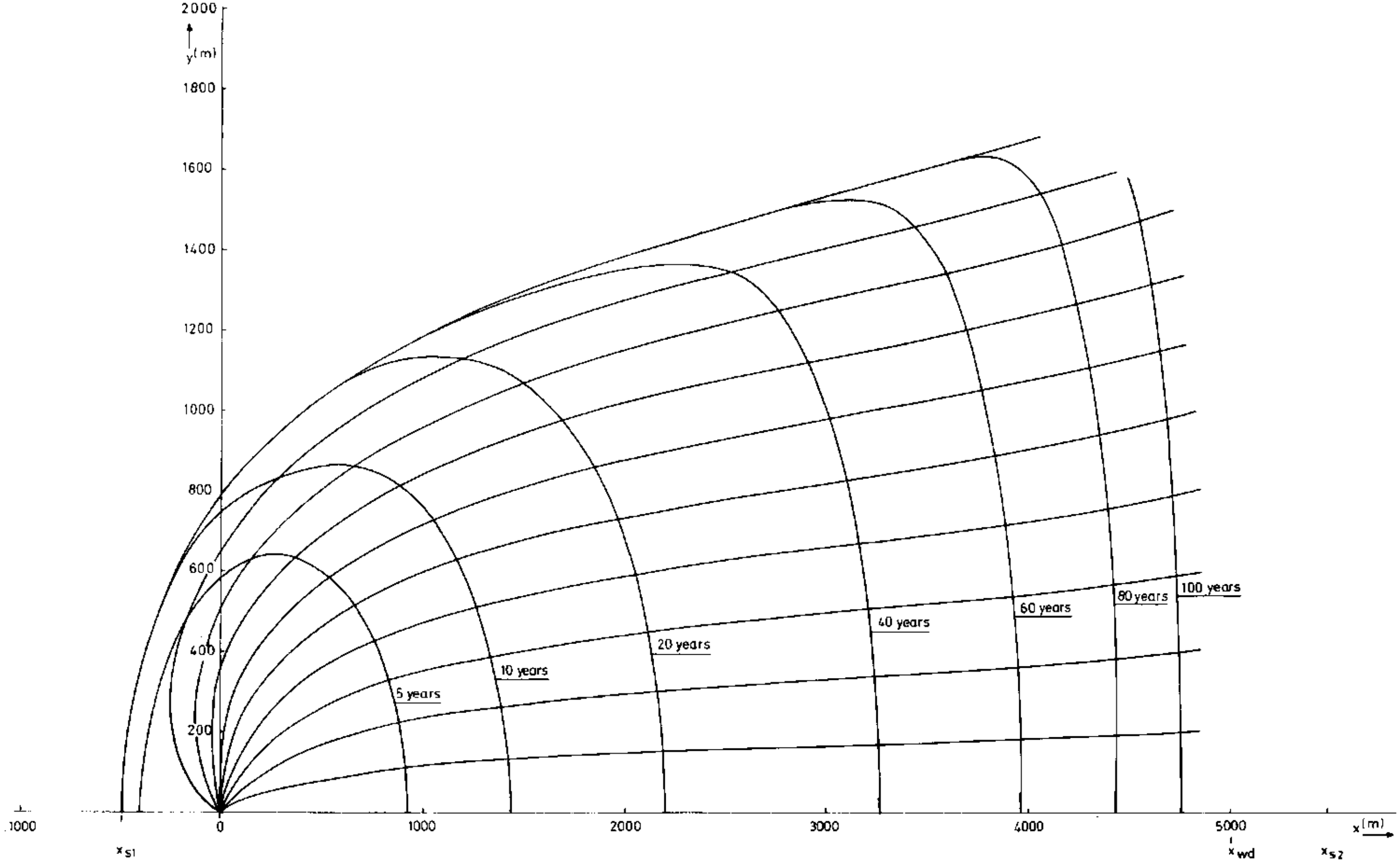

Fig. 5. Isochrones and streamlines concerning flow to a well with a place-dependent baseflow. For reasons of symmetry only one half of the flow net is given.

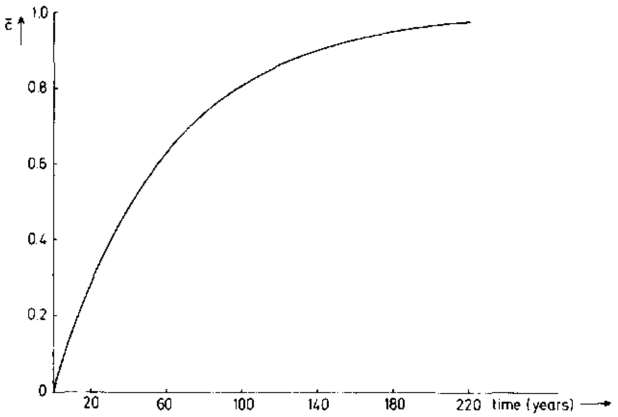

Fig. 6. Relation between the concentration in extracted groundwater and the time for illustration 3; this graph also represents the cumulative distribution of residence times.

This area, multiplied by the recharge rate N, provides that part of the discharge Q_w, originating from the area within the isochrone. Applying plane geometry to the total recharge area yields — evidently — an area equal to Q_w/N.

The relation between the concentration of outflowing groundwater and time has been determined for the case of c_{input} equals one and $c_{\text{orig.}}$ equals zero, and has been depicted in Fig. 6, being the same relation as given by eqn. (6).

In this particular case Fig. 6 shows also the cumulative distribution of residence times (Huisman and Martijn, 1969), being the relation between the fraction of discharge from the system (ordinate) and the age of the outflowing groundwater.

EXTENSION OF THE MODEL TO CONSIDER REACTING SOLUTES

The model describing the transport of a solute from a diffuse source and the outflow from a reservoir in which perfect mixing takes place can be extended to account for different kinds of interaction and decomposition processes.

The basic approach involves deriving the mass balance equation for a perfectly stirred reservoir and adding appropriate terms to account for the processes. This procedure, in general, is restricted to linear processes, although a few non-linear interactions can also be described in this way.

The effects of first-order kinetic reaction and linear adsorption have been described elsewhere (Van Ommen, 1985b). This theory is extended here to account for the chemical decomposition of adsorbed contaminants, non-equilibrium adsorption and adsorption according to a non-linear convex isotherm.

In order to quantify the contribution of each of these processes, the mass balance equation is derived and the solution is presented. Following is a brief discussion of the mathematical formulations of the equations describing the various chemical processes.

(a) *Reaction of adsorbed contaminants.* If this process is described by a first-order mechanism, the following equation holds:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\gamma S \quad [\mathrm{T}^{-1}] \tag{20}$$

where S represents the quantity adsorbed $[\mathrm{MM}^{-1}]$, t is the time [T] and γ the decomposition constant at the solid phase $[\mathrm{T}^{-1}]$.

(b) *Non-equilibrium adsorption.* In this case, the adsorption rate follows a first-order kinetic law with the adsorption rate proportional to the adsorption deficit, i.e. the difference between the actual adsorbed quantity and the adsorbed quantity at equilibrium (see e.g. Van Genuchten and Cleary, 1979):

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \beta(kc - S) \quad [\mathrm{T}^{-1}] \tag{21}$$

where β $[\mathrm{T}^{-1}]$ is the rate coefficient of the adsorption reaction and kc is the quantity adsorbed at equilibrium according to a linear adsorption isotherm, having a slope k $[\mathrm{L}^3\mathrm{M}^{-1}]$.

(c) *The non-linear adsorption isotherm.* Generally the theory is not applicable in the case of non-linear adsorption. However, an analytical solution is possible if the solute is adsorbed according to a convex isotherm ($\mathrm{d}^2S/\mathrm{d}c^2 < 0$), provided the input concentration is constant with time. The migration of the solute can be obtained using the slope of the chord-envelope of the isotherm (Reiniger and Bolt, 1972; Bolt, 1972; Schweich and Sardin, 1981). In fact, the non-linear isotherm is then linearised by a process of filling vacant adsorption sites. This process is described by the lines AB and AC in Fig. 8a.

It should be pointed out that this method of solute transport simulation can only be applied if the aquifer has a uniform initial concentration. This condition, in combination with the constant input concentration, justifies the use of the slope of the chord-envelope between the initial and the input concentration.

Neither decomposition at the adsorption complex or in the liquid phase can be taken into account: in those cases of decomposition the concentration at the solute front will decrease, resulting in a steeper slope of the chord-envelope ($\mathrm{d}^2S/\mathrm{d}c^2 < 0$!), which makes the formerly used linearisation impossible. The breakthrough curve will then have to be found by numerical techniques (see e.g. Van Ommen, 1985c). This is also the case if the adsorption follows a concave isotherm. The process of desorption in an initially contaminated aquifer can not be treated by the outlined theory, unless the adsorption is according to a concave isotherm. In that case, desorption proceeds along the chord-envelope again (Bolt, 1979).

When we consider a system with delayed linear adsorption and first-order decay of solutes, both in the dissolved and adsorbed state, the mass balance equation describing the "breakthrough" of a solute in outflowing groundwater, now reads:

Solid and liquid phase:

$$\varepsilon H \frac{\mathrm{d}c}{\mathrm{d}t} + \varrho H \frac{\mathrm{d}S}{\mathrm{d}t} = \mathrm{N}c_{\text{input}} - Nc - \alpha\varepsilon Hc - \gamma\varrho HS \quad [\mathrm{ML}^{-2}\mathrm{T}^{-1}] \tag{22}$$

Solid phase only:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \beta(kc - S) - \gamma S \quad [\mathrm{T}^{-1}] \tag{23}$$

where c is the concentration of solute in the reservoir $[\mathrm{ML}^{-3}]$, α is the first-order decomposition constant concerning the liquid phase $[\mathrm{T}^{-1}]$, ϱ is the dry bulk density of the aquifer $[\mathrm{ML}^{-3}]$. Rearranging eqns. (22) and (23) yields a system of coupled differential equations of order one:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{Nc_{\text{input}}}{\varepsilon H} - \left(\frac{N}{\varepsilon H} + \alpha + \frac{\beta k\varrho}{\varepsilon}\right)c + \left(\frac{\beta\varrho}{\varepsilon}\right)S \tag{24a}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = (\beta k)c - (\beta + \gamma)S \tag{24b}$$

or:

$$\begin{pmatrix} c'(t) \\ S'(t) \end{pmatrix} = \begin{pmatrix} -B & D \\ E & -F \end{pmatrix} \begin{pmatrix} c(t) \\ S(t) \end{pmatrix} + \begin{pmatrix} A \\ 0 \end{pmatrix} \tag{25}$$

where

$$A = \frac{Nc_{\text{input}}}{\varepsilon H} \tag{25a}$$

$$B = \frac{N}{\varepsilon H} + \alpha + \beta k\varrho/\varepsilon \tag{25b}$$

$$D = \beta\varrho/\varepsilon \tag{25c}$$

$$E = \beta k \tag{25d}$$

$$F = \beta + \gamma \tag{25e}$$

The eigenvalues of this linear system are given by:

$$a_1 = \frac{-(B + F) - \sqrt{(B + F)^2 + 4(ED - BF)}}{2} \tag{26a}$$

$$a_2 = \frac{-(B + F) + \sqrt{(B + F)^2 + 4(ED - BF)}}{2} \tag{26b}$$

Both are smaller than zero because:

$$ED - BF < 0 \rightarrow ED < BF \tag{27a}$$

or:

$$\frac{\beta^2 k\varrho}{\varepsilon} < \frac{\beta^2 k\varrho}{\varepsilon} + \alpha\beta + \frac{N\beta}{\varepsilon H} + \frac{\gamma\beta\varrho k}{\varepsilon} + \alpha\gamma + \frac{N\gamma}{\varepsilon H} \tag{27b}$$

so:

$$0 \;<\; \alpha(\beta + \gamma) + \frac{N}{\varepsilon H}(\beta + \gamma) + \frac{\gamma\beta\varrho k}{\varepsilon} \tag{27c}$$

The right-hand side of eqn. (27c) is always greater than zero, resulting in a stable linear system.

The solution of the system (eqns. (25)) — given the initial conditions c_0 and S_0 at time t_0 — has been obtained using the Laplace transform and is given by:

$$\begin{pmatrix} c(t) \\ S(t) \end{pmatrix} = \begin{pmatrix} c_1 e^{a_1(t-t_0)} + c_2 e^{a_2(t-t_0)}, & c_3 e^{a_1(t-t_0)} + c_4 e^{a_2(t-t_0)} \\ c_5 e^{a_1(t-t_0)} + c_6 e^{a_2(t-t_0)}, & c_7 e^{a_1(t-t_0)} + c_8 e^{a_2(t-t_0)} \end{pmatrix} \begin{pmatrix} c_0 \\ S_0 \end{pmatrix} + \begin{pmatrix} \dfrac{Ac_1}{a_1}(e^{a_1(t-t_0)} - 1) + \dfrac{Ac_2}{a_2}(e^{a_2(t-t_0)} - 1) \\ \dfrac{Ac_5}{a_1}(e^{a_1(t-t_0)} - 1) + \dfrac{Ac_6}{a_2}(e^{a_2(t-t_0)} - 1) \end{pmatrix} \tag{28}$$

where the constants c_1 to c_8 are defined as:

$$\begin{aligned} c_1 &= 1 + \frac{F + a_2}{a_1 - a_2} = 1 - c_2 & c_5 &= \frac{E}{a_1 - a_2} \\ c_2 &= -\frac{F + a_2}{a_1 - a_2} & c_6 &= \frac{E}{a_2 - a_1} = -c_5 \\ c_3 &= \frac{D}{a_1 - a_2} & c_7 &= 1 + \frac{B + a_2}{a_1 - a_2} = 1 - c_8 \\ c_4 &= \frac{D}{a_2 - a_1} = -c_3 & c_8 &= -\frac{B + a_2}{a_1 - a_2} \end{aligned}$$

In case of non-linear adsorption the system of equations will change if the initial concentration is not equal to zero. The solution then reads:

$$\begin{pmatrix} c(t) \\ S(t) \end{pmatrix} = \begin{pmatrix} c_1 e^{a_1(t-t_0)} + c_2 e^{a_2(t-t_0)}, & c_3 e^{a_1(t-t_0)} + c_4 e^{a_2(t-t_0)} \\ c_5 e^{a_1(t-t_0)} + c_6 e^{a_2(t-t_0)}, & c_7 e^{a_1(t-t_0)} + c_8 e^{a_2(t-t_0)} \end{pmatrix} \begin{pmatrix} c_{0,\mathrm{nl}} \\ S_{0,\mathrm{nl}} \end{pmatrix} + \begin{pmatrix} \dfrac{Ac_1 + Gc_3}{a_1}(e^{a_1(t-t_0)} - 1) + \dfrac{Ac_2 + Gc_4}{a_2}(e^{a_2(t-t_0)} - 1) \\ \dfrac{Ac_5 + Gc_7}{a_1}(e^{a_1(t-t_0)} - 1) + \dfrac{Ac_6 + Gc_8}{a_2}(e^{a_2(t-t_0)} - 1) \end{pmatrix} \tag{29}$$

where:

$$A = \frac{Nc_{\mathrm{input}}}{\varepsilon H} + \frac{\varrho\beta S_{0,\mathrm{nl}}}{\varepsilon} + \frac{\varrho\beta k c_{0,\mathrm{nl}}}{\varepsilon} \tag{30a}$$

$$G = \beta(S_{0,\mathrm{nl}} - kc_{0,\mathrm{nl}}) \tag{30b}$$

with $c_{0,\mathrm{nl}}$ as the uniform initial concentration at time t_0. $S_{0,\mathrm{nl}}$ is the corresponding quantity adsorbed according to the isotherm and k represents the slope of the chord-envelope between $S(c_{\mathrm{input}})$ and $S_{0,\mathrm{nl}}$. In case of $c_{0,\mathrm{nl}} = S_{0,\mathrm{nl}} = 0$, solution (29) corresponds with solution (28). Time-dependent input concentration (except in the non-linear adsorption case!) can be accounted for by calculating the convolution integral of the input concentration with the impulse-response of the system using a technique similar to that reported by Van Ommen (1985b). A program, written for HP41CV, to calculate eqns. (28) and (29) is available upon request.

APPLICATION OF THE MODEL

The applicability of the solution depicted in eqns. (28) and (29) is demonstrated with the help of two examples. The first example is a case of non-equilibrium adsorption, where the influence of the adsorption rate coefficient is discussed. The second example shows the breakthrough of a solute adsorbing to a convex isotherm.

Example 1. In Fig. 7 the breakthrough curve of a solute in outflowing groundwater is presented, following a pulse-type course of the input-concentration: between $t = 0$ and $t = 95\,\mathrm{yr}$ $c_{\mathrm{input}} = 1.0\,\mathrm{kg\,m^{-3}}$, outside this range $c_{\mathrm{input}} = 0$. The adsorbed quantities are given by crosses, the concentrations (in the liquid phase) by points. The breakthrough curves for $\beta = 0.027\,\mathrm{yr^{-1}}$ are presented by interrupted lines. This example clearly shows the effect of the rate coefficient β:

If $1/\beta \ll T$ (the time-constant of the migration of the adsorbing solute:

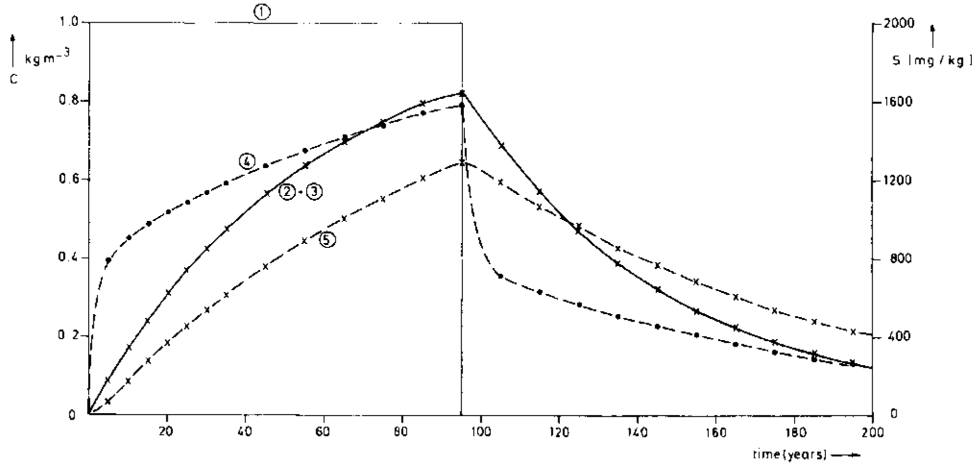

Fig. 7. Example of the non-equilibrium adsorption. $N = 0.3\,\mathrm{m\,yr^{-1}}$; $\varepsilon = 0.3$; $H = 5\,\mathrm{m}$; $\alpha = 0\,\mathrm{yr^{-1}}$; β = different values ($\mathrm{yr^{-1}}$); $\gamma = 0\,\mathrm{yr^{-1}}$; $\varrho = 1500\,\mathrm{kg\,m^{-3}}$; $k = 0.002\,\mathrm{m^3\,kg^{-1}}$. At equilibrium: $T = \varepsilon H(1 + \varrho k/\varepsilon)/N = 55\,\mathrm{yr}$: $\beta = 0.027\,\mathrm{yr^{-1}}$ (interrupted lines); $\beta = 2.7\,\mathrm{yr^{-1}}$ (solid lines). The adsorbed quantities are given as crosses.

1 = the concentration in recharge water; *2*, *3* = the concentration and quantity adsorbed in case of fast adsorption ($\beta = 2.7\,\mathrm{yr^{-1}}$); *4* = the breakthrough curve in case of slow adsorption ($\beta = 0.027\,\mathrm{yr^{-1}}$); *5* = the adsorbed quantity in case of slow adsorption.

$T = \varepsilon H(1 + \varrho k/\varepsilon)/N$), the influence of the adsorption reaction is small (except after a sudden change of the input concentration).

If $1/\beta > T$ (or of the same order of magnitude), the shape of the breakthrough curve changes considerably, while the adsorbed quantity lags behind.

Example 2. In Fig. 8b two breakthrough curves have been constructed for a

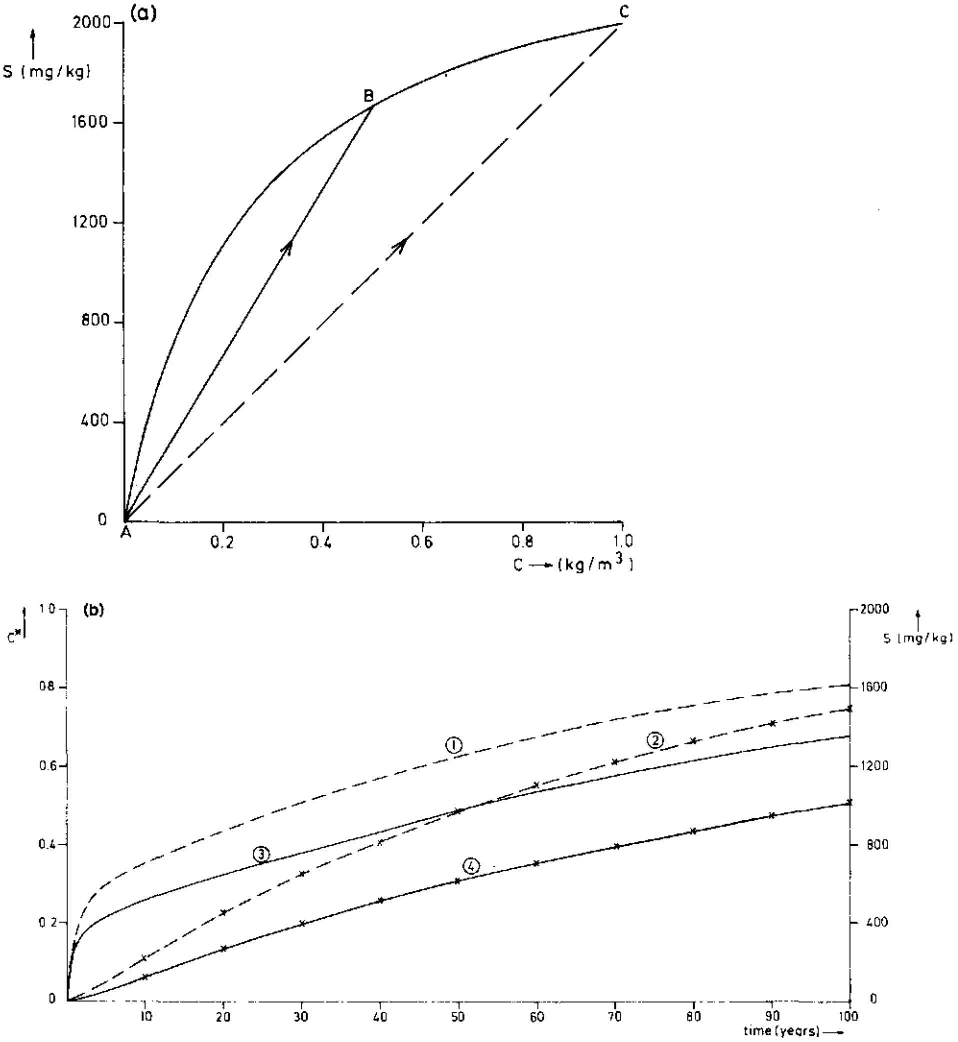

Fig. 8. a. The non-linear adsorption isotherm with the chord-envelopes (AB and AC): $S(c) = 0.01\ c/1 + 4c$ (kg/kg dry soil). b. The influence of the non-linear isotherm on the breakthrough curve. $N = 0.3\,\mathrm{m\,yr^{-1}}$; $\varepsilon = 0.3$; $H = 5\,\mathrm{m}$; $\alpha = 0\,\mathrm{yr^{-1}}$; $\beta = 0.05\,\mathrm{yr^{-1}}$; $\gamma = 0\,\mathrm{yr^{-1}}$; $\varrho = 1500\,\mathrm{kg\,m^{-3}}$. Adsorbed quantities are given as crosses. Interrupted lines: $c_{\text{input}} = 1.0\,\mathrm{kg\,m^{-3}}$; solid lines: $c_{\text{input}} = 0.5\,\mathrm{kg\,m^{-3}}$. *1* = the breakthrough curve for $c_{\text{input}} = 1.0\,\mathrm{kg\,m^{-3}}$; *2* = the quantity adsorbed versus time in case of $c_{\text{input}} = 1.0\,\mathrm{kg\,m^{-3}}$; *3* = the breakthrough curve for $c_{\text{input}} = 0.5\,\mathrm{kg\,m^{-3}}$; *4* = the quantity adsorbed for $c_{\text{input}} = 0.5\,\mathrm{kg\,m^{-3}}$.

solute adsorbing according to a non-linear Langmuir isotherm (Fig. 8a); the first one where $c_{\text{input}} = 0.5\,\text{kg}\,\text{m}^{-3}$ for $t \geqslant 0$, the second where c_{input} equals $1.0\,\text{kg}\,\text{m}^{-3}$. In both cases the initial concentration was uniformly equal to zero. As ordinate the dimensionless concentration c^* is used, defined as:

$$c^* = ((c - c_{\text{orig.}})/(c_{\text{input}} - c_{\text{orig.}}))$$

With a higher input concentration (second breakthrough curve), the breakthrough is faster because of the smaller slope of the chord-envelope resulting in a relatively smaller adsorbed quantity than in the first case.

CONCLUSIONS

Based on the analogy between the transport of an inert solute away from a diffuse source of contamination and the outflow of a perfectly stirred reservoir, the characteristic time for transport of an inert solute in a groundwater flow system can be defined as:

$$T = \frac{\varepsilon H}{N} \quad [\mathrm{T}] \tag{31}$$

This characteristic time is an important factor and for e.g. Dutch circumstances the next rule of thumb may be applied: *the characteristic time (yr) equals the thicknesss of the aquifer (m).* The porosity is about 0.30, where the net annual groundwater recharge equals 250–350 mm.

"Thick" aquifers have a large characteristic time for transport of inert solutes; the concentration of solutes in outflowing groundwater reacts slowly upon changes of the concentration in the recharge water. Using the discussed approach, it is necessary to investigate the magnitude of the time scale of the chemical interaction or decomposition process in order to evaluate the dominating process. With that knowledge, a sound basis for the prediction of groundwater quality in time might be present.

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3. CALCULATING THE IMPACT OF A MOMENTARY INPUT OF A DECAYING SOLUTE - AND ITS DECAY COMPONENTS - ON THE QUALITY OF OUTFLOWING GROUNDWATER

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CALCULATING THE IMPACT OF A MOMENTARY INPUT OF A DECAYING SOLUTE — AND ITS DECAY COMPONENTS — ON THE QUALITY OF OUTFLOWING GROUNDWATER

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ABSTRACT

Van Ommen, H.C., 1986. Calculating the impact of a momentary input of a decaying solute — and its decay components — on the quality of outflowing groundwater. J. Hydrol., 89: 59–64.

Using the analogy between the breakthrough curve of solute transport from a diffuse source and the effluent concentration of a perfectly stirred tank, the evolution of the concentration in outflowing groundwater concerning an arbitrary component of a decay chain is presented. As an illustration of the method, an example of a hypothetical decay chain is presented. Consequences and recommendations for — nevertheless undesirable — practical use are discussed.

INTRODUCTION

At the end of April 1986, large parts of the world's population were frightened by the nuclear disaster which took place at Tsjernobyl, U.S.S.R. As a consequence, considerable amounts of radioactive material were scattered over large parts of the Northern Hemisphere reaching the earth's surface by the processes of wet and dry deposition.

At this early stage, it is very difficult to strike a complete balance concerning the environmental impact of such an event. However, Trouwborst et al. (1986) and Van der Veen (1986) discussed the effects on drinking water produced from surface waters.

As groundwater is another important source for drinking water production, the scope of this article is to provide a simple calculation method in order to predict the effects of an instantaneous input of radioactive material upon the quality of groundwater. These effects include decay and generation of components as is the case in a radioactive decay chain.

After the theoretical development of the method, an example is given to illustrate the theory, followed by some conclusions and recommendations.

TRANSPORT FROM A DIFFUSE SOURCE

As has been derived elsewhere (Van Ommen, 1986), groundwater transport of a solute stemming from a diffuse source can be described by considering the

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aquifer as a reservoir in which perfect mixing takes place. This analogy occurs, if the following assumptions are valid: (1) steady groundwater flow in a phreatic aquifer with uniform recharge; (2) changes in thickness of the saturated zone are small compared to the total thickness of the aquifer; (3) the thickness of the aquifer and its porosity are constant; (4) the Dupuit–Forchheimer assumptions are valid.

The mixing process in a perfectly stirred tank is governed by a first-order linear differential operator. Using the beforementioned analogy and the knowledge that radioactive decay is a first-order linear process as well, it is manageable to incorporate the effects of a radioactive decay chain into the mass balance equation of a perfectly stirred tank.

By applying this approach to groundwater transport from a diffuse source of contamination, it is not necessary to solve a set of dependent convective-dispersive solute transport equations to calculate the breakthrough curve of a component in outflowing groundwater. For problems of pollution by point sources, however, the set of dependent transport equations will have to be solved (see, e.g., Huyakorn and Pinder, 1983). As was implicitly assumed, only saturated transport will be considered for the reason that the transport time in the unsaturated zone can generally be neglected against the transport time in the aquifer (Van Ommen, 1986).

Henceforth is the derivation of the mass balance equations for a perfectly stirred tank in which the processes of adsorption, decay, and generation of components of a decay chain take place.

THE MASS BALANCE EQUATION

In order to predict the effects of a momentary input of the first component in the decay chain, the mass balance equations are derived for a system having a constant input equal to one. From this step-response of the system, the impulse-response is easily determined.

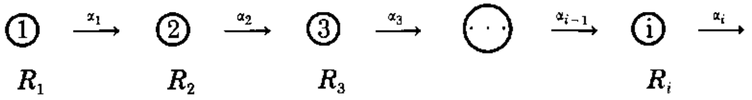
The mass balance equation for an arbitrary component subject to inflow, outflow, adsorption, production and first-order decay reads (Van Ommen, 1985):

$$\varepsilon H(1 + R)\frac{\mathrm{d}c}{\mathrm{d}t} = Nc_{\mathrm{in}} - Nc + P - \alpha\varepsilon Hc - \alpha\varepsilon HRc \qquad (1)$$

where c is the concentration of the component (M L^{-3}), t is the time (T), ε is the porosity of the aquifer, H the thickness of the aquifer (L), N the net recharge rate (L T^{-1}), c_{in} the inflow concentration (M L^{-3}),P the production term (M L^{-2} T^{-1}), α the decay coefficient (T^{-1}) and R the distribution ratio of the component. The fifth term on the right-hand side of eqn. (1) represents the decay of the component in the adsorbed state. The decay coefficient is defined in terms of the half-life, $t_{1/2}$, of a component as:

$$\alpha = \frac{\ln 2}{t_{1/2}} \qquad (2)$$

Considering a decay chain of the following form:



where the number within the circle represents the component, α the decay coefficient of the component and R the distribution ratio.

The mass balance equation concerning the first component, for c_{in} equal to one, is given by:

$$\varepsilon H(1 + R_1)\frac{\mathrm{d}c_1}{\mathrm{d}t} = N - (N + \alpha_1 \varepsilon H + \alpha_1 \varepsilon H R_1)c_1 \tag{3}$$

The subscripts relate to the number of the component in the decay chain.

For component number i, the mass balance equation becomes:

$$\varepsilon H(1 + R_i)\frac{\mathrm{d}c_i}{\mathrm{d}t} = (\alpha_{i-1}\varepsilon H + \alpha_{i-1}\varepsilon H R_{i-1})c_{i-1} - (N + \alpha_i \varepsilon H + \alpha_i \varepsilon H R_i)c_i \tag{4}$$

Note that no inflow takes place and that the generation of component i is equal to the decay of component $i - 1$.

The production term is thus equal to $\alpha_{i-1}\varepsilon H(1 + R_{i-1})\, c_{i-1}$. In reality, a single component — say component number '$i - 1$' — may decay into different decay components, generated by a given fraction of the decaying solute. In this case, the production term on the right-hand side of eqn. (4) will have to be multiplied by the fraction of component '$i - 1$', decaying into component 'i'. For the sake of simplicity, this has been omitted in the derivation, although it is easy to incorporate in the presented approach.

Eqn. (4) may be rearranged to yield a general form:

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = p_i c_{i-1} - q_i c_i \tag{5}$$

where $p_1 = \dfrac{N}{\varepsilon H(1 + R_1)}$ and $c_{i-1} = c_{\text{in}} = 1$ for $i = 1$,

and:

$$p_i = \alpha_{i-1}\frac{1 + R_{i-1}}{1 + R_i} \quad (i > 1) \tag{6}$$

$$q_i = \frac{N}{\varepsilon H(1 + R_i)} + \alpha_i \quad (\text{all } i) \tag{7}$$

Integration of eqn. (5) yields for the concentration of component i in the outflowing groundwater:

$$c_i(t) = \left(p_i \int_0^t c_{i-1}(t) \exp(q_i t)\, \mathrm{d}t + \text{constant}\right) \exp(-q_i t) \tag{8}$$

If the initial concentration of component i in the aquifer is equal to zero, the constant is zero.

The solution of eqn. (8) has been developed in the framework of a transport model to describe single species transport in a heterogeneous soil profile (Van Ommen, 1985). In the latter case, the mathematical nature of the problem is the same, although the physical nature is entirely different; the values of the coefficients p_i and q_i differ considerably in both cases.

For the initial concentration equal to zero, and c_{in} equal to one, the concentration of component n in outflowing groundwater is given by:

$$c_n(t) = K_n(0) + \sum_{i=1}^{i=n} [K_n(i) \exp(-q_i t)] \tag{9}$$

The coefficients are obtained as follows:

$$K_j(0) = K_{j-1}(0) p_j / q_j \tag{9a}$$

$$K_j(1) = K_{j-1}(1) p_j / (q_j - q_1) \tag{9b}$$

$$K_j(i) = K_{j-1}(i) p_j / (q_j - q_i) \tag{9c}$$

$$K_j(j) = -\sum_{i=0}^{i=j-1} [K_j(i)] \tag{9d}$$

Starting with $K_0(0) = 1$, the coefficients $K_n(0)$ and $K_n(1)$ through $K_n(n)$ in eqn. (9) are easily obtained by applying the recursive relationships (9a–9d) until j equals n. In general, $q_j \neq q_i$ for $i, j = 1, \ldots, n\,(j \neq i)$ in order to avoid numerical instabilities (see eqn. (9c)). An example of this calculation is given in Appendix I of Van Ommen (1985).

Having the step-response of the system, given by eqn. (9), the impulse response $c_n'(t)$ can easily be determined by taking the first derivative of the step-response:

$$c_n'(t) = \sum_{i=1}^{i=n} [-q_i K_n(i) \exp(-q_i t)] \tag{10}$$

This unit impulse-response gives the outflow concentration of component n, upon a momentary input of component 1 of N $\mathrm{ML^{-2}}$, i.e. 1 (T, time unit) × 1 ($c_{\text{in}} = 1\,\mathrm{ML^{-3}}$) × N ($\mathrm{LT^{-1}}$).

In the next part, an illustration of the theory will be given in the form of hypothetical breakthrough curves, following a unit input impulse of component 1.

EXAMPLE

In this example, the reaction of groundwater quality upon an instantaneous unit input of the first component in a decay chain is given. This component is finally transformed into component 5, which is assumed to be the last and stable component in the decay chain. The data used in the calculation (see Table 1) are entirely arbitrary values of the recharge rate, thickness and porosity of the aquifer, as well as the values of the distribution ratio and the half-life of the components.

TABLE 1

Data used in the example

Thickness of the aquifer: 10 m
Recharge of the aquifer: 0.3 m yr^{-1}
Porosity of the aquifer: 0.3
Input quantity: 0.3 kg m^{-2}

Component	R	$t_{1/2}$(yr)
1	1.0	1.0
2	2.0	0.1
3	0.0	5.0
4	1.0	20.0
5	1.0	∞ (stable)

The breakthrough curves of the five components are given in Fig. 1. Two important conclusions may be drawn from these breakthrough curves: (1) high concentrations of a component in a decay chain may occur a long time after the momentary input took place; (2) the concentration of a component in outflowing groundwater is highly dependent upon the decay coefficient of a precedent component in the decay chain.

CONCLUSIONS AND RECOMMENDATIONS

Transport of components, which are decaying according to a first-order decay reaction, can be described by using an analogy of the transport process

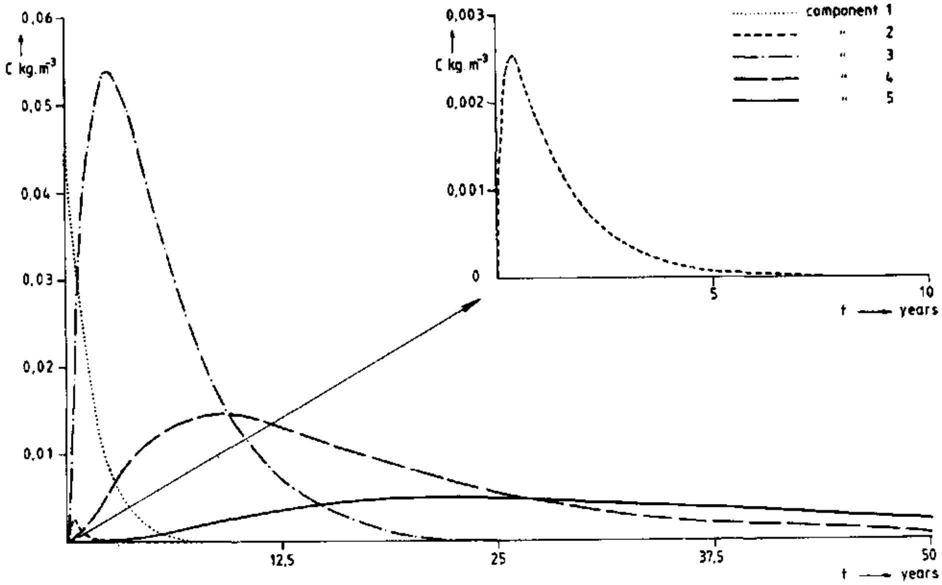


Fig. 1. Breakthrough curves following an instantaneous input of component 1.

from a diffuse source with the outflow from a perfectly stirred tank. The input parameters of a transport model based on that analogy, consist of hydrological parameters such as recharge rate of the aquifer, porosity and thickness of the aquifer and a physical and geochemical parameter: the half-life and the distribution ratio of the component. With a reliable knowledge of these parameters, a sound basis for the prediction of the breakthrough curve might be present.

As was shown in the example, high concentrations of a component may occur a long time after the input took place. For that reason, drinking water produced from infiltration water in the intake area once being exposed to a momentary input of radioactively decaying material, needs a constant quality control on the presence of components accompanied with an amount of radiation.

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4. SYSTEMS APPROACH TO AN UNSATURATED-SATURATED GROUNDWATER QUALITY MODEL, INCLUDING ADSORPTION, DECOMPOSITION AND BYPASS

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SYSTEMS APPROACH TO AN UNSATURATED-SATURATED GROUNDWATER QUALITY MODEL, INCLUDING ADSORPTION, DECOMPOSITION AND BYPASS

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ABSTRACT

Van Ommen, H.C., 1985. Systems approach to an unsaturated-saturated groundwater quality model, including adsorption, decomposition and bypass. *Agric. Water Manage.*, 10: 193—203.

In this paper an unsaturated-saturated model for groundwater pollution from diffuse sources is developed. As a linear systems approach has been applied, a time-dependent input concentration can easily be incorporated. Processes as first-order decomposition and linear adsorption can be accounted for as well as the phenomenon of bypass flow. An example is given of a bimodal breakthrough curve as a reaction on a pulse-type input concentration. A program written for an HP41CV pocket calculator is presented in the appendix.

INTRODUCTION

In the last decade the interest for groundwater quality models has increased due to the growing impact of human activities and intensive land use on the quality of ground- and surface water. Examples of human influence on the quality of groundwater are contamination by solutes from sanitary landfills (MacFarlane et al., 1983) and high nitrogen contents caused by leaching of nutrients in regions where large amounts of fertilizer are used in agriculture (Bruyn, 1984).

A broad distinction can be made between two kinds of models, viz. those which describe the migration of solutes emitted by point sources, and those which describe migration of solutes emitted by diffuse sources. The definition of point and diffuse sources depends, of course, on the scale of the problem. On a regional scale a single field emitting solutes to the groundwater may be considered as a point source. However, on the scale of the parcel itself, the contamination can be considered to stem from diffuse sources.

0378-3774/85/$03.30

Another distinction can be made between: models describing the transport of a solute in the unsaturated zone, and models describing migration of solutes in the saturated zone. Two- and three-dimensional models describing the transport of solutes in the system unsaturated-saturated zone are scarce and often very complicated.

In the following a linear systems approach will be applied to the transport of a solute, stemming from a diffuse source, in the unsaturated and saturated zone. By means of this approach breakthrough curves can be obtained for flow to ditches, drains and wells using data that are relatively easy to obtain.

THEORY

Transport of solutes in the unsaturated zone — derivation of the transport equation

The unsaturated topsoil is assumed to consist of a number of discrete layers having the same thickness and properties. In order to develop the transport equation we start with the mass balance for each arbitrary layer i, in words:

accumulation rate = inflow – outflow – decomposition

The accumulation can take place in the liquid phase (solution) as well as in the solid phase (adsorption). The relation between the concentration of a solute in the liquid phase and the quantity adsorbed at the solid phase, at a constant temperature, is given by the adsorption isotherm. We assume the linear relation:

$$S = KC \tag{1}$$

where S is the quantity adsorbed ($\mathrm{M\ M^{-1}}$); C the concentration of solute in the liquid phase ($\mathrm{M\ L^{-3}}$); and K a constant ($\mathrm{L^3\ M^{-1}}$). The rate of accumulation of solute in the liquid phase in a layer with thickness L and volumetric moisture content θ equals:

$$\theta L \frac{\mathrm{d}C_i}{\mathrm{d}t} \tag{2}$$

and for the solid phase:

$$L\rho \frac{\mathrm{d}S_i}{\mathrm{d}t} \tag{3}$$

where ρ is the dry bulk density of the soil. Substituting equation (1) into equation (3) results in:

$$LR\theta \frac{\mathrm{d}C_i}{\mathrm{d}t} \tag{4}$$

with

$$R = \frac{\rho K}{\theta} \tag{5}$$

R is the so-called distribution ratio, i.e. the ratio of the amount of solute adsorbed to the quantity of the solute present in the liquid phase. Using the retardation factor R^* (Van Genuchten and Alves, 1982):

$$R^* = R + 1 = 1 + \rho K/\theta \tag{6}$$

the accumulation rate in layer i may now be written as:

$$\theta L(1 + R)\,\frac{\mathrm{d}C_i}{\mathrm{d}t} \tag{7}$$

The term 'inflow' in the mass balance equation equals the product of the incoming waterflow (f_d) and the concentration of the solute leaving the ($i - 1$)th layer. For the first layer, the concentration in the rain or irrigation water should be used for the inflowing water. So the first term of the right-hand-side of the mass balance becomes:

$$f_\mathrm{d}\,C_{i-1}(t) \tag{8}$$

The 'outflow' term can be defined analogous to the 'inflow' term as:

$$f_\mathrm{d}\,C_i(t) \tag{9}$$

When complete mixing is assumed the concentration of the outflowing water equals the average concentration (C_i) in layer i.

The decomposition is supposed to be described by a reaction with first-order kinetics so that the decomposition rate is proportional to the amount of solute present:

$$\alpha\theta L\,C_i(t) \tag{10}$$

in which α is the decomposition constant (T^{-1}). Combining equations (7), (8), (9) and (10) results in the transport equation of layer i:

$$\theta L(1 + R)\,\frac{\mathrm{d}C_i}{\mathrm{d}t} = f_\mathrm{d}\,C_{i-1}(t) - f_\mathrm{d}\,C_i(t) - \alpha\theta L\,C_i(t) \tag{11}$$

or

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = A\,C_{i-1}(t) - (A + B)\,C_i(t) \tag{12}$$

with

$$A = \frac{f_\mathrm{d}}{\theta L(1 + R)} \tag{13}$$

$$B = \frac{\alpha}{1 + R} \tag{14}$$

When the input concentration is set equal to one and the initial concentration equal to zero, integration of equation (12) gives for the outflow concentration at the bottom of the unsaturated zone:

$$C_n(t) = \left(\frac{A}{A+B}\right)^{n+1} + \exp[-(A+B)t] \sum_{k=0}^{k=n} \left[\frac{(At)^{n-k}}{(n-k)!} \left(-\left(\frac{A}{A+B}\right)^{k+1}\right)\right] \tag{15}$$

where $n = N - 1$, in which N represents the number of layers. By splitting the soil profile into distinct layers, numerical dispersion occurs. This may be used to represent the physical dispersion of solutes in the soil profile, which is governed by a characteristic dispersion length (Bolt, 1979). A value of L for the soil layers equal to twice this dispersion length gives satisfactory results (Van Hoorn, 1981).

Transport of solutes in the saturated zone

Two cases of transport of a solute in the saturated zone will be considered: the flow to parallel canals, which has been described extensively elsewhere (Ernst, 1973; Gelhar and Wilson, 1974), and the flow of solutes to a fully penetrating well in a phreatic aquifer. In order to establish a relation between the concentration of the water flowing into the saturated zone and the concentration of a solute leaving it, the residence time distributions have to be derived. From these distributions the concentration/time dependence of a solute flowing out of the saturated zone can be obtained.

For the derivation of the breakthrough curve in the case of flow to canals

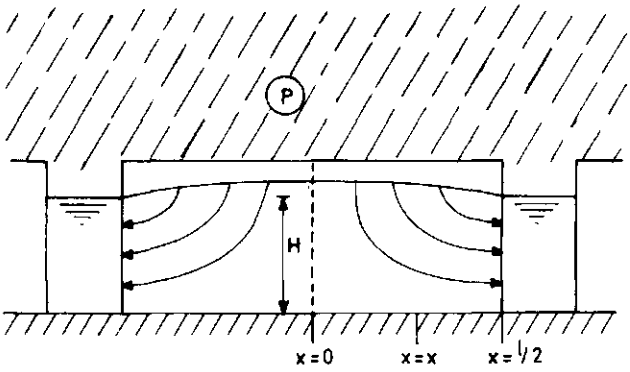

Fig. 1. Flow to parallel canals.

the flow model described by Ernst (1973) is used. Rainfall or irrigation water (P) is drained through an aquifer of thickness H towards parallel canals, having a spacing l. Using the coordinate system given in Fig. 1, the flow at distance x from water divide per unit length of canal (q_x) can be written as:

$$q_x = Px \tag{16}$$

So the residence time of a water drop starting at distance x from the divide is:

$$T_x = \frac{\epsilon H}{P}\,{}^{e}\log\,\frac{l}{2x} \tag{17}$$

where ϵ is the porosity of the aquifer. Assuming an initially 'clean' aquifer with concentration 0, and at time $t = 0$ a concentration equal to one at the top of the saturated zone, the drainage water in the canal is composed of: water with a concentration one, supplied by all streamlines with residence time shorter than T_x, and 'clean' water from all streamlines originating at greater distance from the canal. Applying equation (16), the solute fluxes at $x = l/2$ are:

concentration 1: $q'_s = P(l/2 - x) \times 1$ (18)

concentration 0: $q''_s = Px \times 0 = 0$ (19)

resulting in the average concentration $\bar{c}$ of the outflow:

$$\bar{c} = P(l/2 - x)/(Pl/2) = 1 - 2x/l \tag{20}$$

From equation (17) it follows:

$$2x/l = \exp\,(-PT/(\epsilon H)) \tag{21}$$

Combining equations (20) and (21) leads to:

$$\bar{c} = 1 - \exp\,(-PT/(\epsilon H)) \tag{22}$$

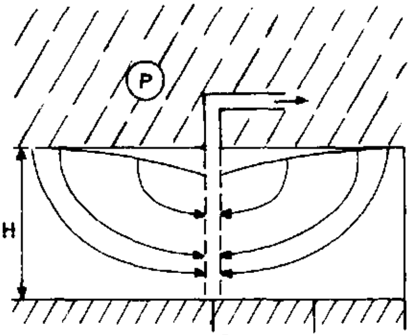

Fig. 2. Flow to a well in a phreatic aquifer.

The breakthrough curve for flow to a fully penetrating well in a phreatic aquifer (Fig. 2) can be treated in the same way. With respect to the concentrations the same initial and boundary conditions as in the first case are used.

The amount of water flowing to the well from a distance greater than r ($Q(r)$) equals:

$$Q(r) = \pi P(r_e^2 - r^2) \tag{23}$$

where r_e is the radius of influence of the well. The concentration of a solute in the well can be obtained by the same reasoning as in the case of flow to canals:

$$\bar{c} = Pr^2/(Pr_e^2) = r^2/r_e^2 \tag{24}$$

The pore flow velocity $u(r)$ at a distance r from the well is determined by dividing $Q(r)$ by the effective cross-sectional area at that distance:

$$u(r) = \frac{(r_e^2 - r^2)P}{2r\epsilon H} \tag{25}$$

From this pore flow velocity the residence time T_r at a point $r = r$ from the well is:

$$T_r = -\frac{\epsilon H}{P}\ {}^{e}\log\left(1 - \left(\frac{r}{r_e}\right)^2\right) \tag{26}$$

Combined with equation (24) this results in the following relation between the concentration in the well and time:

$$\bar{c} = 1 - \exp\left(-PT/(\epsilon H)\right) \tag{27}$$

This is the same result as given in (22), hence there is a similarity between the breakthrough curves for the flow to canals and the flow to a well.

Equations (22) and (27) describing the breakthrough curves are exactly the same as those for the concentration/time dependence of the effluent in a reservoir, having a volume of ϵH and an inflow/outflow rate P, in which complete mixing takes place. This means, that the breakthrough curves may be calculated with equations (11) to (14) and this enables one to give a complete description of the breakthrough of a solute through the unsaturated and saturated zones. The unsaturated zone is schematized as a series of layers with the same properties and residence times, the outflow of which is used as the time-dependent input for the aquifer.

Phenomenon of bypass

In the unsaturated zone, part of the waterflow may take place through macropores and cracks. Especially in clay soils, which are subject to swelling and shrinking, this preferential downward flow may play an important role (Bouma et al., 1981; Dekker and Bouma, 1984). As a consequence, part of the precipitation (and the dissolved solutes) can reach the groundwater much faster than water flowing through the soil matrix itself, and this may cause an accelerated breakthrough of the solute from the unsaturated soil.

In the above cases, bypass can be schematized as follows: a fraction of the precipitation (f) flows directly to the groundwater through the cracks and/or macropores, while the remainder ($1 - f$) flows through the soil matrix. The input concentration to the saturated zone is then composed of two parts:

$$C_{\text{input}} = f C_{\text{inp}} + (1 - f) C_{\text{outf}} \tag{28}$$

where C_{inp} is the concentration in precipitation/irrigation water, and C_{outf} the concentration in the water flowing out of the unsaturated zone. In this way it is possible to achieve a coupling between the unsaturated and saturated zones.

Coupling of the two systems

The relation between the concentration in a canal or well (C) and the time (t) can be described by equations (11) to (14):

$$\frac{\mathrm{d}C}{\mathrm{d}t} = A_{\text{aq}} \left(C_n(t)(1 - f) + f\right) - (A_{\text{aq}} + B_{\text{aq}})\, C(t) \tag{29}$$

where A_{aq} and B_{aq} are analogous to A and B in equations (13) and (14), but now applied to the aquifer, and $C_n(t)$ is the concentration in the water flowing out of the soil matrix at the bottom of the unsaturated zone (equation 15). When the concentration of a solute in the water flowing into the coupled system is equal to unity, the solution of the mass balance equation (29) reads:

$$\begin{aligned} C(t) = \Bigg((1 - f) \Bigg\{ \left(\frac{A_{\text{aq}}}{A_{\text{aq}} + B_{\text{aq}}}\right) \left(\frac{A}{A + B}\right) (\exp ((A_{\text{aq}} + B_{\text{aq}})t) - 1) \\ + A_{\text{aq}} \sum_{k=0}^{k=n} \Bigg\{ A^{n-k} \left(- \left(\frac{A}{A + B}\right)^{k+1} \right) \Bigg(\Bigg(\exp ((A_{\text{aq}} + B_{\text{aq}} - A - B)t) \\ \times \sum_{j=0}^{j=n-k} \left(\frac{t^{n-k-j}(-1)^j}{(n-k-j)!} \quad \frac{1}{(A_{\text{aq}} + B_{\text{aq}} - A - B)^{j+1}} \right) \Bigg) \\ + \left(\frac{-1}{A_{\text{aq}} + B_{\text{aq}} - A - B} \right)^{n-k+1} \Bigg) \Bigg\} \Bigg\} \\ + f \Bigg\{ \left(\frac{A_{\text{aq}}}{A_{\text{aq}} + B_{\text{aq}}}\right) (\exp ((A_{\text{aq}} + B_{\text{aq}})t) - 1) \Bigg\} \Bigg) \exp (-(A_{\text{aq}} + B_{\text{aq}})t) \end{aligned} \tag{30}$$

Due to the linearity of the system involved, the concentration of the output will always be proportional to the input concentration and hence the solution is generally applicable.

Breakthrough curves for a time-dependent input

Equation (30) represents the response of the system to an input represented by a unit stepfunction. For this special case we use the notation $S(t)$ (step-response) for (30). The reaction of a linear system on a time-dependent input can be obtained by calculating the discrete form of the convolution integral of the input concentrations with the T-time salinographs (compare the unit hydrograph method as described by Krayenhoff van de Leur, 1973), which are determined by:

$$\mu(T,t) = S(t) - S(t - T) \quad \text{for } t \geqslant T \qquad (31)$$

These T-time salinographs represent the influence of the input concentration (which is equal to 1) on the output concentration between the times t and $t - T$.

Assuming the time-axis to be divided into time intervals of the same length T, the concentration in the canal or well after a time t (composed of 'i' time intervals of length T) equals:

$$C(t) = \sum_{j=1}^{j=i} \mu(T,jT)\, C_{\text{inp}}(i - (j - 1)) \qquad (32)$$

The coupling of water quality and water quantity is a problem due to the different time scale at which both processes take place. The time scale for water quantity is often an order of magnitude smaller than that of the water quality (Raats, 1983). The latter is for an inert solute in the saturated zone:

$$\epsilon H/P \qquad (33)$$

This leads to the conclusion that the assumption of stationary water flow is justified when the period of variation in water flow is small compared with the water quality time scale. In order words: when considering long term effects of different values for the input concentration on water quality for a system with a time scale of e.g. 30 years, it is justified to use the average net yearly precipitation and stationary flow instead of a non-stationary water flow caused by time-dependent precipitation.

EXAMPLE

As an example we carried out a calculation with the following input data: net precipitation 300 mm/year; decomposition factor and the distribution ratio equal to zero; thickness unsaturated zone: 2 m, represented by five layers of 0.4 m each, with a volumetric moisture content of 0.15; thickness saturated zone (aquifer): 2 m, porosity: 0.30; bypass flow factors: 1.0, 0.5 and 0.0. In Fig. 3 the specified pulse-type input and the reaction of the system for three values of the bypass coefficient are given. Striking is the appearance of a two-peak breakthrough curve for a bypass factor equal to 0.5. The first peak represents the reaction of the system to the input concentration which arrives at the top of the saturated zone by the process of bypass. The second one is due to the breakthrough of the solute flowing through the soil matrix itself. However, this breakthrough takes place later than the moment at which the input concentration changes from one to zero. The very slight decrease in concentration between the peaks is the result of the combined process.

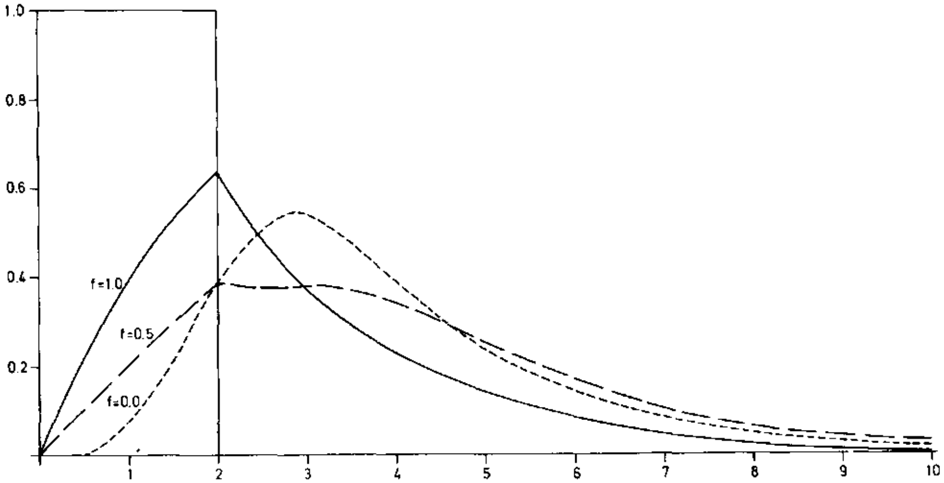

Fig. 3. Breakthrough curves as a function of the specified input data and bypass coefficients.

The calculation of these breakthrough curves was performed on a HP41CV programmable pocket calculator. The program is presented in the Appendix.

APPENDIX

Program for HP41CV (XEQ size 100; maximum number of time steps: 19)

```
 01♦LBL "WATQUAL"
"NLAY ?"  PROMPT  1  -
STO 41  "TEND ?"  PROMP
STO 42  "DELTIME ?"
PROMPT  STO 43
"PRECIP. ?"  PROMPT
STO 44  "MOIST.CONT. ?"
PROMPT  STO 45
"DISRAT.SOIL ?"  PROMPT
STO 46  "DISRAT.AQUI ?"
PROMPT  STO 47
"EFF.POR. ?"  PROMPT
STO 48  "DEC.FAC.SOIL ?"
PROMPT  STO 49
"DEC.FAC.AQUI ?"  PROMPT
STO 50  "TH.LAYERS ?"
PROMPT  STO 51
"TH.AQUIFER ?"  PROMPT
STO 52  "FR.BYPASS ?"
PROMPT  STO 53  RCL 42
RCL 43  /  STO 61  0
STO 62

 49♦LBL 00
1  ST+ 62  "CIN "
RCL 62  INT  FIX 0
ARCL X  "├ ?"  PROMPT
STO IND 62  RCL 61
RCL 62  X<Y?  GTO 00
RCL 46  1  +  RCL 51  *
RCL 45  *  1/X  RCL 44
*  RCL 53  CHS  1  +  *
STO 54  RCL 46  1  +
1/X  RCL 49  *  STO 55
RCL 47  1  +  RCL 52  *
RCL 48  *  1/X  RCL 44
*  STO 56  RCL 47  1  +
1/X  RCL 50  *  STO 57
RCL 54  RCL 55  +  1/X
RCL 54  *  STO 44
RCL 56  RCL 57  +  1/X
RCL 56  *  STO 45
RCL 56  RCL 57  +
RCL 54  -  RCL 55  -
STO 46  RCL 46  1/X  CHS
STO 47  RCL 41  1  +
RCL 44  X<>Y  Y↑X
RCL 45  *  RCL 53  CHS
1  +  *  ENTER↑  RCL 53
RCL 45  *  +  STO 48  0
STO 63

152♦LBL 01
1  ST+ 63  RCL 63
RCL 43  *  STO 64  0
STO 65  0  STO 66

163♦LBL 02
0  STO 67  0  STO 68
RCL 41  RCL 66  -
STO 69

172♦LBL 03
RCL 69  ENTER↑  RCL 68
-  STO 70  RCL 46
ENTER↑  RCL 68  1  +
Y↑X  RCL 70  FACT  *
1/X  ENTER↑  RCL 64
ENTER↑  RCL 70  Y↑X  *
-1  RCL 68  Y↑X  *
ST+ 67  1  ST+ 68
RCL 69  RCL 68  X<=Y?
GTO 03  RCL 54  RCL 69
Y↑X  STO 71  RCL 44
RCL 66  1  +  Y↑X  CHS
ST* 71  RCL 47  RCL 41
RCL 66  -  1  +  Y↑X
ENTER↑  RCL 46  RCL 64
*  E↑X  RCL 67  *  +
ST* 71  RCL 71  ST+ 65
1  ST+ 66  RCL 41
RCL 66  X<=Y?  GTO 02
RCL 56  ST* 65  RCL 53
CHS  1  +  ST* 65  20
RCL 63  +  STO 72
RCL 56  RCL 57  +
RCL 64  *  E↑X  1  -
RCL 48  *  RCL 65  +
ENTER↑  RCL 56  RCL 57
+  CHS  RCL 64  *  E↑X
*  STO IND 72  RCL 61
ENTER↑  RCL 63  X<Y?
GTO 01  1  STO 73
RCL 21  STO 81  81
STO 80

284♦LBL 04
1  ST+ 73  1  ST+ 80
RCL 73  20  +  STO 74
RCL 73  19  +  STO 75
RCL IND 74  RCL IND 75
-  STO IND 80  RCL 61
RCL 73  X<Y?  GTO 04  0
STO 76  TONE 9

308♦LBL 05
1  ST+ 76  0  STO 77  0
STO 78

315♦LBL 06
1  ST+ 78  RCL 76
RCL 78  -  1  +  80  +
RCL IND X  RCL IND 78  *
ST+ 77  RCL 78  RCL 76
X>Y?  GTO 06  RCL 77
FIX 3  "C= "  ARCL X
AVIEW  STOP  RCL 76
RCL 61  X>Y?  GTO 05
STOP  END
```

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5. CALCULATING THE QUALITY OF DRAINAGE WATER FROM NON-HOMOGENEOUS SOIL PROFILES WITH AN EXTENSION TO AN UNSATURATED-SATURATED GROUNDWATER QUALITY MODEL INCLUDING BYPASS FLOW

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CALCULATING THE QUALITY OF DRAINAGE WATER FROM NON-HOMOGENEOUS SOIL PROFILES WITH AN EXTENSION TO AN UNSATURATED-SATURATED GROUNDWATER QUALITY MODEL INCLUDING BYPASS FLOW

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ABSTRACT

Van Ommen, H.C., 1985. Calculating the quality of drainage water from non-homogeneous soil profiles with an extension to an unsaturated-saturated groundwater quality model including bypass flow. *Agric. Water Manage.*, 10: 293—304.

Based on the mass balance equation, a pseudo-analytical solution for the chemical concentration in drainage water from a soil profile is given. The effects of linear adsorption, decomposition and plant water uptake as well as the water content and layer thickness may be specified separately for each layer. The phenomenon of bypass flow can also be taken into account. From the obtained relationship between the concentration of solute in the drainage water leaving the soil profile and the time, a coupling between the unsaturated and the saturated zone can be achieved as was described earlier. This leads to breakthrough curves of the solute leaving the combined system of unsaturated and saturated zones. Time-dependent input concentrations can easily be incorporated through the systems approach. The computer programs (written for an HP41CV pocket calculator), describing the quality of drainage water from non-homogeneous profiles and the breakthrough of a solute leaving the combined system, are given as an appendix.

INTRODUCTION

One-dimensional solute transport plays an important role in problems concerning leaching of salts from the soil profile and contamination of groundwater by pollution at the surface. The concentration of a solute in water leaving the unsaturated zone may impose a heavy burden on the quality of groundwater.

Several kinds of solutions of the solute transport equation are possible; a distinction can be made between analytical solutions and numerical solutions. Van Genuchten and Alves (1982) give a variety of solutions for the steady-state transport equation subject to various initial and boundary conditions. These solutions are only valid for homogeneous soil profiles, i.e. soil

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profiles of which transport properties such' as pore flow velocity, solute distribution ratio and decomposition constant are assumed to be constant with depth. Numerical solutions generally use the finite difference or finite element approach and are flexible with respect to flow conditions (steady and non-steady and transport parameters (Gureghian et al., 1979; Van Genuchten, 1978).

Both types of solutions have their advantages and disadvantages. Sometimes non-steady flow conditions and heterogeneous distribution of transport parameters forces one to apply a numerical solution to the problem at hand (Leistra et al., 1980). On the other hand, numerical methods require a large amount of input data especially when non-steady flow is taken into account. Apart from this, discretization of time and space imposes severe limitations on time- and space steps and may cause problems in connection with stability and convergency of the solution (Duynisveld, 1983).

In the following, a model to describe the evolution of the concentration of a solute leaving the unsaturated zone, consisting of layers with different transport properties and flow conditions, is developed. The water flow is assumed steady. Starting from the solution of the solute transport equation in heterogeneous profiles, a coupled unsaturated-saturated groundwater quality model is derived (see Van Ommen, 1985). Finally, an illustration of the theory is given.

THEORY

Transport of solutes in the unsaturated zone

For the derivation of the desired relationship, the following assumptions are made: stationary water flow, i.e. water fluxes and water contents are independent of time; the soil is divided into a number of layers in which complete mixing takes place; no precipitation and/or dissolution of salts takes place; and solute uptake by plants is neglected. We assume a layer of thickness L (L), of unit cross-section, with water inflow q_{in} (L T^{-1}) and outflow q_{out}. Because the water content (θ) of the layer is assumed to be constant, we have:

$$q_{\mathrm{out}} = q_{\mathrm{in}}(1 - S) \tag{1}$$

where the sink term S represents water uptake by plant roots (or evaporation) expressed as a fraction of the inflow in the layer under consideration ($0 \leqslant S \leqslant 1$). Decomposition of the solute is assumed to be described by a first-order equation; the decomposition being proportional to the amount of solute present in the layer. This process is characterized by the rate constant α (T^{-1}). Adsorption of solute at the solid phase is quantified by the distribution ratio R being the ratio of the amount of solute adsorbed to the amount of solute present in the liquid phase.

Inflow of solute in an arbitrary layer is equal to the product of the incoming water flow (q_{in}) and the concentration of the solute leaving the overlying layer (C_{i-1}). For the first layer, the concentration in rain- or irrigation water should be used. The mass balance equation for any arbitrary layer i then reads:

$$(1 + R_i)\theta_i L_i \frac{\mathrm{d}C_i}{\mathrm{d}t} = q_{\text{in},i} C_{i-1}(t) - q_{\text{out},i}\, C_i(t) - \alpha_i \theta_i L_i\, C_i(t) \tag{2}$$

where t is the time (T); and C_i the concentration in layer i (M L^{-3}); or:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = p_i\, C_{i-1}(t) - q_i\, C_i(t) \tag{3}$$

in which

$$p_i = \frac{q_{\text{in},i}}{\theta_i L_i (1 + R_i)} \tag{4}$$

and

$$q_i = \frac{q_{\text{out},i}}{\theta_i L_i (1 + R_i)} + \frac{\alpha_i}{1 + R_i} \tag{5}$$

Integration of equation (3) yields for the concentration of a solute in any arbitrary layer i:

$$C_i(t) = (p_i \int_0^t C_{i-1}(t) \exp\,(q_i t)\,\mathrm{d}t + \text{constant}) \;\; \exp\,(-q_i t) \tag{6}$$

If the initial concentration of layer i is equal to zero, the constant = 0. Assuming a unit input concentration to an initially clean layer, the concentration in layer 1 is:

$$C_1(t) = \frac{p_1}{q_1}\;(1 - \exp\,(-q_1 t)) \tag{7}$$

Bypass through cracks, fissures or root channels can be accounted for by considering a fraction f of the infiltrating water N flowing directly to the bottom of the soil profile through the macropores, while the remainder $1 - f$ flows through the soil matrix (Fig. 1). In this case the concentration of a solute in the drainage water (C_{dw}) is composed of two contributions:

$$C_{\text{dw}} = \frac{fNC_{\text{inf}} + q_{\text{out},n} C_{\text{outf}}}{fN + q_{\text{out},n}} \tag{8}$$

where C_{inf} is the concentration of solute in the infiltrating water, C_{outf} the concentration of the solute flowing out of the soil matrix at the bottom of

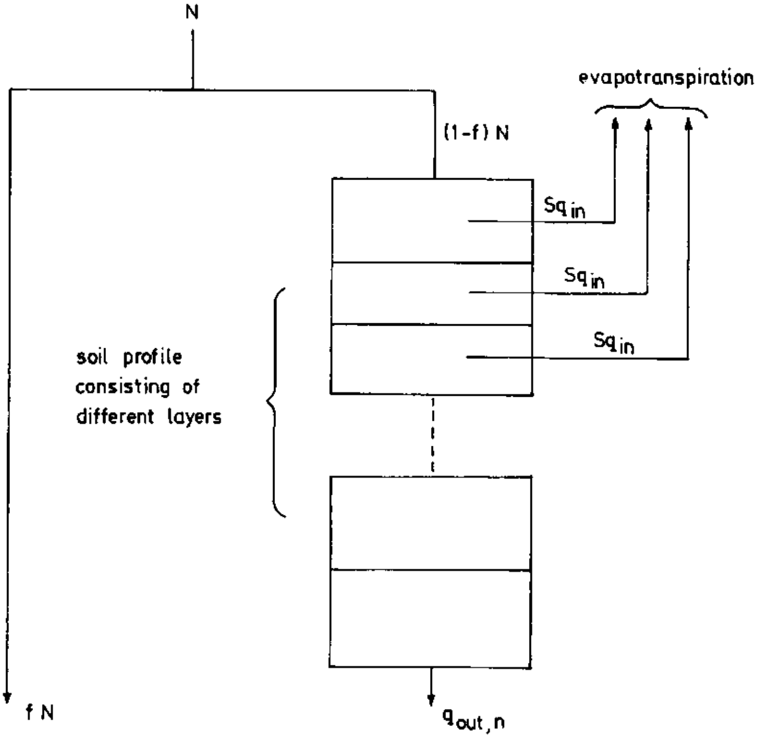

Fig. 1. Schematization of the soil profile.

the profile, and $q_{out,n}$ water flux leaving layer n at the bottom of the profile. Successive integration of equation (6) yields for the concentration of a solute ($C_n(t)$ in layer n at the bottom of the soil profile, when the input concentration is 1 ($C_{inf} = 1$) and the initial concentration is zero:

$$C_n(t) = K_n(0) + \sum_{i=1}^{i=n} (K_n(i) \exp(-q_i t)) \tag{9}$$

For the coefficients the following relationships are valid:

$$K_j(0) = K_{j-1}(0) p_j/q_j \tag{9a}$$

$$K_j(1) = K_{j-1}(1) p_j/(q_j - q_1) \tag{9b}$$

$$K_j(i) = K_{j-1}(i) p_j/(q_j - q_i) \tag{9c}$$

$$K_j(j) = - \sum_{i=0}^{i=j-1} (K_j(i)) \tag{9d}$$

Starting with $K_0(0) = 1$, the coefficients $K_n(0)$ and $K_n(1)$ through $K_n(n)$ in equation (9) are easily obtained by applying the recursive relationships (9a—9d) until j equals n. An example of this calculation is given in Appendix I for $n = 3$. In general, $q_j \neq q_i$ for $i, j = 1, \ldots, n$ $(j \neq i)$ in order to avoid numerical instabilities (see equation 9c).

In cases of a uniform soil profile where no decomposition takes place, hence $p = q$ for all layers involved, the concentration in layer n is given by Van Hoorn (1981):

$$C_n(t) = 1 - \exp(-qt)\left(\sum_{i=0}^{i=n-1} \frac{q^i t^i}{i!}\right) \tag{10}$$

It should be remarked that the concentration of a solute in water flowing out of the soil profile is equal to the concentration of the bottom layer n itself, due to the assumption of complete mixing. This means, that C_{outf}, as defined in equation (8), is identical to $C_n(t)$ in equations (9) and (10).

The combination of equations (8) and (9) or equations (8) and (10) gives the concentration in the drainage water.

In the case of a uniform soil profile, it was possible to attach a physical value of the dispersion length to the layer thickness L, on the basis of comparing the analytical solution of the transport equation with the schematization of solute transport in a series of reservoirs in which complete mixing takes place (Goudriaan, 1973; Van Hoorn, 1981).

In the case of a non-homogeneous soil profile divided into discrete layers with different properties, it is not possible to attach a value of the dispersion length to the layer thickness explicitly. As a first approximation the same rule as in the case of homogeneous soil profiles may be applied: the layer thickness equals twice the dispersion length.

Transport of solutes in the saturated zone

The transport of solutes in the saturated zone is treated using the analogy between the breakthrough curve for the case of solute flows to canals and wells and the concentration/time dependence of the outflow from a reservoir in which complete mixing takes place (Van Ommen, 1985). When assuming a unit input concentration ($C_{\text{inf}} = 1$) to the unsaturated zone with initial zero concentration, the concentration of the drainage water leaving the unsaturated zone is:

$$C_{\text{dw}} = \frac{fN + q_{\text{out},n}\, C_n(t)}{fN + q_{\text{out},n}} \tag{11}$$

Using the above analogy, the mass balance equation becomes:

$$\epsilon H(1 + R)\,\frac{\mathrm{d}C}{\mathrm{d}t} = (fN + q_{\text{out},n})\,C_{\text{dw}}(t) - (fN + q_{\text{out},n})\,C(t) - \alpha\epsilon H\,C(t) \tag{12}$$

where ϵ is the effective porosity of the aquifer; H the thickness of the aquifer (L); R distribution ratio of the solute in the aquifer; $C(t)$ concentration of the solute in the reservoir (M L^{-3}) = concentration of solute in well or canal (M L^{-3}); α rate constant of the first-order decomposition of the solute in the aquifer (T^{-1}). Substituting equation (11) into (12) leads to:

$$\epsilon H(1+R)\,\frac{dC}{dt} = fN + q_{\text{out},n}\,C_n(t) - (fN + q_{\text{out},n})\,C(t) - \alpha\epsilon H\,C(t) \tag{13}$$

Integration of equation (13), using equation (9), yields:

$$C(t) = \left(\frac{A}{D} + \frac{B\,K_n(0)}{D}\right)(1 - \exp(-Dt)) + B\sum_{i=1}^{i=n}\left\{\frac{K_n(i)}{(D-q_i)}\,(\exp(-q_i t) - \exp(-Dt))\right\} \tag{14}$$

with constants:

$$A = \frac{fN}{\epsilon H(1+R)} \tag{14a}$$

$$B = \frac{q_{\text{out},n}}{\epsilon H(1+R)} \tag{14b}$$

$$D = \frac{fN + q_{\text{out},n}}{\epsilon H(1+R)} + \frac{\alpha}{1+R} \tag{14c}$$

The computation of breakthrough curves in the case of time-dependent input concentration can be realised by the determination of the T-time salinographs from the response of the system to an input represented by a unit step function. The output of the system is then given by the convolution integral of the T-time salinographs with the input of the system. For details, see Van Ommen (1985).

EXAMPLES

Two examples of breakthrough curves (BTC's) are given here. The first BTC describes the concentration of drainage water leaving the unsaturated zone, the second one describes the concentration of a solute in water leaving the combined system of the unsaturated and saturated zone. In both cases the unsaturated zone has been schematized in the same way. The unsaturated soil profile is assumed to consist of five layers with different properties, as given in Table 1. The time-dependent input concentration and the response of the system are given in Fig. 2; the computation was performed on an HP41CV calculator. For the reaction immediately after a change of input concentration, an extra calculation was made to obtain a more detailed response curve. The presence of a bypass leads to an im-

TABLE 1

Physical data used in the examples

Properties of the unsaturated soil profile

Parameter	Layer					
	1	2	3	4	5	
L	0.3	0.2	0.2	0.2	0.1	(m)
θ	0.15	0.20	0.20	0.25	0.30	(—)
R	1.00	0.50	0.10	0.00	0.00	(—)
α	0.50	0.30	0.00	0.00	0.00	(year^{-1})
S	0.50	0.40	0.00	0.00	0.00	(—)

Properties of the aquifer

Parameter	
H	2 m
ϵ	0.3
R	0.0
α	0.0 year^{-1}

Annual precipitation (N): 0.800 m.
Fraction of bypass (f): 0.2.

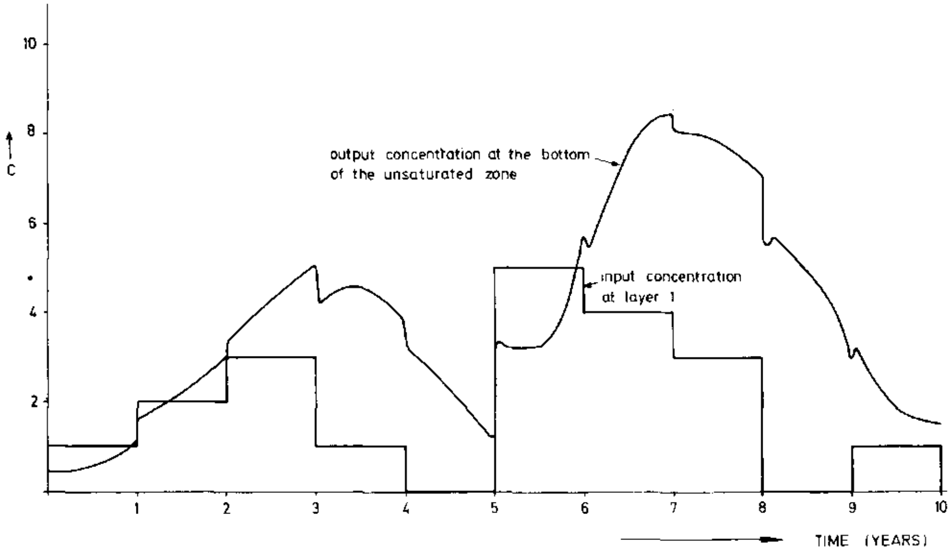

Fig. 2. Concentration in drainage water leaving the unsaturated zone, as a function of the specified input data.

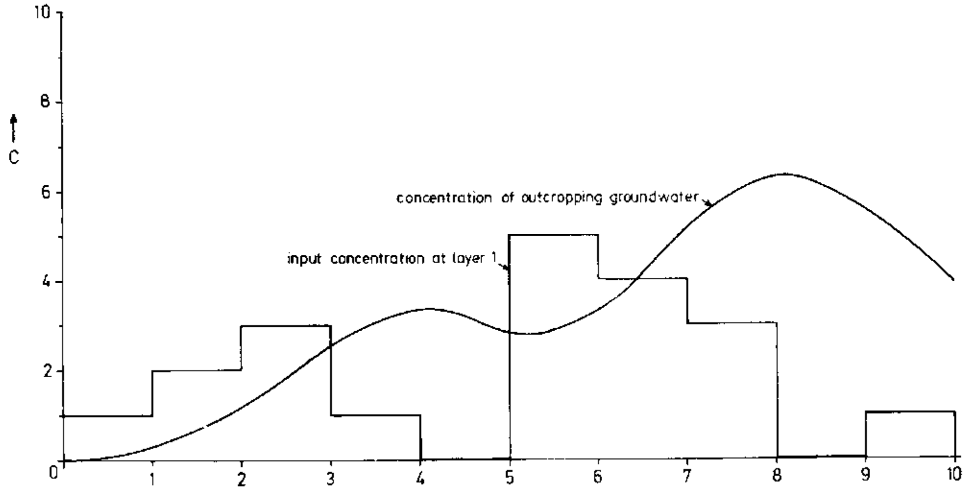

Fig. 3. Concentration in water leaving the integrated system of unsaturated-saturated zone, as a function of the specified input data.

mediate response upon changes of the input concentration, followed by a slower reaction due to the processes in the soil matrix. Extraction of water by plant roots leads to a higher concentration of the solute in the drainage water.

The breakthrough curve for the combined system has been computed using the same schematization of the unsaturated zone and the same input concentrations. The physical data of the saturated zone are listed in Table 1. The results of the calculation are given in Fig. 3. When comparing Fig. 2 with Fig. 3, it appears that the reaction of the combined system upon changes of the input concentration is less pronounced than the reaction of the unsaturated system alone. This is caused by the larger time-constant of the saturated system (Raats, 1983). Besides, the presence of a bypass flow in the unsaturated zone causes no abrupt change of the output concentration from the saturated zone.

The programs for the computation of the BTC's in the case of the unsaturated and combined system are given in Appendix II.

APPENDIX I

Calculation of the coefficients according to equations (9a—9d).

The soil profile is assumed to consist of three layers each with their own properties, resulting in values of p_1, p_2, p_3 and q_1, q_2 and q_3. Hence $n = 3$.

The derivation of the coefficients in equation (9) is as follows:

$j = 1$

$$- i = 0\colon K_1(0) = K_0(0)\frac{p_1}{q_1} = \frac{p_1}{q_1}$$

$$- i = 1\colon K_1(1) = -\frac{p_1}{q_1}$$

$j = 2$

$$- i = 0\colon K_2(0) = K_1(0)\frac{p_2}{q_2} = \frac{p_1 p_2}{q_1 q_2}$$

$$- i = 1\colon K_2(1) = K_1(1)\ \frac{p_2}{q_2 - q_1} = -\ \frac{p_1 p_2}{q_1(q_2 - q_1)}$$

$$- i = 2\colon K_2(2) = -\sum_{i=0}^{i=1} K_2(i) = \frac{p_1 p_2}{q_1(q_2 - q_1)} - \frac{p_1 p_2}{q_1 q_2}$$

$j = 3$

$$- i = 0\colon K_3(0) = \frac{p_1 p_2 p_3}{q_1 q_2 q_3}$$

$$- i = 1\colon K_3(1) = -\ \frac{p_1 p_2}{q_1(q_2 - q_1)}\ \frac{p_3}{(q_3 - q_1)} = -\ \frac{p_1 p_2 p_3}{(q_3 - q_1)(q_2 - q_1)q_1}$$

$$- i = 2\colon K_3(2) = \left(\frac{p_1 p_2}{q_1(q_2 - q_1)} - \frac{p_1 p_2}{q_1 q_2}\right)\left(\frac{p_3}{(q_3 - q_2)}\right)$$

$$- i = 3\colon K_3(3) = -\sum_{i=0}^{i=2} K_3(i) = -\frac{p_1 p_2 p_3}{q_1 q_2 q_3} + \frac{p_1 p_2 p_3}{(q_3 - q_1)(q_2 - q_1)q_1}$$

$$+\left(\frac{p_1 p_2}{q_1 q_2} - \frac{p_1 p_2}{q_1(q_2 - q_1)}\right)\left(\frac{p_3}{(q_3 - q_2)}\right)$$

APPENDIX II

Programs for HP41CV (XEQ size 100, maximum number of time steps: 19; maximum number of layers: 10)

```
 01♦LBL "WATQ2"
0  STO 32  1  STO 21
"N.LAYERS ?"  PROMPT
STO 00  1  -  STO 34
"FR.BYPASS ?"  PROMPT
STO 01  "ENDTIME ?"
PROMPT  STO 02
"DELTIME ?"  PROMPT
STO 03  "INF.RATE ?"
PROMPT  STO 04  RCL 04
RCL 01  *  STO 41
RCL 01  CHS  1  +
ST* 04

 33♦LBL 01
1  ST+ 32  RCL 32
ENTER↑  RCL 00  X<Y?
GTO 02  "DATA LAYER "
RCL 32  INT  FIX 0
ARCL X  AVIEW
"TH.LAYER ?"  PROMPT
STO 05  "MOIST.CONT.?"
PROMPT  STO 06
"DEC.FAC. ?"  PROMPT
STO 07  "DISTR.RAT. ?"
PROMPT  STO 08
"FR.EVAPTR. ?"  PROMPT
STO 09  XEQ "P"  XEQ "Q"
XEQ "COEF"  GTO 01

 66♦LBL 02
0  STO 35

 69♦LBL 03
1  ST+ 35  RCL 35
RCL 03  *  ENTER↑
RCL 02  X<Y?  GTO 12
X<>Y  STO 36  XEQ "CONC"
RCL 04  ST* 40  RCL 41
ST+ 40  RCL 41  RCL 04
+  ST/ 40  RCL 35  60  +
ENTER↑  RCL 40
STO IND Y  GTO 03

 97♦LBL 12
RCL 02  RCL 03  /
STO 00  0  STO 06

104♦LBL 11
1  ST+ 06  "CIN "
RCL 06  INT  FIX 0
ARCL X  "⊢ ?"  PROMPT
ENTER↑  40  RCL 06  +
X<>Y  STO IND Y  RCL 00
RCL 06  X<Y?  GTO 11
RCL 61  STO 81  61
STO 01  81  STO 02
```

```
130♦LBL 04
1  ST+ 01  1  ST+ 02
RCL IND 01  ENTER↑
RCL 01  1  -  RCL IND X
X<>Y  RDN  -  STO IND 02
RCL 01  60  -  ENTER↑
RCL 00  X>Y?  GTO 04  0
STO 03  TONE 9  0
STO 03

157♦LBL 09
1  ST+ 03  0  STO 04  0
STO 05

164♦LBL 10
1  ST+ 05  RCL 03
RCL 05  -  1  +  80  +
RCL IND X  ENTER↑
RCL 05  40  +  RCL IND X
X<>Y  RDN  *  ST+ 04
RCL 05  RCL 03  X>Y?
GTO 10  RCL 04  FIX 3
"C= "  ARCL X  AVIEW
STOP  RCL 03  RCL 00
X>Y?  GTO 09  STOP

199♦LBL "P"
RCL 08  1  +  RCL 06  *
RCL 05  *  1/X  RCL 04
*  STO 10  RTN

212♦LBL "Q"
RCL 32  10  +  STO 33
RCL 08  1  +  RCL 06  *
RCL 05  *  1/X  RCL 09
CHS  1  +  RCL 04  *
STO 04  *  RCL 08  1  +
1/X  RCL 07  *  +
STO IND 33  RTN
```

```
242♦LBL "COEF"
RCL 21  RCL 10  *
RCL IND 33  /  STO 21  0
STO 37

251♦LBL 05
1  ST+ 37  RCL 37
ENTER↑  RCL 32  1  -
X<Y?  GTO 06  RCL 37  21
+  STO 05  RCL 37  10  +
STO 06  RCL IND 05
RCL 10  *  RCL IND 33
ENTER↑  RCL IND 06  -  /
STO IND 05  GTO 05

279♦LBL 06
0  STO 38  0  STO 39

284♦LBL 07
RCL 38  21  +  RCL IND X
ST+ 39  1  ST+ 38
RCL 38  ENTER↑  RCL 32
1  -  X<>Y  X<=Y?
GTO 07  -1  ST* 39
RCL 32  ENTER↑  21  +
ENTER↑  RCL 39
STO IND Y  RTN

310♦LBL "CONC"
RCL 21  STO 40  0
STO 07

315♦LBL 08
1  ST+ 07  10  ENTER↑
RCL 07  +  RCL IND X
CHS  RCL 36  *  E↑X
ENTER↑  21  RCL 07  +
RCL IND X  X<>Y  RDN  *
ST+ 40  RCL 07  ENTER↑
RCL 00  X>Y?  GTO 08
RTN  END
```

```
 01♦LBL "WATQ3"
0  STO 32  1  STO 21
"N.LAYERS ?"  PROMPT
STO 00  1  -  STO 34
"FR.BYPASS ?"  PROMPT
STO 01  "ENDTIME ?"
PROMPT  STO 02
"DELTIME ?"  PROMPT
STO 03  "INF.RATE ?"
PROMPT  STO 04  RCL 04
RCL 01  *  STO 41
RCL 01  CHS  1  +
ST* 04

 33♦LBL 01
1  ST+ 32  RCL 32
ENTER↑  RCL 00  X<Y?
GTO 02  "DATA LAYER "
RCL 32  INT  FIX 0
ARCL X  AVIEW
"TH.LAYER ?"  PROMPT
STO 05  "MOIST.CONT.?"
PROMPT  STO 06
"DEC.FAC. ?"  PROMPT
STO 07  "DISTR.RAT. ?"
PROMPT  STO 08
"FR.EVAPTR. ?"  PROMPT
STO 09  XEQ a  XEQ b
XEQ c  GTO 01

 66♦LBL 02
"DATA AQUIFER"  AVIEW
PSE  "THICKNESS ?"
PROMPT  STO 42
"EFF. POR. ?"  PROMPT
STO 43  "DEC.FAC. AQ. ?"
PROMPT  STO 44
"DISTR.RAT.AQ.?"  PROMPT
STO 45  RCL 43  RCL 42
*  RCL 45  1  +  *
STO 46  RCL 41  RCL 46
/  STO 47  RCL 04
RCL 46  /  STO 48
RCL 47  RCL 48  +
ENTER↑  RCL 44  RCL 45
1  +  /  +  STO 49
RCL 47  RCL 49  /
STO 50  RCL 48  RCL 49
/  STO 51  0  STO 35

119♦LBL 03
1  ST+ 35  RCL 35
RCL 03  *  ENTER↑
RCL 02  X<Y?  GTO 12
X<>Y  STO 36  XEQ d
RCL 35  60  +  ENTER↑
RCL 40  STO IND Y
GTO 03

139♦LBL 12
RCL 02  RCL 03  /
STO 00  0  STO 06
```

```
146♦LBL 11
1  ST+ 06  "CIN "
RCL 06  INT  FIX 0
ARCL X  "⊦ ?"  PROMPT
ENTER↑  40  RCL 06  +
X<>Y  STO IND Y  RCL 00
RCL 06  X<Y?  GTO 11
RCL 61  STO 81  61
STO 01  81  STO 02

172♦LBL 04
1  ST+ 01  1  ST+ 02
RCL IND 01  ENTER↑
RCL 01  1  -  RCL IND X
X<>Y  RDN  -  STO IND 02
RCL 01  60  -  ENTER↑
RCL 00  X>Y?  GTO 04  0
STO 03  TONE 9  0
STO 03

199♦LBL 09
1  ST+ 03  0  STO 04  0
STO 05

206♦LBL 10
1  ST+ 05  RCL 03
RCL 05  -  1  +  80  +
RCL IND X  ENTER↑
RCL 05  40  +  RCL IND X
X<>Y  RDN  *  ST+ 04
RCL 05  RCL 03  X>Y?
GTO 10  RCL 04  FIX 3
"C= "  ARCL X  AVIEW
STOP  RCL 03  RCL 00
X>Y?  GTO 09  STOP

241♦LBL a
RCL 08  1  +  RCL 06  *
RCL 05  *  1/X  RCL 04
*  STO 10  RTN

254♦LBL b
RCL 32  10  +  STO 33
RCL 08  1  +  RCL 06  *
RCL 05  *  1/X  RCL 09
CHS  1  +  RCL 04  *
STO 04  *  RCL 08  1  +
1/X  RCL 07  *  +
STO IND 33  RTN

284♦LBL c
RCL 21  RCL 10  *
RCL IND 33  /  STO 21  0
STO 37
```

```
293♦LBL 05
1  ST+ 37  RCL 37
ENTER↑  RCL 32  1  -
X<Y?  GTO 06  RCL 37  21
+  STO 05  RCL 37  10  +
STO 06  RCL IND 05
RCL 10  *  RCL IND 33
ENTER↑  RCL IND 06  -  /
STO IND 05  GTO 05

321♦LBL 06
0  STO 38  0  STO 39

326♦LBL 07
RCL 38  21  +  RCL IND X
ST+ 39  1  ST+ 38
RCL 38  ENTER↑  RCL 32
1  -  X<>Y  X<=Y?
GTO 07  -1  ST* 39
RCL 32  ENTER↑  21  +
ENTER↑  RCL 39
STO IND Y  RTN

352♦LBL d
RCL 21  RCL 51  *
RCL 50  +  STO 40
RCL 36  CHS  RCL 49  *
E↑X  CHS  1  +  ST* 40
0  STO 07

370♦LBL 08
1  ST+ 07  10  ENTER↑
RCL 07  +  RCL IND X
CHS  RCL 36  *  E↑X
STO 52  RCL 36  ENTER↑
RCL 49  CHS  *  E↑X
ST- 52  21  RCL 07  +
RCL IND X  ST* 52
RCL 48  ST* 52  10
ENTER↑  RCL 07  +
RCL IND X  CHS  RCL 49
+  1/X  ST* 52  RCL 52
ST+ 40  RCL 07  ENTER↑
RCL 00  X>Y?  GTO 08
RTN  END
```

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6. EXPERIMENTAL AND THEORETICAL ANALYSIS OF SOLUTE TRANSPORT FROM A DIFFUSE SOURCE OF POLLUTION

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EXPERIMENTAL AND THEORETICAL ANALYSIS OF SOLUTE TRANSPORT FROM A DIFFUSE SOURCE OF POLLUTION

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ABSTRACT

Transport processes governing soil and groundwater contamination by a diffuse (non-point) source were studied by means of a field tracer experiment in the Hupselse Beek catchment area in The Netherlands. A bromide tracer was applied to the intake area (11 m x 260 m) of a drain, and subsequently monitored in the unsaturated zone, as well as in the drain effluent. Data from the unsaturated zone were analyzed using both the classical convection-dispersion solute transport equation (CDE) and a regional stochastic model (RSM) which assumes lognormal distributions of the pore water velocity and the dispersion coefficient across the field. Both models described the data equally well, with the CDE model giving a somewhat better mass balance of the recovered bromide. Calculated solute fluxes leaving the unsaturated were used as input into a mixing cell type model for transport in the saturated zone. Drain effluent concentrations predicted with the coupled unsaturated-saturated transport model were compared with the observed breakthrough curve; results indicate the presence of preferential flow in the unsaturated zone.

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INTRODUCTION

Public awareness and concerns about the leaching of nutrients and pesticides from agricultural lands has never been higher than it is today. This is not surprising as more and more evidence showed that diffuse (non-point) sources of pollution play a major role in the degradation of the quality of our soil and groundwater systems (Bruyn, 1984; van der Veen, 1986; Funk, 1987).

Groundwater pollution stemming from diffuse agricultural sources typically involves first transport through the unsaturated zone, followed by transport in the underlying saturated groundwater system. The time scale for transport in the saturated zone is usually much larger than that for transport in the unsaturated zone, thus further contributing to the time-consuming and costly nature of field tracer experiments involving coupled unsaturated-saturated systems. Because of these considerations, field experimental studies of the migration of solutes from diffuse sources are best carried out in shallow aquifers with relatively short residence times. An aquifer of this type is located in the Hupselse Beek catchment area of the Netherlands. Soils in the region consist of an approximately 2 m thick surface layer of thin fluviatile and aeolian deposits, underlain by a thick Miocene clay layer of low permeability.

In this paper we present the results of a field transport experiment in the above Hupselse Beek groundwater basin using bromide as a tracer. The experiments were carried out in a 1 ha field with recently installed subsurface drains. A diffuse source of pollution was simulated by uniformly applying a small pulse of KBr solution to a strip of land, 260 m long and having a width twice the drain spacing (11 m). Main objective of the experiment was to study and evaluate field-scale solute transport processes operative in the unsaturated zone, and in a coupled unsaturated-saturated soil/groundwater system. Transport in the unsaturated zone will be analyzed by means of the classical convection-dispersion solute transport equation, and a regional stochastic model accounting for field-scale heterogeneity in the transport process. Transport in the saturated zone is described using a recently developed mixing cell type model (van Ommen, 1986).

THEORETICAL

Transport in the unsaturated zone

Numerous theoretical studies of solute transport in the vadose zone have been carried out over the last several decades. Initially, solute transport was often simulated by applying the classical Fickian-type convection-dispersion equation to field conditions. The CDE equation for nonreactive transport is given by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - V \frac{\partial c}{\partial x} \qquad [1]$$

where t is time (T), x is soil depth (L), c is the solution concentration (ML^{-3}), D is the dispersion coefficient (L^2T^{-1}), and V is the average pore water velocity (LT^{-1}).

The CDE has been shown to describe solute transport under laboratory conditions quite satisfactorily (Danckwerts, 1953; Nielsen and Biggar, 1962; Lindstrom et al., 1967). Its extension to field conditions affects primarily the value of the dispersion coefficient, which presumably relates to the scale of the heterogeneities present in the flow field (Anderson, 1979; Dagan, 1986). This flow field is often considered to be at steady-state with respect to water flow, and homogeneous with respect to water content. This was shown to be justified by experimental and theoretical studies by Cassel et al. (1975) and Wierenga (1977). The assumption of steady state water flow associated with an average water content for the soil gave similar solute distributions as those obtained by modeling solute transport during transient water flow.

The dispersion coefficient D in Eq. (1) is often expressed mathematically by

$$D = D_0 + \alpha V \qquad (L^2T^{-1}) \qquad [2]$$

where D_0 is the porous medium ionic or molecular diffusion coefficient (L^2T^{-1}), and α is the dispersivity (L). The applicability of this expression to transport in unsaturated soils has often been questioned (e.g., Beese and Wierenga, 1983). Still there is reasonably strong evidence that Eq. [2] holds if the scalar dispersivity is equal to a few centimeters

(Sposito et al., 1986). In most cases the effect of D_0 on the value of the dispersion coefficient is negligible as compared to the effect of the dispersivity term in Eq. [2] (e.g., Biggar and Nielsen, 1976; Schulin et al., 1987a). In practice, D is often used as an empirical parameter representing the effects of all solute spreading mechanisms, such as transient water flow, or various physical and chemical nonequilibrium conditions (Nielsen et al., 1986). In our case we will assume that the dispersion coefficient is linearly related to the local pore water velocity, i.e.,

$$D = \alpha V \qquad [3]$$

There is now increasing evidence that solute transport in field soils cannot be adequately described by the CDE (Biggar and Nielsen, 1976; van de Pol et al., 1977; Bowman and Rice, 1986; Richter and Jury, 1986). This appears specially true during surface ponding, when local variations in the pore water velocity can become so large that the dispersion process can no longer be described with a physically realistic value of the dispersivity. Dagan and Bresler (1979) introduced a method to determine variations in the pore water velocity in terms of the statistical distribution of the hydraulic conductivity. From these variations in the velocity, first- and second-order spatial and temporal moments of the concentration distribution can be derived. An application of this theory was given by Bresler and Dagan (1979) for constant input concentration. These authors compared solute profiles based on spatially variable data with solute profiles computed with the classical CDE. For both cases they derived expressions for the length of the transition zone, defined as the difference between the depths at which the concentration equalled 0.1 and 0.9 of the input. In case of the CDE, this zone expands as the square root of time, whereas in the Bresler-Dagan model the length of this zone increases linearly with time. The profile calculated with the proposed model could also be obtained with the CDE, provided the dispersivity used for predicting the concentration at 1 m depth ranged from 16.1 cm for low recharge cases to 334.0 cm for high recharge rates. From this the authors concluded that pore-scale dispersion is not significant for transport in heterogeneous fields.

Two years later Bresler and Dagan (1981) incorporated pore-scale dispersion into their earlier model. This had very little effect on the calculated solute distributions, as already had been foreseen in the 1979 paper. Finally, Bresler and Dagan (1983b) developed expressions for the first- and second-order moments of the concentration distribution as a function of depth and time, using a simplified solution (Dagan and Bresler, 1983; Bresler and Dagan, 1983a) of the non-steady water flow equation. The transient water flow description gave approximately the same results as the steady-state approach.

Jury (1982) introduced the concept of the transfer function model as a means of describing solute transport in heterogeneous fields. In this approach, a soil system is characterized uniquely by the way in which it transforms an input function into an output function, and assuming a log-normal distribution of travel times and no local dispersion. Jury et al. (1986) later gave a more general derivation of transfer function models for transport of solutes in soils. Solutes in the model may be conservative, or may undergo physico-chemical or biological transformations in a soil with spatially or temporally variable flow properties. The authors conclude that any mechanistic solute transport model which maintains mass balance can be made consistent with the transfer function concept.

A slightly different approach was followed by Amoozegar-Fard et al. (1982) who used Monte-Carlo simulation techniques to obtain various solute concentration distributions as affected by variabilities in the pore water velocity and the dispersion coefficient. This approach assumes that the field can be represented by a large number of independent noninteracting soil columns in which vertical transport is described by the CDE. Each column has its own pore water velocity V, which is considered to be lognormally distributed among the individual columns. The lognormal distribution, $\rho(V)$, with mean μ and standard deviation σ is given by:

$$\rho(V) = \frac{1}{V\sigma\sqrt{(2\pi)}} \exp\left\{\frac{-(\ln(V)-\mu)^2}{2\sigma^2}\right\} \qquad [4]$$

The first moment of this distribution is the field average (global) velocity, <V> given by

$$\langle V\rangle = \exp\,(\mu + \sigma^2/2) \qquad [5]$$

The probability density function of the dispersion coefficient D is considered to be completely defined in terms of $\rho(V)$ and deterministic α.

The spreading of a solute pulse in a 'field-averaged' soil profile can thus be attributed to two mechanisms: (1) local dispersion in the columns themselves, and (2) differences in the pore-water velocities among the columns.

Results of the Monte-Carlo simulations by Amoozegar-Fard et al. show that the variability of V has a dominant effect on the field-averaged solute profile. In the limiting case of zero dispersivity, the approach is analogous to the transfer function model of Jury (1982).

In our study we will consider two methods of describing solute transport in the unsaturated soil profile: the classical CDE, and the method introduced by Amoozegar-Fard et al. (1982) commonly referred to as regional-stochastic model (RSM) (Parker and van Genuchten, 1984a; Schulin et al., 1987b). To partially account for the transient flow regime in the system, we will use the amount of drainage water, rather than time, as independent variable. This approach is somewhat similar to the linearization method used by Parker and van Genuchten (1984a).

Transport in the saturated zone

Once the bromide tracer leaves the unsaturated zone to reach the ground water table, transport occurs in the saturated zone along flow lines in the direction of the drains. Transport in this part of the system is simulated by considering the saturated zone to be a perfectly mixed reservoir. Previous examples of such an analogy are given by Eldor and Dagan (1972), Ernst (1973), Gelhar and Wilson (1974), Raats (1983) and van Ommen (1986), among others. The approach assumes that 1) groundwater flow is at steady-state in which case the drain discharge from the system becomes equal to the recharge rate multiplied with the total recharge area, 2) the thickness of the aquifer and its porosity are constant and 3) groundwater flow is horizontal, thus making the Dupuit-Forchheimer assumptions valid. The concentration in the drainage water for a unit step input of a diffuse pollution source is then given by

$$C(t) = 1 - e^{-Nt/(\epsilon H)} \qquad [6]$$

where C is the concentration of the drainage water, t is the time, N is the steady groundwater recharge rate (LT^{-1}) and ϵ (L^3L^{-3}) is the porosity of the aquifer of thickness H (L). As before, the total amount of outflow, Nt, can be used as a substitute variable for time if the flow regime is transient.

Whereas flow in the direct vicinity of the drain is essentially radial, the effect of this on the solute breakthrough curve is only of importance for values of $H/L > 0.1$, where L is the drain distance (Ernst, 1973). Groenendijk (1986) showed that the concentration of the drainage water can be corrected for radial flow within a distance H from the drain by using a modified travel time distribution as first derived by Ernst (1973). Groenendijk's analysis leads to

$$c(t) = 1 - A \qquad [7]$$

where:

$$A = 1 - 2\sqrt{(2Nt)/(\pi\epsilon L)} \qquad \text{for } t \leq (\pi\epsilon H^2)/(2NL)$$

and:

$$A = (1 - 2H/L)\exp(-(Nt)/(\epsilon H) + (\pi H)/(2L))$$

$$\text{for } t > (\pi\epsilon H^2)/(2NL)$$

Although H/L is generally smaller than 0.1 in our study, we still included the above correction for radial flow near the drain into our solution.

Drain water concentrations as a function of the cumulative amount of drainage is now calculated by the convolution integral of the impulse response of the saturated transport system with the solute loading rate leaving the unsaturated zone. We refer to the study of van Ommen (1985) for a more detailed description of this technique.

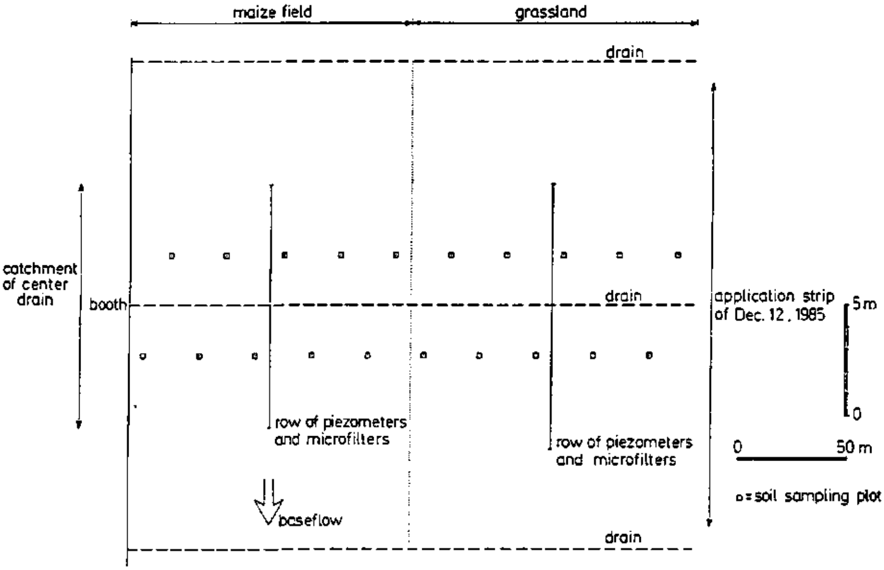

Figure 1a Schematic plane view of the experimental field. The small squares indicate the sampling spots.

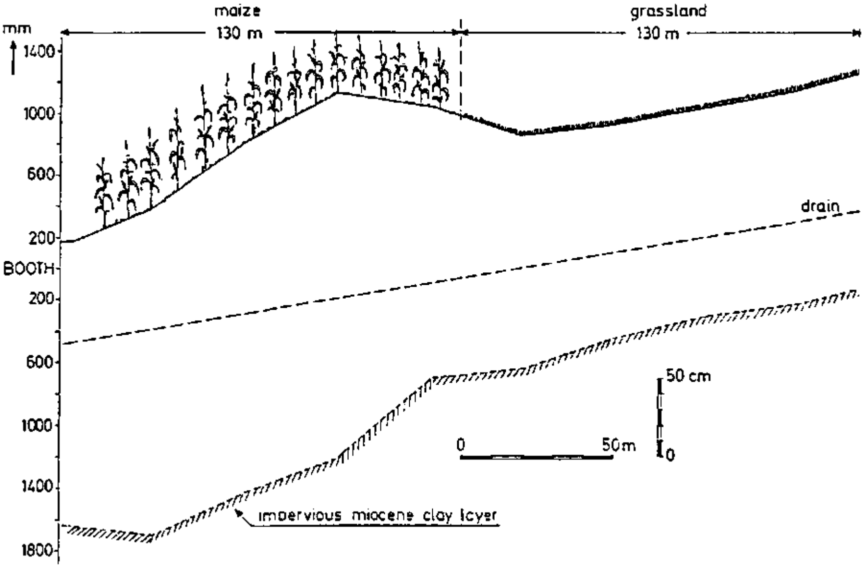

Figure 1b Vertical cross-section of the experimental field.

MATERIALS AND METHODS

Geographical setting

The experimental field was located in the Hupsel catchment area in the Eastern part of the Netherlands. The field met the requirements with respect to the thickness of the saturated zone (see Introduction). Drains were first installed in the area in 1982. Soil type is a loamy sand Haplaquod (Wösten et al., 1985) with a top soil having a finer texture than the deeper soil layers (Dekker, 1986). Beneath these layers at a depth ranging from 1.5 to 2.5 m, a 20 to 30 m thick impervious clay layer of Miocene age was found. This clay layer forms a natural boundary for the unconfined groundwater flow system (Studygroup Hupselse Beek, 1974). One half of the drained field was under permanent grass and the remainder under corn during the growing season.

Tracking the drains

The bromide tracer was applied to the catchment area of one drain after this area had been determined in the field. Drains in the field were located by using the 'TRACKA' system (manufacturer HORMANN) which consisted of a radio wave emitter attached to a special jethead normally used for cleaning drainage tubes. At places where the emitted signals were most clearly received, a marker was put in the soil. Having tracked a whole drainage tube in this way, a cord was stretched along the markers. Three drains were jetted and tracked in this way: the drain to be sampled and the two adjacent ones. The average drain distance between the center drain and its two neighbors was taken to be half the distance between the outer drains. This resulted in an average drain spacing of about 10.85 m. Because the drains were approximately 260 m long, the catchment area comprised about 2850 m^2. The markers of the outer drains also served as boundaries for the tracer application. After application of the tracer the center drain was dug up at several places to determine its depth in the field. Figure 1a gives a schematic plane view of the experimental field; a vertical cross-section is shown in Fig. 1b.

Application of the tracer

The tracer used in our study was the negatively charged bromide ion, often recommended as a soil water tracer (Jury et al. 1982; Bowman, 1984). Application took place on December 12, 1985 in the form of a 4.5 mm KBr solution (2.55 g L^{-1}) using a sprinkler irrigation system (Fig. 2) with a high application uniformity (the coefficient of variation was less than 2% when not driving, Institute for Soil Fertility, 1985).

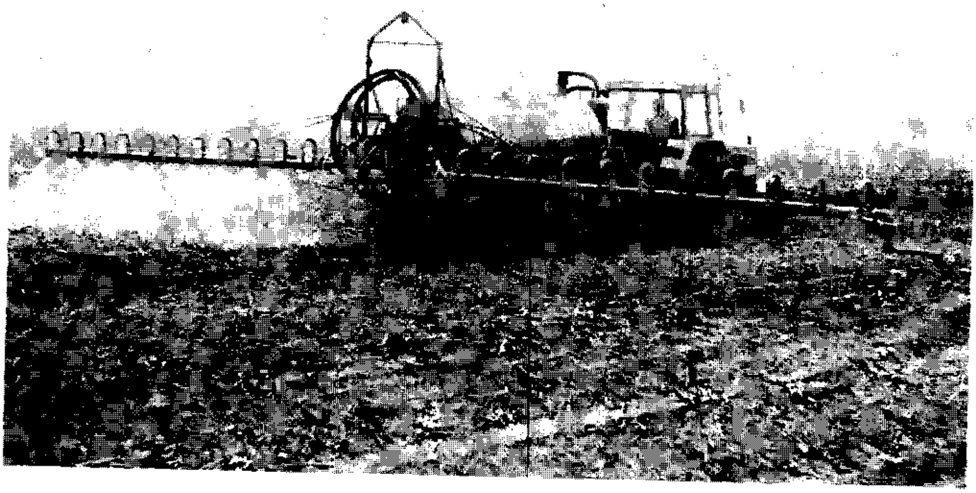

Figure 2 Application of the tracer solution.

Two strips of 5 m width each on both sides of the drain were sprayed four times, resulting in a total application rate of 60 kg Br^- to a surface area of 20 m x 260 m. Thus, we treated an area nearly twice as large as the catchment area of the center drain. This was done to account for possible irregularities in the water divide between the drains. No ponding or surface runoff was observed during the application.

Soil sampling

To quantify solute transport processes in the unsaturated zone, soil samples after 69.5, 167.0, 225.0 and 304.5 mm of drain discharge were collected. At each sampling time, the soil was sampled at 20 plots regularly distributed along the drain: 10 plots in the corn field and an equal number in the grassland. Each plot was located in the center of the first 'application strip' next to the central drain. The first plot was located in the corn field at the right-hand-side of the central drain, the second plot at the left-hand-side, etc. (Fig. 1a). Sampling within a plot consisted of taking soil samples every 5 cm with a 6 cm diameter auger up to a depth of 70 cm. Deeper sampling would sometimes lead to samples of the saturated zone (see Fig. 1b). Distances within each sampling plot never exceeded 30 cm. This procedure thus resulted in 20 x 14 = 280 soil samples at each sampling time. Analysis of these samples in the laboratory involved the preparation of 1:2 soil-water extracts, followed by bromide concentration determination.

Piezometers and sampling of the saturated zone

Rows of piezometers were installed perpendicular to the drain in the middle of the corn and grass fields (Fig. 1a). Bromide concentrations of the ground water at these same locations were monitored by means of microfilters (3/4" inner diameter and 10-cm length) which had been installed at different depths in the saturated zone. Groundwater samples were withdrawn after 109.5, 193.5, 278.0 and 353.0 mm of drain discharge. Piezometer readings were taken at irregular intervals.

Drain discharge measurements and sampling

Drain water was collected using a tank which was partially sunken into the bottom of the ditch at the drain outlet. Water was pumped automatically from this tank in increments of 0.089 m^3 whenever the water level reached a floating contact. Once every 16th time of pumping, an automatic water sampler (Manning S4400) received a signal to operate. In this way (16 x

0.089 m^3/2850 m^2 soil surface area) a water sample was taken after every 0.5 mm of drain discharge. Samples were thus collected on a discharge-proportional basis. The entire system was controlled with a Hewlett Packard 75B programmable calculator. The equipment was installed in a booth with an electrical heating system to protect it against severe colds during the winter season.

Bromide analysis

Soil water extracts, drainage water samples and groundwater samples were analyzed for bromide using a high performance ion-chromatographic method with UV-detection at a wavelength of 193 nm (Neele, 1987).

Bromide uptake by plants

In order to account for possible bromide uptake during the winter season, grass samples were taken at the end of March, 1986. Grass was sampled at 6 plots, each randomly located in the application strip. The corn field remained uncultivated until the end of May, 1986.

RESULTS AND DISCUSSION

Local water balance

During the summer and early autumn preceding the experiment, the drain did not discharge and the ditches were dry. The bromide tracer was applied a few weeks after the drain started to flow. Precipitation data were obtained from the meteorological station 'Assink', located some 900 m from the experimental field (Warmerdam, 1981). Figures 3 and 4 show the precipitation and the cumulative amounts of precipitation and drain discharge from day 1 (December 12, 1985) to day 191 (June 20, 1986) at the end of the percolation period when drainflow again ceased. The very dry period from day 47 to day 84 corresponded with a long period of frost (February 1986 was the dryest month of February on record in The Netherlands). The differences between cumulative amounts of discharge and precipitation increased during the experiment because of increased evapotranspiration in the spring.

The experiment was continued until the summer of 1987. At the beginning of the experiment we assumed that drain discharge would result exclusively from water infiltrating the application strip between the water divides at each side of the center drain. Unfortunately, piezometer readings in the corn field later indicated that a regional baseflow was superimposed upon the local flows between the drains, at least during part of the experimental period (Fig. 1a). A simple hydrological calculation showed that this baseflow had a flux of at most a few cm per day, at least in the corn field. No head gradient was observed perpendicular to the drain in the grass area. Because the tracer was applied to a strip that extended 5 m beyond the water divide between the drains, horizontal inflow of bromide by water from the catchment of the central drain would only be guaranteed for some 250 days. Therefore, only results for the first percolation season ending in June, 1986, will be considered here. Drain water samples in autumn 1986 showed bromide concentrations of 1.4 mg L^{-1} for the upstream drain, 14.0 mg L^{-1} for the centre drain, and 11.8 mg L^{-1} for the downstream drain, thus confirming the presence of the baseflow. Note that the average of the upstream and downstream drainage water concentrations is about half the concentration in the center drain, as would have been expected.

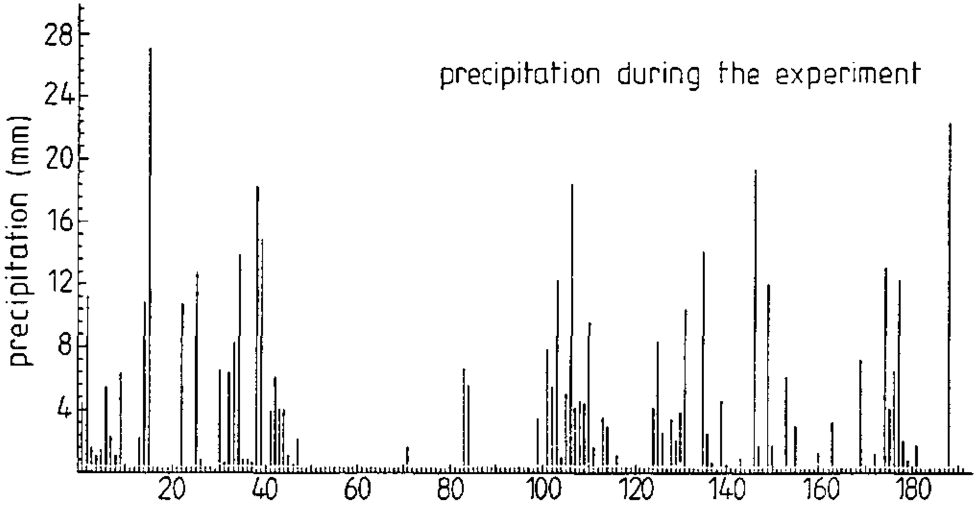

Figure 3 Precipitation during the experiment.

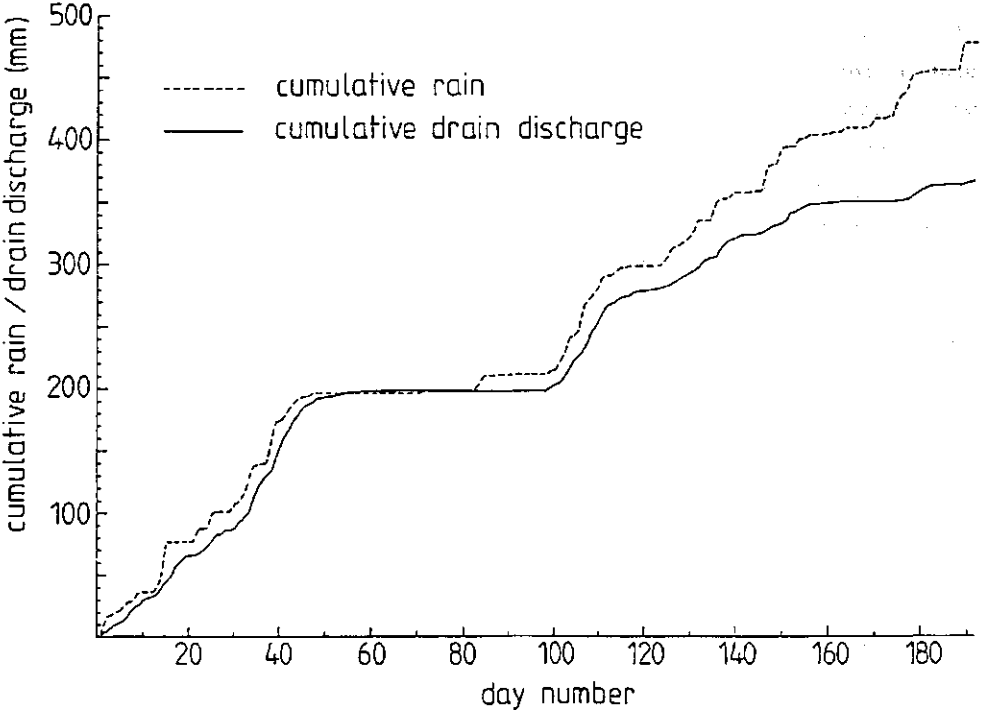

Figure 4 Cumulative precipitation and drain discharge during the experiment.

Soil samples and unsaturated transport

Soil bromide concentrations were grouped according to land use: grass or corn. They will be treated separately, even though about half of the concentration distributions from the grass field were statistically not significantly different from those of the corn land, as predicated by the Kolmogorov-Smirnov statistic (based on the maximum difference between two empirical cumulative distribution functions), and the Wilcoxon test (based on the rank of the data in both groups). Because the grass and corn fields were treated separately, the number of soil sample replications at each time and depth was ten. Distributions of the concentrations were tested for normality and log-normality by the tests of Kolmogorov-Smirnov, Cramer-Von Mises (Rao et al., 1979) and Shapiro-Wilk (Shapiro and Wilk, 1965). No clear distinction could be made from these analyses: sometimes the distributions were better described by a normal probability density function (PDF), sometimes by a log-normal PDF, and sometimes neither of the two could adequately describe the concentration data. Hence, spatially-averaged (global) bromide concentrations at given depths and times were determined by simply taking arithmetic mean of the concentrations. Confidence intervals (90%) were calculated using the bootstrapping procedures (Dane et al., 1986) which do not require a-priori assumptions regarding the probability distribution. The number of bootstrap replications was chosen at 5000. Concentration profiles for the four sampling times are presented in Figures 5 (corn) and 6 (grass), together with the optimized curves for the CDE and RSM transport models.

The nonlinear least-squares optimization program developed by Parker and van Genuchten (1984a) was used for the analysis of the field data. This program (called 'CXTFIT', version 1985) can be used to estimate the unknown parameters in several one-dimensional solute transport models from spatial distributions of the resident concentration (Parker and van Genuchten, 1984b). In our study where the flow rate varied greatly in time, the controlling independent variable was taken to be the amount of drain discharge, expressed in mm. By doing so, the pore water velocity MV is given with respect to the flux density of the drain discharge. Thus, a computed velocity MV of, say, 4.0 means that the pore water velocity is four times larger than the water flux density. Its reciprocal ($MV^{-1}=0.25$), corresponds then with the mobile water content of the system.

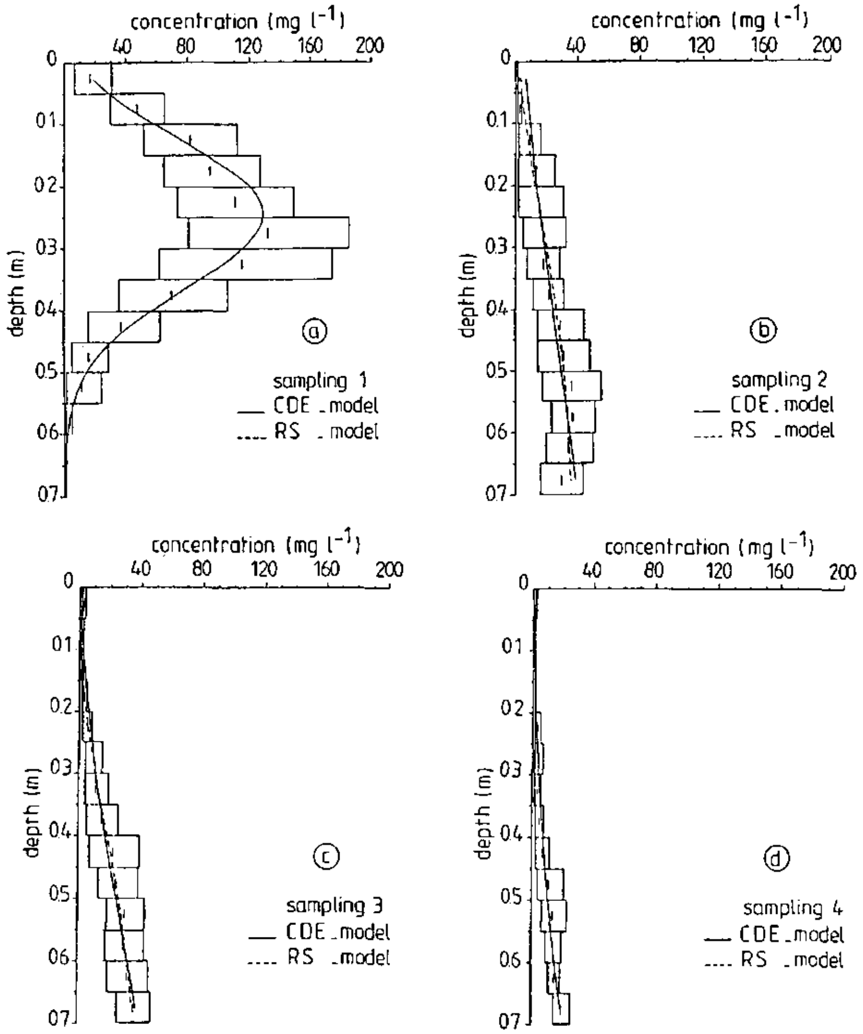

Figure 5a-d Concentration profiles in the corn field at different sampling times.

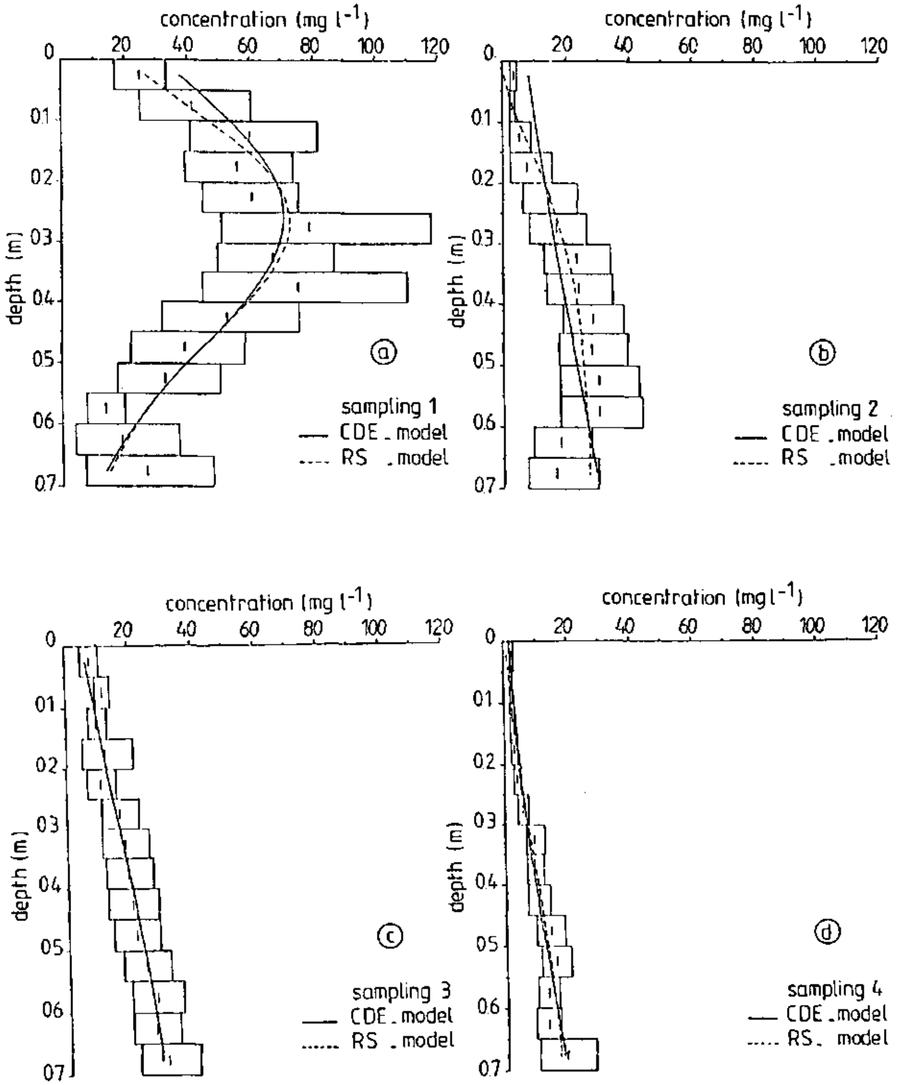

Figure 6a-d Concentration profiles in grassfield at the different sampling times.

CDE-results

Parameter estimation results for the convection-dispersion equation (CDE) are given in Table 1. The sampling number refers to the accumulated drain discharge when the soil was sampled (i.e., sampling 1 corresponds with a discharge of 69.5 mm, 2 with 167.0 mm, 3 with 225.0 mm and 4 with 304.5 mm). Because the application of the tracer solution was uniform, the applied tracer pulse length t_0 was 4.5 mm. This value was not corrected for bromide uptake by grass as only an estimated 3% of the amount of bromide applied was recovered from the grass.

Sampling	Number of observations	MV (-)	α (mm)	mass balance
		Land use: corn		
1	14	3.27	37.	0.981
2	14	5.40	196.	0.988
3	14	3.77	95.	0.992
4	14	3.68	95.	1.00
1-4	56	3.19	62.	0.911
1,3,4	42	3.33	42.	0.957
2,3,4	42	4.31	178.	0.953
		Land use: permanent grass		
1	14	3.04	145.	0.966
2	14	7.16	322.	0.984
3	14	3.28	211.	1.01
4	14	3.78	173.	0.997
1-4	56	3.03	198.	0.931
1,3,4	42	3.09	154.	0.951
2,3,4	42	4.15	353.	0.934

Table 1 Parameter estimation results for the convection dispersion equation (CDE).

Initially, we optimized the pore water velocity MV and the dispersion coefficient D, of the CDE model. The mass balance was verified by carrying out a second optimization with unknown t_0 but with MV and D fixed at their values from the first run. The optimized t_0-value was divided by the known t_0-value to yield the recovered fractions of the tracer as viewed by the CDE model. These mass balance ratios are also indicated in Table 1. Values range between 0.911 and 1.00 times the amount applied. Optimizations were carried out for all four samplings, and for various combinations of these as shown in Table 1. Optimizations were also performed using data from all plots separately, instead of using areally-averaged values. Results for the individual plots were generally very similar to the global estimates except for substantially lower correlation coefficients between the fitted and observed concentrations because of fewer sampling replicates and the inclusion of spatial variability.

Because the relative pore water velocity in this study is the inverse of the volumetric water content, one should be able to estimate the average mobile volumetric water contents of the corn and grass plots from the optimized parameter values for MV in Table 1. Results compare well with the measured gravimetric water content distributions for the grass and corn fields shown in Fig. 7 and 8, respectively. These globally averaged distributions, with their 90% confidence intervals, were based on measured gravimetric water contents at the four sampling times. Dry soil bulk densities derived from open pit measurements ranged from 1.3 g cm^{-3} for the topsoil to about 1.7 for the deeper layers. At a few locations we found some thin peat layers with dry bulk densities of about 0.9 g cm^{-3}. Unfortunately we were unable to measure the volumetric moisture content and the tracer concentration on the same soil sample. Confidence intervals of the water contents in Figs 8 and 9 were based on the normal distribution of the gravimetric water content. Validity of this assumption was verified with the same three statistical tests used previously. The inverses of the MV-values in Table 1 correspond well with the measured water content profiles provided the bulk density factor of 1.3 to 1.7 is taken into account. An exception to this is the second sampling when the optimization procedure resulted in an unreasonably high pore water velocity. Note that pore water velocities for the corn field seem to be somewhat higher than those for the grass because of lower water contents.

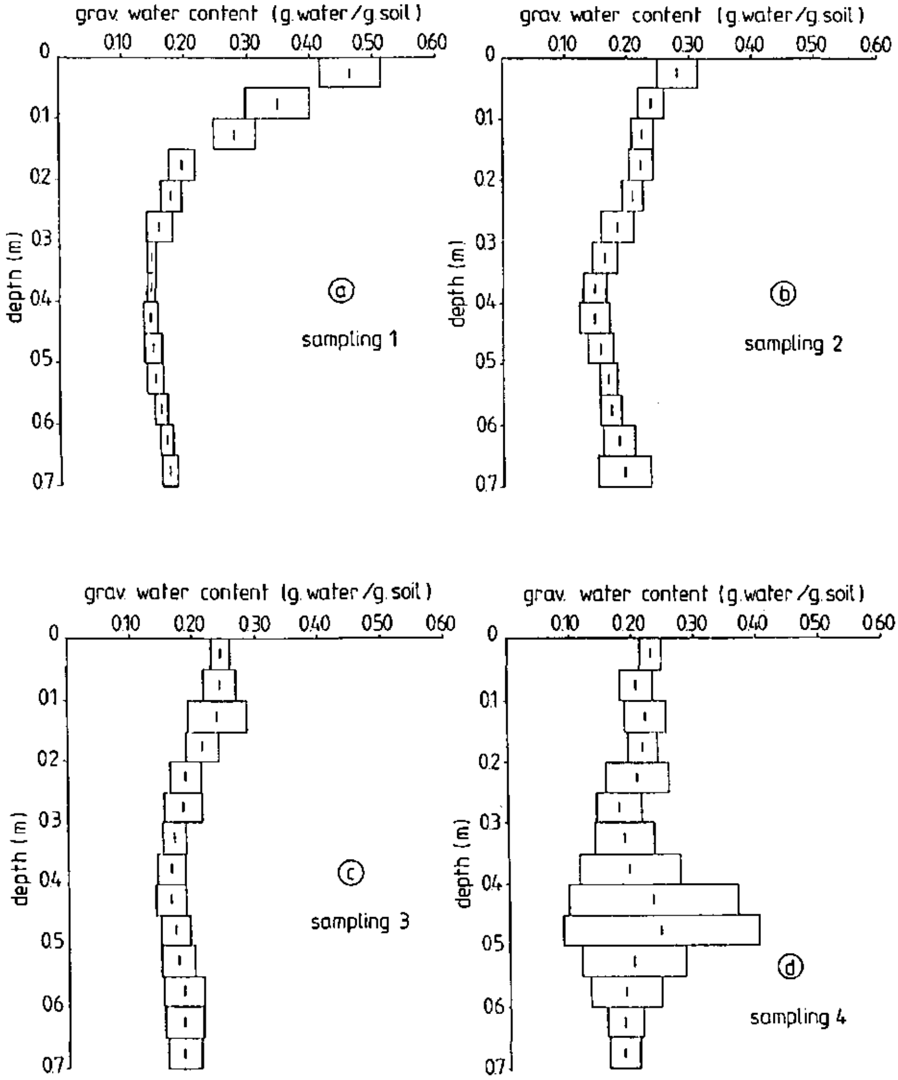

Figure 7a-d Gravimetric moisture content profiles in the corn field at different sampling times (90% confidence intervals are all indicated).

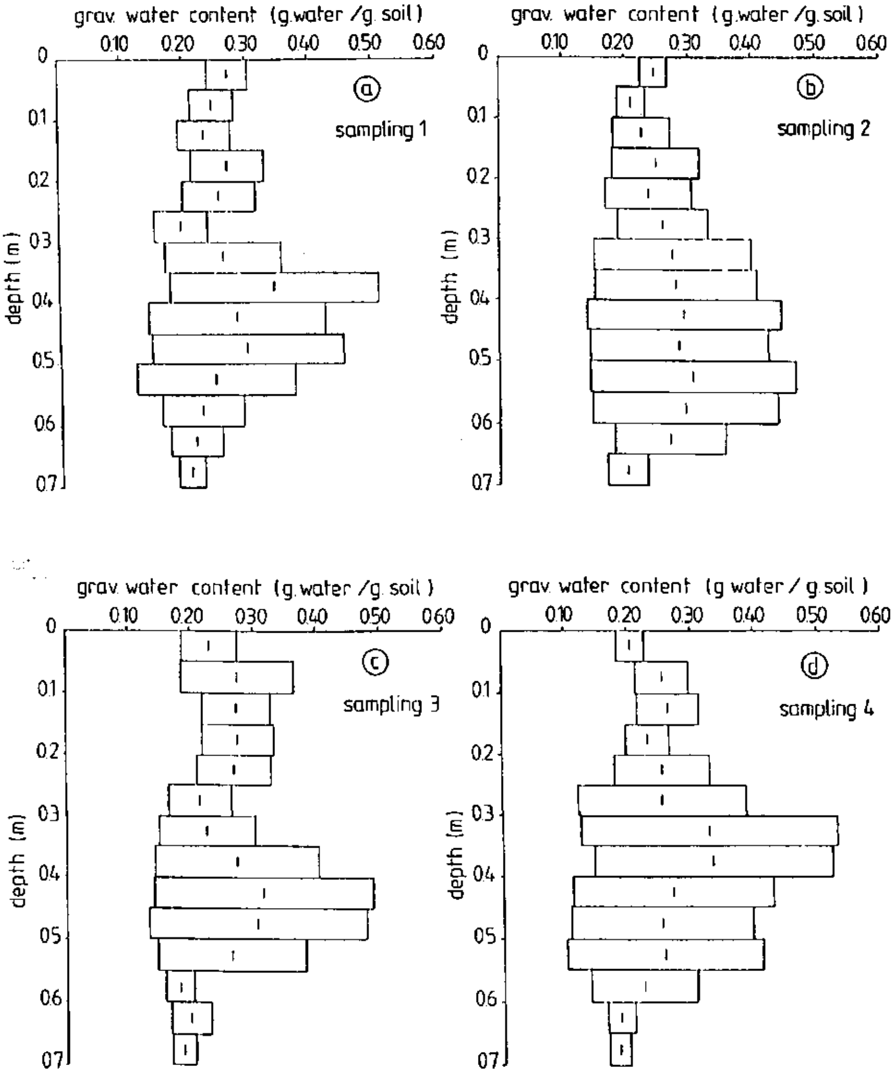

Figure 8a-d Gravimetric moisture content profiles in grassfield at the different sampling times.

The dispersivities α show an analogous behavior: for corn they are in reasonable agreement with values reported in the literature, except for the second sampling when a relatively large value resulted. The dispersivities for the grassfield were always larger than those for the corn field with the second sampling again showing a much larger value. The larger values of α for grass may be attributed to more prominent preferential flow paths in the soil because of continuous plant root activity in the winter, which in turn could have resulted in a larger variation of pore flow velocities.

Taking all four samplings together, ('1-4' in Table 1) yields values for MV which are in good agreement with the measured water content profiles, both for the corn field and the grassland. Note, however, that the first sampling has a disproportionally large influence on the results. This is because sampling 1 has by far the largest contribution to the sum of squares than the other samplings with much lower concentrations.

The parameter optimizations above could or also have been executed with all three transport parameters as unknown (i.e., MV, D and the amount of applied solute t_0). This would have given a more direct check on the mass balance. Such a procedure is only successful if the solute concentration profiles exhibit clear maxima. Otherwise, a non-unique set of transport parameters (notably for t_0) can describe the concentration profile. For example during the optimizations MV and t_0 will be positively correlated in case of increasing concentrations with depth, and negatively correlated for decreasing concentrations. Hence, the 3-parameter optimization can only be applied to the first sampling time when a distinct maximum is present. Results for this case are given in Table 2; they show relatively good mass recoveries. Velocities and dispersivities agree quite well with those found earlier, especially for the corn field.

Convection dispersion equation

MV (-)	α (mm)	t_0 (mm)	mass balance
		Land use: corn	
3.31	36.	4.398	0.977
		Land use: permanent grassland	
3.41	101.	3.812	0.847

Regional stochastic model

Land use: grassland

<MV> (-)	α (mm)	$\sigma_{\ln(MV)}$	mass balance
3.61	92.	0.210	0.812

Table 2 Mass balance results as based on data from the first sampling time.

RSM-results

Parameter estimation results for the regional stochastic model (RSM) are presented in Table 3. Optimizations in this case were carried out for three transport parameters $\mu_{\ln(MV)}$, $\sigma_{\ln(MV)}$ and α, instead of two as was done for the CDE model. A mass balance check was also made, similarly as for the CDE. Some results have been omitted since $\sigma_{\ln(MV)}$ at times converged towards zero during the optimization procedure, thus giving the same values of the transport parameters as the CDE optimization. Most values of the average pore water velocity <MV> are somewhat higher than those calculated with the convection dispersion approach. The velocities calculated for the second sampling are again remarkably higher than the others. The mass balance checks generally showed a substantial decrease in the sum of squares when the amount of applied bromide (t_0) was also optimized. This amount was always less than the actually applied amount (4.5 mm x 2.55 g L^{-1} = 11.48 g $Br^- \ m^{-2}$), thus resulting in mass balances of less than 100%.

Sampling number	Number of observations	<MV> (-)	α (mm)	$\sigma_{\ln(MV)}$	mass balance
Land use: corn					
1	14	----	---	-----	----
2	14	8.26	64.	0.651	0.65
3	14	4.71	33.	0.457	0.801
4	14	----	---	-----	----
1-4	56	4.19	15.	0.411	0.748
1,3,4	42	3.53	33.	0.186	0.917
2,3,4	42	6.42	46.	0.607	0.665
Land use: grassland					
1	14	3.85	85.	0.303	0.779
2	14	20.03	0.2	1.010	0.352
3	14	----	---	-----	----
4	14	5.97	70.	0.647	0.628
1-4	56	4.71	61.	0.521	0.651
1,3,4	42	3.70	103.	0.300	0.825
2,3,4	42	8.85	33.	0.840	0.463

Table 3 Parameter estimation results for the regional stochastic model.

A direct check on the mass balance was only carried out for the first sampling for the grass, again resulting in the relatively low recovery of 81.2% (Table 2). No explanation for this low recovery could be found.

Statistical properties of the transport parameters

The transport parameters were also determined for every vertical concentration profile separately, using a two-parameter fit for MV and D for the CDE (Table 4). The resulting distributions of velocities and dispersivities of the CDE optimization process were again tested for normality and log-normality by the Kolmogorov-Smirnov, Cramer-Von Mises and Shapiro-Wilk tests. In some cases we could not discriminate between these distributions as often neither the normal, the lognormal, or both, were found to be acceptable. This is indicated with a question mark in Table 4.

Land use: corn

Sampling	Number of observations	Distribution of MV	Distribution of D
1	10	normal	log-normal
2	10	log-normal	?
3	10	log-normal	log-normal
4	10	?	log-normal
1-4	40	?	?

Sampling	Number of observations	Correlation between MV-D	Correlation between ln(MV)-ln(D)
1	10	-0.194	0.045
2	10	0.993	0.844
3	10	0.933	0.900
4	10	0.997	0.969
1-4	40	0.915	0.861

Sampling	Number of observations	$\langle MV \rangle$ (-)	$\sigma_{\ln(MV)}$
1	10	3.04	0.358
2	10	7.55	0.906
3	10	4.51	0.506
4	10	8.67	1.096
1-4	40	5.49	0.778

Land use: permanent grass

Sampling	Number of observations	Distribution of MV	Distribution of D
1	10	?	log-normal
2	10	log-normal	log-normal
3	10	log-normal	log-normal
4	10	?	log-normal
1-4	40	?	log-normal

Sampling	Number of observations	Correlation between MV-D	Correlation between ln(MV)-ln(D)
1	10	0.111	0.490
2	10	0.806	0.957
3	10	0.921	0.720
4	10	0.925	0.865
1-4	40	0.831	0.024

Sampling	Number of observations	$\langle MV \rangle$ (-)	$\sigma_{\ln(MV)}$
1	10	3.06	0.467
2	10	14.89	1.202
3	10	4.38	0.614
4	10	5.16	0.560
1-4	40	5.90	0.819

Table 4 Statistical properties of the fitted transport parameters.

The table also shows correlations between MV and D, and between ln(MV) and ln(D). The values for <MV> assume a log-normal distribution of MV as based on Eq. [5]. Correlations are often close to one, with some exceptions.
Linear relations between V and D assuming zero intercepts are presented in Table 5. If the intercept was not set equal to zero, the regression line would have crossed the D-axis often at values below the origin, which is physically not correct. Table 5 showes that very high values of the dispersivity will occur when the power of the velocity in Eq. [5] is set equal to one, as is often assumed in the literature.

<u>Land use: corn</u>

Sampling	Number of observations	$D = \alpha\,MV$	$D = \alpha\,(MV)^n$
1	10	$D = 46.9\,MV$	$D = 70.1\,MV^{0.14}$
2	10	$D = 758\,MV$	$D = 10.2\,MV^{1.94}$
3	10	$D = 309\,MV$	$D = 3.37\,MV^{2.90}$
4	10	$D = 3770\,MV$	$D = 7.46\,MV^{2.49}$
1-4	40	$D = 2870\,MV$	$D = 8.36\,MV^{2.23}$

<u>Land use: permanent grassland</u>

1	10	$D = 182\,MV$	$D = 82\,MV^{1.23}$
2	10	$D = 1520\,MV$	$D = 18.9\,MV^{2.15}$
3	10	$D = 452\,MV$	$D = 22.3\,MV^{2.10}$
4	10	$D = 527\,MV$	$D = 16.1\,MV^{2.66}$
1-4	40	$D = 1380\,MV$	$D = 523\,MV^{0.06}$

Table 5 Relations between the fitted dispersion coefficient and the local relative pore water velocity.

The calculated values for <MV> and $\sigma_{\ln(MV)}$ (Table 4) at samplings 2 and 3 (corn) and 2 and 4 (grass) corresponded rather well with the values as determined from the field-averaged profiles (Table 3) and the RSM parameter estimation process. Note that in the latter case, the effect of dispersion has been omitted, so that the results are not quite comparable. However, if we assume that the effect of dispersion is negligible with respect to the variability in the velocity as characterized by $\sigma_{\ln(MV)}$, then the comparison is justified.

We concluded that both the convection-dispersion equation and the regional-stochastic model describe the field data reasonably well. Because of the surprisingly large local variations across a seemingly quite homogeneous and small area, a definite preference for one of the two models cannot be established from the available data. On the other hand, the CDE, performs somewhat better than the RSM in terms of the mass balance accuracy. Therefore, in the following we will only use the CDE description of the processes in the unsaturated zone.

Samples of the saturated zone

When the field tracer experiment was first initiated we planned to construct two-dimensional contour maps of the measured groundwater bromide concentrations perpendicular to the drain, and to hopefully use the plots for discerning information about the transport of bromide along streamlines towards the drains. Unfortunately, ground water samples withdrawn from the microfilters installed at different depths in the aquifer yielded such an erratic concentration pattern that any attempt to analyze them in terms of the above objective was judged to be useless. We were also unable to clearly deduce the presence of a base flow in the saturated zone from the measured solute concentrations, especially under the corn field. Still, as expected, concentrations at greater depths tended to increase somewhat with time during the experiment. The large variability of the measured ground water concentrations may be attributed to a large variability in the permeability of the aquifer at the scale of the sampling program, a feature which was recently described by Sudicky (1986), and/or to irregular bromide solute fluxes across the catchment from the unsaturated zone into the ground water system.

Drainage water sampling and coupled breakthrough curves

Figure 10 shows the measured concentration distribution of the drain water. The plot reflects the behavior of the coupled unsaturated-saturated transport system upon an instantaneous input of bromide across the catchment are. Careful analysis of this showed that about 53% of the total amount of applied bromide was recovered during the first 6 months of the experiemnt.

Having determined the parameters of the two transport models for solute transport in the unsaturated zone, and assuming that transport in the saturated zone obeys Eq. [7], it should be possible to predict the bromide concentration of the drainage water as a function of the drain discharge.

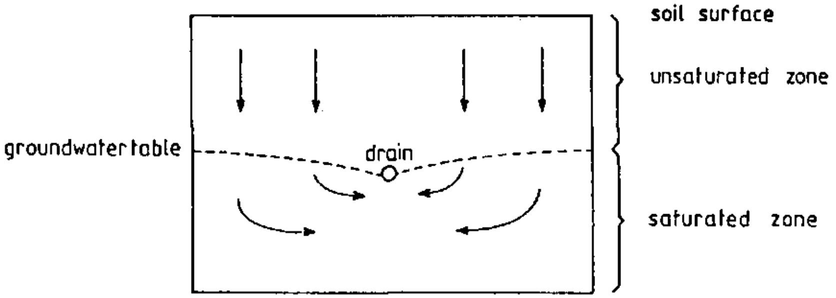

Figure 9 Vertical cross-section of the coupled transport system.

The calculation procedure is schematically shown in Fig. 9 which gives a vertical cross section of the coupled unsaturated-saturated transport system perpendicular to the drain. The input concentration as a function of the amount (mm) of drain discharge for the saturated transport system is obtained by calculating the breakthrough curve from the unsaturated zone at the groundwater table. In this case, flux concentrations as defined by Parker and van Genuchten (1984b) were used, and not the resident concentrations employed in the parameter estimation process of the unsaturated transport models. The concentration of the drainage water was obtained by numerically evaluating the convolution integral of the time-dependent input concentration with the proposed impulse response for the saturated transport system. Because the thicknesses of the unsaturated and saturated zones were not constant along the drain, the concentration of the drain water was calculated as the average solute concentration of 20 equally-spaced locations, each having its own coupled transport system. The breakthrough curve for a certain location along the drain then depends on land use, the thickness of the unsaturated zone, the thickness of the saturated zone, and its water content. The thickness of the unsaturated zone at a given location could be equated to the drain depth, except that piezometric observations during winter indicated that the unsaturated zone was about 10 to 20 cm less. This correction increased the thickness of the saturated zone as well.

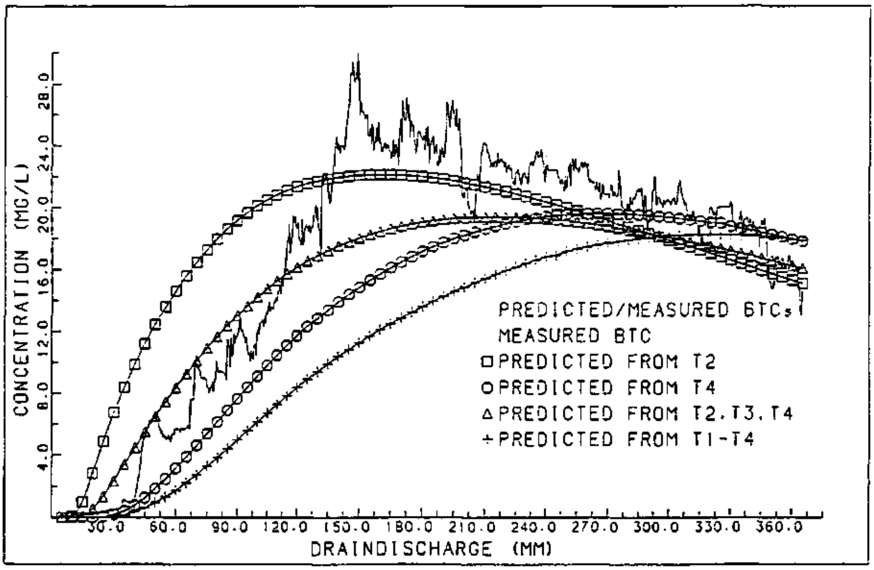

Figure 10 Measured and predicted drain effluent BTC's using the fitted unsaturated solute transport parameters.

The liquid-filled porosity of the aquifer was determined from soil samples taken from the deepest layers (about 110 cm below the soil surface) exposed in 10 profile pits; From measured dry bulk densities, the mean porosity was estimated to be 0.33; this value will be used in all subsequent calculations.

Figure 10 compares the measured breakthrough curve (BTC) with 4 predicted curves which were chosen such that the full range of transport velocities as determined by CXTFIT was considered, including the highest velocities for sampling 2, and the lowest velocity resulting from the simultaneous fit of all four sampling times. The simultaneous fit considerably underestimated the drain water concentrations, especially at early times, even though the MV-values were in good agreement with the measured soil water contents, while at the same time the dispersivity α agreed well with literature values. The predicted BTC based on the combined fit of samplings 2, 3 and 4 shows a slightly better fit although the breakthrough still starts too early, and the concentrations are still too low after about 120 mm of drain discharge. The fastest BTC obtained for sampling 2 considerably overestimates the drain water concentrations up to about 130 mm of discharge, after which value the concentrations are being somewhat underestimated.

From Fig. 10 we conclude that solute transport in this soil system cannot be described adequately by assuming one average water flow velocity for the entire unsaturated zone. We believe that preferential flow may have caused some of the observed discrepancies.

Although solute transport in the topsoil was described quite well with the CDE, we speculate that at a certain depth water flow could have become instable, causing water to flow downwards along preferential flow paths (Glass et al., 1987). This type of preferential flow would result in an accelerated transport through the subsoil. Thus, 'slow' transport in the topsoil may have been followed by relatively 'fast' transport in the subsoil, thus resulting in a BTC that fits the measured data better.

Given the above considerations, we tried to predict the drain effluent curve by assuming a layered soil profile consisting of a uniform topsoil characterized by relatively slow bromide transport, and a more heterogeneous subsoil with relatively fast transport caused by some type of shortcircuiting. Transport in this layered system was calculated with a numerical finite element solution (van Genuchten, 1986) of the steady-state transport equation for layered profiles. For transport in the topsoil we used the fitted parameter values as listed in Table 1 for sampling 1. However, transport velocities for the subsoil were calculated from the fitted MV-value of the second sampling. Since MV for this second sampling also included the residence time of the tracer in the topsoil, its value was corrected accordingly to yield a relative pore water velocity MV of 7.21 for the subsoil of the corn field, and 11.6 for the grass field. Dispersivities were assumed to be the same as for the first sampling time.

The BTC obtained in this way is shown in Figure 11. The curve was found to be rather insensitive to changes of +/- 5 cm in the thickness of the topsoil; hence only the BTC for a topsoil of 25 cm is presented.

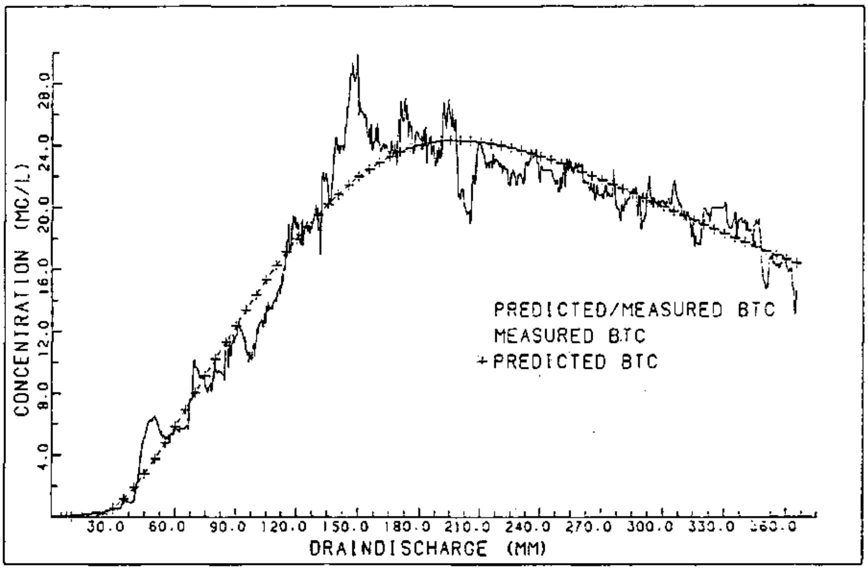

Figure 11 Measured and the predicted drain effluent BTC using a numerical model for a layered soil system.

Close examination of this figure shows that the peak concentration after about 150 mm discharge is still somewhat underestimated but in general the measured BTC is predicted surprisingly well. Thus we conclude that the assumption of accelerated transport in the subsoil is justified. It still remains an open question, whether the transport parameters from the second, third and fourth samplings have a physical basis, or should be considered as a set of parameters describing a fast breakthrough only.

Additional evidence of accelerated (preferential) transport in the subsoil can be found in the literature, especially in cases where a fine-textured layer overlies a coarse-textured horizon. Starr et al. (1978, 1986) found similar results for field measurements, while Glass et al. (1987) showed this fingering phenomenon to be present during elaborate laboratory experiments. The occurrence of preferential flow in our study is indirectly supported by

1) the presence of a textural change from a low permeable topsoil to a more permeable subsoil at approximately 25 cm depth (see Materials and Methods), which may cause unstable wetting fronts (Raats, 1973), and thus contribute to preferential flow even during wet conditions (Glass et al., 1987),
2) the presence of water repellent layers throughout the profile. As shown by Hendrickx et al. (1987), these layers can also trigger the formation of preferential flow paths.

Experimental evidence of the presence of preferred flow zones in this field was further presented by van Ommen et al. (1988), who were able to visualize these zones by means of a iodide-starch color technique described in van Ommen et al. (1987).

SUMMARY AND CONCLUSIONS

Transport of a non-reactive tracer (bromide) was studied in an unsaturated-saturated transport system. Two models were used to describe unsaturated transport: the convection-dispersion equation (CDE) and a regional stochastic model (RSM). Both transport model could describe the observed data reasonably well, although the CDE model performed slightly better in predicting the amount of recovered bromide.

Solute migration velocities and dispersivities for transport in the topsoil generally agreed well with measured water contents and dispersivity values found in the literature. In the subsoil, however, transport velocities were not in agreement with observed water contents, especially for the grassfield. The accelerated breakthrough of the subsoil was probably caused by preferential flow ("shortcircuiting") originating at the transition between topsoil and subsoil.

Using measured tracer concentration distributions for the unsaturated zone, the drain water quality could be predicted accurately only when the effects of fast transport in the subsoil was accounted for in the unsaturated-saturated transport system.

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7. A NEW TECHNIQUE FOR EVALUATING THE PRESENCE OF PREFERENTIAL FLOW PATHS IN NON-STRUCTURED SOILS

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A NEW TECHNIQUE FOR EVALUATING THE PRESENCE OF PREFERENTIAL FLOW PATHS IN NON-STRUCTURED SOILS[1]

H.C. van Ommen, L.W. Dekker, R. Dijksma, J. Hulshof and W.H. van der Molen[2]

ABSTRACT

A new technique for determining the presence of preferential flow paths in a non-structured soil profile is described. The presented method is easily applicable in the field, and is based on the formation of an intensely colered complex of I_2 with starch. Moreover, the method can be applied to all kinds of non-structured soils, irrespective of their color. An illustration of the technique is given in case of water and solute movement in a water-repellent soil, where formation of preferential flow paths was known to occur.

Additional Index Words: water-repellent soils, unstable wetting fronts, iodine-starch complex

INTRODUCTION

Many studies concerning solute movement through the unsaturated soil profile have shown that the leaching mechanism depends upon the variability of water fluxes in the field. (e.g. Van de Pol et al., 1977; Nielsen et al., 1986; White et al., 1986). In structured soils, such as clay and peat soils, cracks and macropores may contribute an important part to this variability. Techniques to visualize these macropores and cracks, and their capacity of transporting water and solutes have been introduced by Bouma and Dekker (1978), Bouma et al. (1978) and Bouma et al. (1979). These often involve the application of an amount of dye solution to the soil surface. The presence of the dye, which adsorbes at the walls of the cracks and macropores, can be studied, for example, by micromorphological techniques.

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[2] Hydrologist, Soil Scientist, Research Assistants and Professor of Agrohydrology respectively.

In non-structured soils, the phenomenon of flow through preferential paths is not linked with the presence of cracks or macropores; its occurrence can be induced by several mechanisms. The mechanism of formation of unstable wetting fronts, possibly generated by an increase of the hydraulic conductivity with depth (Raats, 1973), causes the development of preferential paths through the soil matrix. Another mechanism concerns the formation of preferential paths in a soil profile with water-repellent characteristics, as has been described by Bond (1964). An important difference between water and solute flow in structured and non-structured soils, is the depth at which a preferential flow path develops: in structured soils it originates principally from the soil surface; in non-structured soils, the development of a preferential flow path may take place at any depth, depending upon soil horizons and water repellent characteristics. For this very reason, the use of dyes - most of which have a strong tendency to be absorbed by the soil matrix - is limited to those that are not adsorbed by the soil matrix and have the same migration velocity as water. In addition, the color of the dye has to be in contrast to the soil matrix. The objective of this study was to develop a method to investigate the occurrence of preferential flow paths in non-structured soils.

METHODS AND MATERIALS

The presence of an applied tracer in the soil is visualized by a color reaction. The tracer is the I^- ion, having about the same transport properties as the often used soil water tracers, Cl^- and Br^-. However, Bowman (1984) found that a considerable amount of the applied I^- can be oxidized under aerobic field conditions, resulting in a mass recovery <100%. As the color reaction is very sensible to the presence of I^-, even a fraction of the applied I^- concentration (5 to 15 g L^{-1}) is visualized.

After application of the I^- solution to the soil under investigation, horizontal cross-sections of the soil profile are obtained by removing slices of the soil. At each depth, the excavated soil surface is carefully powdered with very dry starch until the soil surface is only just visible.

Five to ten minutes later the film of starch will be wetted by the soil solution, and shows a milky colored surface. This surface is treated with a mist of bleaching-liquor. At places where I^- is present, it is oxidized to I_2 by Cl_2:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad [1]$$

The generated I_2 immediately forms an intensely colored dark blue complex with the starch, and the prefential paths of solute flow are visualized. In this way, a whole soil profile can be excavated in order to obtain a series of two dimensional pictures of the phenomenon.

Particular care must be taken concerning the applications of starch and the bleaching-liquor mist. A starch film which is relatively thick will not be wetted entirely by the soil solution. As a consequence, the reaction between Cl_2 and I^- to form the dark blue starch complex is prevented: I^- is present at the 'bottom' of the film, while Cl_2 is sprayed on its top. Having applied a starch film of the correct thickness, a large dose of the bleaching-liquor - for example by use of a spray - can leach the very thin starch film so that the color disappears quickly. Careful application of both the starch and the bleaching-liquor mist is therefore essential for the success of this method.

EXPERIMENTS AND RESULTS

To illustrate the described methodology, an experiment was carried out on a soil profile having water-repellent characteristics. The soil was located near Ouddorp (The Netherlands), and has been subject to a study of the existence of preferential flow paths.
The I^- solution (15 g L^{-1}) was uniformly sprayed on a soil surface covered with grass (area 0.8 m x 0.9 m) in three portions of 14 mm each. The time interval between these applications was about 2 hours. Ponding did not occur; although the soil surface was flat a distinct wetter location developed within the treated surface. Later, this location appeared to correspond with the occurrence of numerous preferential flow paths. Half an

hour after the final application, the soil profile was horizontally excavated and the described method was applied. The application of starch (normal potato-starch) took place with three sieves of 150 μm placed on top of each other. By placing the starch in the top sieve, and gently shaking, a fine dust of starch was formed. The bleaching-liquor was applied by means of a plant sprayer with a special nozzle to obtain a fine mist of liquid.

Figure 1 shows the visualized preferential pathways at about a 15-cm depth. Three zones can be distinguished:

1) a dry zone, appeared where the starch is still dry (the upper right part of the picture)
2) a wet zone, shown by milky grey colored starch film (the lower left part of the picture)
3) in this wet zone, a dark blue colored zone appeared, indicating a preferential path.

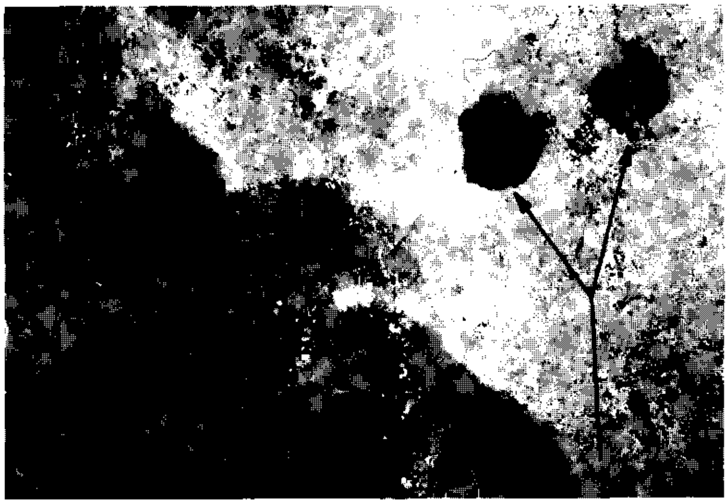

Figure 1 Visualized pathways of preferential flow paths in a non-structured soil using the I_2-starch color reaction.

Isolated preferential wet-flow paths can be found in the dry zone as well, as indicated by the arrow. After removing the starch layer, the color of the soil under it is essentially unaltered.

The discussed color reactions thus are clearly the result of the physical processes playing a role in this particular soil. The method is promising due to its simplicity and applicability, and can be used in non-structured soils, irrespective of their color or chemical properties.

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8. EXPERIMENTAL ASSESSMENT OF PREFERENTIAL FLOW PATHS IN A FIELD SOIL

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EXPERIMENTAL ASSESSMENT OF PREFERENTIAL FLOW PATHS IN A FIELD SOIL

H.C. van Ommen[1], R. Dijksma[1], J.M.H. Hendrickx[2], L.W. Dekker[2], J. Hulshof[1], and M. van den Heuvel[1]

ABSTRACT

Preferential flow paths in the subsoil can cause an accelerated movement of solutes in unsaturated-saturated transport systems. To visualize these zones of preferred flow, an iodide-coloring technique was applied to 10 plots in a field. Results indicate the existence of a non-uniform solute front in the subsoil. However, this non-uniformity could be adequately accounted for by using the convection-dispersion equation for describing the relative amount of colored area in the system. Pore water velocities agreed well with measured volumetric water contents, while dispersivities were roughly of the same order of magnitude as those reported in the literature for field-scale experiments. Results did not agree with the accelerated movement found in a previous unsaturated-saturated flow experiment on the same field. The study indicates that the antecedent moisture regime and rainfall intensity have an important effect on the formation of preferential flow paths in a subsoil, thus showing the dynamic nature of this physical phenomenon.

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INTRODUCTION

To study the transport mechanisms in a coupled unsaturated-saturated system, a non-reactive tracer was applied to a catchment area of a drain (see van Ommen et al., (1988a) for an extensive report on this experiment). An analysis of observed bromide concentration data in the unsaturated zone showed that transport in the topsoil could be described well with the convection-dispersion equation using values of the transport parameters that seemed physically correct. Once the pulse of solute moved into the subsoil, however, the migration velocities appeared to increase significantly. These observations were in poor agreement with observed water content profiles, and therefore suggested that part of the soil water may not have been active in the transport process towards the groundwater table.

Observed tracer concentrations in the drain water at this site showed an accelerated breakthrough of the tracer from the system if all soil water was assumed to be mobile. The prediction of the drainage water concentration as a function of the amount of drain discharge was only successful if the soil was divided into two zones: a 25 cm topsoil with relatively slow transport, and a subsoil, with relatively high solute migration velocities.

The topsoil was a loamy sand, while the material of the subsoil had a coarser texture. This stratification indicates an increase of the hydraulic conductivity at the interface between topsoil and subsoil. This situation has been shown to favor the development of preferential flow paths (Raats, 1973).

The objective of this paper is to examine to what extent these preferential flow paths can be visualized by using a recently developed iodide-coloring technique (van Ommen et al., 1988b). Results from a color tracer experiment will be analyzed in terms of the classical convection-dispersion solute transport equation, and compared with data from the bromide tracer experiment.

METHODS AND MATERIALS

The catchment area of the drain consisted of one half permanent grassland, and one half corn field, which was still bare at the time of the experiment. Details of the bromide tracer experiment are given by van Ommen et al (1988a). On April 13 and 14, 1987, ten irrigations of 10 mm each of an iodide solution (7.5 g $I^{-}l^{-1}$) were applied to 5 plots in the bare corn field of the catchment area. The tracer was applied to each 1 m^2 plot using a high pressure sprinkling apparatus. Ponding and surface runoff were not observed during the application. After the irrigations, the plots were covered to prevent evapotranspiration and the infiltration of rain. Two days later, the plots were excavated, and the iodide distribution in the topsoil and subsoil were visualized with the coloring technique, described by van Ommen et al. (1988b). This technique was previously used successfully in the field by Hendrickx et al. (1988). Basically this technique consists of oxydizing the iodide-ions with a chlorine containing solution, and tracing the iodine liberated with starch powder. Blue streaks and stains then indicate the places where iodide has been present. Some soil core samples (230 cm^3 rings) were taken during the excavation to determine the volumetric water content.

Six weeks later, the same procedure was applied to the grassland. This time, a more intensive soil sampling program was carried out for the purpose of comparing moisture contents within and outside the preferred flow zones. At every depth three pairs (as dictated by the size of the flow paths) of soil core samples (100 cm^3 rings) were taken. Such a pair consisted of a sample taken within the preferred flow zone and another one directly adjacent to the previous in the region where no iodide was made visible by the color reaction.

It should be remarked, that the corn field and the grassland applications followed relatively wet periods, when the drains were discharging.

RESULTS AND DISCUSSION

Visualized solute fronts

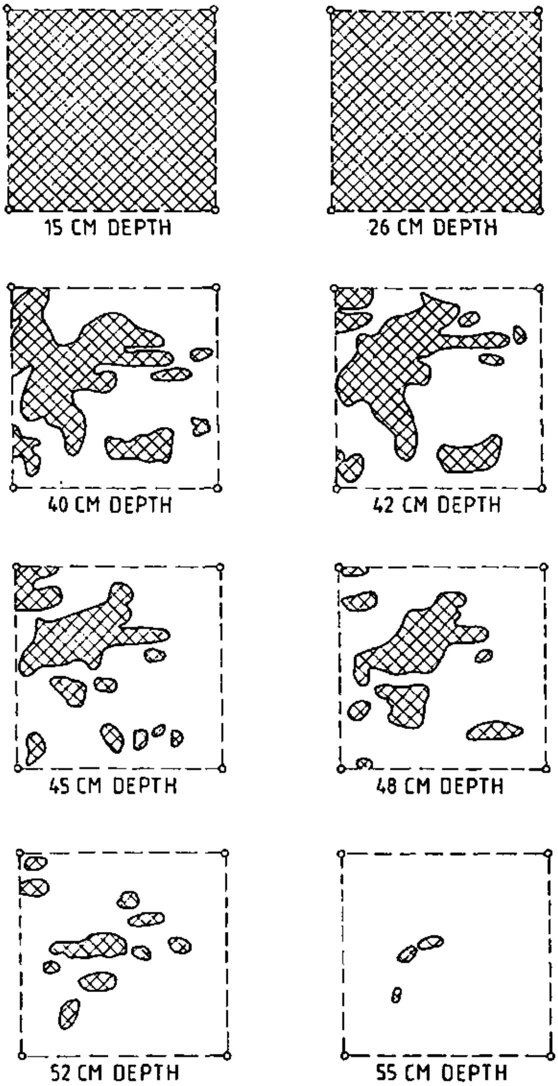
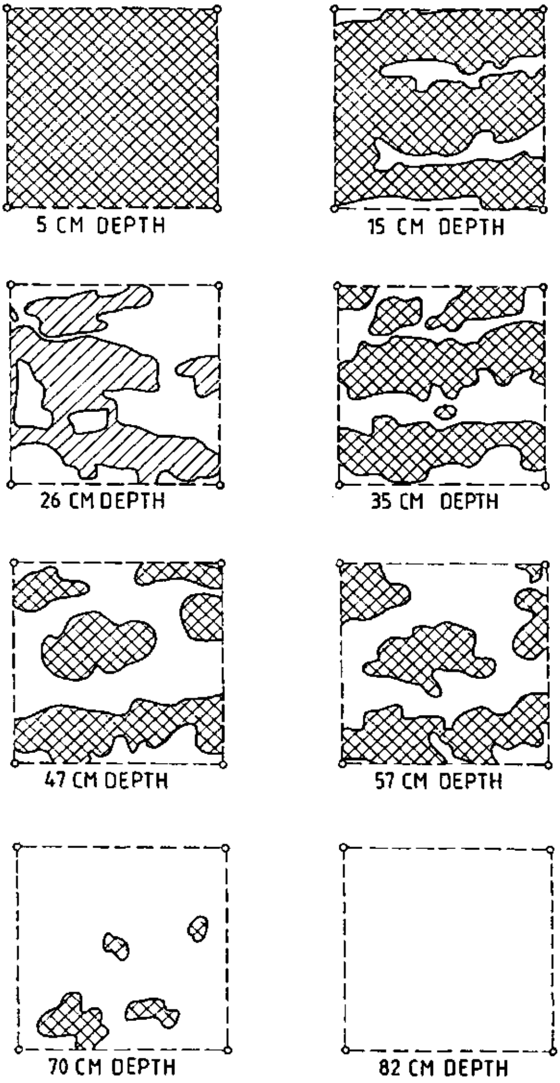


Figure 1a Horizontal cross sections showing the presence of iodide different depths in bare field plot 3.



5 CM DEPTH

15 CM DEPTH

26 CM DEPTH

35 CM DEPTH

47 CM DEPTH

57 CM DEPTH

70 CM DEPTH

82 CM DEPTH

Figure 1b Horizontal cross sections showing the presence of iodide at different depths in grassland plot 8.

Figure 1 presents horizontal cross sections showing the area of colored soil surface at different depths for two representative plots: one located in the corn field (a) and the other in the grassland (b). Note that the solute front had a more irregular shape in the grassland than in the corn field. Figure 2 shows the relation between the fraction of colored area and soil depth for each plot separately in both the corn (a) and the grassland (b).

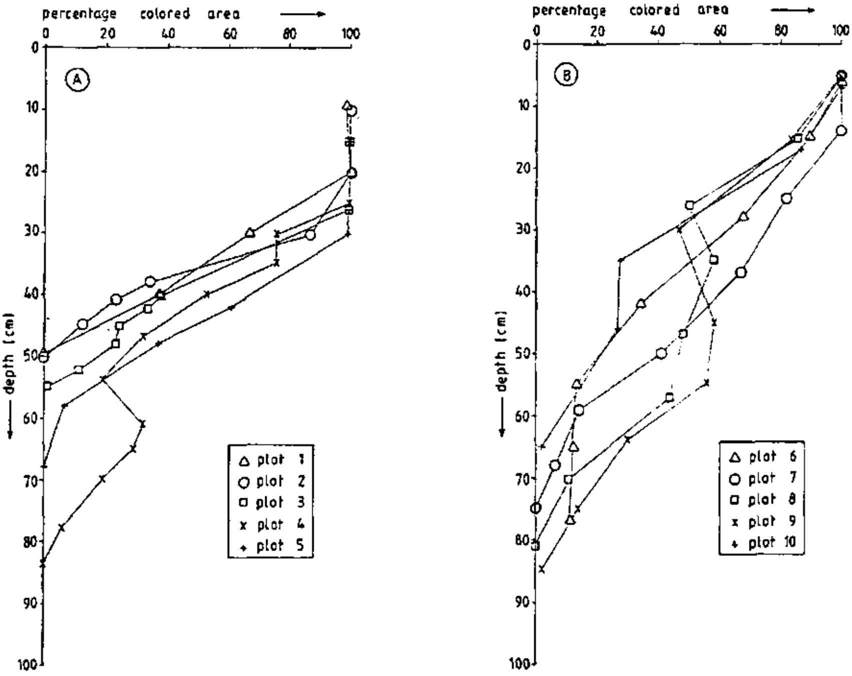


Figure 2 Relationship between percentage colored area and depth for five plots in the corn field (a) and for five plots in the grassland (b).

These figures show that the average penetration depth of the solute front in the corn field is not different from that in the grassland; only the scatter around this depth is much larger in the latter case.

Soil moisture contents

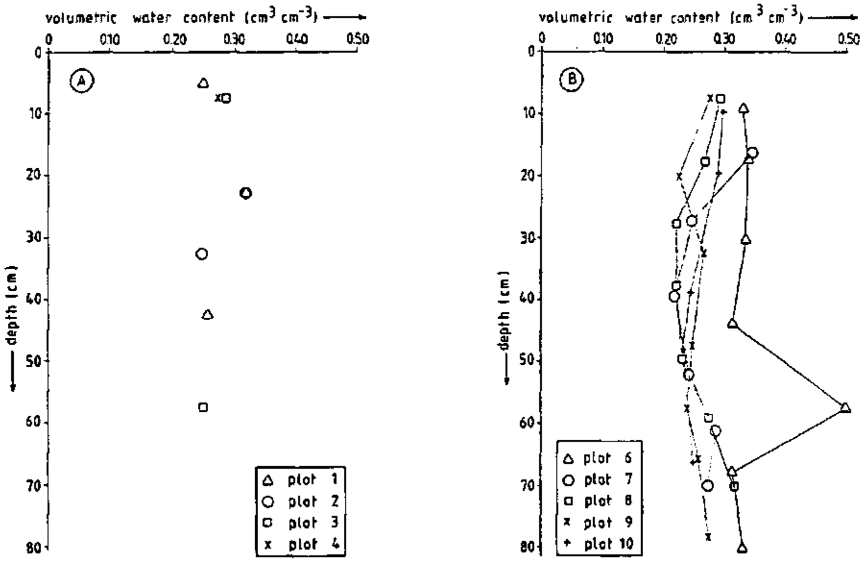


Figure 3 Volumetric water content as a function of depth in the corn field (a) and the grassland (b).

Figure 3a shows the moisture content as a function of depth in the corn field. Every point represents the average of three measurements. Although this figure is based on a limited number of data, we conclude that an average moisture content of 25% would not be far from the real value. No distinction was made on the basis of presence or absence of a preferred flow zone. To study if these differences were statistically significant, signed rank tests and sign tests were applied to the data. These tests indicated that there was no significant difference between the moisture content within and outside a preferred flow zone. Moisture profiles for the five plots located in the grassland are presented in Fig. 3b. Each point represents an average of four or six samples. From this figure it appears that the volumetric moisture content is also about 25%. The wetter subsoil of plot 6 is caused by a layer high in organic matter.

Predicted solute profiles from the bromide experiment

We assume that the fraction of colored area at a given depth is representative for the average iodide concentration at that depth. The iodide profiles can then be predicted using the convection-dispersion equation (CDE) with parameters from the bromide experiment, if the transport conditions of the two experiments are similar. For this particular case the iodide profiles can be described by the solution of the CDE for a step input of unity.

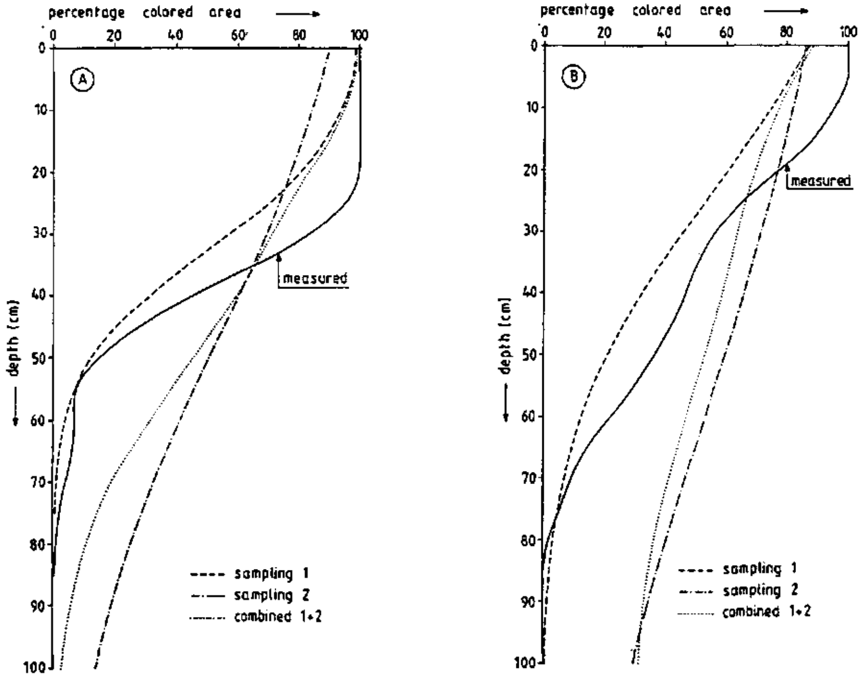


Figure 4 Measured and predicted iodide profiles for the corn field (a) and the grassland (b).

Figure 4 shows the measured (based on the average of the 5 plots) and predicted iodide profiles using transport parameters from the bromide tracer experiment for the corn field (a) and the grassland (b). Pore water velocities (relative to the flux density) and dispersivities were obtained from the first sampling (after 70 mm of drain discharge), from the second sampling (after 169 mm of drain discharge), and from a combination of these (Table 1). Details are given by van Ommen (1988a).

sampling	relative pore water velocity (-)	dispersivity (mm)
1, corn field	3.27	37.0
1, grassland	3.04	145.0
2, corn field	5.40	196.0
2, grassland	7.16	322.0
1+2, topsoil*, corn	3.27	37.0
1+2, subsoil, corn	7.21	37.0
1+2, topsoil, grass	3.04	145.0
1+2, subsoil, grass	11.16	145.0

* The thickness of the topsoil was 25 cm.

Table 1 The CDE parameters determined from the bromide sampling.

Predictions using the CDE parameters of the first bromide sampling underestimate the average solute penetration depth, both for the corn field and the grassland. Transport evidently occurs at lower mobile water contents (hence higher relative pore water velocities) in case of the iodide tracer experiment. The CDE parameters of the second sampling lead to an overestimation of the average penetration depth in the maize field and the grassland. Dispersion at these depths is also more pronounced. Because the high values of the pore water velocities and dispersivities for the second sampling are probably associated with the preferential flow paths in the subsoil, transport velocities here were calculated from the pore water velocities of the second sampling, corrected for the slower transport in the top 25 cm of the soil. This yielded a non-uniform velocity field from which

the drain water quality could be predicted satisfactorily.
The predicted iodide profiles from these heterogeneous velocity fields are located between the solute fronts that were calculated from the first and second samplings. However, these two profiles also do not correspond well with the measured iodide patterns.

From the above comparisons we conclude that transport parameters obtained from the bromide tracer experiment are not representative for the field transport conditions during the iodide tracer experiment.

Description of the iodide solute front with the CDE

As stated before, the fraction of colored surface is assumed to be representative for the average iodide concentration. It should then be possible to describe the mean penetration depth and its variation with the CDE using an average pore water velocity and dispersivity. Expressing the pore water velocity in terms of the amount of water applied (100 mm), the transport parameters of the system were determined using the nonlinear least-squares optimization program 'CXTFIT' described by Parker and van Genuchten (1984). Results are shown in Fig. 5 for both the corn (a) and grass (b) areas.
We assumed that the dispersion coefficient is linearly related to the relative pore water velocity so that their ratio denotes a characteristic length, the dispersivity. For the corn field, the optimized value of the relative pore water velocity (pore water velocity divided by flux density) was found to be 3.94, and that of the dispersivity 13.3 mm.
For grassland these values were 3.98 and 83.7 mm, respectively.
The inverse of these pore water velocities for the corn field would correspond with a mobile moisture fraction of $3.94^{-1} = 0.254$, and for grassland of $3.98^{-1} = 0.251$. These values agree well with the observed volumetric moisture content profiles, presented in Figure 3.
The dispersivity for the grassland is higher than that for the corn field, which is in agreement with results of the bromide tracer experiment (Table 1).

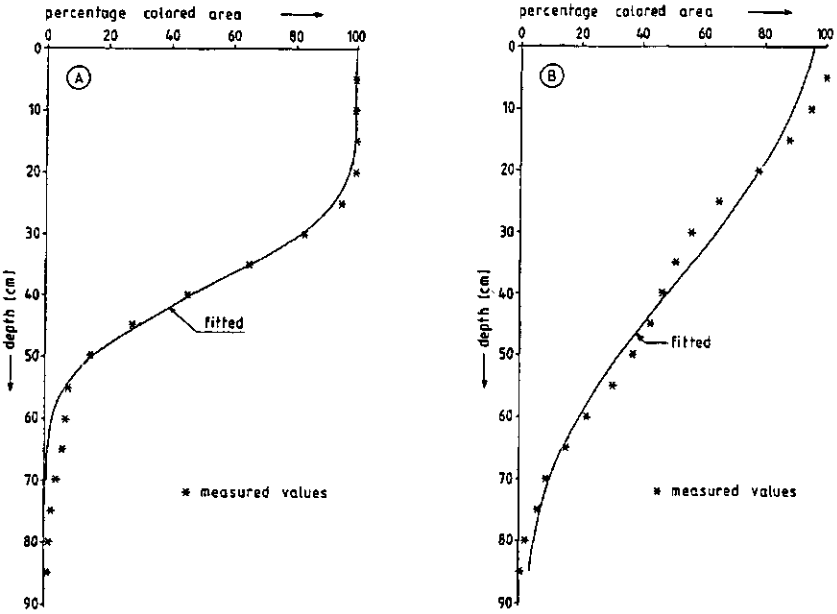


Figure 5 Observed average iodide profiles for the corn field (a) and the grassland (b), and their fit to the convection-dispersion transport model.

In summary, the non-uniform solute front could be described well with the convection-dispersion equation. The average penetration depth was consistent with the measured volumetric water contents, indicating that all soil water was mobile under the experimental conditions. Variations in the solute front penetration depth were such, that the field-average profile could be described accurately with a physically acceptable value of the dispersivity.

Prediction of the bromide breakthrough in the drain water

The CDE parameters as determined from the iodide color experiment were used to predict the breakthrough of bromide in the drain effluent from the unsaturated-saturated transport system. Details of the calculation are given by van Ommen et al. (1988a). The calculated and measured breakthrough curves are presented in Figure 6. The figure shows that transport parameters derived from the iodide tracer experiment cannot be used to predict the fast breakthrough as related to the soil sampling during the bromide experiment.

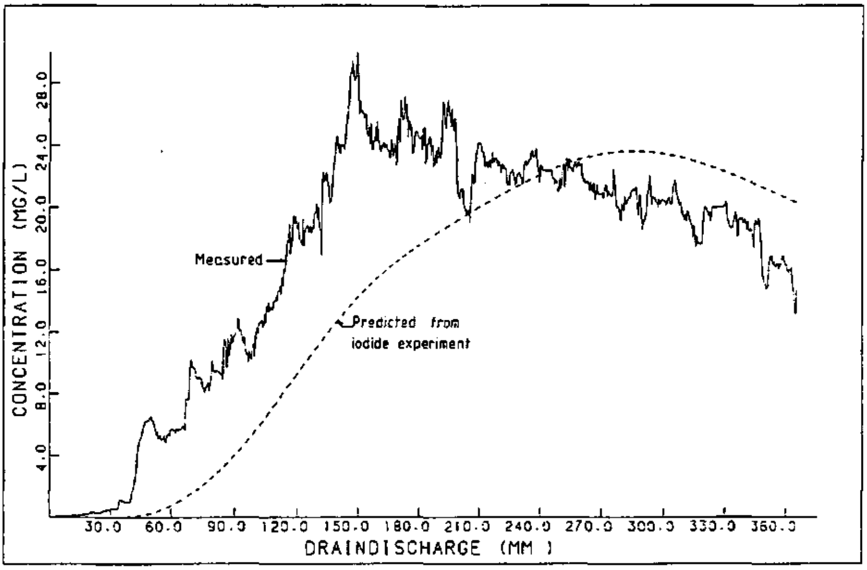


Figure 6 Measured bromide breakthrough curve of the drain water, and the predicted breakthrough based on transport parameters from the iodide experiment.

SUMMARY AND CONCLUSIONS

An iodide-starch coloring technique was successfully used to visualize zones of preferred flow in an undisturbed field soil profile. No statistically significant difference could be observed between values of the water content within or outside a zone of preferred flow. From results of treated plots (5 in a corn field and 5 in a grassland), the solute penetration depths could be determined by assuming validity of the CDE model. The iodide dispacement pattern was quite irregular; however, this irregularity could be adequately captured by a realistic value of the dispersivity. The average solute penetration depth was in good agreement with measured soil water contents.

The accelerated breakthrough that was observed during the bromide field experiment at the same site could not be reproduced with the iodide tracer experiment. We believe that the antecedent moisture regime and the rainfall intensity may have an important effect on the formation of preferred flow zones in the subsoil.

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9. PREDICTION OF SOLUTE BREAKTHROUGH FROM SCALED SOIL PHYSICAL PROPERTIES

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PREDICTION OF SOLUTE BREAKTHROUGH FROM SCALED SOIL PHYSICAL PROPERTIES

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ABSTRACT

Solute transport in unsaturated soil may be described with a transfer function model in which the travel time distribution for a non-reactive solute depends on the distribution of the flow velocity (V). When the spatial variable V is described with the scaling theory of similar media, the travel time distribution follows from the scaling factor (δ) distribution.

Using an experimentally assessed distribution for δ, the travel time distributions were calculated with Monte Carlo simulation. By comparison of travel time distributions found by assuming that the hydraulic conductivity ($K(\theta)$), the volumetric moisture fraction θ, or both are stochastic variables, we found that the stochastic nature of $K(\theta)$ was the dominant factor in the transport process. Assuming θ constant, an analytical approximation was derived for the travel time distribution in a soil system that is homogeneous with depth. The approach was used to predict the breakthrough of an inert tracer from an unsaturated-saturated system. Comparison of these predictions with the observed breakthrough suggests a relatively fast breakthrough that could not be accounted for by our simplified model.

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INTRODUCTION

A quantitative understanding of solute transport under field conditions is needed for predicting field-scale behavior and transport of contaminants and nutrients. At first, the Convection-Dispersion Equation (CDE) was assumed to describe transport adequately, but as experimental information increased it became apparent that the CDE model was unable to accurately quantify transport under field conditions due to, among others, soil heterogeneity (Biggar and Nielsen, 1976; Bowman and Rice, 1986; Richter and Jury, 1986).

To take such heterogeneity into account, Jury (1982) introduced the 'Transfer Function' concept. His approach is based on the expectation that processes in soils are too complex to be adequately modeled in a deterministic manner, but that the overall response of a system may be measured. In view of the breakthrough often observed in natural soil systems, the response upon an input impulse is explained by a lognormally distributed residence time of solute in the system. In later work, Jury et al. (1986) gave a physical interpretation of the transfer function representing the field by a macroscopically homogeneous column. White et al. (1986) and Jury et al. (1982) applied the concept to both columns and field plots. Because the CDE model predicts a normally distributed residence time for realistic dispersion coefficients and column lengths, this model is often less adequate than the Transfer Function Model (TFM). The CDE model remains popular moreover, because of the simplicity to evaluate analytical solutions of the CDE, and the simplicity in obtaining a field average flow velocity (from the average moisture content and the net recharge rate), which is necessary as model input. The residence time in the TFM approach varies around an average value which may be very small for solutes transported in macropores, and very large for solutes that enter a stagnant soil water phase. As was shown by Sposito et al. (1986), this may lead to a non-normal distribution of travel times not accounted for by the CDE.

Both modeling approaches require a parameter which accounts for soil heterogeneity. For the CDE model this is the dispersion coefficient, which becomes very large if the residence time is not normally distributed. In view of the physical background of the dispersion coefficient (Bolt, 1979) there is little inclination to accept such large values (Bresler and Dagan, 1979). On the other hand, the TFM approach lumps heterogeneity into a variance of the residence time without giving a physical meaning to the model parameters. However, due to increased interest by soil physicists and hydrologists to describe flow and transport in spatially variable flow domains, it has now become feasible to give a physical background and a quantification of the residence time distribution.

A promising way to describe water flow, taking into account the spatial variability of soil hydraulic properties, is offered by means of the scaling theory of similar media. The concept of scaling soil hydraulic properties was introduced by Miller and Miller (1955, 1956), and has been later applied successfully by Warrick et al. (1977), Russo and Bresler (1980), and Hopmans (1987). The scaling theory was used by Bresler and Dagan (1979), Dagan and Bresler (1979) to describe field-averaged transport of a non-reactive solute, and by van der Zee and van Riemsdijk (1987) for a reactive solute.

In this paper, we present a method to predict the solute residence time distribution from the scaling factor distribution. The method is illustrated by application to a field situation.

THEORY

The scaling technique

The purpose of scaling is to provide a simple mechanistic description of part of the variance of properties of interest. By scaling, the spatial variability of soil hydraulic properties is expressed by the variability of an ensemble of scale factors, δ_i, that relate the soil hydraulic properties at each sampled location, i, to a reference.

The scaling parameter, δ_i, is defined as the ratio of a microscopic characteristic length, λ_i, of a soil at location i, and the characteristic length, λ_m, of a reference soil (Peck et al., 1977)

$$\delta_i = \lambda_i/\lambda_m \qquad [1]$$

Scaling theory results in a relation of the soil water retention and hydraulic conductivity curve at any location i, with a mean pressure head h_m and hydraulic conductivity K_m, such that for the soil water pressure head (negative in the unsaturated zone):

$$h_i = h_m/\delta_i \qquad [2]$$

and for the unsaturated hydraulic conductivity:

$$K_i = \delta^2_i \cdot K_m \qquad [3]$$

For similar media, Eqs. [2] and [3] hold for h_i and K_i measured at different water contents. Owing to the fact that soils in general do not have identical values of porosity, h and K are written as a function of degree of saturation S rather than volumetric moisture fraction θ.
Reference soil water retention curves and reference $K(\theta)$ relations, and the corresponding scaling factor distributions can be assessed with techniques as described by Hopmans (1987). In accordance with Rao et al. (1979), a distribution of the scaling factors may be tested for log-normality. If true, the continuous scaling factor distribution may be used for interpolation and extrapolation to other retention functions $\theta(h)$ than those found experimentally. In case there is good agreement between the scale factors determined from conductivity and water retention data, the distribution characteristics of the latter are sufficient to describe the variation of both hydraulic functions. With the Probability Density Functions (PDF's) of δ and the reference curves, the hydraulic properties are fully characterized, and flow may be calculated once initial and boundary conditions are specified.

Derivation of the residence time distribution

To derive the travel time distribution we assume that the following conditions are met: (1) gravity flow, i.e., a unit hydraulic gradient; (2) steady-state water flow; (3) a uniform soil profile with respect to the hydraulic properties and (4) a purely convective vertical transport. Based on these assumptions, the controlling variable time may be expressed as the amount of water drained (van Ommen et al., 1988).

The pore water velocity V (LT^{-1}) under unit gradient follows from $K(\theta)$ and the volumetric water content θ:

$$V = K(\theta)/\theta \qquad [4]$$

The variability in both the conductivity, $K(\theta)$ and water content ($\theta(h)$) relations can be expressed in terms of the variability of the scaling parameter, δ (Eqs. [2] and [3]). In a layer of thickness L the residence time, T (T), equals

$$T = L\theta/K(\theta) \qquad [5]$$

Transformation of time T into the equivalent amount of drain discharge T' is done by multiplication of T with the areally averaged flux density, $\bar{K}$, which equals (Bresler and Dagan, 1979):

$$\bar{K} = K_m \cdot \exp\ (2\mu_y + 2\sigma^2{}_y) \qquad [6]$$

K_m is defined as in Eq. [3], and the exponential term is the expectation of the log-normally distributed δ^2, where $Y = \ln\delta$, and μ_Y and σ_Y are the mean and standard deviation of Y respectively.

Combination of Eqs. [3], [5], and [6] yields the travel time T'(L), now expressed as percolated water depth:

$$T' = L\theta/\delta^2 \cdot \exp\ (2\mu_Y + 2\sigma^2{}_Y) \qquad [7]$$

From the representative soil water pressure head in the field, and the distribution of the scaling parameter δ, the distribution of travel times to a soil depth L, and thus the breakthrough curve for an instantaneous input of unit magnitude, can be constructed using Monte Carlo simulations. However, the statistical properties of the travel time distribution can also be derived analytically if it is assumed that the variability in T' is mainly determined by the variation in downward flux, $K(\theta)$, and to a lesser extent by the variation in θ, i.e., the water content is kept fixed at a 'field-average value'. It can then easily be shown (see e.g. van der Zee and van Riemsdijk, 1987) that:

$$\mu_{\ln T'} = \ln(L\theta) + 2\sigma^2_Y \qquad [8]$$

$$\sigma_{\ln T'} = 2\sigma_Y \qquad [9]$$

where $\mu_{\ln T'}$ and $\sigma_{\ln T'}$ are the mean and standard deviation of ln(T') respectively. The PDF of T' is

$$\rho(T') = (T'\sigma_{\ln T'}\sqrt{(2\pi)})^{-1} \cdot \exp\,(-(\ln T'-\mu_{\ln T'})^2/2\sigma^2_{\ln T'}) \qquad [10]$$

which corresponds with the PDF of the transfer function model (Jury, 1982).

APPLICATIONS

The soil hydraulic properties and their variations, pertaining to both applications to follow, were measured on samples taken from an experiment field in the study area 'Hupselse Beek' in the Netherlands. The watershed and the soil physical measurement techniques were described by Hopmans and Stricker (1987). In Table 1 we present the scale factor statistics and the parameters of the analytical hydraulic model of van Genuchten (1980). The data describe the scaled mean hydraulic functions for both the A and BC-horizon.

	Horizon	
Parameter of van Genuchten model for scaled mean hydraulic functions	A(25)*	BC(46)
α	0.0282	0.0238
n	1.451	1.669
θ_s	0.403	0.316
θ_r	0.000	0.000
K_s (cm day^{-1})	72.0	60.0
Statistics scale factor values		
μ_Y	-0.3050	-0.1960
σ_Y	0.8531	0.6492

* Number of sampled locations

Table 1 Parameter values for description of variability of soil hydraulic functions.

Solute breakthrough for the unsaturated soil

For a first illustration we consider a hypothetical soil profile (L = 1 m) consisting of a BC-horizon only. The soil water retention curves of the 46 sample locations within the 0.5 ha field before and after scaling are shown in Figure 1a and 1b, respectively. The solid line in Fig. 1b represents the scaled mean water retention curve. Clearly, scaling was very successful in explaining the variations in the h(S)-relation.

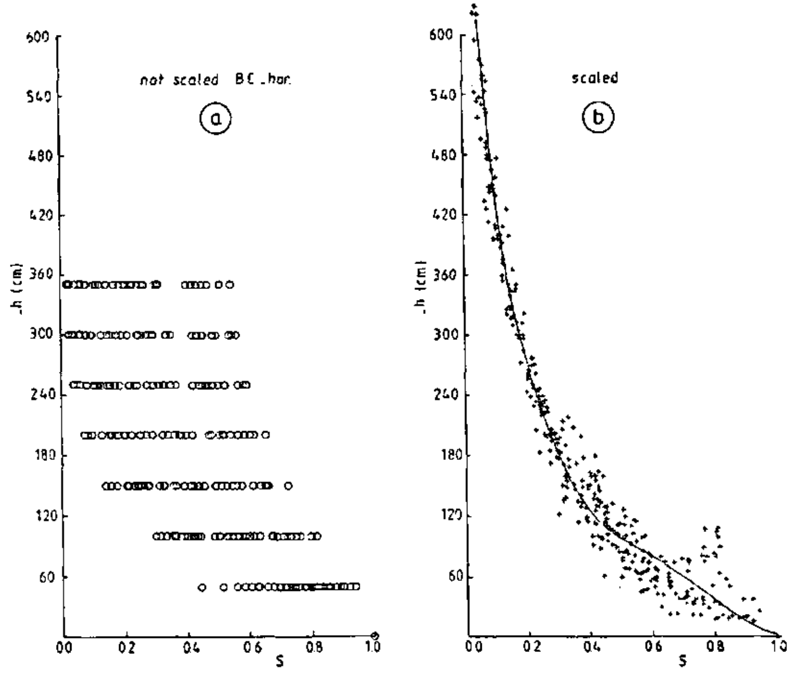

Figure 1 Unscaled (a) and scaled (b) soil water retention curves of the BC-horizon.

Figure 2 shows four travel time PDF's, three of which are the result of a Monte Carlo (MC) simulation, while the fourth is determined from the analytical solution (Eq. [10]), to check the accuracy of the MC-simulation results. The uniform soil water pressure head at which solute transport is

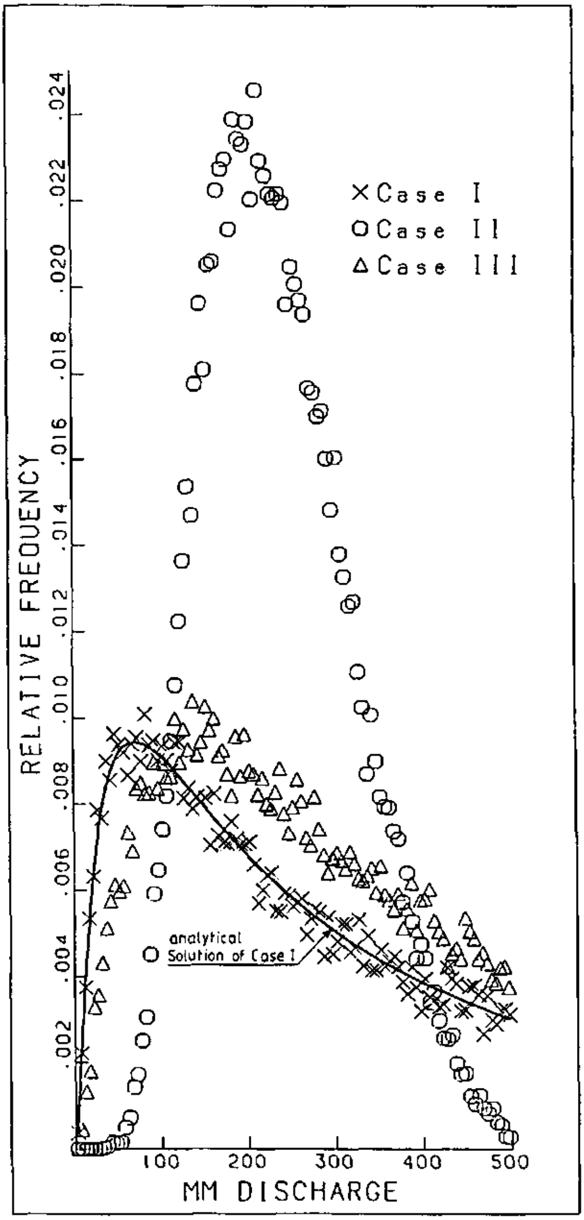

Figure 2 Travel time distribution functions (h = -100 cm) determined from the MC-simulations for case I (flux density variable), case II (volumetric water content variable), case III (both flux density and volumetric water content variable), and analytical solution for case I.

assumed to occur was set equal to -100 cm. Three cases with respect to the origin of the travel time variation are shown: (I) contribution of the flux variability only, (II) contribution of the moisture content variability only, as was done by Bresler and Dagan (1979), and (III) contribution from both the moisture content and flux variability. The number of MC replicates, from which the PDF's were determined, was chosen to be 40,000. The travel times on the horizontal axis of Fig. 2 were sorted into 100 classes of 5 mm width.

From Figure 2 it appears that the results of the MC-simulation for case I (variable flux) is in good agreement with the analytically derived PDF. Furthermore, the travel time distributions of cases I and III are not very different. Figure 2 also shows that the travel time distribution based on a uniform flux (δ=1 in Eq. [7]), and a variable moisture content (case II) is completely different from all other cases. The variation in travel time for case II is far less than those for a variable flux. We therefore conclude that the variability of the residence time is much more affected by the variability of the flux than by the variability of the moisture content.

Field experiment

In order to investigate which case would approach the actual solute breakthrough the best in a field soil, we applied the presented theory to a field experiment.

The field experiment involved the study of solute migration in a unsaturated-saturated transport system in the 'Hupselse Beek' catchment area. Bromide tracer solution was uniformly applied to the 260 m long, 11 m wide catchment area of a drain. From the measured bromide concentrations in the drain water, the breakthrough curve from the coupled unsaturated-saturated transport system could be constructed. The experiment is described in detail by van Ommen et al. (1988). A study in the same field was also carried out to describe the spatial variability of soil physical properties (Hopmans and Stricker, 1987). Since the variability study discriminated between topsoil (A-horizon) and subsoil (BC-horizon), the simulated flow system was adapted to this situation.

The field transport system is discretized by means of 'flow blocks' along the drain. In our case such a flow block consisted of the topsoil, the subsoil, and the saturated zone (Figure 3). Each block has its own value for the thickness of the subsoil and the thickness of the saturated zone depending on the position along the drain. The thickness of the topsoil was 25 cm.

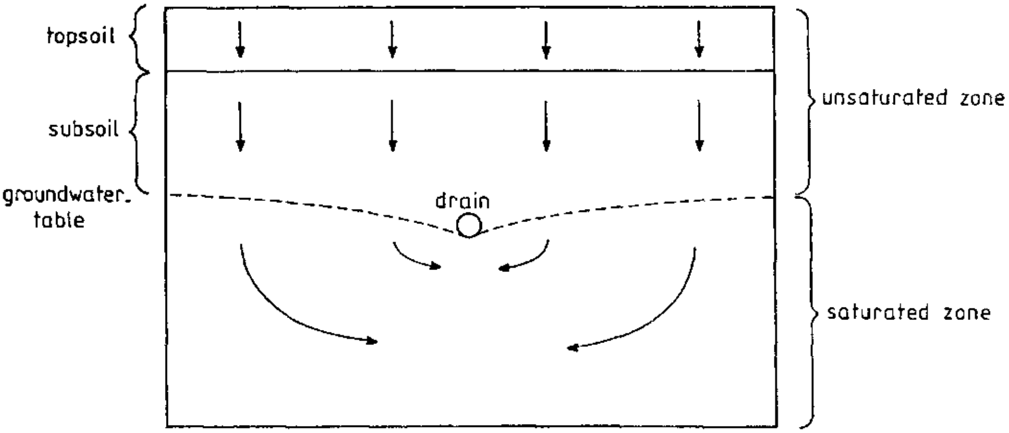

Figure 3 Flow block of unsaturated-saturated soil water transport system.

Transport within a flow block was modeled as follows. Based on MC-simulations using Eq. [7], the impulse response for the topsoil transport system was determined. The breakthrough curve at a depth of 25 cm served as input for the second transport system, of which the impulse response could be determined in a similar way. Convolution of the impulse response of the subsoil with the input from the topsoil resulted in a breakthrough curve at the groundwater level. Finally, the concentration in the drainage water of one flow block was calculated from convolution of the concentration at the groundwater level with the impulse response of the saturated transport system. This last procedure is described in detail by van Ommen et al. (1988a). After averaging of the flow block concentrations, the concentration of the drain water at the outlet of the coupled transport system was determined as a function of the amount of drainage (mm).

Figure 4 shows drain effluent breakthrough curves assuming a variable flux and a fixed moisture content (case I) for various standard deviations in Y.

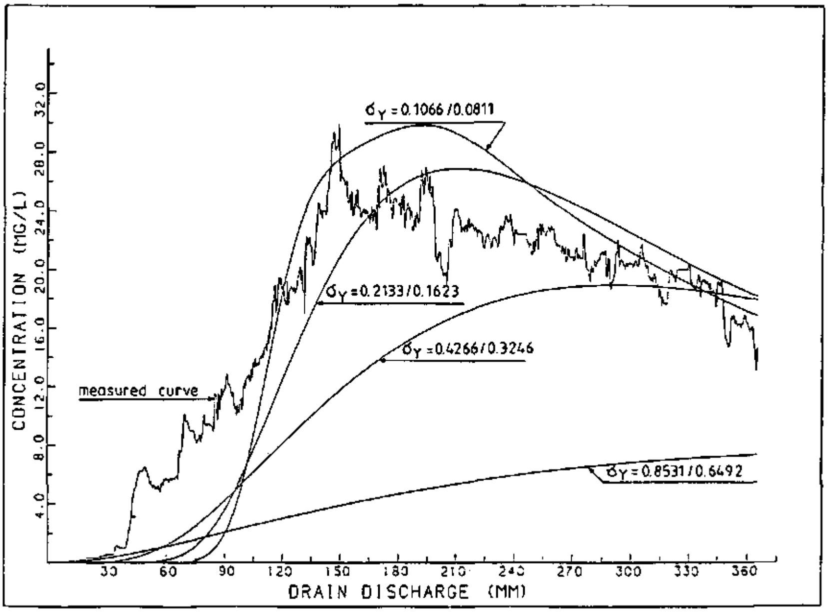

Figure 4 Observed field breakthrough curve and predicted breakthrough curves (h = -100 cm) with variable fluxes only (case I) and for different values of σ_Y for the top and subsoil, respectively. The lowest curve is based on measured variability of scale factors.

The measured variability of soil physical parameters, expressed in the standard deviations of the scale factor, appears to result in a variation of travel times which is much larger than that derived from the measured solute breakthrough curve. For values of σ_Y smaller than measured (Table 1), calculated solute breakthrough curves were in better agreement with the experimentally determined curve. Although the fit improved at lower variabilities, the measured breakthrough curve still begins sooner than predicted. The value of the soil water pressure head used in this simulation was equal to -100 cm while decreasing this value to -500 cm (not shown) did result in slightly higher concentration values; it did not affect $\sigma_{\ln T}$, (Eq. [9]).

Figure 5 shows the breakthrough curves for a fixed flux and a variable moisture content (case II). The calculated breakthroughs are for soil water pressure head values of -100 cm and -500 cm. We emphasize that the period of drain discharge up to 250 mm coincides with the winter and spring percolation season, during which the discharge rates are high and transpiration low. Therefore, a representative soil water pressure head of -100 cm should much closely mimic the actual field situation than a value of

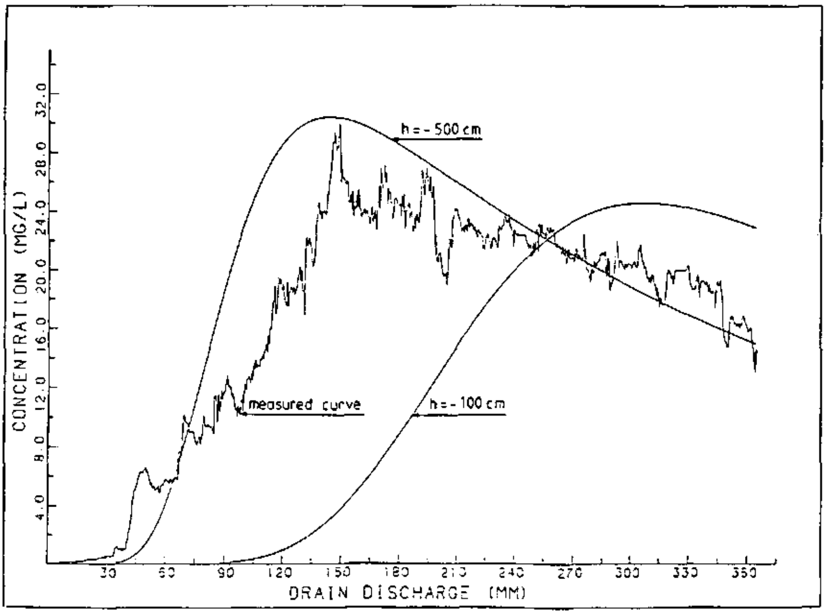

Figure 5 Observed and predicted drain water breakthrough curves with variable volumetric moisture content only (case II) and for different values for the uniform soil water pressure head.

-500 cm, which produced a reasonable fit. From Figure 4 and 5 it appears that in this case the measured variability of travel times seems to be more determined by the variability of moisture contents than by variable fluxes.

This statement must be made cautiously since preferential flow in the subsoil caused an accelerated breakthrough to the groundwater table from the transport system (van Ommen et al., 1988a). If the experiment had been carried out under ponded infiltration conditions, the variability of fluxes might have been in far better agreement with the predicted breakthrough based on flux variability only.

CONCLUSIONS

We presented a simple model to predict solute breakthrough for an unsaturated soil. The residence time distribution was expressed by means of the statistical properties of the scale factors, and a value for the effective soil water pressure head at which transport presumably occurred. A simple analytical solution could be presented if the water content is uniform in the system.

Application of the model showed that the variability in solute travel times is dominated by the variability in fluxes, rather than the variability in volumetric water content.

The model was verified with a field experiment involving the application of bromide to the intake area of a drain, and the measurement of concentrations the drain water. Model results did not agree with the measured breakthrough curve when the measured variability in scale factors and a realistic soil water pressure head were substituted in the model.

We believe that the negative outcome of the field verification experiment does not necessarily prove that the presented model is invalid. However, the simple physically-based expression that translates the parameters of the transfer function concept into measurable quantities, might be more successful under different experimental conditions.

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10. SAMENVATTING

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'Het transport vanaf een diffuse bron van verontreiniging en de toepassing hiervan op een gekoppeld onverzadigd-verzadigd systeem'.

De aantasting van de kwaliteit van het grondwater is de laatste jaren vaak in het nieuws. Aanvankelijk eisten de vele gevallen van verontreiniging ten gevolge van lokale bronnen de aandacht op; voorbeelden zijn o.a. vuilnisbelten en stortplaatsen van chemisch afval. Naarmate de sanering van deze puntbronnen verder ter hand genomen werd, bleek dat de bedreiging van de grondwaterkwaliteit door verspreid voorkomende bronnen van verontreiniging - diffuse bronnen van verontreiniging - een ernstig probleem vormde. Omdat maatregelen ter preventie en bestrijding van deze bronnen belangrijke implicaties hebben, is het van groot belang om de effecten hiervan te kunnen kwantificeren en te vertalen naar een beleid op grond waarvan de kwaliteit van het grondwater op lange termijn gewaarborgd is. Bovendien is in hoofdstuk 1 uiteengezet in hoeverre grondwater kwetsbaar kan zijn ten aanzien van het indringen van verontreinigingen vanaf het aardoppervlak.
In hoofdstuk 2 werd een theorie afgeleid, met behulp waarvan de effecten van diffuse bronnen van verontreiniging op de kwaliteit van dagzomend grondwater kon worden gekwantificeerd. Deze theorie berust op een analogie van het onderhavige transport mechanisme met het optreden van volledige menging in een reactorvat. Dit maakt het mogelijk om de kwaliteitsveranderingen van het uittredende grondwater, ten gevolge van een diffuse belasting, uit te drukken als functie van eenvoudig te verkrijgen hydrogeologische parameters.
Hoofdstuk 3 vormt een illustratie van het gemak waarmee moeilijkere transportproblemen opgelost kunnen worden als gebruik wordt gemaakt van de analogie, die in hoofdstuk 2 beschreven is. Het betreft hier de reactie van de grondwaterkwaliteit op een eenmalige belasting van het grondwater met een stof, die radioactief verval vertoont. Overigens, voor de eenvoud is het transport van een dergelijke stof door de onverzadigde bodem niet verdisconteerd: in werkelijkheid kan dit echter van grote invloed zijn.
Het effect van de onverzadigde zone op het transport van een opgeloste stof vanaf het bodemoppervlak is nader beschreven in hoofdstuk 4. Het transport door de onverzadigde bodem wordt dan gesimuleerd met behulp van het transport door een reeks identieke reactorvaatjes, waarin volledige menging

optreedt. Tevens werd in dit hoofdstuk uiteengezet op wat voor wijze het effect van tijdsafhankelijke invoer-concentraties berekend kon worden.

Aangezien bodemeigenschappen met de diepte sterk kunnen varieren, werd in hoofdstuk 5 een rekenmethode gepresenteerd waarmee de stroming van een opgeloste stof door zo'n heterogeen systeem beschreven wordt. Aan ieder bodemlaagje afzonderlijk kan dan een waarde van het vochtgehalte, de dikte, de retardatiefactor of de afbraakconstante worden toegekend. Een speciaal geval hiervan is een gekoppeld onverzadigd-verzadigd transportsysteem, waarin het laatste bodemlaagje dan de verzadigde zone voorstelt.

Om nu de theorie, die in de voorgaande hoofdstukken is gepresenteerd, te verifiëren, is een veldexperiment uitgevoerd. Dit experiment, waarvan in hoofdstuk 6 uitgebreid verslag is gedaan, bestond uit het toedienen van een merkstof op een gedraineerd perceel. Hierna zijn zowel monsters van de bodem, van het grondwater en van het drainwater genomen om het transport van de merkstof door de onverzadigde en verzadigde zones kwantitatief te kunnen beschrijven. Op basis van de bodembemonsteringen en de theorie, zoals die gepresenteerd is in de voorgaande hoofdstukken, was het mogelijk om de concentratie van de merkstof in het drainwater te voorspellen en te vergelijken met de gemeten waarden. Deze voorspelling was alleen dan in goede overeenstemming met het gemeten verloop, als het transport van de merkstof in de ondergrond versneld plaatsvond. Omdat er indirecte aanwijzingen bestonden voor het ontstaan en de aanwezigheid van preferente stroombanen, waardoor de merkstof sneller naar het grondwater kon bewegen dan op grond van de meest gangbare theorieën zou worden verwacht, werd een methode ontwikkeld waarmee het bestaan van deze stroombanen in het veld aangetoond kon worden.

De techniek van de methode werd in detail beschreven in hoofdstuk 7 en berust op het principe dat jodium met zetmeel een intensief donkerblauw gekleurd complex vormt. Dit jodium wordt verkregen door oxidatie van het jodide-ion, dat als inerte merkstof aan de bodem is toegevoegd.

In hoofdstuk 8 kwam de toepassing van de in hoofdstuk 7 ontwikkelde methode aan de orde. Op tien plaatsen in het perceel, waar ruim een jaar geleden de merkstof was toegediend, werd nu 100 mm jodide oplossing toegediend. Na afgraving werden de donker gekleurde vlekken, die op de aanwezigheid van jodide duidden, gefotografeerd en de fractie blauwkleuring als functie van de diepte uitgezet. Op deze manier werd informatie verkregen in hoeverre het transport door preferente stroombanen plaatsvond. Op grond van de resultaten, die met deze kleurstofmethode werden geboekt, bleek, dat de versnelde doorbraak, zoals die was waargenomen tijdens het voorgaande experiment, niet kon worden gereproduceerd. De omstandigheden waaronder de jodide-kleurstofproeven waren uitgevoerd, verschilden blijkbaar zodanig met die tijdens het eerste merkstof experiment, dat de eerder waargenomen versnelde uitspoeling niet optrad. Hiermee wordt onderstreept dat het ontstaan van preferente stroombanen een dynamisch proces is, waarnaar nog veel onderzoek gedaan moet worden.

Op hetzelfde perceel was in het zeer recente verleden een studie verricht naar de ruimtelijke variabiliteit van bodemfysische parameters. Op basis van de resultaten van dat onderzoek werd getracht om de verblijftijdspreiding - en hiermee het transport door het gekoppeld onverzadigde-verzadigde systeem - te beschrijven op basis van de gemeten ruimtelijke variabiliteit van genoemde parameters (hoofdstuk 9). Indien verondersteld werd, dat de verblijftijd in de onverzadigde zone hoofdzakelijk toe te schrijven zou zijn aan de variabiliteit van de waterflux, dan resulteerde dit in een verblijftijdspreiding, die groter was dan die op grond van de waargenomen merkstofconcentraties in het drainwater was waargenomen. Vermoedelijk speelt de variabiliteit van de waterflux een grotere rol in situaties waarbij infiltratie optreedt vanaf een geïnundeerd bodemoppervlak.

CURRICULUM VITAE

Hendrikus Coenraad van Ommen werd op 25 juni 1959 geboren te Rhenen. In 1977 behaalde hij het diploma V.W.O.-B aan het Christelijk Lyceum Veenendaal.

In 1977 begon hij met zijn studie aan de Landbouwhogeschool te Wageningen, studierichting bodemkunde en bemestingsleer met als oriëntatie de bodemnatuur en -scheikunde. Na het behalen van zijn kandidaatsdiploma in 1980, bracht hij zijn stage en een gedeelte van zijn studie door aan het "Institut de Mécanique de Grenoble" (Frankrijk) door. In februari 1983 rondde hij zijn studie af met als vakken bodemnatuurkunde en bodemscheikunde (hoofdvak), meteorologie en omgevingsnatuurkunde (hoofdvak), en de agrohydrologie (bijvak).

Sinds januari 1983 is hij in dienst bij de Vakgroep Cultuurtechniek, sectie agrohydrologie, waar hij zich voornamelijk heeft beziggehouden met onderzoek en onderwijs op het gebied van het transport van opgeloste stoffen in en naar het grondwater. Deze dissertatie vormt een weerslag van het grootste gedeelte van zijn onderzoeksresultaten gedurende de periode 1983-1988.

Sinds het najaar van 1988 is hij werkzaam als milieutechnisch adviseur bij het ingenieurs- en adviesbureau Grontmij N.V.