Modeling non-point source pollutants in soil: Applications to the leaching and accumulation of pesticides and cadmium

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2.1 Application of the Pesticide Transport Assessment Model to a Field-study in a Humic Sandy Soil in Vredepeel


Co-authors: Ton van der Linden and Leo van der Pas.

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2.2 Application of Nine Pesticide Leaching Models to the Vredepeel Dataset. Pesticide Fate

*Agricultural Water Management* (accepted).

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2.3 Modeling the Long-Term Effect of Cadmium Deposition in Acid Sandy Soils

Submitted in a slightly revised form to *Geoderma*.

Co-authors: Hans van Grinsven and Koos Verstraten.
CHAPTER 2

Application of the Radiative Transfer Assessment Model to a Field Study in Hoomei Sandy Soil in '`

Application of the Radiative Transfer Assessment Model to a Field Study in Hoomei Sandy Soil in `
2.1 Application of the Pesticide Transport Assessment Model to a Field-Study in a Humic Sandy Soil in Vredepeel

Abstract

The Pesticide Transport Assessment model (PESTRAS) is a process-oriented model to simulate the fate and movement of water and pesticides in a cropped field soil. The model was evaluated using field data of bromide, ethoprophos and bentazone, collected from a field experiment in a humic sandy soil near Vredepeel, the Netherlands. Model predictions were generally within the 95% confidence intervals of the observations when site-specific model inputs were used. If generic parameter values were used, the model predictions sometimes deviated strongly from the observed data. This was especially the case for pesticide degradation properties. The bromide simulations showed that preferential flow was not an important process for this field soil. A significant fraction of the applied ethoprophos disappeared by surface volatilization. The downward movement of this pesticide was slightly overestimated, probably due to ignorance of sorption kinetics. The depth-dependence of pesticide transformation was atypical. An important fraction of the applied bentazone was transformed under micro-aerobic to anaerobic conditions in the subsoil.

Introduction

During the eighties it became clear that the total pesticide use per hectare of arable land was high in the Netherlands compared to other European countries (RIVM, 1989). At the same time, results of extensive groundwater monitoring programs showed approximately 50 pesticides at observable concentrations in the groundwater of western Europe and the USA (Leistra and Boesten, 1989; Hallberg, 1989; Koshiek, 1991). For these reasons, the Dutch government released a declaration with the intent of reducing both the total pesticide use, and the emission of pesticides to groundwater, surface water and the atmosphere. These objectives have been worked out in more detail in the Multi-Year Crop Protection Plan (LNV, 1991). Models play an important role in the evaluation of this policy.
plan (Van der Linden et al., 1996). As a part of this evaluation, the pesticide leaching model PESTRAS (Tiktak et al., 1994c; Freijer et al., 1996) in combination with an information system on pesticide use (Merkelbach et al., 1997) was applied to obtain quantitative information on pesticide emissions to the groundwater on a regional-scale (Tiktak et al., 1996a,b).

Before PESTRAS can be used for quantitative assessment of expected pesticide leaching to the groundwater, its ability to simulate the movement and distribution of pesticides in soil should be evaluated ('model validation'). A crucial part of such a validation study is the comparison of model results with independent field observations. In the case of a regional-scale model, such a study should include an evaluation of both the predicted spatial pattern, and the temporal variation of pesticide leaching. However, regional-scale observations of pesticide leaching are scarce or non-existing, and are usually limited to one point-in-time (e.g. Kohsiek, 1991). As an alternative, the model is applied to a number of field-plots where most model-inputs can be obtained from direct measurements, and where the fate of a pesticide is measured as a function of time. For validation of a regional-scale model, the field-plots should be selected carefully, so that they cover a broad range of soils, pesticides, and hydrological conditions.

The main objective for the presented study was to evaluate the ability of PESTRAS to simulate the movement and distribution of bromide and two pesticides in the soil system. To achieve this, the model was applied to a data set collected from a field experiment in a humic sandy soil near Vredepeel, the Netherlands (Boesten and Van der Pas, 1997). In this model application on-site measured data were available. As many of these model inputs were not available for regional-scale applications, we evaluated the effect of using generic parameter values instead of on-site measured parameter values.

Materials and Methods

Field Study
The field study was conducted at the experimental farm ‘Vredepeel’ in the south-eastern part of the Netherlands (51°32’N; 5°52’E), and is described in detail by Boesten and Van der Pas
APPLICATION OF THE PESTRAS MODEL

(1997). Annual average precipitation is approximately 750 mm; potential evapotranspiration is 530 mm, and average temperature 9.3 °C. All experiments were carried out at a plot of size 54x80 m², which was part of an agricultural field (size 60x160 m²). There were drain lines at 1.2 m depth, but all drains were closed during the experiments. The water table resided at 0.5-1.5 m below the soil surface. Table 1 summarizes some general soil properties.

Table 1
Selected properties of the Vredepeel soil.

<table>
<thead>
<tr>
<th>Soil layer</th>
<th>pH_{\text{so}}</th>
<th>Organic matter (%)</th>
<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
<th>Bulk density (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00–0.32 m †</td>
<td>5.3</td>
<td>4.90</td>
<td>3</td>
<td>6</td>
<td>91</td>
<td>1315</td>
</tr>
<tr>
<td>0.32–1.00 m</td>
<td>4.7</td>
<td>0.23</td>
<td>2</td>
<td>2</td>
<td>96</td>
<td>1666</td>
</tr>
<tr>
<td>1.00–2.00 m</td>
<td>4.6</td>
<td>0.25</td>
<td>3</td>
<td>9</td>
<td>88</td>
<td>1700</td>
</tr>
</tbody>
</table>

† Depth of layer boundary inferred from color transition in the field

The experimental plot was sown with winter wheat before pesticide and bromide applications. Bromide (sodium bromide solution) and two pesticides (ethoprophos [O-ethyl S,S-dipropyl phosphorodithioate] and bentazone [3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one 2,2 dioxide]) were sprayed on November 22, 1990 at rates of 111, 3.4, 0.8 kg active ingredient ha⁻¹, respectively. The wheat crop was harvested in August 1991. After a short bare period, mustard was sown and it was harvested at the end of November 1991.

Soil profile samples were taken from 16 soil columns (diameter 0.1 m) on 1, 22, 42, 103, 214, 278, 347, and 474 days after pesticide application. Sampling depth was down to 1.2 m. After sampling, the columns were sliced into layers, and pesticide and bromide contents and the volume fraction in the liquid phase were determined. Also the gravimetric soil water content and the dry bulk density were determined. Soil samples from one particular layer were pooled to four samples before pesticide analysis. Sixteen groundwater tubes were installed with filters at 0.8-1.0 m, 1.2-1.4 m, and 1.9-2.1 m depth. On each sampling day groundwater samples were taken from the filters situated below the groundwater level. The water samples were combined to four samples and analyzed for ethoprophos and bentazone. At the experimental field, soil- and air-temperatures, rainfall, and groundwater level were recorded continuously. Before pesticide application, 70 samples were
taken from the top 0.25 m of the soil; the samples were mixed and were used for laboratory experiments on transformation rate and adsorption of both pesticides. At the same time samples were taken from the 0.5-1.0 m and the 1.2-2.0 m soil layers. The latter layer was water-saturated at the time of sampling. These samples were used for laboratory experiments on transformation rates in the subsoil. Duplicate samples (volume 300 cm$^3$) were taken for the determination of the water retention characteristic for the 0.1-0.18, 0.45-0.53 and 0.70-0.78 m soil layers. The unsaturated hydraulic conductivity function was measured using the evaporation method of Wind (1968).

The pesticide transport assessment model

For this study, the mechanistic, process oriented model PESTRAS (Pesticide Transport Assessment, Tiktak et al., 1994c; Freijer et al., 1996) was used. PESTRAS is a one-dimensional, dynamic, multi-layer model for simulating transient flow, hydrodynamic dispersion, equilibrium sorption, transformation, uptake and volatilization of pesticides by plant roots in the unsaturated zone and the uppermost part of the saturated zone. The model consists of three major submodels: (i) hydrology, (ii) heat transport, and (iii) pesticide transport, sorption, transformation and volatilization.

**Hydrology**

The hydrological submodel (Tiktak and Bouten, 1992) uses a finite-difference method to solve the Richards equation:

$$\frac{C(h)}{t} \frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[ K(h) \frac{\partial h}{\partial z} + 1 \right] - S_w(h)$$  \hspace{1cm} (1)

where $C$ (m$^{-1}$) is differential water capacity, $t$ (d) is time, $z$ (m) is vertical position, $h$ (m) is soil water pressure head, $K$ (m d$^{-1}$) is unsaturated hydraulic conductivity, and $S_w$ (d$^{-1}$) is a sink term accounting for water uptake by roots. The driving force for the water uptake sink term is the potential transpiration, $T^*$ (m d$^{-1}$). It is calculated from the reference evapotranspiration ($ET^*$):

$$T^* = f_c(1-e^{-0.6LAI})ET^*$$ \hspace{1cm} (2)

where $f_c$ (-) is an empirical crop factor, $LAI$ (m$^2$ m$^{-2}$) is the Leaf Area Index, and $ET^*$ (m d$^{-1}$) is the potential evapotranspiration.
APPLICATION OF THE PESTRAS MODEL

due to Makkink (1957). The potential uptake from a specific soil layer is calculated by distributing the potential transpiration over all soil layers using the root length distribution and simulated water contents. Vertical feedback mechanisms are simulated with preferential uptake from layers with high water saturation fractions (Herkelrath et al., 1977). The actual water uptake is calculated by multiplying the potential uptake with a dimensionless reduction function for that particular layer (Belmans et al., 1983).

PESTRAS contains several options for the lower boundary condition. In this particular study, a flux condition was chosen:

\[ J_{\text{bot}} = a_b \exp \left( b_v |H| \right) + c_b \]  

where \( J_{\text{bot}} \) (m d\(^{-1}\)) is soil water flux through the bottom of the system, \( H \) (m) is groundwater depth, and \( a_b \) (m d\(^{-1}\)), \( b_v \) (m\(^{-1}\)), and \( c_b \) (m d\(^{-1}\)) are parameters.

Heat transport

The model takes into account conductive and convective transport of heat in the soil:

\[ \frac{\partial C_v T}{\partial t} = \frac{\partial}{\partial z} \left[ \lambda \frac{\partial T}{\partial z} - J_w \rho_w H_w T \right] \]  

where \( C_v \) (J m\(^{-3}\) K\(^{-1}\)) is the specific heat capacity, \( T \) (K) is temperature, \( \lambda \) (J m\(^{-1}\) d\(^{-1}\) K\(^{-1}\)) is the effective heat conductivity, \( J_w \) (m d\(^{-1}\)) is soil water flux, \( \rho_w \) (kg m\(^{-3}\)) is specific density of water, and \( H_w \) (J kg\(^{-1}\) K\(^{-1}\)) is the specific heat capacity of water. The upper boundary condition is the air temperature; and the lower boundary condition is a fixed temperature.

Pesticide transport, transformation and sorption

The pesticide fate model considers a three-phase one-dimensional soil column:

\[ \frac{\partial}{\partial t} \left( \rho X + \theta c + \varepsilon Y \right) = \frac{\partial}{\partial z} \left[ \theta D \frac{\partial c}{\partial z} - \theta u c + D e_{\text{fi}} \frac{\partial Y}{\partial z} - J_p \right] - S_s - R_s \]  

where \( \rho \) (kg m\(^{-3}\)) is dry bulk density of the soil, \( X \) (kg kg\(^{-1}\)) is solid phase mass content, \( \theta \) (m\(^3\) m\(^{-3}\)) is volumetric water content, \( c \) (kg m\(^{-3}\)) is mass concentration in the liquid phase, \( D \) (m\(^2\) d\(^{-1}\)) is
the hydrodynamic dispersion coefficient, \( v \) (m d\(^{-1}\)) is flow rate of the pore water, \( \varepsilon \) (m\(^3\) m\(^3\)) is the volumetric air content, \( Y \) (kg m\(^{-3}\)) is concentration in the gas phase, \( D_{\text{eff}} \) (m\(^2\) d\(^{-1}\)) is the effective Fickian diffusion coefficient of gas in soil, \( J_r \) (kg m\(^2\) d\(^{-1}\)) is the pressure adjustment flux (Freijer and Leffelaar, 1996), \( S_\varepsilon \) (kg m\(^3\) d\(^{-1}\)) is rate of plant uptake of the pesticide, and \( R_s \) (kg m\(^3\) d\(^{-1}\)) is rate of transformation of the pesticide. The hydrodynamic dispersion coefficient is comprised of terms from molecular diffusion and dispersion due to mechanical mixing during advection:

\[
D = a_i D_o + L |v|
\]  

(6)

where \( a_i (-) \) is soil matrix factor quantifying reduction of diffusion in porous medium, \( D_o \) (m\(^2\) d\(^{-1}\)) is molecular diffusion coefficient in water, \( L \) (m) is dispersivity, and \( v \) (m d\(^{-1}\)) is flow rate of the pore water. The effective Fickian diffusion coefficient is calculated according to Bakker and Hidding (1970):

\[
D_{\text{eff},F} = a_g (\varepsilon - \varepsilon_o) D_{o,F}
\]  

(7)

where \( D_{o,F} \) (m\(^2\) d\(^{-1}\)) is the effective diffusion coefficient of gas in free air, \( a_g \) is an empirical parameter, and \( \varepsilon_o \) (m\(^3\) m\(^3\)) is the air content at a pressure head corresponding to the air-entry value.

Equilibrium sorption onto the soil solid phase is described with the Freundlich equation:

\[
X = K_F c^{1/n}
\]  

(8)

where \( K_F \) (m\(^{3/n}\) kg\(^{-1/n}\)) is the Freundlich sorption coefficient and \( 1/n \) is the Freundlich exponent. The Freundlich coefficient is calculated from the coefficient for distributing the substance over organic matter and water, \( K_{om} \) (m\(^3\) kg\(^{-1}\)) (Boesten and van der Linden, 1991):

\[
K_F = f_{om} K_{om} c_e^{1-1/n}
\]  

(9)

where \( f_{om} \) (kg kg\(^{-1}\)) is the mass fraction of organic matter, and \( c_e \) (kg m\(^3\)) is the concentration at which \( K_F \) has been calculated (usually 1 g m\(^3\)). The dissolved and gaseous phases are assumed to be in equilibrium in accordance with Henry’s law:

\[
Y = K_H c
\]  

(10)

where \( K_H \) (m\(^3\) m\(^3\)) is the Henry coefficient.
The transformation of a pesticide in the soil, \( R_s \), is described with a first-order rate equation (Boesten and van der Linden, 1991):

\[
R_s = f_T f_p f_z \frac{\ln(2)}{DT_{so}} c^*
\]

(11)

where \( f_T, f_p \) and \( f_z (-) \) are reduction factors accounting for the influence of temperature, soil-water pressure head and depth in soil, \( DT_{so} (d) \) is the disappearance half-life under reference conditions (i.e. measured in freshly sampled top-soil at a temperature of 293 K, and at a soil water pressure head of -1 m), and \( c^* (kg \ m^{-3}) \) is the total content of pesticide in the soil system.

The reduction factors are described by:

\[
f_T = \exp(\gamma (T - T_{ref}))
\]

(12)

and

\[
f_p = \min\left(1, \left(\frac{h_{ref}}{h}\right)^B\right)
\]

(13)

where \( B (-) \) and \( \gamma (K^{-1}) \) are empirical parameters, \( T (K) \) is prevailing soil temperature, \( T_{ref} (K) \) is reference temperature (293 K), \( h (m) \) is soil-water pressure head, \( h_{ref} (m) \) is reference soil-water pressure head (usually -1 m), and \( \min \) refers to 'minimum of'. The depth-in-soil function, \( f_z \), accounting for depth distribution of microbial activity, is described through a table.

The uptake rate of a pesticide by plant roots from soil, \( S_s \), is described by:

\[
S_s = f_{uc} S_u c
\]

(14)

where \( f_{uc} (-) \) is an empirical transpiration stream concentration factor, \( S_u (d^{-1}) \) is the sink term accounting for water uptake by plant roots, and \( c (kg \ m^{-3}) \) is mass concentration of pesticide in the liquid phase.

Before the first rainfall, the pesticide is assumed to reside in a thin surface film. Volatilization of pesticide from this thin surface layer is assumed to occur by vapor diffusion through a stagnant air boundary layer of thickness \( d (m) \), above which the chemical concentration is zero (Jury et al., 1990). The mass balance for the surface film can be simplified to:

\[
\frac{dC}{dt} = - \frac{J_s}{d}
\]

(15)
where $J_s$ (kg m$^{-2}$ d$^{-1}$) is the volatilization flux, which is calculated by

$$J_s = R_0^{-1} Y_s$$

(16)

where $R_0$ (d m$^{-1}$) is the transport resistance and $Y_s$ (kg m$^{-3}$) is the concentration in the gas phase. During the first rainfall, the pesticide is assumed to enter the soil, and the boundary condition becomes a known concentration at the soil surface. See Freijer et al. (1996) for details.

**Derivation of input data**

**Physical properties**

Soil hydraulic properties are represented in PESTRAS by the Mualem and Van Genuchten functions (Van Genuchten, 1980). The measured data were fitted to these functions, using a nonlinear optimization algorithm (Nelder and Mead, 1965). Parameter $I$ was not optimized. Instead, the average value derived by Mualem (Van Genuchten et al., 1991) was used. Although the saturated hydraulic conductivity was measured, it was not used. Instead, it was obtained by substituting the hydraulic conductivity at a pressure head of -1 m (which was also measured) into the optimized functions. In this way, the extreme variability due to macropore flow at saturation was avoided. Table 2 gives the parameters for the soil hydraulic properties.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>$\theta_s$ (m$^3$ m$^{-3}$)</th>
<th>$\theta_r$ (m$^3$ m$^{-3}$)</th>
<th>$\alpha$ (m$^{-1}$)</th>
<th>$n$ (-)</th>
<th>$K_s$ (m d$^{-1}$)</th>
<th>$I$ (-)</th>
<th>SSQR (m$^3$ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00-0.32</td>
<td>0.4495</td>
<td>0.0000</td>
<td>21.08</td>
<td>1.3358</td>
<td>0.50</td>
<td>0.5</td>
<td>3.56x10$^2$</td>
</tr>
<tr>
<td>0.32-0.60</td>
<td>0.4051</td>
<td>0.0000</td>
<td>4.97</td>
<td>1.4500</td>
<td>0.15</td>
<td>0.5</td>
<td>4.62x10$^2$</td>
</tr>
<tr>
<td>&gt; 0.60</td>
<td>0.2951</td>
<td>0.0000</td>
<td>2.41</td>
<td>1.9910</td>
<td>0.05</td>
<td>0.5</td>
<td>2.78x10$^2$</td>
</tr>
</tbody>
</table>

$\theta_s$ is saturated soil water content, $\theta_r$ is residual soil water content, $K_s$ is saturated hydraulic conductivity, $\alpha$, $n$, and $I$ are parameters, and SSQR is Sum of Squares of Residuals.

The dispersion length was initially set to 0.05 m, which is the average of values found by van Ommen et al. (1989). The soil bulk density was inferred from the data set, and is listed in Table 1. The pore volume, $\varphi$, was calculated by multiplying the saturated soil water content with a factor 1.2. This factor was included to account for the effect of residual air during soil
wetting (Freijer, 1994). The density of the soil solid phase, \( \rho_s \) (kg m\(^{-3}\)), was calculated by:

\[
\rho_s = \frac{\rho}{(1 - \phi)}
\]

(17)

The air content at the air-entry value, \( \epsilon_0 \), was calculated from \( \phi - \theta_a \), where \( \theta_a \) is the water content at a pressure head equal to the air-entry value (-1/a). Parameter \( a_q \) (Eqn. 7) was derived from Freijer (1994) and was set to 0.5.

**Crop related properties**

The reduction function for water uptake was set to 1 (no reduction) for \( h > -5 \) m, and decreased linearly to 0 between \( h = -5 \) m and \( h = -80 \) m. These values were based on a field study for maize (Boesten and Van der Linden, 1991). The Leaf Area Index was calculated from the observed soil coverage according to Belmans et al. (1983). Its maximum value was 5.42 m\(^2\) m\(^{-2}\) for mature winter wheat and 4.00 m\(^2\) m\(^{-2}\) for mature yellow mustard. The crop factor, \( f_c \), was taken from Feddes (1987). For full-grown winter wheat a crop factor of 1.2 was used, which declined to 0.6 after maturation of the crop. For yellow mustard, a crop factor of 1 was used. The root depth of the mature crops was set to -0.4 m. Root density was assumed to be constant with depth.

**Relationship between groundwater-level and drainage**

No information about the local hydrological situation was available in the data set, so parameter values for the relationship between groundwater-level and drainage could only be obtained by calibration. We used an automated calibration procedure in which the parameters were optimized by minimizing the sum of squares of residuals between the simulated and measured groundwater levels. PESTRAS was coupled to a program based on the Simplex optimization algorithm (Nelder and Mead, 1965). Approximately 250 runs were required to find the optimum parameter set. Although the Simplex algorithm is not very sensitive to local minima in the parameter space, we repeated the optimization with different initial parameter settings. The first guess of these parameters was taken from De Visser and De Vries (1989). They gave the following parameter
values for a sandy soil in Brabant: \( a_s = -0.00133 \) m d\(^{-1}\), \( b_s = -1.0 \) m\(^{-1}\), and \( c_s = -0.0003 \) m d\(^{-1}\).

**Bromide properties**

Bromide was assumed to be conservative with no interactions with the solid and gas phases, so the half-life was set to \(10^{10}\) days, and \( K_w \) and \( K_H \) were set to zero. The diffusion coefficient of bromide in water was set to \(1.6 \times 10^4\) m\(^2\) d\(^{-1}\) based on Weast (1974). Bromide was initially assumed not to be taken up by plants, thus the transpiration stream concentration factor \( f_{ws} \) was set to 0.

**Pesticide data**

Adsorption isotherms were determined at different temperatures with soil sampled from the topsoil (Boesten and Van der Pas, 1997). The sorption points available in the data set were fitted to the Freundlich model. Two different fitting procedures were used, i.e. linear regression of log-transformed data, and non-linear curve fitting. Table 3 summarizes the results of the fitting. Notice that there is a distinct difference between sorption of ethoprophos at 5 °C and 25 °C, both for \(1/n\) and \(K_w\). We decided to use the 5 °C sorption isotherm, as this temperature closely resembles field conditions at the time of pesticide application. Notice that the value of \(1/n\) is somewhat more affected by the fitting procedure than \(K_w\). Although the choice is arbitrary, we used the results from the non-linear curve fitting.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ethoprophos</th>
<th>Bentazone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log-transformed</td>
<td>Non-linear</td>
</tr>
<tr>
<td>(5^\circ\mathrm{C})</td>
<td>(25^\circ\mathrm{C})</td>
<td>(5^\circ\mathrm{C})</td>
</tr>
<tr>
<td>(K_w) (L kg(^{-1}))</td>
<td>59</td>
<td>88</td>
</tr>
<tr>
<td>(1/n)</td>
<td>0.83</td>
<td>0.90</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\(\dagger\) Calculated from \(K_c\) using the organic matter content of the topsoil

The rate of transformation in the topsoil was measured in the laboratory at 5 and 15 °C in the case of bentazone and 5, 15 and 25 °C in the case of ethoprophos. Soil, 50 g portions for the 0-25 cm layer and 100 g portions for the 50-100 and 100-200 cm layers were incubated for periods up to 450 days. Initial concen-
trations in the top layer soil sample were 5.7 mg kg\(^{-1}\) for etho-
prophos and 1.2 mg kg\(^{-1}\) for bentazone; for the deeper layers the
initial concentrations were 12 µg kg\(^{-1}\) and 120 µg kg\(^{-1}\), respec-
tively. Incubation jars were capped with Al-foil. Soil from the
100-200 cm layer was incubated under water-logged (5 mm
water layer) conditions. Redox measurements in the field
showed a fairly constant value of approximately 200 mV during
a 6 month period. The incubation method for the 100-200 cm
layer was chosen to approximate field conditions, i.e. to have
micro-aerobic to anaerobic conditions. First-order rate-
constants, \(k\) (d\(^{-1}\)), were calculated for each temperature using
two fitting procedures, i.e. linear regression of In-transformed
data and non-linear curve fitting. With the rate constants ob-
tained for different temperatures, parameter \(\gamma\) (Eqn. 12) had to
be calculated according to Boesten and Van der Linden (1991).
Finally, the half-life at 20 °C was calculated with Eqn. 12. Trans-
formation in the subsoil was measured at one temperature only
(10 °C), so the half-life in the subsoil at 20 °C was calculated us-
ing parameter \(\gamma\) for the topsoil. Results shown in Table 4 indi-
cate that the calculated half-lives were strongly affected by the
fitting procedure. This is caused by the large scatter in the data-
points as shown by Boesten and Van der Pas (1997): In the case
of linear regression on In-transformed data, lower points are
given relatively more weight, whereas the opposite is true for
non-linear curve fitting. As the choice is rather arbitrary we
performed simulations with results from both fitting proce-
dures. The parameter \(\gamma\) was 0.126-0.170 for bentazone, which is
outside the range of 50 experiments reviewed by Boesten
(1986). Probably, the temperature of 5 °C chosen as the lower
range of temperatures in the transformation experiment was
outside the range for which the Arrhenius equation applies, re-
sulting in an overestimation of \(\gamma\). For ethoprophos, parameter \(\gamma\)
was close to the average value reported by Boesten (1986). The
depth-dependence of transformation is rather curious. Lowest
transformation rates were found in the middle soil layer for
both pesticides. Independent incubation studies with 2,4D [(2,4-
dichlorophenoxy)-acetic acid] and acetate showed the same
general depth-dependence of transformation (Bogte, personal
communication, 1997), so an experimental artifact could be ex-
cluded.
Parameter $B$ describing the pressure head dependence of the transformation rate was set to 0.25 (Boesten, 1986). Notice that parameter $B$ was originally obtained for the relationship $f_0 = (\theta/\theta_{ref})^B$. We converted the value given by Boesten (1986) to the value required in Eqn. 13 using the measured water retention characteristic.

The transpiration stream concentration factor for pesticide uptake, $f_{uc}$, was initially set to 0.5, which is the average of values reported in Briggs et al. (1982). As the range of probable values for $f_{uc}$ is considerable, it is considered a calibration parameter. For ethoprophos the range is 0-1 as it is a non-ionic substance. Bentazone, on the other hand, is an ionic substance, so the range to be considered is as large as 0-3 (Van den Bosch and Boesten, 1994).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ethoprophos</th>
<th>Bentazone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In-transformed</td>
<td>Non-linear</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>$V$</td>
<td>0.094</td>
<td>0.094</td>
</tr>
<tr>
<td>$DT_{sp}$ A layer (d)</td>
<td>105</td>
<td>83</td>
</tr>
<tr>
<td>$DT_{sp}$ B layer (d)</td>
<td>186</td>
<td>210</td>
</tr>
<tr>
<td>$DT_{sp}$ C layer (d)</td>
<td>146</td>
<td>125</td>
</tr>
</tbody>
</table>

† Molar energy of activation in Arrhenius equation
‡ At $T = 20\, ^\circ C$

The diffusion coefficients of ethoprophos and bentazone in water were estimated to be $3.5 \times 10^{-5} \, m^2 \, d^{-1}$ (Van den Bosch and Boesten, 1994). The effective diffusion coefficient of pesticide in free air was estimated at $0.4 \, m^2 \, d^{-1}$ (Freijer et al., 1996). The Henry coefficient was calculated from the water solubility and saturated vapor pressure published by Tomlin (1990). Its value was $6.1 \times 10^{-8} \, m^3 \, m^{-3}$ for ethoprophos and $7.9 \times 10^{-8} \, m^3 \, m^{-3}$ for bentazone. Following Jury et al. (1990) surface volatilization is simulated using a stagnant air boundary layer thickness, $d$, of 0.005 m. The surface resistance for volatilization was initially set to $10 \, d \, m^3$. Its final value was obtained by calibration.

Model calibration
Calibration is necessary for parameters that cannot be measured independently. Model calibration may also be necessary
APPLICATION OF THE PESTRAS MODEL

when only generic (i.e. not site specific) model parameters are available. In the present study, only a limited number of parameters were obtained by calibration. Moreover, a logical sequence for calibration was adapted based on the strength of interactions between hydrology, soil chemical transport and pesticide behavior. Table 5 shows the parameters that were calibrated.

When comparing the model predictions with the observed data, both qualitative and quantitative techniques were employed. Quantitative techniques try to express the agreement between model and data numerically, while qualitative techniques are based on (subjective) visual inspection of the results. As indicated by Janssen and Heuberger (1995) results from both techniques should be interpreted with due care, and only a combination of both techniques is bound to be successful. In this study we used two performance measures, i.e. the Normalized Root Means Square Error (NRMSE) and the Modeling Efficiency (ME):

\[
NRMSE = \sqrt{\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n}}
\]

(18)

\[
ME = \frac{\sum_{i=1}^{n} (O_i - \bar{O})^2 - \sum_{i=1}^{n} (P_i - \bar{P})^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2}
\]

(19)

Table 5
Pestras parameters that were calibrated.

<table>
<thead>
<tr>
<th>#</th>
<th>Parameter</th>
<th>Description</th>
<th>Calibration criterion</th>
<th>Eqn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$a_p$, $b_p$, and $c_p$</td>
<td>Groundwater level-drainage parameters</td>
<td>Groundwater-level</td>
<td>(3)</td>
</tr>
<tr>
<td>2</td>
<td>$\theta_s$</td>
<td>Saturated water content</td>
<td>Water content</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$L$</td>
<td>Dispersion length</td>
<td>Bromide content</td>
<td>(6)</td>
</tr>
<tr>
<td>4</td>
<td>$f_{\text{up,b}}$</td>
<td>Uptake factor for bromide</td>
<td>Bromide content</td>
<td>(14)</td>
</tr>
<tr>
<td>5</td>
<td>$R_v$</td>
<td>Transport resistance</td>
<td>Total mass of pesticide</td>
<td>(16)</td>
</tr>
<tr>
<td>6</td>
<td>$f_{\text{uc,pesl}}$</td>
<td>Uptake factor ethoprophos and bentzone</td>
<td>Pesticide content</td>
<td>(14)</td>
</tr>
</tbody>
</table>
where $P_i$ and $O_i$ denote the predicted value and observed value respectively, $\bar{O}$ and $\bar{P}$ are their means, and $n$ is the number of observations. The Normalized Root Mean Square Error expresses the spread around the measurements, while the Modeling Efficiency indicates whether the model describes the data better than simply the average of the predictions. Optimal values are zero and one, respectively.

Results and Discussion

Hydrology

Measurements of groundwater levels and soil water contents were available for comparison with the simulations. These data and the simulation results are presented in Figures 1 and 2. Statistical performance measures are presented in Table 6.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRMSE</td>
<td>0.2401</td>
<td>0.0858</td>
<td>0.0899</td>
<td>0.3594</td>
<td>0.2808</td>
</tr>
<tr>
<td>ME</td>
<td>-0.3069</td>
<td>0.8331</td>
<td>0.8210</td>
<td>-0.0544</td>
<td>0.3563</td>
</tr>
</tbody>
</table>

Run 1: Before calibration; Run 2: Relationship between groundwater level and drainage adjusted; Run 3: profile description adjusted.

Model parameters for the first run are given in the section on model inputs. Both Figure 1 and Table 6 show that there is considerable disagreement between the simulated and measured groundwater levels. This is not surprising, because we started with generic relationships between groundwater level and drainage (De Visser and De Vries, 1989). As there was no information on the local hydrological situation, parameters for this relationship could only be obtained by calibration. We decided to use an automated calibration procedure as described in the section on model inputs. Final optimized parameters were $a = -0.042$ m d$^{-1}$, $b = -3.8$ m$^{-1}$, and $c = -0.001$ m d$^{-1}$. The simulation of groundwater levels is now quite reasonable, both statistically and derived from qualitative judgement. Notice that the model does not reproduce the peak around day 100, and that there is almost no rainfall preceding this groundwater rise. Probably, an external factor has caused this particular rise.
Figure 1
Measured and simulated groundwater levels. Run 1: Before calibration; Run 2: groundwater level-drainage relationship adjusted; Run 3: profile description adjusted.

Table 6 shows that soil water contents were overestimated in the 0.3-0.6 m layer. This implies that the measured water retention characteristics are not representative for the field profile. The reason for this may be that the samples for the determination of the water retention characteristics were too small to be representative for the field soil. The measured saturated soil water content for the second layer was almost as high as that of the upper soil layer (Table 2). In the same time, both the profile description and measurements of the organic matter content indicate that it is rather improbable for the hydraulic properties of the middle soil layer to resemble those of the topsoil. Therefore, we decided to perform a third run using a two-layer hydraulic system, i.e. the 0.3-0.6 m layer was given the same hydraulic properties as the lower soil layer. Figure 2 shows that there is considerable improvement of the simulated soil water contents. Notice that the groundwater levels were almost not affected by dropping the second layer.

Although there remain some differences between the model predictions and the observations, further calibration was not carried out. The reason for this is that soil water contents were measured at a limited number of times, so that it was difficult to judge model response in terms of temporal variability. Moreover, the aim of the application of the hydrological part of the model was not to provide a pure fit to the measured data.
but to quantify the most important water balance components. Table 7 shows that the water balance was hardly affected by the calibration procedure. Also the occurrence of unfavorable conditions for pesticide transformation was not or hardly affected, as indicated by the time-integrated average value of parameter $f_p$ in Eqn. 13.

**Figure 2**
Simulated and measured soil water profiles at 1, 103, 278 and 474 days after application. See description of figure 1 for explanation of model runs.

**Bromide**
There are two calibration parameters relevant to bromide transport, i.e. the dispersion length, $L$, and the transpiration concentration stream factor, $f_{icr}$. As a first step we optimized the dispersion length. The range considered was 0.025-0.10 m, which is the range given by Van Ommen et al. (1989). Table 8 gives the simulated and observed bromide profiles at 103 and 278 days after application. The lower and upper bounds of the observed values are the approximate 95% confidence intervals, calculated by subtracting and adding 2.13 times the standard error of the average observed concentration. As the overall performance could not objectively be judged from graphical comparison, we decided to rely fully on the statistical performance measures listed in Table 8. From these measures it followed that a dispersion length of 0.075 m could best be used in the rest of the simulations. This value is somewhat higher than the value

<table>
<thead>
<tr>
<th>Day</th>
<th>Soil water content ($m^3 m^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Simulated profile" /></td>
</tr>
<tr>
<td>103</td>
<td><img src="image2" alt="Simulated profile" /></td>
</tr>
<tr>
<td>278</td>
<td><img src="image3" alt="Simulated profile" /></td>
</tr>
<tr>
<td>474</td>
<td><img src="image4" alt="Simulated profile" /></td>
</tr>
</tbody>
</table>

95% confidence interval of observations run 1 run 2 run 3

...
Table 7
Overview of results from the hydrological submodel.

<table>
<thead>
<tr>
<th>Run</th>
<th>Components of the water balance (mm)</th>
<th>$f_t$ (-) $\S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P$</td>
<td>$ET$</td>
</tr>
<tr>
<td>1</td>
<td>768</td>
<td>616</td>
</tr>
<tr>
<td>2</td>
<td>768</td>
<td>616</td>
</tr>
<tr>
<td>3</td>
<td>768</td>
<td>616</td>
</tr>
</tbody>
</table>

† See description of table 6 for explanation of model runs.
‡ Calculated for the period November 22, 1990 until March 9, 1992. $P$ is precipitation; $ET$ is reference evapotranspiration; $E_r$ is actual transpiration; $q_{25}$ is drainage at 0.25 m depth; $q_{50}$ is drainage at 0.5 m depth; $q_{100}$ is drainage at 1 m depth; $\Delta W$ is Storage change.
§ $f_t$: Pressure head dependence of pesticide transformation (Eqn. 13).

Table 8
Statistical performance measures and mass balance for the bromide simulations.

<table>
<thead>
<tr>
<th>$L$ (m)</th>
<th>$f_w$ (-)</th>
<th>NRMSE †</th>
<th>$ME$ †</th>
<th>Mass balance (% of dose) †</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$f_{wp}$</td>
</tr>
<tr>
<td>Case A: Effect of dispersion length, $L$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>0.5</td>
<td>2.9</td>
<td>0.28</td>
<td>16.5</td>
</tr>
<tr>
<td>0.050</td>
<td>0.5</td>
<td>2.4</td>
<td>0.53</td>
<td>22.4</td>
</tr>
<tr>
<td>0.075</td>
<td>0.5</td>
<td>2.0</td>
<td>0.68</td>
<td>24.9</td>
</tr>
<tr>
<td>Case B: Effect of transpiration concentration stream factor, $f_w$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>0.0</td>
<td>2.0</td>
<td>0.68</td>
<td>0.0</td>
</tr>
<tr>
<td>0.075</td>
<td>0.5</td>
<td>2.0</td>
<td>0.68</td>
<td>24.9</td>
</tr>
<tr>
<td>0.075</td>
<td>1.0</td>
<td>2.0</td>
<td>0.68</td>
<td>30.2</td>
</tr>
</tbody>
</table>

† Calculated for 1, 103, 278 and 474 days after application. 
‡ $f_{wp}$ is fraction taken up; $f_l$ is fraction leached; $f_{sys}$ is fraction left in upper meter

APPLICATION OF THE PESTRAS MODEL

used by Tiktak et al. (1996a,b) in regional-scale simulations of pesticide leaching.

In a second step the transpiration concentration stream factor was calibrated. Also these results are given in Figure 3 and Table 8. Table 8 shows that the statistical performance measures were not affected by $f_{wp,Br}$. Figure 3, however, shows considerable differences between model results for day 278. From this graph it follows that bromide concentrations were seriously overestimated in the 0.15-0.45 m soil layer when $f_{wp,Br}$ was set to zero. The predictions for day 103 were not sensitive to $f_{wp,Br}$ as this is a winter situation with almost no water uptake. Notice that the observations show elevated concentrations of bromide in the upper soil layer that are not predicted by the model. This is most probably due to physical non-equilibrium conditions
resulting from diffusion limited mass-transport (Biggar and Nielsen, 1962).

Table 8 shows the mass balance for the five model runs. The effect of the dispersion length on the mass balance is considerable. Apparently, a slightly different distribution of bromide yields a significant difference in bromide uptake. Notice that a considerable fraction of the total dosage of bromide was taken up. This complicates the interpretation of bromide profiles in a cropped field situation. Nevertheless, the agreement between the model and the observations indicates that preferential flow is of limited importance for this field soil. This confirms the observations by Hamminga et al. (1994) who did not find indications for fingered flow, despite the fact that the soil was known to be water-repellent.

**Ethoprophos**

As discussed before, different values for $DT_{50}$ and $K_{om}$ may be derived from the experimental data. Although arbitrarily, we decided to use pesticide properties obtained by non-linear curve fitting, so $DT_{50}$ was set to 83 d and $K_{om}$ to 63 L kg$^{-1}$. The only calibration parameter was the transport resistance for surface volatilization, $R_s$. This parameter was fitted using the observed areic mass of pesticide in the soil system. Its optimized value was $1.4 \times 10^4$ d m$^{-1}$. Results are shown in Table 9 and Figure 4.
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Figure 4 shows a rapid decrease of ethoprophos due to surface volatilization directly after application. This fast decrease stops after the first rainfall, and almost 60% of the applied dose has than disappeared (Table 9). This implies that a significant fraction of surface applied pesticides may disappear by volatilization, even if they are only moderately volatile ($10^6 < K_H < 10^5$). Ignorance of this process will thus overestimate the leaching of pesticides. However, although the model is able to reproduce the observed fast decrease of ethoprophos, predictions of surface volatilization remain too uncertain to be applied for regional-scale modeling. The major restriction is that not enough experimental data are available for a reliable parameterization of this submodel. Moreover, the transport resistance is highly dependent upon the atmospheric conditions after application (Jury et al., 1990; Freijer et al., 1996).

Both the measurements and the model indicate that there was no ethoprophos below 0.3 m depth at the end of the experiment, so the leaching potential of ethoprophos is negligible. Nevertheless, the move-met of ethoprophos is slightly overestimated (Figure 4). This may be caused by the adsorption in the field being stronger than expected on the basis of 24-h equilibrium isotherms obtained in the laboratory. A possible explanation is that sorption in soils is a non-instantaneous process.
(Boesten and Van der Pas, 1983; Ma et al., 1996) resulting in an increase of the distribution coefficient with time (Pignatello and Huang, 1991). The latter authors showed that the distribution coefficient was approximately 2 to 40 times greater than the 24-h $K_o$, depending on the time after application.

The model reproduced the areic mass of ethoprophos until 214 days after application (Figure 4). From this day onwards, the model overestimated the residual mass. As transformation is the most important loss pathway for ethoprophos during the later stages of the experiment (Table 9), it can be concluded that this is caused by underestimation of the rate of transformation. There are a number of explanations for this phenomenon. First, the pressure head dependency of transformation may have been overestimated. The occurrence of low soil-water pressure heads coincides with the time that model predictions started to deviate from the measured areic mass. A run with $f_p$ set to zero, however, showed almost no difference with the presented results. An alternative explanation is accelerated transformation due to adaptation of the microbial population. Smelt et al. (1987) found higher rates of transformation of ethoprophos from annually treated soils compared with soils not previously treated. As PESTRAS does not account for this effect, this hypothesis could not be tested.

Four simulations were done to show the effect of different fitting procedures for calculating $DT_{50}$ and $K_{om}$ (see section on model inputs). Figure 4 shows limited differences between the four model runs. This is due to the fact that both $K_{om}$ and $DT_{50}$ were in a range where according to an earlier sensitivity analyses (Tiktak et al., 1994b) model output was relatively insensitive to variations of these parameters.

### Table 9

<table>
<thead>
<tr>
<th>$K_{om}$ (L kg$^{-1}$)</th>
<th>$DT_{50}$ (d)</th>
<th>NRMSE †</th>
<th>$ME$ †</th>
<th>Mass balance (% of dose) ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$f_{vol}$</td>
</tr>
<tr>
<td>63</td>
<td>83</td>
<td>0.768</td>
<td>0.169</td>
<td>59.2</td>
</tr>
</tbody>
</table>

† Calculated for 1, 103, 278 and 474 days after application.
‡ $f_{vol}$ is fraction volatilized; $f_{trans}$ is fraction transformed; $f_{sys}$ is fraction taken up; $f_r$ is fraction left in system; $f_r$ is fraction leached from the upper meter of the soil profile.
Bentazone
As with the ethoprophos simulations, pesticide properties obtained by non-linear curve fitting were used, so \( K_{ow} \) was set to 2.8 L kg\(^{-1} \) and \( DT_{50} \) was set to 16 d. With the \( R_v \) values obtained in the ethoprophos simulations, the surface volatilization fluxes of bentazone were negligible. Therefore, to speed-up the calculations the gas transport submodel was switched off.

Simulated and measured concentration profiles are shown in Figure 5. Generally, the model results are within the approximate 95% confidence intervals of the observations. Both the model and the observations indicate significant transport of bentazone to the subsoil compared to ethoprophos. Approximately 30% of the applied dose leached below the depth of 1 m (Table 10). At 214 days after application the model overestimated the bentazone concentration in the topsoil. At the end of the experiment (day 474) all bentazone was removed from the system according to the observations while the model still predicted some bentazone to be present in the soil system.

The most important loss pathway for bentazone is transformation (Table 10). The depth dependence of transformation as derived from the laboratory incubation experiments (Table 4) is in contradiction with the standard application of PESTRAS (Tiktak et al., 1996a,b) where no transformation below 1 m was assumed, based on literature data (Boesten and Van der Linden, 1991). As a result, the model calculated a significant fraction of bentazone (21% of the applied dose) to be removed by transformation from the 1-2 m soil layer. The laboratory experiments indicated no transformation in the 0.5-1 m soil layer. The already mentioned overestimation of the calculated bentazone concentration at 474 days after application probably results from transformation rates being underestimated for this particular soil layer. To check this, an additional simulation was performed with \( f_j \) set to 0.25 between 0.5 and 1 m depth. Results indicate better agreement at the end of the experiment (Figure 5), but at day 278 the calculated concentration profile diverged from the average measured concentration. It can be concluded that the simulations do not contradict the results from the incubation experiments. An explanation for the curious depth dependence of transformation cannot be found in the literature. A possible explanation could be that in this soil there are two distinct microbiological populations: In the topsoil, bentazone is
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transformed aerobically, while in the 1-2 m soil layer bentazone is primarily transformed by micro-aerophilic or anaerobic organisms. In the middle soil layer, where aerobic and anaerobic conditions alternate, none of the two populations may have been adjusted.

Table 10
Statistical performance measures and mass balance for the three model runs described in the section on bentazone.

<table>
<thead>
<tr>
<th>f_r (-) †</th>
<th>f_u (-) †</th>
<th>NRMSE ‡</th>
<th>ME ‡</th>
<th>Mass balance (% of dose) § ¶</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.5</td>
<td>2.055</td>
<td>0.414</td>
<td>0.0 66.7 23.3 10.1 30.4</td>
</tr>
<tr>
<td>0.25</td>
<td>0.5</td>
<td>2.139</td>
<td>0.430</td>
<td>0.0 73.4 21.0 5.6 23.5</td>
</tr>
<tr>
<td>0.00</td>
<td>2.0</td>
<td>1.987</td>
<td>0.511</td>
<td>0.0 59.8 30.9 9.3 29.6</td>
</tr>
</tbody>
</table>

† f_r for the 0.5-1.0 m soil layer. Other values not adjusted.
‡ Calculated for 1, 103, 278 and 474 days after application.
§ f_r vd is fraction volatilized; f_r r is fraction transformed; f_r ut is fraction taken up; f_r s is fraction left in system; f_r l is fraction leached from the upper meter of the soil profile.
¶ Notice that the sum is not 100%, because the system considered was 0-2 m.

The overestimation of bentazone contents in the root zone at day 278 is likely to be caused by underestimation of the transpiration concentration stream factor, f_u. As bentazone is an ionic substance, f_u is highly uncertain. Shone and Wood (1974), for example, empirically derived a f_u value of 3.1 for the 2,4 D anion, so preferential uptake of bentazone cannot be excluded. An additional simulation with f_u set to 2 was carried out to test this hypothesis. Figure 5 and Table 10 indeed show that the model performed better with a higher f_u value. Notice that although the fraction of bentazone taken up increased, the fraction leached below 1 m was hardly affected due to competition between transformation and uptake. This phenomenon was already reported by Tiktak et al. (1996b).

With the transpiration concentration stream factor set to 2, the effect of fitting procedures in the interpretation of laboratory experiments was analyzed. As the differences were minor, results are not presented here. The marginal differences were caused by the fact that the higher value of γ was compensated for by a lower value of DT50. This resulted in almost equal transformation rates in the temperature range 5-15 °C.
Simulated and observed concentration of bentazone as a function of depth at 103, 278 and 474 days after application.

Effect of calibration procedure on major indices of pesticide behavior

Although in this study PESTRAS was used as a plot-scale pesticide transport assessment tool, it was primarily developed for simulating pesticide leaching on a regional-scale (Tiktak et al., 1996a,b). It is therefore interesting to quantify the effect of the calibration procedure on indices of pesticide leaching and accumulation, i.e. the maximum concentration of pesticide in the 1-2 m soil layer ($c_{max}$) and the residual fraction in the plough layer at one year after application ($f_{rp}$). To accomplish this, a number of simulations were carried out with generic parameter values instead of the calibrated or on-site measured parameter values. Results are shown in Table 11.

The use of generic pesticide degradation parameters had a major impact on both the residual fraction of ethoprophos and the maximum concentration of bentazone. With default values for the half-life, the accumulation of ethoprophos was underestimated by a factor 7. With default values for the temperature dependence of transformation, the leaching of bentazone was also underestimated, but it was overestimated when default values for the depth-dependence of transformation were used. Generic pesticide properties are usually averages of values obtained from a series of laboratory-studies with a considerable standard deviation. The default half-life of ethoprophos, for ex-
Table 11
Effect of using generic data instead of on-site measured or calibrated data on the maximum concentration of pesticide in the shallow groundwater (\(c_{\text{max}}\)) and the fraction of pesticide in the plough layer (\(f_{\text{p}}\)).

<table>
<thead>
<tr>
<th>#</th>
<th>Parameter considered</th>
<th>Ethoprophos</th>
<th>Bentazone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Site specific data</td>
<td>0.00</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.7</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>(pF, K(h)) by transfer function</td>
<td>0.00</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.1</td>
<td>0.07</td>
</tr>
<tr>
<td>3</td>
<td>(a_{\alpha}, b_{\alpha}, c_{\alpha}) from the literature</td>
<td>0.00</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.0</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>(L) set to 0.05 m (default value)</td>
<td>0.00</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.2</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>(K_{\alpha}) from default database</td>
<td>0.00</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.2</td>
<td>0.02</td>
</tr>
<tr>
<td>6</td>
<td>(DT_{50}) from default database</td>
<td>0.00</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>0.04</td>
</tr>
<tr>
<td>7</td>
<td>(\gamma) set to 0.08 (default value)</td>
<td>0.00</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.3</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>(f_{\alpha}) set to 0.5 (default value)</td>
<td>0.00</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.5</td>
<td>0.01</td>
</tr>
<tr>
<td>9</td>
<td>(f_{\gamma}) set to 0.5 (default value)</td>
<td>0.00</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.7</td>
<td>0.16</td>
</tr>
<tr>
<td>10</td>
<td>(f_{z}) set to default values</td>
<td>0.00</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.7</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Some other parameters (dispersion length, transpiration concentration stream factor) affected the two indices, but to a far lesser extent. Conclusions on the effect of these parameters, however, must be made with care. The transpiration concentration stream factor, for example, may be much more important for pesticides that are applied in spring. Also the effect of the relationship between the groundwater level and drainage on bentazone leaching is ambiguous: The effect is such that the peak concentration is not affected, but with generic groundwater level-drainage relationships the peak concentration is retarded due to slower downward transport.
Conclusions

For the soil and conditions in this field-study, the PESTRAS model is found to predict the movement of a non-adsorbed compound (bromide) and two pesticides (ethoprophos and bentazone) reasonably well when site-specific parameter values were used. When generic parameter values were used, the model predictions sometimes deviated strongly from the observed data. This implies that predictions of pesticide leaching on a regional-scale as carried out by Tiktak et al. (1996a,b) should always be accompanied by estimations of confidence intervals obtained by appropriate uncertainty analyses (Loague et al., 1996).

The observed bromide profiles could only be reproduced if it was assumed that a considerable fraction of the applied bromide was taken up. This complicated the interpretation of the observed bromide profiles in this cropped field-soil. Nevertheless, the bromide simulations showed that the convection-dispersion model was able to describe the observed concentration profiles, indicating that preferential flow was not an important process in this sandy soil.

Almost 60% of the applied dose of ethoprophos volatilized directly after application. Although PESTRAS was able to reproduce this observed fast decrease of ethoprophos, predictions of volatilization of surface applied pesticides remain too uncertain to be applied for regional-scale modeling. Not enough data are available for a reliable parameterization of this submodel, so there is an urgent need for research in this field. Both the simulations and the observations indicated that there was no ethoprophos below 0.3 m depth, so the leaching potential was negligible. The movement of ethoprophos was slightly overestimated, probably due to ignoring long-term sorption kinetics. Transformation rates were reasonably described until 214 days after application. From that day onwards, transformation in the field was faster than predicted, probably due to adaptation of the microbial population.

The concentration profiles of bentazone could only be explained if it was assumed that bentazone was taken up preferentially ($f_{ur} > 1$). The effect of uptake on leaching, however, was negligible due to competition between transformation and uptake. With the on-site measured atypical depth-dependence of
transformation, we could reproduce the observed bentazone profiles. The model calculated almost 30% of the applied bentazone to leach below 1 m depth. However, almost 20% of the total dose disappeared from the 1-2 m soil layer by transformation under micro-aerobic to anaerobic conditions. As anaerobic transformation is a key process in the predicting the risk of contamination of drinking-water wells by pesticides, research of transformation in the saturated zone is required. The occurrence of bentazone in some drinking-water wells (Versteegh et al., 1995) at least indicates that anaerobic transformation does not always occur.

In this study, the procedure of deriving pesticide properties from the original sorption and dissipation data did not affect the simulations to a great extent. This conclusion, however, may not be generally applicable as indicated by for example Boekhold et al. (1993). With results from non-linear curve fitting or linear regression of In-transformed data they could either reject or validate the model. Work should be done to reduce subjectivity in deriving model inputs.

The conclusions in this paper pertain to the current application only. As PESTRAS is developed for simulating pesticide leaching on a regional-scale, the model must be evaluated in a broader range of soils, pesticides and hydrological conditions.
Application of Nine Pesticide Leaching Models to the Vredepeel Dataset. Pesticide Fate

Abstract

The performance of nine deterministic, one-dimensional, dynamic pesticide leaching models with different complexity was evaluated using a field experiment with bentazone and ethoprophos on a humic sandy soil with a shallow groundwater table. All modelers received an extensive description of the experimental data. Despite this fact, the interpretation of the experimental data was ambiguous, leading to tremendous user dependent variability of selected model inputs. Together with the fact that most modelers calibrated at least part of their model, the possibility for evaluating model concepts was limited. In the case of bentazone, most model predictions were within the 95% confidence intervals of the observations. In the case of ethoprophos, model performance was often poor due to the ignorance of volatilization, kinetic sorption and adaptation of the microbial population. Most models were calibrated using on-site measured data, limiting the possibility for extrapolation for policy-oriented applications.

Introduction

Pesticide residues were found in groundwater all over Europe (Leistra and Boesten, 1989) and the United States (Hallberg, 1989). Agriculture is a dominant source of these pesticide residues. Although the environmental hazard associated with the observed environmental concentrations is poorly defined, it is generally accepted that leaching losses within agricultural fields should be minimized.

The fate of pesticides in the soil is determined by a considerable number of processes, such as solute transport, degradation, sorption, plant-uptake, and volatilization. The interaction between these processes is complex and non-linear (Boesten, 1991; Tiktak et al., 1994b), making the use of mechanistic pesticide fate models in quantitative groundwater management indispensable. The use of these models for registration purposes and regional-scale assessments, however, is hampered by the short-
age of sufficiently detailed experimental data to allow appropriate validation tests. The resulting low validation status of most pesticide leaching models is a critical issue. An aspect that has not received much attention in model evaluation is the level of variation in model outputs introduced by user-dependent subjectivity during derivation and selection of model input parameters (Brown et al., 1996; Boesten, 1999).

The main objective for the study presented in this paper was to evaluate and compare the ability of a number of well-established pesticide leaching models to simulate the movement and distribution of two pesticides in the soil system. Specific attention was given to user-dependent subjectivity during derivation of model input parameters. The models were applied to a dataset collected from a field experiment in a humic sandy soil near Vredepeel, the Netherlands (Boesten and Van der Pas, 1999). This paper deals with the pesticide behavior part of the models, the waterflow and solute transport submodels are evaluated by Vanclooster and Boesten (1999).

Materials and Methods

The models
A total number of nine pesticide leaching models was considered in this comparison study (Table 1). All models were deterministic, dynamic, one-dimensional, multi-layer in their approach. All processes required for a proper description of pesticide fate were incorporated into the models. The models differed mainly in the complexity by which the various processes are modeled.

Waterflow is the main medium by which the pesticide is transported, so a proper description of waterflow is required. Basically, there are two approaches to describe water flow through the soil matrix. In the physically based approach, waterflow is described by Richard’s equation where waterflow is determined by hydraulic gradients and a hydraulic conductivity function (LEACHM, PESTLA, PESTRAS, MACRO and WAVE). The second more simple approach, which is used in the other models, does not consider hydraulic gradients. In these capacity models drainage only occurs above a user-specified soil water content. Disadvantage of most capacity models is their inability
APPLICATION OF NINE PESTICIDE LEACHING MODELS

to deal with upward fluxes and groundwater tables. MACRO is the only model dealing with macropore flow; none of the models deals with preferential flow in the soil matrix due to heterogeneous conditions. See Vanclooster and Boesten (1999) for details on waterflow.

Solute transport is either determined by taking the product of the soil water flux and the chemical concentration (VARLEACH and GLEAMS), or by solving the convection-dispersion equation (CDE; other models). The latter approach is more physically based, and considers an explicit description of the hydrodynamic dispersion and molecular diffusion coefficients. In models that do not explicitly simulate hydrodynamic dispersion, a correct combination of layer thickness and timestep must be used to obtain a numerical dispersion comparable to real dispersive fluxes.

In the simplest description of sorption, it is assumed that sorption is a reversible, linear, equilibrium process (GLEAMS, PRZM, MACRO and WAVE). In MACRO, the sorption sites are partitioned into a fraction that equilibrates with the macropores and another fraction that equilibrates with the soil matrix. The linear equilibrium approach requires only a few input parameters, i.e. the linear distribution coefficient (Kd), or a combination of the organic matter content (fom) and the coefficient for distributing the substance over organic matter or organic carbon and the soil liquid (Kom or Koc). LEACHM and PESTRAS also assume equilibrium sorption, but these models consider non-linear (Freundlich) sorption. These models require one extra input parameter, i.e. the Freundlich exponent, n, to describe the non-linearity of the sorption isotherm. VARLEACH, PELMO and PESTLA also consider kinetic (non-equilibrium) sorption.

All models consider the degradation process to obey first order kinetics. The most important input parameter is the degradation rate (rd) or the degradation half-life (DT50), which is often allowed to vary with depth, soil water content and temperature (see Table 1).

Plant uptake of pesticide is considered in all models except VARLEACH (in fact, VARLEACH does not consider the presence of crops at all). Plant uptake is assumed to be passive, that is uptake is proportional to the transpiration rate and the pesticide
### Table 1
Overview of models used in this study.

<table>
<thead>
<tr>
<th>Model</th>
<th>No. of modellers</th>
<th>Waterflow</th>
<th>Preferential flow</th>
<th>Solute transport</th>
<th>Sorption</th>
<th>Degradation</th>
<th>Plant uptake</th>
<th>Volatilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>VARLEACH v2.0</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Linear equilibrium and kinetic</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>GLEAMS v2.1</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Linear equilibrium and kinetic</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>PRZM v2</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Freundlich equilibrium and kinetic</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>PELMO v2.01</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Freundlich equilibrium and kinetic</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>LEACHM v3.1</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Freundlich equilibrium and kinetic</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

† 8 is soil water content, T is temperature, z is depth

Concentration. Four out of nine models (PRZM, PESTLA, PESTRAS and MACRO) incorporate a 'concentration stream factor' to account for selective uptake.

Transport in the gas phase and surface volatilization is accounted for in LEACHM and PESTRAS. In these models, volatilization is assumed to occur through a thin surface layer. The driving force is the concentration gradient of pesticide across this layer, and the concentration of the pesticide in the atmosphere above the layer is assumed to be zero. Input data are the Henry's law constant, the gas phase diffusion coefficient of the pesticide, and the surface resistance for volatilization.

**Evaluation procedure**

The models were compared with the observed total pesticide content profiles at three selected times (i.e. 103, 278 and 474 days after application; see Figure 1 and Figure 2). Using this information, the model predictions were mutually compared using a statistical performance indicator, which tries to express the agreement between model predictions and observations based on objective criteria. Various performance indicators exist (Janssen and Heuberger, 1995; Loague and Green, 1991) from which we choose the Modeling Efficiency (ME):
### Results and Discussion

#### Model parameterization

Table 2 and Table 3 show the range of pesticide dosages, sorption distribution coefficients and half-lives assumed by the models. The models differ in their assumptions and methods to calculate these parameters. Some examples of these methods include analytical recovery, field application rates, and laboratory measurements. The application rates are important as they affect the input to the models, which in turn affects the results. In the tables, the range of dosages and coefficients is shown, along with the model's assumptions for each parameter. The models also have different assumptions for water flow, preferential flow, and solute transport, which can affect the models' predictions of pesticide movement.

#### Reference

Boesten and Van der Linden, 1991
Leonard et al., 1987
Mullin et al., 1992
Klein, 1995

#### Waterflow

Richards
Richards
Richards
Richards

#### Preferential flow

no
no
yes
yes

#### Solute transport

CDE
CDE
CDE
CDE

#### Solute transport

Freundlich equilibrium
Freundlich equilibrium
Linear equilibrium
Linear equilibrium

#### Sorption

1st order, 8, T and z dependent
1st order, 8, T and z dependent
1st order, 8 and T dependent
1st order, 8 and T dependent

#### Degradation

CDE
CDE
CDE
CDE

#### Plant uptake

no
no
yes
yes

#### Volatilization

no
no
no
no

---

\[
ME = \frac{\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - \overline{P})^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2}
\]  

(1)

in which \(P_i\) and \(O_i\) denote the predicted value and observed value \(i\), \(\overline{O}\) and \(\overline{P}\) are their means, and \(n\) is the number of observations. The Modeling Efficiency indicates whether the model describes the data better than simply the arithmetic average of the observations. The optimal value is one. As indicated by Janssen and Heuberger (1995) results should be interpreted with care, and only a combination of statistical comparison and graphical representations is useful. In the graphs, the spread in the measurements was considered by plotting the lower and upper bounds of the 95% confidence intervals of the observations.
various modelers. The range of parameter values is listed per model. Despite the fact that all modelers used the same description of the experimental data, the table shows tremendous user-dependent variability of the selected model inputs. Variability is highest for the half-life in the subsoil, and lowest for the sorption coefficient in the topsoil. A first examination of the list of model parameters did not show a relationship between the general experience of the modeler in deriving pesticide properties and the parameter values chosen. The range of model inputs observed amongst the three most experienced experts in the field of pesticide modeling was as high as the range of values listed in Table 2 and Table 3.

Generally, there are three reasons for the extreme user-dependent variability of model inputs, i.e. (i) calibration of pesticide properties, (ii) use of literature data instead of measured data, and (iii) ambiguity in the interpretation of laboratory data. The first two in fact reflect different modeling strategies.

Some modelers calibrated pesticide properties. They justified this by the fact that the laboratory experiments did not necessarily represent processes occurring under field conditions. The microbial population, for example, may have been disturbed during sampling, so that field-degradation rates were higher than laboratory degradation rates. Some modelers believed that this was especially true for the subsoil where microaerobic to anaerobic conditions occurred. This explains why the range of half-lives is higher for the subsoil than for the topsoil.
The second reason for user-dependent variability is that some modelers used generic (literature) data for pesticide properties. They stated that fair statements about the predictive power of a model for pesticide registration purposes could only be made if the model was parameterized using generic data. The most important reason for user-dependent variability is that the interpretation of the experimental data is ambiguous. Some examples follow in the remainder of this chapter; however, other problems in data-derivation exist.

### Table 3

Overview of major model inputs for ethoprophos. The table shows the lowest and highest parameter values selected per model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Dose (kg)</th>
<th>( DT_{50} ) (d)</th>
<th>( K_f ) (L kg(^{-1}))</th>
<th>( n ) (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VARLEACH</td>
<td>3.0-3.35</td>
<td>132-219</td>
<td>2.7-3.6</td>
<td>1.0-1.0</td>
</tr>
<tr>
<td>GLEAMS</td>
<td>3.0-3.35</td>
<td>25-90</td>
<td>3.2-3.6</td>
<td>1.0-1.0</td>
</tr>
<tr>
<td>PRZM-2</td>
<td>3.0-3.35</td>
<td>17-157</td>
<td>1.8-4.3</td>
<td>1.0-1.0</td>
</tr>
<tr>
<td>PELMO</td>
<td>1.3-3.35</td>
<td>153-166</td>
<td>3.5-4.3</td>
<td>0.86-0.87</td>
</tr>
<tr>
<td>LEACHM</td>
<td>1.3-3.35</td>
<td>132-153</td>
<td>2.7-3.5</td>
<td>0.8-1.0</td>
</tr>
<tr>
<td>PESTLA</td>
<td>1.3</td>
<td>196</td>
<td>4.2</td>
<td>0.87</td>
</tr>
<tr>
<td>PESTRAS</td>
<td>3.35</td>
<td>212</td>
<td>3.2</td>
<td>0.81</td>
</tr>
<tr>
<td>MACRO</td>
<td>2.7-2.7</td>
<td>102-231</td>
<td>2.4-6.0</td>
<td>1.0-1.0</td>
</tr>
<tr>
<td>WAVE</td>
<td>1.3</td>
<td>83</td>
<td>9.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

| \( DT_{50} \) (d) of bentazone at 10 °C and field-capacity |
| \( K_f \) (L kg\(^{-1}\)) |
| \( n \) (-) |

- Calculation based on the concentration of the chemical in the spraying solution, the water flow rate and the speed of the spraying device (0.80 kg ha\(^{-1}\)),
- Estimation based on the mass recovered directly after application (0.63 kg ha\(^{-1}\)), or
- Calculation based on the mass recovered directly after application, but with correction for analytical recovery (0.73 kg ha\(^{-1}\)).

In the case of ethoprophos, some modelers used the dose recovered after 23 days to account for the rapid volatilization after application. From the models reviewed in this paper, only
PESTRAS, GLEAMS and LEACHM contain a description of surface volatilization.

Pesticide sorption parameters
Adsorption isotherms were determined at 5 and 15 °C (bentazone) and 5 and 25 °C (ethoprophos) with soil sampled from the topsoil (Boesten and Van der Pas, 1999). Subjectivity was introduced because one could either fit a sorption isotherm to the low-temperature sorption points, the high-temperature sorption points, or even fit all sorption points simultaneously. Further subjectivity was introduced by the possibility of using different fitting procedures. Tiktak et al. (1998c), for example, showed that non-linear curve fitting of the original data yielded different results than linear regression of log-transformed data (Table 4 in chapter 2.1). A final point of concern is how modelers parameterized their sorption isotherms for the subsoil. Most modelers used the $K_{oc}$ concept in which it is assumed that the distribution coefficient is proportional to the organic matter content. Some modelers, however, decided to use one distribution coefficient for the entire soil profile (see Table 2 and Table 3).

Degradation
The rate of transformation in the topsoil was measured in the laboratory at 5 and 15 °C in the case of bentazone and 5, 15 and 25 °C in the case of ethoprophos. Most modelers fitted first-order rate degradation constants for the individual temperatures, after which the temperature dependence of degradation was calculated; however, those people who used a model in which the half-life was independent of soil temperature usually decided to fit the 5 °C and 15 °C degradation points only. As shown by Tiktak et al. (1998c), the calculated half-lives and the molar activation energy in the Arrhenius equation were strongly affected by the fitting procedure (Table 5 in chapter 2.1). This is caused by the large scatter in the data-points as shown by Boesten and Van der Pas (1999): In the case of linear regression on ln-transformed data, lower points are given relatively more weight, whereas the opposite is true for non-linear curve fitting. The value of the molar energy of activation for bentazone is outside the range of 50 experiments reviewed by Boesten (1986) indicating that the temperature of 5 °C chosen as
the lower range of temperatures in the transformation experiment may have been outside the range for which the Arrhenius equation applies. Some modelers decided not to use this high activation energy and used model defaults, introducing yet another source of user-dependency. In the case of bentazone, further differences resulted from the fact that the laboratory degradation rates did not exactly meet the assumption of first-order rate kinetics. Some modelers fitted the rate constant to the initial, faster, degradation phase. Some models (e.g. MACRO) assume different degradation half-lives of pesticide in the soil solution and pesticide sorbed at the soil solid phase. As the experiments only consider the overall degradation rates, the derivation of such figures added additional subjectivity.

Subsoil degradation studies were carried out for the 50-100 and 100-200 cm soil layers. The degradation studies suggested very low degradation rates for the 50-100 cm soil layers, while the degradation rates for the deepest soil layer were almost as high as the topsoil degradation rates (Table 5 in chapter 2.1). Not all modelers trusted the experiments, so they decided to keep degradation constant with depth or they used default values for the depth dependence of transformation. However, independent incubation studies with 2,4D [(2,4-dichloro-phenoxy)-acetic acid] and acetate, carried out after most modelers already made their model runs, also suggested lower activity in the 50-100 cm soil layer.

**Model performance for bentazone**

Observed and simulated bentazone concentration profiles at 103, 278 and 474 days after application are shown in Figure 1, Table 4 shows the range of Modeling Efficiencies per model. The second row of graphs in Figure 1 shows the range for all simulations, the third row is added to show the sensitivity of the simulated concentration profiles to user-dependent subjectivity in the derivation of the degradation half-life and the sorption coefficient. For this purpose, simulations were carried out with the half-life and sorption coefficient set at the average value ±2 times the standard deviation. The model PESTRAS was used for this purpose. The average half-life at 10 °C derived from the laboratory experiments was 74 days with a coefficient
Figure 1
Bentazone mass content as a function of depth at 103, 278 and 474 days after application: a) 95% confidence intervals of observed contents; b) Full range of all simulations provided by the participants to the ring-test; c) Range resulting from user dependent variability of half-life and the sorption coefficient, simulated with the PESTRAS model.
Figure 2
Ethoprophos mass content as a function of depth at 103, 278 and 474 days after application. 95% confidence intervals of observed contents; b) Full range of all simulations provided by the participants to the ring-test; c) Range resulting from user dependent variability of half-life and the sorption coefficient simulated with the PESTRAS model.
of variation of 42%, the average sorption coefficient was 0.11 dm³ kg⁻¹ with a coefficient of variation of 14% (Boesten, 1999). Figure 1b shows that there is considerable variation in the predicted concentration profiles, and a considerable part of this variation could be caused by user-dependent subjectivity during the derivation of model inputs (Figure 1c).

Table 4 shows that the performance for the same model varied amongst users. In line with the general conclusions drawn from Figure 1c we can state that this user dependency of modeling is most likely caused by subjectivity during derivation of model inputs. The best Modeling Efficiency was generally found by those users who allowed pesticide properties to be calibrated. This is most striking in the case of VARLEACH and GLEAMS, where one of the users calibrated the degradation half-life and sorption coefficients, while the others didn’t.

User dependent variability of model-inputs limits the possibility for selecting the best model in terms of ability to reproduce the observed concentration profiles. Consider the following example. Vanclooster and Boesten (1999) evaluated the models with respect to the waterflow and solute transport components. An important conclusion from their comparison was that the Richards’ models performed better than the capacity type of models. As bentazone is a mobile component it is to be expected that Richards’ models also perform better for the pesticide part of the model. This, however, cannot be concluded from Table 4. For example, the Modeling Efficiency for PRZM-2 and GLEAMS is good while the Modeling Efficiency for PESTLA is negative. This is a typical example of the fact that ‘model-error’ (capacity models could not describe water- and solute transport) can be cancelled out by ‘parameter error’ (a reasonable value for the Modeling Efficiency of GLEAMS could only be obtained after calibration of pesticide properties).

Despite the problems with data-derivation, all models and the observations indicated significant transport of bentazone; however, the magnitude of the leaching differed considerably (Table 5). Tiktak et al. (1998c) calculated a maximum concentration of bentazone in the 1-2 m soil layer of 15.2 µg L⁻¹, which is approximately 150 times the EU-drinking water standard. Table 5 shows that there was no agreement about plant-uptake rates. A number of models did not include a module for pesticide uptake. Modelers using a model lacking a routine for pes-
Pesticide uptake usually lumped pesticide uptake and transformation resulting in high degradation rates. The Dutch models PESTLA and PESTRAS calculated that a significant fraction of the applied bentazone was taken up. However, as bentazone is an ionic substance, parameter values for bentazone uptake are highly uncertain. Tiktak et al. (1998c) showed that with the observed atypical depth dependence of degradation, an important fraction of the applied bentazone disappeared from the 1-2 m soil layer by transformation under micro-aerobic to anaerobic conditions. Anaerobic transformation is a key process in the prediction of the risk of contamination of drinking-water wells by pesticides, so research on transformation under anaerobic conditions is required.

Table 4
Modeling Efficiency (ME) for predictions of bentazone and ethoprophos in the soil profile. The table shows the worst and the best runs for each model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Bentazone</th>
<th>Ethoprophos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Worst</td>
<td>Best</td>
</tr>
<tr>
<td>VARLEACH</td>
<td>-5.7</td>
<td>-1.0</td>
</tr>
<tr>
<td>GLEAMS</td>
<td>-1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>PRZM-2</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>PELMO</td>
<td>-0.7</td>
<td>-0.4</td>
</tr>
<tr>
<td>LEACHM</td>
<td>-4.5</td>
<td>0.8</td>
</tr>
<tr>
<td>PESTLA</td>
<td>-</td>
<td>-0.1</td>
</tr>
<tr>
<td>PESTRAS</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>MACRO</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Model performance for ethoprophos
The observations indicate a rapid decrease of ethoprophos directly after application (Figure 3). This fast decrease stops after the first rainfall, and almost 60% of the applied pesticide has then disappeared. The initial decrease is due to surface volatilization of the applied chemical, and could only be reproduced by the PESTRAS model (Figure 3). However, most models do not contain a description of surface volatilization, and can therefore not deal with this initial decline. Modelers used the following methods to avoid this problem: (i) use of high degradation rates directly after application, and (ii) use of a lower pesticide dosage of 1.33 kg ha\(^{-1}\), which is the amount recovered at 23 days after pesticide application. Although it is thus possible to describe the fate of ethoprophos during later stages of the experiment, it is clear that a proper description of surface volatiliza-
tion is required for surface applied, moderately volatile or volatile pesticides \((K_H > 10^5)\). The PESTRAS model did contain a module for surface volatilization, but the most important parameter governing volatilization (the surface resistance, \(R_s\)) could only be obtained by calibration. Moreover, as the surface resistance is strongly dependent upon the atmospheric conditions after application (Jury et al., 1990; Freijer et al., 1996), predictions of surface volatilization remain too uncertain to be used for pesticide registration purposes or regional-scale modeling (Tiktak et al., 1998c).

Table 5

<table>
<thead>
<tr>
<th>Model</th>
<th>(fr_{vol})</th>
<th>(fr_{trans})</th>
<th>(fr_{up})</th>
<th>(fr_{sys})</th>
<th>(fr_{leached})</th>
<th>(fr_{err})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEACHM</td>
<td>0.0</td>
<td>88.0</td>
<td>0.0</td>
<td>4.1</td>
<td>6.9</td>
<td>1.0</td>
</tr>
<tr>
<td>MACRO</td>
<td>0.0</td>
<td>65.2</td>
<td>0.0</td>
<td>6.8</td>
<td>28.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PESTLA</td>
<td>0.0</td>
<td>37.1</td>
<td>28.0</td>
<td>6.7</td>
<td>28.2</td>
<td>0.0</td>
</tr>
<tr>
<td>PESTRAS</td>
<td>0.0</td>
<td>36.2</td>
<td>23.3</td>
<td>10.1</td>
<td>30.4</td>
<td>0.0</td>
</tr>
<tr>
<td>PRM-2</td>
<td>0.0</td>
<td>47.0</td>
<td>0.0</td>
<td>10.0</td>
<td>43.0</td>
<td>0.0</td>
</tr>
<tr>
<td>WAVE</td>
<td>0.0</td>
<td>83.0</td>
<td>0.0</td>
<td>3.0</td>
<td>10.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

† Calculated for the end of the experiment and for the upper meter of the soil profile
‡ \(fr_{vol}\) is fraction volatilized; \(fr_{trans}\) is fraction transformed; \(fr_{up}\) is fraction taken up; \(fr_{sys}\) is fraction left in system; \(fr_{leached}\) is fraction leached from the upper meter of the soil profile and \(fr_{err}\) is numerical mass balance error

Both the observations and the model predictions indicate that there was no ethoprophos below 0.3 m depth during the experiment (Figure 2a-b), so the models were conclusive about the leaching potential of ethoprophos (which is negligible). Nevertheless, the majority of models slightly overestimated the movement of ethoprophos (model results were outside the 95% confidence intervals), caused by ignorance of kinetic sorption (Ma et al., 1996). Results from long-term sorption experiments indeed confirmed that the distribution coefficient increased with time (Boesten and Van der Pas, 1999). Some modelers tried to imitate kinetic sorption by using a higher distribution coefficient. They indeed succeeded to calibrate the center of mass of pesticide residues in the soil profile, but they did not well describe the tail of the ethoprophos profile. The latter is significant from a pesticide registration point of view, as kinetic sorption may result in long-term leaching of pesticides at low concentrations (Wagenet and Hutson, 1996; Pignatello and Huang,
After the initial volatilization phase, the areic-mass observations still show a two-phase behavior: From 214 days after applications onwards, pesticide dissipation accelerates (Figure 3). As degradation is the most important loss pathway during the later stages of the experiment (Table 6), it can be stated that this is most probably caused by accelerated degradation due to adaptation of the microbial population. This was also found by Smelt et al. (1987) who found higher rates of transformation from annually treated fields compared with soils not previously treated. No single model was able to deal with this process, indicating that the first-order representation of degradation is not sufficient in this particular case.

The third row in Figure 3 shows the effect of user-dependent variability of pesticide properties on ethoprophos concentration profiles. The average half-life at 10 °C was 172 d with a coefficient of variation of 32%. For the sorption coefficient, these figures amounted to 3.4 dm³ kg⁻¹ and 21% (Boesten, 1999). Figure 2 shows that the variation in concentration profiles caused by user-dependent variability is higher than the variation of all simulations. This is caused by the fact that a number of model-
ers calibrated their model, so that the effect of variation of model-inputs is partly cancelled out.

Table 6
Mass balance of ethoprophos as a fraction of the applied dose for a selection of models. †

<table>
<thead>
<tr>
<th>Model</th>
<th>( f_{\text{vol}} )</th>
<th>( f_{\text{rav}} )</th>
<th>( f_{\text{at}} )</th>
<th>( f_{\text{sys}} )</th>
<th>( f_{\text{i}} )</th>
<th>( f_{\text{aw}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEACHM</td>
<td>0.0</td>
<td>89.8</td>
<td>0.0</td>
<td>1.3</td>
<td>0.0</td>
<td>8.9</td>
</tr>
<tr>
<td>MACRO</td>
<td>0.0</td>
<td>57.0</td>
<td>0.0</td>
<td>39.0</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>PESTLA</td>
<td>0.0</td>
<td>75.2</td>
<td>1.5</td>
<td>9.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PESTRAS</td>
<td>59.2</td>
<td>29.9</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PRZM-2</td>
<td>0.0</td>
<td>75.0</td>
<td>0.0</td>
<td>25.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>WAVE</td>
<td>0.0</td>
<td>94.0</td>
<td>0.0</td>
<td>5.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

† Calculated for the end of the experiment and for the upper meter of the soil profile
†† See table 5 for an explanation of symbols

Summary and Conclusions

Within this study the performance of the pesticide fate part of nine well established pesticide leaching models was evaluated using a dataset collected on a humic sandy soil with a shallow groundwater table. The models were deterministic, dynamic, one-dimensional, multi-layer in their approach, and differed mainly in the complexity by which the various processes are modeled.

All modelers received an extensive description of the experimental data. Despite this fact, no single model run was parameterized in the same way. The most important reason for user-dependent variability of model inputs was that the interpretation of the experimental data was ambiguous. Subjectivity in deriving model inputs should be reduced when the models are to be used for registration purposes, so it is an important task for the modeling community to provide policy-oriented users with strict guidelines and additional tools for deriving model inputs.

The tremendous range in model-inputs used by the modelers hampered the possibility for evaluating model concepts. This was enhanced by the fact that only three pesticide profiles were available for evaluation, so that the identifiability of model-parameters was limited. Future studies on comparison of model concepts could use input mapping (Rose et al., 1991) and consider the effect of model complexity on parameter identifi-
ability (Van der Perk, 1997). Evaluation of model concepts themselves is bound to be most successful when using one model in combination with a library of modules with different complexity of the included process descriptions (Tiktak et al., 1994a).

All models and the experimental data were conclusive with respect to the leaching potential of the two pesticides considered. The models indicated significant transport of bentazone to the 1-2 m soil layer, whereas the transport of ethoprophos below 0.3 m depth was negligible. Nevertheless, the magnitude of the simulated concentrations differed strongly between the models. In the case of bentazone, most model predictions were within the 95% confidence interval of the observations, but calibration was often necessary to accomplish this. This limits the general applicability of the models when used for pesticide registration purposes or regional-scale modeling. This problem becomes even more serious when generic (literature) data are used for model parameterization, and this is usually the practice in policy oriented applications. The accumulation of ethoprophos, for example, was underestimated by a factor 7 when generic pesticide properties were used (Tiktak et al., 1998c). It is an important task for modelers to provide decision makers with this kind of uncertainty (Loague and Corwin, 1996; Tiktak et al., 1998b).

Despite the above mentioned problems with parameter identifiability, some general conclusions about model concepts could be drawn:

- Almost 60% of the applied ethoprophos disappeared by surface volatilization, so models lacking a module for surface volatilization were not successful in describing the fate of this pesticide.
- The transport of ethoprophos was overestimated by models not dealing with kinetic sorption.
- Degradation of ethoprophos could reasonably be described using first-order kinetics until 214 days after applications. From that day onwards, degradation in the field was faster than predicted by the models probably due to adaptation of the microbial population.
- The depth-dependence of transformation for bentazone was atypical. Almost 30% of the applied bentazone leached below 1 m depth, and 20% disappeared from the 1-2 m soil
layer by transformation under micro-aerobic to anaerobic conditions (Tiktak et al., 1998c). Anaerobic transformation is a key process in predicting the risk of contamination of drinking-water wells.

Future research should be directed towards solving these problems. However, caution must be taken not to fall into the trap of building new model versions that contain a lot of parameters which cannot be derived from experimental data as the applicability of such models for regional-scale applications is limited. Finding the balance between model complexity and parameter identifiability is also a challenge for future model developments (Loague and Corwin, 1996).
Modeling the Long-Term Effect of Cadmium Deposition in Acid Sandy Soils

Abstract

Contamination of soil with cadmium is a common problem in the Netherlands. Field-studies in combination with a dynamic, process-oriented model are required to identify and quantify the processes that have led to the presently observed distribution of cadmium in the soil profile. We applied the METRAS model to simulate the fate of cadmium at three contaminated fields under natural land-use in the vicinity of a zinc-smelter. METRAS describes transient flow, hydrodynamic dispersion, equilibrium sorption, speciation and biocycling of metals in soils. Specific model inputs such as sorption isotherms were derived from the literature using pedotransfer functions. Using these data, the model could reproduce the currently observed depth-profiles of cadmium. However, the sorption constant of the litter layer had to be lowered by a factor of 10 to account for the lower affinity of fresh organic matter for metal sorption. Biocycling could explain the considerable amount of organically bound cadmium that is found in the ectoorganic layer and upper part of the mineral soil. Also, the current and the steady-state cadmium concentration in the upper soil compartment were underestimated without bio-cycling. The model predicted considerable leaching of cadmium to the groundwater with concentrations exceeding the Dutch groundwater quality standard by a factor of 50-100.

Introduction

Diffuse contamination of soil and groundwater with cadmium is a common problem in the Netherlands, both under natural and agricultural land uses. The main sources of diffuse soil pollution with cadmium are animal manure, fertilizers and atmospheric deposition (Van Eerdt and Stiggelbout, 1992). An inventory based on 2544 point observations showed strong accumulation of cadmium in the topsoil across large areas of land (Tiktak et al., 1998a). Moreover, in a survey of the quality of the uppermost aquifer (5-17 m depth) Pebesma and de Kwaad-
steniet (1994) found cadmium concentrations over 1.2 μg L⁻¹ in acid sandy soils. Policy makers, however, are not only interested in information on the current state of the environment, they also need quantitative information on the long-term response of environmental quality to reduced pollutant loads. It is clear that models are indispensable tools in making quantitative predictions.

Due to the ubiquitous nature of diffuse soil pollution, decision makers are primarily interested in regional-scale model applications (Corwin and Loague, 1996). A number of regional-scale model assessments of cadmium accumulation have yet been published (Von Steiger et al., 1998; Tiktak et al., 1998ab). However, comparison of the simulated and observed cadmium contents showed serious underestimation of cadmium in soils under natural land-use (Tiktak et al., 1998a). Additionally, field-studies in nature reserves (Pedroli et al., 1990; Dijkstra, 1996; Wilkens et al., 1997) showed that there were strong concentration gradients within the first few centimeters of the topsoil. Finally, laboratory studies (Takken, 1993) showed that the sorption coefficient was considerably lower in the ecto-organic soil layer than in the mineral soil underneath. It became clear that proper understanding of cadmium behavior required application of a mechanistic model to the plot-scale, where information on the vertical distribution of cadmium in soil and the shallow groundwater is available.

We therefore applied the dynamic, mechanistic, multi-layer model METRAS (Metal Transport Assessment; Makaske et al., 1995) to simulate the fate of cadmium at three contaminated fields under natural land-use in the ‘Kempen’ area (Wilkens, 1995; Wilkens and Loch, 1997). Clay-content, organic matter content and present-day pH were measured on-site, all other model-inputs were derived from pedotransfer functions (Breeuwsma et al., 1986; Bouma and Van Lanen, 1987; Elzinga et al., 1999), or were obtained from the literature (generic data). This implies that the model was parameterized in the same way as was done earlier for the regional-scale model (Tiktak et al., 1998a).

The objectives of this modeling study are: (i) to identify and quantify the soil processes that have led to the presently observed cadmium profiles, (ii) to evaluate whether a general purpose model of metal behavior in combination with generic
process parameters can simulate the observed cadmium profiles, and (iii) to predict future soil and groundwater concentrations of cadmium.

Materials and Methods

Field study
The field study was conducted in the Dutch-Belgian ‘Kempen’ region, which is contaminated as a result of atmospheric deposition of cadmium and zinc due to the presence of zinc smelters. The ‘Kempen’ region is flat lowland, situated at an elevation of 35-40 m above sea-level. Soils in the area are generally sandy and acidic (Figure 1). The climate of the area is humid and temperate with mean July and January temperatures of 19 and 4 °C, respectively, and annual precipitation averaging 700 mm. Here, only a brief summary of the field study is given, details can be found in Wilkens (1995) and Wilkens and Loch (1997).

For sampling, three fields (size 60x60 m$^2$) were selected in the direction of the prevailing wind (N-E) from the zinc-smelter Overpelt (Table 1). The fields were situated in nature reserves, and were covered by Molinia caerulea vegetation. The soil at field 1 is developed in eolian dune-deposits, and is very low in organic matter (Figure 1). Field 2 and 3 have well developed podzol profiles with a humic-B horizon situated at 10-25 cm below the soil surface. An important difference between the Arenosol and the Carbic Podzol is that the latter shows a sharper gradient with respect to organic matter.

Soil samples were taken in August and September 1990 (Wilkens, 1995). Groundwater level at the time of sampling was at 1.5 m below surface at all fields. At each field, nine soil profiles situated in a rectangular grid were sampled to a depth of 1.3 m. Sampling was carried out in pits excavated for this purpose. The samples were air dried at room temperature, and passed through a 2 mm nylon sieve.

<table>
<thead>
<tr>
<th>Field</th>
<th>Distance (km)</th>
<th>Soil type (FAO, 1988)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.9</td>
<td>Arenosol</td>
</tr>
<tr>
<td>2</td>
<td>2.3</td>
<td>Carbic Podzol</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>Carbic Podzol</td>
</tr>
</tbody>
</table>
For the determination of total heavy-metals contents, 0.5 g of sample was finely ground and destructed in a mixture of 10 ml of concentrated HClO₄·HNO₃ (3:2 by volume) and 10 ml of concentrated HF. Cadmium was analyzed by graphite furnace AAS. The detection limit for cadmium in the soil material was 0.05 mg kg⁻¹. Soil pH was determined in double distilled water after equilibration of 24 h. Total organic matter content was measured according to Black (1965).

From November 1991 to November 1992 groundwater was sampled at four sites per field using polyethylene piezometric tubes (Wilkens, 1995). The tubes varied in length from 2.1 to 5.0 m below the soil surface and measured 41 mm in diameter. Filter screens were placed just below the expected local range of water-table levels. pH was measured on-site. After sampling, the samples were stored in polyethylene bottles and acidified to pH 2 with concentrated nitric acid. Samples were stored at 4 °C. Metals were measured in the laboratory by ICP-AES.

Model description
For this study, the mechanistic, process-oriented model METRAS (Metal Transport Assessment) was used. METRAS is a one-dimensional, dynamic, multi-layer model simulating transient...
MODELING THE LONG-TERM EFFECT OF CADMIUM DEPOSITION

flow, hydrodynamic dispersion, equilibrium sorption, speciation and biocycling of metals in soil.

Solute transport
Transport is calculated for all relevant components by the convection-dispersion equation:

\[ \frac{\partial c_j^*}{\partial t} = \frac{\partial}{\partial z} \left[ \theta D_j \frac{\partial c_T}{\partial z} \right] - \frac{\partial \theta v c_T}{\partial z} - S_j \]  

(1)

where \( c_j^* \) (kg kg\(^{-1}\)) is the total mass content of component \( j \) in the soil system, \( z \) (m) is vertical position, \( \theta \) (m\(^3\) m\(^{-1}\)) is volumetric water content, \( c_T \) (kg m\(^{-3}\)) is the total component solute concentration, \( D_j \) (m\(^2\) d\(^{-1}\)) is the hydrodynamic dispersion coefficient for component \( j \), \( v \) (m d\(^{-1}\)) is the flow rate of the pore water, and \( S_j \) (kg m\(^{-3}\) d\(^{-1}\)) is volumetric uptake rate of component \( j \). The hydrodynamic dispersion coefficient is composed of terms from molecular diffusion and dispersion due to mechanical mixing during advection:

\[ D_j = a D_0 + L |v| \]  

(2)

where \( a \) (-) is soil matrix factor quantifying reduction of diffusion in a porous medium, \( D_0 \) (m\(^2\) d\(^{-1}\)) is molecular diffusion coefficient of component \( j \) in water and \( L \) (m) is the dispersivity.

Mass balance and mass action equations
All geochemical problems can be characterized by a series of mass balance and mass action equations (McBride, 1994). Metals are involved in a large number of geochemical reactions. As the solution of a large set of mass balance and mass action equations is computationally expensive, only a subset of reactions was considered in the simulations. Whether a species is relevant for a particular application was deduced from an inventory with the general purpose geochemical program MINEQL\(^+\) (Schecher and McAvoy, 1991).

The total mass content of component \( j \) is described by the following general mass balance equation:

\[ c_j^* = Q_j + \frac{\theta c_T}{\rho} \]  

(3)
where $Q_j$ (kg kg$^{-1}$) is the solid phase mass content of component $j$ and $\rho$ (kg m$^{-3}$) is the dry bulk density. The total solution concentration of component $j$ is described by:

$$c_{T_j} = \sum_{i=1}^{m} a_{i,j} c_i$$

(4)

where $a_{i,j}$ (-) is the stoichiometric coefficient of component $j$ in species $i$, and $c_i$ (kg m$^{-3}$) is the solution concentration of species $i$.

The concentration of species $i$ in component $j$ can be deduced from the mass action of formation of species $i$ from component $j$:

$$c_i = \frac{K_i}{\gamma_j} \prod_j \left( \frac{X_j}{Y_j X_j} \right)^{a_{i,j}}$$

(5)

in which $K_i$ (-) is the thermodynamic formation constant, $X_j$ (kg m$^{-3}$) is the concentration of free, uncomplexed component $j$, and $\gamma_j$ (-) is the activity coefficient, which is calculated using the Davies extension of the Debye-Hueckel equation (Stumm and Morgan, 1997):

$$\log(\gamma_j) = -0.5 |z|^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

(6)

where $I$ (-) is the ionic-strength and $z$ is the ion valence.

Several authors have shown that sorption of complexed metal species is negligible (e.g. Boekhold et al., 1993; Christensen, 1984). Sorption is therefore described as a function of free metal activity:

$$Q = K_F \gamma X^n$$

(7)

where $K_F$ (m$^n$ kg$^{-1}$) is the Freundlich sorption constant, and $n$ (-) is the Freundlich sorption exponent. $K_F$ is related to basic soil properties by a pedo-transfer function (Elzinga et al., 1999):

$$K_F = K_f (H^+)^{-m} CEC^a$$

(8)

where $K_f$ (kg$^{1-n}$ kg a$^{-1}$ m$^{2(n-m)}$ mmol$^{-a}$ mol$^{n}$) is the sorption coefficient, CEC (mmol, kg$^{-1}$) is the Cation Exchange Capacity at neutral pH, and $m$ and $a$ are empirical parameters. See further the section on model inputs.
The uptake rate of component $j$ is assumed to be dependent on the concentration of free, uncomplexed component $j$ (Cabrera et al., 1988; Asp and Berggren, 1990):

$$S_j = f_{\text{pref},j} S_w X_j$$  \hspace{1cm} (9)

where $f_{\text{pref},j}$ (-) is preference factor for component $j$ and $S_w$ (m$^3$ m$^{-3}$ d$^{-1}$) is volumic volume rate of water uptake. The total uptake rate of component $j$ is allocated to leaves and roots on the basis of a (fixed) allocation factor, $f_{\text{al},j}$.

The remainder of the biocycling module in METRAS is based upon the RESAM model (De Vries et al., 1995). Litterfall and root decay are described by first-order rate reactions:

$$\begin{align*}
 v_{\text{Lf},j} &= k_{\text{Lf},j} Am_{\text{Lv}} ct_{\text{Lv},j} \\
 v_{\text{Rd},j} &= k_{\text{Rd},j} Am_{\text{Rt}} ct_{\text{Rt},j}
\end{align*}$$

where $v_{\text{Lf},j}$ (kg m$^{-2}$ d$^{-1}$) is the litterfall flux of component $j$, $v_{\text{Rd},j}$ (kg m$^{-2}$ d$^{-1}$) is the root decay flux of component $j$, $k_{\text{Lf},j}$ (d$^{-1}$) is the litterfall rate constant, $k_{\text{Rd},j}$ (d$^{-1}$) is the root decay constant, $Am_{\text{Lv}}$ (kg m$^{-2}$) is the areic leaf mass, $Am_{\text{Rt}}$ (kg m$^{-2}$) is the areic root mass, and $ct_{\text{Lv}}$ and $ct_{\text{Rt}}$ (kg kg$^{-1}$) are the contents of component $j$ in leaves and roots, respectively. Root decay is restricted to the decay of fine roots. The distribution of root decay with depth is determined by the distribution of fine roots. Reallocation in leaves and fine roots is considered negligible.

For the simulation of the decomposition of above ground organic matter (litter) a distinction is made between a rapidly decomposing pool of fresh litter (less than 1 year old) and a slowly decomposing pool of old litter (older than 1 year) (Janssen, 1984). The mineralization flux of fresh litter is proportional to the litter fall flux:

$$v_{\text{MiLf},j} = f_{\text{mi},j} v_{\text{Lf},j}$$

where $v_{\text{MiLf},j}$ is the mineralization flux of component $j$ in fresh litter, and $f_{\text{mi},j}$ (-) is a mineralization factor. The mineralization flux of old litter and root necromass are described by a first-order rate reactions:

$$\begin{align*}
 v_{\text{MiLt},j} &= k_{\text{MiLt},j} Am_{\text{Lt}} ct_{\text{Lt},j} \\
 v_{\text{MdRn},j} &= k_{\text{MdRn},j} Am_{\text{Rn}} ct_{\text{Rn},j}
\end{align*}$$

(12)
where $v_{MiLt}$ and $v_{MiRn}$ (kg m$^{-2}$ d$^{-1}$) are the mineralization fluxes of component $j$ in old litter and root necromass, $k_{MiLt}$ and $k_{MiRn}$ (d$^{-1}$) are the mineralization constants, and $c_{iLt}$ and $c_{iRn}$ (kg kg$^{-1}$) are the contents of component $j$ in litter and root necromass, respectively.

**Model parameterization**

Aim of this study was to reconstructed the currently observed depth-distribution of cadmium using independent estimates of historical cadmium loads (‘hind-cast simulation’). The zinc-smelter started its activities in 1890. for this reason, simulations were carried out for the period 1890-2000. According to Edelman (1984), cadmium contents in uncontaminated Dutch soil are close to the analytical detection limit (usually less than 0.15 mg kg$^{-1}$), so we assumed that in 1890 there was no cadmium present.

Clay-content, organic matter content and present-day pH were measured on-site, all other data were derived from pedo-transfer functions or were obtained from the literature (generic data). As mentioned before, nine profiles were sampled per field. Simulations were carried out for all these profiles, after which we calculated the averages and standard deviations. The advantage of this procedure is that it gives insight into variability of metal accumulation and leaching caused by soil heterogeneity.

**Chemical complexes**

To determine the most important chemical species for the current model application, MINEQL$^+$ was run for the system Cd$^{2+}$, Cl$^-$, SO$_4^{2-}$, H$^+$, CO$_3^{2-}$, PO$_4^{3-}$ and A$^2$ (where A refers to a dissolved organic acid). Acid-base titrations were carried out for the entire range of concentrations for diffusely contaminated natural soils in the Netherlands found by Leeters et al. (1994) and Römkens and Salomons (1998). Equilibrium constants for inorganic complexes were taken from the NIST Standard Reference Database 46 (NIST, 1993), organic complexation constants were taken from Mantoura et al. (1978). The dissociation of organic acids was represented by a diprotic acid analogue

$$H_2A^0 \leftrightarrow HA^- + H^+ \quad \log(K) = -4.3$$

$$HA^- \leftrightarrow A^{2-} + H^+ \quad \log(K) = -9.5$$

(13)
Dissociation constants were calculated with the equation (Oliver et al., 1983):

\[ pK = 0.96 + 0.90pH - 0.039(pH)^2 \]  

(14)

The total concentration of organic anions (μmol L\(^{-1}\)) in the soil solution was related to the Dissolved Organic Carbon concentration by:

\[ [A]_t = [A^{2-}] + [HA^-] + [H_2A^0] = M_D[DOC] \]  

(15)

where \( M_D \) represents the concentration of organic anions in DOC. \( M_D \) was set to 5.5 μmol mg\(^{-1}\) C in accordance to Henrik-sen and Seip (1980). This value is within the range of values (3.4-8 μmol mg\(^{-1}\) C) obtained from monitoring programs in Dutch forest soils (Tiktak et al., 1988; Verstraten et al., 1990).

In the METRAS simulations, only those chemical species contributing more than 1% to the total dissolved metal concentration were considered. These complexes and their corresponding complexation constants are listed in Table 2.

### Table 2
Metal complexation equilibria considered in the METRAS simulations.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log K )†</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdCl(^+) ↔ Cd(^{2+}) + Cl(^-)</td>
<td>-1.98</td>
</tr>
<tr>
<td>CdSO(_4)(^2-) ↔ Cd(^{2+}) + SO(_4)(^2-)</td>
<td>-2.46</td>
</tr>
<tr>
<td>CdCO(_3)(^2-) ↔ Cd(^{2+}) + CO(_3)(^2-)</td>
<td>-5.40</td>
</tr>
<tr>
<td>CdHCO(_3) ↔ Cd(^{2+}) + H(^+) + CO(_3)(^2-)</td>
<td>-12.40</td>
</tr>
<tr>
<td>CdA(^-) ↔ Cd(^{2+}) + A(^-)</td>
<td>-6.10</td>
</tr>
<tr>
<td>CdHA(^-) ↔ Cd(^{2+}) + H(^+) + A(^-)</td>
<td>-2.60</td>
</tr>
</tbody>
</table>

† \( \log K \) at 298 K and 1000 hPa

Sorption isotherms

The cadmium sorption isotherm was based on a large number of batch data published in the scientific literature (Elzinga et al., 1999). Data were inferred from the original sources by either digitizing the graphical isotherms, or by evaluating fitted isotherms. The original solution data were concentration data, which were transformed to free cadmium activities by correction for activity and complexation effects. The data were fitted using a linearized, logarithmic transform of the extended Freundlich equation (Table 3). To compensate for the lower affinity for metal sorption of fresh organic matter (Herms and Brümmer, 1984), the sorption coefficient of ecto-organic soil material was set at 10% of its value for mineral soil. This is in
line with results from sorption experiments in acid sandy soils (Takken, 1993).

Other soil data
The CEC at near neutral pH values was estimated from the organic matter content and the clay content according to (Breeuwsma et al., 1986):

\[
\text{CEC} = 5f_{\text{clay}} + 27.25f_{\text{oc}}
\]

(16)

where CEC (mmol kg\(^{-1}\)) is Cation Exchange Capacity at a reference pH of 6.5, \(f_{\text{clay}}\) (g 100g\(^{-1}\)) is the clay content and \(f_{\text{oc}}\) (g 100g\(^{-1}\)) is the organic carbon content.

The bulk-density of the soil, \(\rho\) (kg m\(^{-3}\)) was calculated according to Bollen et al. (1995):

\[
\rho = 1800 + 12.36f_{\text{om}} - 291\sqrt[3]{f_{\text{om}}}
\]

(17)

where \(f_{\text{om}}\) (g 100g\(^{-1}\)) is the organic matter content.

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression results for the Freundlich isotherms of cadmium.</td>
</tr>
<tr>
<td>The model is given by:</td>
</tr>
</tbody>
</table>
| \[
\log(Q) = \log(K) + n \log(Cd) + m \, \text{pH} + a \log(\text{CEC})
\] |

<table>
<thead>
<tr>
<th>log(K) (\dagger)</th>
<th>(n)</th>
<th>(m)</th>
<th>(a)</th>
<th>(R^2_{\text{adj}})</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.92</td>
<td>0.83</td>
<td>0.44</td>
<td>0.66</td>
<td>0.76</td>
<td>1125</td>
</tr>
</tbody>
</table>

\(\dagger\) CEC at near neutral pH. The pH effect on the number of sorption sites, which is equivalent with the pH effect on CEC, is accounted for in the regression coefficient for pH.

The concentration of DOC (mg L\(^{-1}\)) was calculated from the organic carbon content by a pedotransfer function (Reinds et al., 1995):

\[
\log(\text{DOC}) = 1.629 + 0.38 \log(f_{\text{oc}})
\]

(18)

Long-term average soil water fluxes, soil water contents and soil water uptake rates were calculated with the hydrological model SWIF (Tiktak and Bouten, 1992). Soil physical properties were taken from the Winand Staring Soil Series (Wösten et al., 1994), crop-factors were taken from De Visser and De Vries (1989). The long-term average net-precipitation amounted to 280 mm a\(^{-1}\).

The dispersion length was set to 0.05 m, which is the average of values found by van Ommen et al. (1989). The diffusion coefficient in water was based on Weast (1974).
Historic depth profiles of soil pH were calculated by superimposing a time-trend factor on the on-site measured vertical pH profiles (Figure 1). This time-trend factor was derived from simulations with the soil acidification model RESAM (De Vries et al., 1995). Deposition data were taken from Heij and Schneider (1991). RESAM runs were carried out for both vegetation-soil combinations considered, i.e. non-agricultural grassland on a carbic podzol and non-agricultural grassland on an arenosol (Table 1).

**Biocycling parameters**

Parameters that must be input to the model include the areic biomasses of leaves and fine-roots, and various rate-constants. These data were taken from a literature survey (De Vries et al., 1990). The areic litter mass and areic root necromass were calculated by integrating the various mineralization equations, using an age of 90 years. All data are listed in Table 4.

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Areic leaf mass †</td>
<td>AmlLv</td>
<td>0.345</td>
<td>kg m^2</td>
</tr>
<tr>
<td>Areic fine-root biomass †</td>
<td>AmRt</td>
<td>0.462</td>
<td>kg m^2</td>
</tr>
<tr>
<td>Rooting depth †</td>
<td></td>
<td>0.2</td>
<td>m</td>
</tr>
<tr>
<td>Preference factor for cadmium ‡</td>
<td>fPref</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Leaf-root allocation factor †</td>
<td>FrLv</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Leaf fall rate constant †</td>
<td>kLf</td>
<td>1.0</td>
<td>a'</td>
</tr>
<tr>
<td>Root decay rate constant †</td>
<td>kRd</td>
<td>2.0</td>
<td>a'^1</td>
</tr>
<tr>
<td>Mineralization factor †</td>
<td>fMi</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Litter mineralization constant †</td>
<td>kMILt</td>
<td>0.15</td>
<td>a'^1</td>
</tr>
<tr>
<td>Root necromass mineralization constant †</td>
<td>kMiRn</td>
<td>0.19</td>
<td>a'^1</td>
</tr>
<tr>
<td>Areic litter mass §</td>
<td>AmLt</td>
<td>1.382</td>
<td>kg m^2</td>
</tr>
<tr>
<td>Areic root necromass §</td>
<td>AmRn</td>
<td>4.863</td>
<td>kg m^2</td>
</tr>
</tbody>
</table>

† Values for grassland described by De Vries et al. (1990)
‡ Taken from Alloway (1995)
§ Calculated by integrating the mineralization equations, using an age of 90 years.

**Cadmium deposition**

The ‘Kempen’ area has received cadmium deposition originating from zinc-smelters in Budel (NL), Overpelt (B) and Balen (B). The field-plots described here are situated close to the Overpelt smelter, so the influence of the two other smelters can reasonably be neglected. Annual average deposition rates were available for five locations situated around the Overpelt smelter.
for the year 1989 (Lisec, 1989). These data showed an extremely sharp decrease of cadmium deposition with distance (Figure 2a). Interpretation of the field-data, however, revealed that this distance function could not explain the fate of cadmium for all field-plots simultaneously. We therefore used the distance relationship obtained for zinc deposition as an alternative. This relationship shows a considerable smaller decrease with distance (Figure 2a). This was justified by the fact that cadmium and zinc preferentially condense on fine particles of approximately equal diameter.

Past deposition rates were obtained by superimposing the so obtained 1989 deposition rates on a time-trend function (Figure 2b), which is based upon the annual zinc production rates (Lisec, 1989). Zinc can be extracted by thermal or electrolytic processes. Before the mid-seventies, thermal processes were generally used. Zinc-smelters using the old thermal process are a major source of cadmium, with Cd emission factors ranging from 10 to 100 g Mg\textsuperscript{-1} (Button, 1982). After the mid-seventies, electrolytic processes were used with very low Cd emission factors (approximately 0.2 g Mg\textsuperscript{-1}). The sharp decrease during the seventies is caused by this change in production process.
Results and Discussion

Cadmium profiles

Figure 3 shows the presently observed average depth profiles of cadmium for the three fields (Wilkens and Loch, 1997). The observations show elevated contents of cadmium in the top mineral soil and ecto-organic soil layers. Comparison of Figure 1 and Figure 3 shows a strong relationship between organic matter and cadmium content, which is confirmed by a moderate correlation between these two soil parameters ($r^2 = 0.47$). As there was no correlation found between the major sesquioxides and cadmium (Wilkens and Loch, 1997), it can be concluded that organic matter is the most important adsorbent in these acid sandy soils. Figure 3 shows that the carbic podzols (field 2 and field 3) show a sharper gradient with respect to cadmium contents than the arenosol (field 1), which is to be expected from the depth distribution of organic matter in the soil profile (Figure 1). Figure 3 also shows that cadmium contents are slightly higher in the B-horizons (10-25 cm depth) of the carbic podzols than in the A-horizons (< 10 cm depth), which indicates illuviation of cadmium in these B horizons.

Figure 3 also shows the simulated depth profiles obtained by hind-cast simulation. Visual inspection shows reasonable agreement between the observations and the simulations for fields 1 and 2 and underestimation of cadmium contents for all depths in field 3. The most probable explanation for this mismatch is underestimation of the cadmium deposition for this particular field.

Acknowledging that virtually all model inputs have been derived from literature data and pedotransfer functions, the agreement between the observed and simulated cadmium contents for fields 1 and 2 is striking. An important point of discussion is the use of generic Freundlich sorption isotherms obtained from laboratory experiments (Elzinga et al., 1999). Application of these sorption isotherms to field partition data on 20 Dutch soils revealed that the amount of cadmium sorbed onto the soil solid phase was systematically underestimated. This underestimation increased with cadmium content, and ranged from a factor of less than 2 at cadmium contents of 0.1 mg kg$^{-1}$ to 10 at cadmium contents above 100 mg kg$^{-1}$. The reason for this systematic underestimation is that laboratory based
isotherms only consider the metal fractions that are sorbed within the equilibrium time, which is usually 24 h. The field data, on the other hand, include slowly desorbing metal incorporated in organic matter and clay minerals. The present study applies to the lower concentration range and acid sandy soils, where application of the laboratory sorption isotherms is most appropriate. Another point of concern is that the presented results could only be obtained after reduction of the Freundlich constant for the ecto-organic layer by a factor of 10 (see page 80). Application of the unreduced Freundlich constant to the ecto-organic soil layer yielded completely unrealistic results with almost no leaching to the subsoil. It is clear that proper parameterization of METRAS requires the use of at least two sorption constants, i.e. one for the ecto-organic soil layer and one for the mineral soil underneath.

Figure 3 shows that the model generally reproduced the observed high cadmium contents in the ecto-organic soil layer. Analysis of the model results showed that approximately 50% (field 1) to 80% (field 2) of total cadmium in the ecto-organic soil layer was incorporated into the organic matter by metal cycling, while the remainder was sorbed onto the soil solid phase. This is consistent with results from metal fractionation studies in the topsoil and ecto-organic soil layers of acid sandy soils, which showed that approximately 60% of total cadmium was in
an organically bound (pyrophosphate-extractable) fraction (Dijkstra, 1996; Pottjegort and Wilms, 1998; Johnson and Petras, 1998).

**Cadmium time-trends**

Figure 4 shows the total concentration of cadmium in the soil solution as a function of time for three selected depths. Figure 4 shows that the maximum concentration of cadmium in the shallow groundwater exceeded the Dutch groundwater quality standard (0.4 μg L⁻¹) by a factor of 50 in the case of field 3 to 100 for fields 1 and 2. Notice that Figure 4 shows considerable retardation of cadmium in the lower soil horizons, particularly in field 1. This indicates that the presence of small amounts of adsorbents in the subsoil can have a strong effect on cadmium leaching. As the Freundlich exponent \( n \) is smaller than one, this is particularly true for the low concentration levels reported in this study. Figure 4 also shows that the interpretation of the timing of the maximum concentration in the groundwater is complicated. On the basis of organic matter content and pH one would expect the fastest breakthrough for the arenosol (field 1). When comparing results for field 1 and field 2, this is indeed true. In field 3, however, the maximum concentration was reached at the same time as in field 1. Apparently, the slightly lower pH in the topsoil (field 3) compensates for the higher organic matter content (field 1).

Regional-scale models of heavy-metal accumulation often use a single soil compartment. For the Dutch assessments, the thickness of this single compartment was set to 5 cm (Tiktak et al., 1998a). It is therefore interesting to verify the effect of biocycling on the average concentration in the upper 5 cm of the soil. We therefore performed an alternative model run, with the preference factor for cadmium uptake set to zero. Results shown in Figure 5 suggest limited effect of biocycling on the average cadmium contents. This is primarily caused by the small thickness of the ecto-organic soil layer in combination with its low bulk density (110 kg m⁻³). In soils with a thick ecto-organic soil layer, however, effects will be more pronounced. Figure 5 also shows that cadmium decreased slightly sharper in response to reduced atmospheric deposition if the preference factor for cadmium uptake was set to zero. Even after a long-
Figure 4
Simulated total soil solution concentration of cadmium at three depths in the soil profile. The observed groundwater concentration and its standard deviation is also indicated.

Concentration of cadmium (µg L⁻¹) (field 1)

Concentration of cadmium (µg L⁻¹) (field 2)

Concentration of cadmium (µg L⁻¹) (field 3)
period of constant deposition, cadmium storage in the upper soil compartment stays at a slightly lower level. This suggests a slight underestimation of steady-state cadmium contents by models that do not consider biocycling.

Figure 5
Time trend of cadmium in the upper 5 cm of the soil showing the effect of biocycling.

Figure 6 shows the influence of variability of organic matter content on the concentration in the lower soil compartment, which is an indicator for the leaching concentration. The figure shows a clear effect on metal retardation. In one field, one can find profiles where the concentration is already declining, and profiles were the cadmium concentration has not yet reached its maximum value. Also the magnitude of the leaching flux was considerably affected by this variability: The coefficient of variation of the accumulated leaching flux for all nine profiles was 33% for field 1 and 43% for field 2. This example shows that interpretation of field-averages should be carried out with care. Jury (1986) even stated than an estimate of the variation of each parameter to construct a crude sample frequency diagram may be of greater value than an accurate average.
Chapter 2.3

Figure 6
Total solute concentration of cadmium in the soil solution at 125-150 cm depth, showing the effect of variability of organic matter.

Cadmium mass balance
Table 5 shows the major terms of the cadmium mass balance for the three fields at three selected times, i.e. 1950, 1975 and 2000. The table shows that in 2000 approximately 30% of the cadmium load has leached to the groundwater. The table also shows that cadmium leaching has already started in 1950 (see also Figure 4). These results suggest that, despite the strong retention of cadmium in the topsoil, leaching is a considerable problem. This is confirmed by Pebesma and de Kwaadsteniet (1994), who carried out a nationwide survey of the quality of the uppermost aquifer (5-17 m depth). They found cadmium concentrations over 1.2 μg L⁻¹ across large areas.

In 2000, approximately 40% of the cadmium load is taken up by the vegetation. However, only 4% of the total cadmium is then stored in the vegetation and necromass. Despite this fact, cadmium contents in the ecto-organic soil layer and living biomass are high (5-10 mg kg⁻¹).
Table 5
Calculated mass balance for the three fields.

<table>
<thead>
<tr>
<th>Year</th>
<th>Compartment (mg m⁻²)</th>
<th>Accumulated flux since 1890 (mg m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Biomass ‡</td>
<td>Necromass ‡</td>
</tr>
<tr>
<td>Field 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>5</td>
<td>24</td>
</tr>
<tr>
<td>1975</td>
<td>12</td>
<td>74</td>
</tr>
<tr>
<td>2000</td>
<td>6</td>
<td>41</td>
</tr>
<tr>
<td>Field 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td>1975</td>
<td>15</td>
<td>86</td>
</tr>
<tr>
<td>2000</td>
<td>9</td>
<td>59</td>
</tr>
<tr>
<td>Field 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>1975</td>
<td>5</td>
<td>31</td>
</tr>
<tr>
<td>2000</td>
<td>3</td>
<td>22</td>
</tr>
</tbody>
</table>

‡ Sum of mass in leaves and fine-roots
† Sum of mass in litter and root-necromass, excluding metals in the sorbed phase.
§ Mineral soil, including metals sorbed in the ecto-organic soil layer.
¶ At 150 cm depth.

Conclusions

The METRAS model was used to simulate the fate of cadmium at three contaminated fields under natural land-use in the Dutch-Belgian ‘Kempen’ area. METRAS describes transient flow, hydrodynamic dispersion, equilibrium sorption, speciation and biocycling of metals in soil. Clay-content, organic matter content and present-day pH were measured on-site, all other model-inputs were generic. This implies that the model was parameterized in the same way as was done previously with a regional-scale model of cadmium accumulation (Tiktak et al., 1998a). With this combination of on-site measured data and generic data, the model could generally reproduce the currently observed depth-profiles of cadmium, both in the ecto-organic layer and in the mineral soil. The model could also reproduce...
the observed high concentration of cadmium in the shallow groundwater.

These findings indicate that the generic sorption isotherms, which were based on batch experiments (Elzinga et al., 1999) were appropriate for the soils and situation described here (i.e. relatively low cadmium contents and acid sandy soils). An important point of concern, however, was that the observed concentration profiles could only be reconstructed after reduction of the Freundlich constant for the ecto-organic soil layer by a factor of 10. This implies that proper parameterization of METRAS requires the use of at least two Freundlich constants, i.e. one for the ecto-organic soil layer and one for the mineral soil.

Biocycling was indispensable to explain the currently observed high cadmium concentration in the ecto-organic soil layer. The simulations indicate that approximately 50 to 80% of total cadmium was stored in the biomass. This is consistent with results from metal fractionation studies in the topsoil and ecto-organic soil layers of acid sandy soils in the same region, which showed that approximately 60% of total cadmium was in an organically bound (pyrophosphate-extractable) fraction.

A simulation without biocycling indicated that the average cadmium content in the upper 5 cm of the soil was hardly affected. This indicates that the use of so-called box-models, which consider only one homogeneous soil compartment and therefore usually ignore biocycling, can be justified if only average concentrations are wanted. If, however, separate information of cadmium in the ecto-organic soil layer is wanted, then at least two layers should be distinguished.