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# Comparison of Pesticide Transport Processes in Three Tile-Drained Field Soils Using HYDRUS-2D

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## ABSTRACT

**The purpose of this study was to assess the transport of the herbicide bentazone [3-(1-methylethyl)-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide] in three contrasting tile-drained cultivated field soils subject to otherwise similar experimental conditions. Observed drain discharge rates and chemical concentrations in the drainage water reflected the different transport processes at the three sites in the same area of northeastern France: a sandy loam site (Villey), a silt loam site (Bouzule-1), and a silty clay site (Bouzule-2). The sandy loam site showed very little tile drainage (240 $m^3$ $ha^{-1}$) during the 100-d study in the spring of 2002, as well as low chemical losses in the drainage water (0.16% [v/v] of the applied amount). While little drainage was observed also for the silty clay soil (175 $m^3$ $ha^{-1}$), observed pesticide losses were considerably larger (1.25% of the applied amount). The silt loam soil, in comparison, showed much more drainage (521 $m^3$ $ha^{-1}$) and the highest chemical loads in the drainage water (2.7% of the applied amount). Numerical simulations of drain discharge with the HYDRUS-2D variably saturated flow and solute transport model compared well with the observed data for the relatively homogeneous sandy loam (Villey) and the silt loam (Bouzule-1) soils. The saturated hydraulic conductivity of the bottom layer in both cases was key to correctly predicting the drainage fluxes. Accurate predictions of the silty clay field data (Bouzule-2) could be obtained only when the soil hydraulic functions were modified to account for preferential flow through drying cracks near the soil surface. Chemical concentrations could be better described using a dual-porosity (mobile–immobile water type) transport model for all three soils, including the sandy loam. Results indicate that water and pesticide transport in soils is governed by site-specific processes. Optimal use of the HYDRUS-2D flow and transport model allowed a reasonable description of the field-scale pesticide processes using only a limited number of adjustable parameters.**

Application of pesticides to cultivated fields often leads to their unintentional leaching through the vadose zone toward underlying and down-gradient water resources. Since excessive leaching compromises soil and water quality, and indirectly human health (Garcia, 2003; Wong et al., 2003; Miersma et al., 2003), many studies have been performed to assess the fate and transport of a variety of pesticides in different soils and for different soil management practices. Experiments focusing on the governing transport processes are often performed using repacked soil columns in the laboratory (Davidson and Chang, 1972; van Genuchten et al., 1977; Gamerdinger et al., 1990; Kookana et al., 1993; Guo and Wagenet, 1999). While useful, such experiments are generally not representative of field conditions and often underestimate the leaching potential of chemicals in the field because of preferential flow or other processes (Flury, 1996).

Field experiments provide a more realistic assessment of pesticide transport processes. Tile-drained agricultural fields in particular have been shown to be attractive for studying field-scale flow and solute transport processes. Many studies have demonstrated the merit of such systems for studying the transport of tracers (Vanderborght et al., 2002; Fox et al., 2004; Gerke and Köhne, 2004), N (Mohanty et al., 1998; de Vos et al., 2000; de Vos, 2001), and pesticides (Abbaspour et al., 2001; Kohler et al., 2001; Zehe and Flühler, 2001; Jaynes et al., 2001; Novak et al., 2003; Larsbo and Jarvis, 2005). Tile drainage systems, in essence, function as large undisturbed field-scale lysimeters (Gerke and Köhne, 2004; Kung et al., 2000) since they integrate the site-specific flow and transport processes within the full transport domain that contributes to drainage outflow.

Optimally interpreting tile drainage response (e.g., drain discharge rates and solute concentrations) is still a challenge because of field-scale spatial and temporal variability and the related problems of preferential flow (Southwick et al., 1995; van Genuchten et al., 1999; Larsson et al., 1999; Hendrickx and Flury, 2001; Kohler et al., 2003). During the past two decades, several models have been developed to simulate water flow and solute transport in the vadose zone. These models range from relatively simplistic approaches to more complex, physically based, dual-porosity, dual-permeability, and multiregion models (Jarvis, 1994; Banton et al., 1995; Abbaspour et al., 2001; Kohler et al., 2003; Pruess, 2004; Larsbo et al., 2005). A review of various approaches to simulate preferential, nonequilibrium flow and transport was recently given by Šimůnek et al. (2003). Although the more sophisticated of these models seem to be able to describe the outflow patterns from tile-drained fields, this may be partly due to the large number of parameters that are often fitted to the observed field data (e.g., Haws et al., 2005). The resulting parameter estimation process by itself can be quite problematic because of problems of parameter uniqueness, identifiability, and stability (e.g., Hopmans and Šimůnek, 1997).

One challenge when simulating the outflow response from tile drains at a given site is that different conceptual formulations sometimes will lead to equally acceptable

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**Abbreviations:** ADE, advection–dispersion equation; MIM, mobile–immobile solute transfer model.

predictions of observed field data (Blazkova et al., 2002). Problems related to identification of the actual physical processes at a site often become more apparent when solute transport is simulated simultaneously with water flow (e.g., Abbaspour et al., 2001; de Vos et al., 1999, 2002). A good example is given by Pang et al. (2000), who studied the field-scale transport of Br and three pesticides using the HYDRUS-2D variably saturated flow and transport model of Šimůnek et al. (1999). They found that the model was able to accurately describe soil water contents, with only relatively minor discrepancies between simulated and observed data; however, predicted concentrations of Br and pesticide showed major differences with the observed data. The HYDRUS-2D model was unable to simulate preferential flow through drying cracks near the soil surface, which caused higher Br and pesticide concentrations at greater depths. Results of the field study by Pang et al. (2000) suggest the need for a more detailed dual-permeability approach for simulating preferential flow. Unfortunately, the many parameters needed for such detailed models are generally not available, unless fitted to comprehensive field data sets, with resultant problems of parameter uniqueness and parameter equifinality (Beven, 1993) in that different conceptualizations and multiple combinations of input parameters may lead to equally acceptable simulations of the field data. The importance of estimating the additional parameters required for the MACRO dual-permeability model, and the significance of data availability in general for simulating pesticide transport in a tile-drained structured field soil, was prominently demonstrated in a recent study by Larsbo and Jarvis (2005).

This study concerns the transport of the herbicide bentazone, sprayed in the spring of 2002 onto three different tile-drained agricultural fields: a sandy loam, a silt loam, and a silty clay soil. The soils were selected because of their contrasting flow and transport properties, while most other experimental conditions were very similar (i.e., weather conditions, pesticide applications, and soil management). Also, several data sets were already available for the sites (Novak et al., 2001, 2003), thus providing additional information helpful for running numerical models and comparing observed and simulated data.

The use of bentazone is a major issue since this pesticide is relatively mobile and frequently detected in surface waters and groundwater (Halfon et al., 1996; Lagana et al., 2002; Institut Français de l'Environnement, 2003, 2004). Previous laboratory experiments conducted with the same soils showed that bentazone degradation and sorption are relatively minor compared with other pesticides (Boivin et al., 2004, 2005). Carrizosa et al. (2000), for this same reason, used bentazone as a model chemical for very mobile herbicides.

Observed tile drain discharge and chemical concentrations in this study were simulated with HYDRUS-2D. One major challenge in using HYDRUS-2D, or any other model, is that for most field-scale applications, only limited information is available about the key parameters and processes involved. In this study, we assessed the utility of HYDRUS-2D to simulate drain discharge and solute concentrations with limited input data and for different field settings. Our aim was to compare observed and simulated water fluxes and solute concentrations using readily available information. Different options in HYDRUS-2D were used in attempts to better simulate the preferential flow of water and solutes. These options included the use of modified soil hydraulic properties (Vogel and Císlerová, 1988) to account for increased flow near saturation, and the use of a dual-porosity (mobile–immobile water) type model for solute transport (Šimůnek et al., 2003).

## MATERIALS AND METHODS

### The Three Field Sites

Three field sites in northeastern France (Lorraine) were selected for the experiments, one site in Villey-St-Etienne (designated as *Villey*), and two sites in La Bouzule (designated as *Bouzule-1* and *Bouzule-2*), approximately 25 km from the Villey site. Winter wheat (*Tritcum aestivum* L.) was grown on the three sites using the same standard management practices in the area. Because of their close proximity, the three sites were also subject to approximately the same weather conditions. Figure 1 shows a layout of the tile drainage systems at the three sites. Cross-sections of the layered profiles, including the locations of the drains, are shown in Fig. 2. The Villey site (Table 1) consisted of sandy loam derived from alluvial deposits (Moselle River) on a marl layer (a very soft, calcareous rock with a chalky clay texture usually formed from a mixture of clay and limestone). The PVC tile drains (0.05-m diameter) at this site were located at an average depth of 0.9 m, with a spacing of 12 m (Fig. 1 and 2).

The Bouzule-1 and Bouzule-2 sites were located on adjacent fields. The 2.83-ha Bouzule-1 site consisted of a medium-textured silt loam (Table 1), while the 1.85-ha Bouzule-2 site contained a finer textured silty clay. The latter site had a 5 to

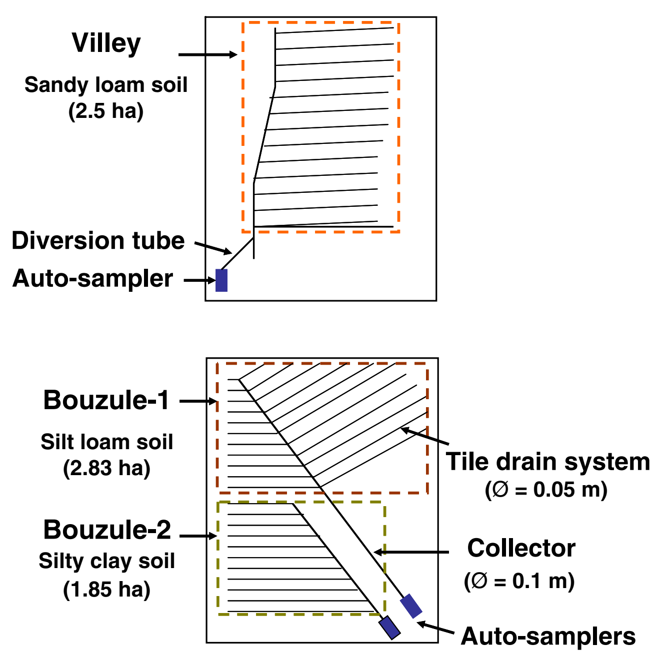


**Fig. 1. Schematics of the layouts of the tile drainage systems at the Villey, Bouzule-1, and Bouzule-2 experimental sites.**

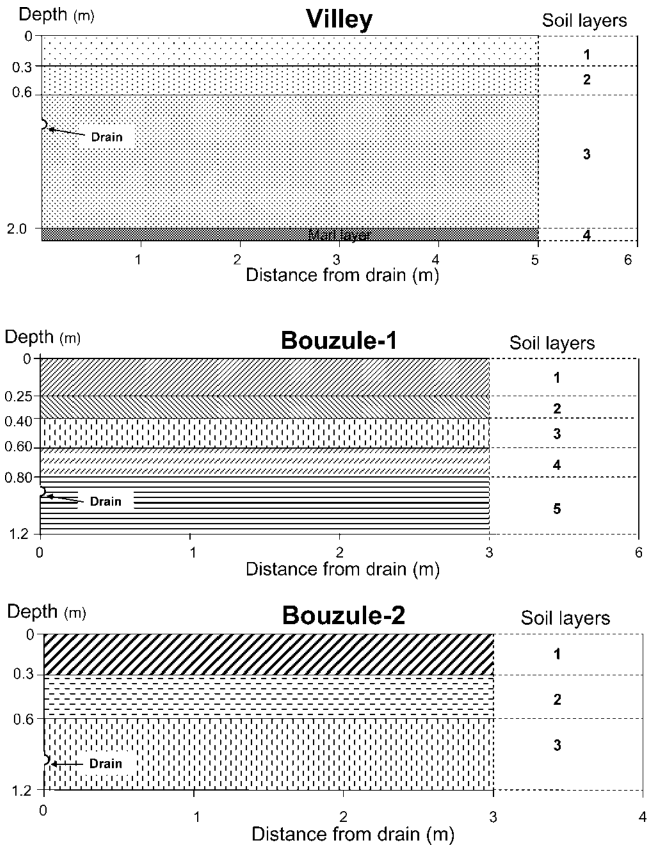


**Fig. 2. Distribution of different soil horizons in the transport domain representing half the drain spacings at the Villey sandy loam site, the Bouzule-1 silt loam site, and the Bouzule-2 silty clay site.**

6% slope toward the Bouzule-1 silt loam site, which had a slope of only 1 to 2% (Fig. 1). The two Bouzule sites were equipped with individual subsurface PVC tile drain systems (0.05-m diameter), with tile drains at an average depth of 0.9 m and having spacings of 12 m in the silt loam (Bouzule-1) and 8 m in the silty clay (Bouzule-2).

**Table 1. Selected physical and chemical properties of the Villey-St-Etienne (Villey) and La Bouzule (Bouzule-1 and Bouzule-2) tile-drained field sites in the Lorraine area of northeastern France.**

| Layers | Clay | Loam | Sand | Bulk density | C content | pH in water |
|---|---|---|---|---|---|---|
| cm | | % | | g cm$^{-3}$ | % | |
| | | | Villey (sandy loam) | | | |
| 0–30 | 11 | 19 | 70 | 1.52† | 0.87 | 5.8 |
| 30–60 | 6.2 | 3.7 | 90.1 | 1.52† | 0.46 | 6.5 |
| 60–200 | 6.2 | 3.7 | 90.1 | 1.50‡ | -§ | – |
| >200 | 54.2 | 40.5 | 5.3 | 1.40‡ | – | – |
| | | | Bouzule-1 (Silt loam) | | | |
| 0–25 | 26 | 52 | 22 | 1.28¶ | 1.36 | 6.6 |
| 25–40 | 31.2 | 52.1 | 16.7 | 1.37¶ | 1.36 | 6.6 |
| 40–60 | 37.2 | 48.8 | 14 | 1.55¶ | 0.41 | 5.8 |
| 60–80 | 40.2 | 49 | 10.8 | 1.53¶ | 0.41 | 5.8 |
| 80–100 | 39.8 | 52.6 | 7.6 | 1.58¶ | 0.32 | 5.2 |
| | | | Bouzule-2 (Silty clay) | | | |
| 0–30 | 54.2 | 40.5 | 5.3 | 1.17¶ | 1.9 | 8.2 |
| 30–60 | 54.1 | 42.8 | 3.1 | 1.30¶ | 0.88 | 8.2 |
| 60–100 | 53 | 43 | 4 | 1.40¶ | 0.51 | 8.3 |

† from Bartoli et al. (2006).
‡ Estimated.
§ Not determined.
¶ From Waleed (1983).

## Meteorological Conditions

Precipitation and potential evapotranspiration rates and other meteorological variables were obtained from the Météo France weather station in Toul (www.meteofrance.fr), about 8 km from the Villey site, and the INRA weather station in Champenoux, about 2 km from the two Bouzule sites (Fig. 3). Measured precipitation during February 2002 in Toul was 143.0 mm and in Champenoux 123.5 mm, more than twice the monthly average (52 mm) for February in this area of France during the previous three decades (1967–1997). The high rainfall rates caused the silty clay and silt loam at the two Bouzule sites to be very wet at that time. Similar conditions occurred at the Villey site. Compared with February, far less precipitation was recorded in March 2002 (a total of 70.2 mm at Villey and 49.0 mm at the Bouzule sites), with most rainfall (94% at the Bouzule sites and 93% at Villey site) occurring during the week immediately after application of the bentazone. Little or no precipitation was recorded thereafter until the end of the spring season.

## Bentazone Application

When wheat at the sites reached the second- or third-leaf stages, the three fields each received an application of bentazone, equivalent to a dose of 1.2 kg ha$^{-1}$. The spray application occurred on 4 Mar. 2002 at the Villey site but not until 11 March at the two Bouzule sites to allow the soils there to dry out enough for the tractor to be able to go onto the fields. No drainage was observed at any of the three sites between the

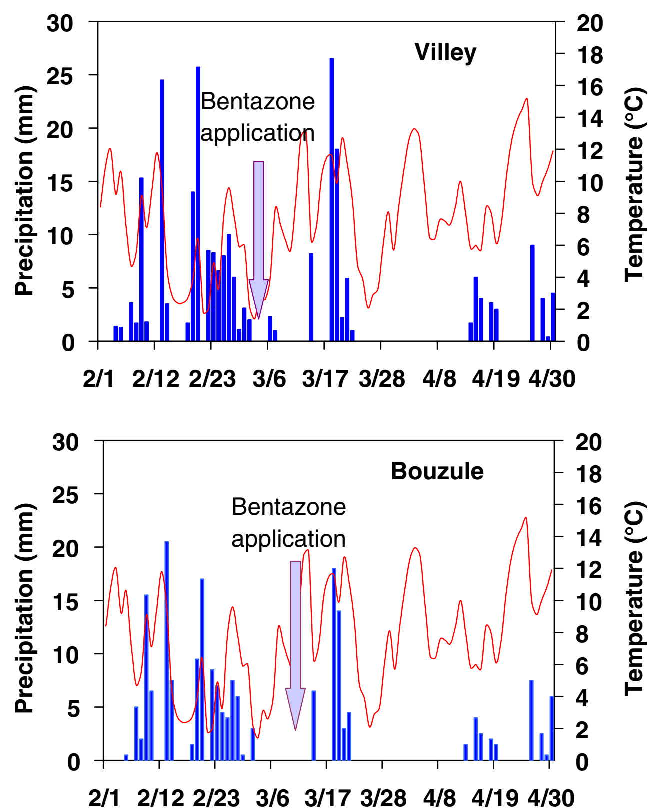


**Fig. 3. Daily precipitation rates (solid bars) and temperatures (lines) recorded by the Météo France meteorological station in Toul (adjacent to the Villey site) and the INRA meteorological station at Champenoux (adjacent to the two Bouzule sites) during the experiments. The two vertical arrows indicate the times of bentazone application.**

two applications since little or no precipitation was recorded during this period. The herbicide was applied using the commercial formulation Bazamais (BASF Agro, Genay, France) by spraying onto the fields as a standard spring treatment by farmers using their own equipment (a 2 by 6 m tractor draw ramp sprayer). Bentazone is a selective contact herbicide locally used on many different crops. The chemical is weakly acidic (pKa 3.3), has a relative molecular mass of 240.3 g mol$^{-1}$ and a solubility of 570 mg L$^{-1}$ (in water at pH 7, 22°C).

### Bentazone Sorption and Degradation

Previous laboratory experiments using surface samples from the three sites showed very low mineralization rates for bentazone. Boivin et al. (2004) observed that, after 7 d of incubation, the mineralized amounts (as a percentage of the applied dose) ranged from 0.11 to only 0.3% for the three soils. Sorption was also found to be very minor, with 97 to 98% of the applied dose being available immediately after application of bentazone to the different soil samples. After 7 d of incubation, 91 to 96% of the applied herbicide was still available. Boivin et al. (2005) found that bentazone adsorption was not correlated with the soil organic matter contents of 13 soils, which included soil samples from the three sites in this study. Bentazone adsorption data could be described using linear isotherms with distribution coefficients ($k_D$) of 1.4 ± 0.1, 1.4 ± 0.1, and 1.2 ± 0.1 L kg$^{-1}$ for the Villey, Bouzule-1, and Bouzule-2 sites, respectively.

### Tile Drain Sampling

The sampling system at each site consisted of a Sigma 900-PMAX automatic sampler (Sigma-Aldrich, St. Louis, MO) coupled to a container with a V-notch weir. This system made it possible to link drainage-water herbicide sampling with the water flux recordings (taken at 10-min intervals). Water samples were collected with the automatic sampler proportionally to the measured flow rate and stored into 10-L glass bottles.

Bentazone in the tile drainage water was analyzed using high performance liquid chromatography coupled with a C18 Merck Lichro CART 250–4 (250 mm long, 4 mm i.d.) column and a diode-array detector (Varian 9065, Varian BV, Middelburg, the Netherlands). Concentrations were determined by twice extracting the drain-water samples with dichloromethane (5:1 v/v water/dichloromethane). Since bentazone is weakly acidic, drainage water samples were acidified to pH 2 by adding HCl (0.1 *M*). The dichloromethane phase was recovered and evaporated to dryness under reduced pressure using a Heidolph 94200 evaporator (Heidolph Instruments, Schwabach, Germany) and then redissolved in high-quality methanol (2 mL). The extracted samples were stored in the dark at −20°C. The recovery rate of this method was 92 ± 4%. Analyses were performed using the following conditions: a wavelength of 220 nm, an injection volume of 20 μL, 30-min run times, 0.8 mL min$^{-1}$ flow rates, and elution with an acetonitrile plus phosphate buffer solution (70:30 by volume). The detection limit for these experimental conditions was 0.1 μg L$^{-1}$.

## THEORETICAL ANALYSIS

### Governing Flow and Transport Equations

We used the HYDRUS-2D software package (Šimůnek et al., 1999) to simulate the flow and pesticide transport processes at the three field sites. Since the various processes in HYDRUS-2D are described in detail in the user manual, we provide here only a brief synopsis of those features most relevant to our experiments. Two-dimensional variably saturated flow was calculated using the standard Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}\left[K\left(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iz}^A\right)\right] - S \qquad [1]$$

where θ is the volumetric water content (L$^3$ L$^{-3}$), $h$ is the pressure head (L), $S$ is a sink term for root water uptake (T$^{-1}$), $x_i$ ($i$ = 1,2) are the spatial coordinates (L), $t$ is time (T), and $K_{ij}$ are components of the unsaturated hydraulic conductivity tensor (L T$^{-1}$). In this study, we assumed isotropic media such that the conductivity tensor is diagonal, with both entries, $K_{xx}$ and $K_{zz}$, equal to the unsaturated hydraulic conductivity function, $K(h)$. The soil water retention, $\theta(h)$, and hydraulic conductivity, $K(h)$, properties needed in Eq. [1] were described using the functions of van Genuchten (1980) as follows:

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \qquad [2]$$

$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \qquad [3]$$

where $\theta_r$ and $\theta_s$ are the residual and saturated water contents (L$^3$ L$^{-3}$), respectively; $K_s$ (L T$^{-1}$) is the saturated hydraulic conductivity, α (L$^{-1}$) and $n$ (unitless) are empirical shape parameters, $m = 1 - 1/n$ (unitless), and $S_e$ is effective saturation given by

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad [4]$$

The effects of macroporosity on variably saturated flow are often described using composite hydraulic properties (e.g., Durner et al., 1999; Mohanty et al., 1997). In this study, we used the composite hydraulic conductivity model of Vogel and Císlerová (1988), which assumes that Eq. [3] can be used for pressure heads less than some critical value, $h_k$, but with the conductivity increasing linearly from $K_k$ to $K_s$ between $h_k$ and saturation to account for noncapillary, macropore-dominated flow as follows:

$$K(h) = \begin{cases} K_s K_r(h) & h \leq h_k \\ K_k + \dfrac{(h - h_k)(K_s - K_k)}{h_s - h_k} & h_k < h < h_s \\ K_s & h \geq h_s \end{cases} \qquad [5]$$

where $K_k$ is the hydraulic conductivity at $h_k$. This equation assumes that the predicted hydraulic conductivity function is matched to a measured value of the hydraulic conductivity, $K_k = K(h_k)$, at some water content $\theta(h_k)$ less than $\theta_s$ (Vogel and Císlerová, 1988). Most of the hydraulic parameters in Eq. [2] and [3] for the different soil layers at the three sites (Table 2) were obtained from direct measurements, while others were estimated from available soil textural data using the Rosetta pedotransfer functions of Schaap et al. (2001). Equation [5] was applied only to the more macroporous Bouzule-2 silty clay site.

**Table 2. Soil hydraulic and solute transport parameters used in the simulations of the three tile-drained field sites: $\theta_r$ is the residual water content, $\theta_s$ is the water content at saturation, $K_s$ is the saturated hydraulic conductivity, $\alpha$ and $n$ are empirical parameters, $\theta_k$ is the water content at the transition point in hydraulic conductivity function close to saturation, $K_k$ is the hydraulic conductivity at $\theta_k$, $\theta_{im}$ is the immobile water content (set equal to $\theta_r$), and $\alpha_s$ is the first-order mass transfer coefficient for exchange between mobile and immobile liquid regions.**

| Layer | $\theta_r$ | $\theta_s$ | $\theta_k$ | $\alpha$ | $n$ | $K_s$ | $K_k$ | $\theta_{im}$ | $\alpha_s$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $cm^{-1}$ | | $cm\ d^{-1}$ | | | $d^{-1}$ |
| | | | | Villey (sandy loam) | | | | | |
| 1 | 0.258† | 0.477† | –‡ | 0.029§ | 2.000§ | 140† | –‡ | 0.258¶ | 0.05# |
| 2 | 0.258† | 0.477† | – | 0.031§ | 2.341§ | 100† | – | 0.258¶ | 0.05# |
| 3 | 0.258§ | 0.477§ | – | 0.031§ | 2.341§ | 70§ | – | 0.258¶ | 0.05# |
| 4 | 0.104§ | 0.510§ | – | 0.014§ | 1.334§ | 0.1§ | – | 0.104¶ | 0.05# |
| | | | | Bouzule-1 (silt loam) | | | | | |
| 1 | 0.179†† | 0.528†† | – | 0.007§ | 1.588§ | 225‡‡ | – | 0.179¶ | 0.08# |
| 2 | 0.246†† | 0.504†† | – | 0.008§ | 1.527§ | 162‡‡ | – | 0.246¶ | 0.08# |
| 3 | 0.229†† | 0.450†† | – | 0.010§ | 1.419§ | 100‡‡ | – | 0.229¶ | 0.08# |
| 4 | 0.235†† | 0.459†† | – | 0.011§ | 1.401§ | 49‡‡ | – | 0.235¶ | 0.08# |
| 5 | 0.235†† | 0.459†† | – | 0.011§ | 1.397§ | 0.1‡‡ | – | 0.235¶ | 0.08# |
| | | | | Bouzule-2 (silty clay) | | | | | |
| 1 | 0.305†† | 0.566†† | 0.556 | 0.018§ | 1.311§ | 25# | 10‡‡ | 0.305¶ | 0.027# |
| 2 | 0.324†† | 0.519†† | 0.509 | 0.016§ | 1.318§ | 10# | 1.5‡‡ | 0.324¶ | 0.027# |
| 3 | 0.308†† | 0.505†† | 0.495 | 0.015§ | 1.322§ | 1.7# | 0.1‡‡ | 0.308¶ | 0.027# |

† Measured data from Bartoli et al. (2006).
‡ Not applicable.
§ Estimated with ROSETTA (Schaap et al., 2001).
¶ Same as residual water content.
# Adjusted to the modeled system.
†† Measured data from Waleed (1983).
‡‡ Measured data from Ailliot (1972).

Solute transport was described using the advection–dispersion equation (ADE) given by:

$$\frac{\partial \theta c}{\partial t} + \frac{\partial \rho s}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial c}{\partial x_j}\right) - \frac{\partial q_i c}{\partial x_i} \qquad (i,j = 1,2) \qquad [6]$$

where $c$ (M $L^{-3}$) and $s$ (M $M^{-1}$) are solute concentrations in the liquid and solid phases, respectively, $q_i$ is represents water flux density (L $T^{-1}$), $\rho$ is the bulk density (M $L^{-3}$), and $D_{ij}$ is the dispersion tensor ($L^2$ $T^{-1}$), which was described using standard expressions (e.g., Bear, 1972) in terms of the longitudinal and transverse dispersivities and contributions arising from molecular diffusion in the liquid phase (Šimůnek et al., 1999). Degradation of bentazone in Eq. [6] was neglected based on laboratory experiments that showed little or no degradation within time periods such as those used for the field experiments (Boivin et al., 2004).

Equation [6] represents the standard ADE, which is known to have limitations for transport in many field soils (Šimůnek et al., 2003). We additionally considered a dual-porosity (mobile–immobile water) type formulation, which assumes that the liquid phase can be partitioned into mobile, $\theta_m$, and immobile, $\theta_{im}$, regions, with advective–dispersive transport being restricted to the mobile region, and with first-order mass transfer between the mobile and immobile liquid regions. The transport equations for this model, further referred to as the MIM model, are given by

$$\frac{\partial \theta_m c_m}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_m D_{ij}\frac{\partial c_m}{\partial x_j}\right) - \frac{\partial q_i c_m}{\partial x_i} - \alpha_s(c_m - c_{im}) \qquad [7a]$$

$$\frac{\partial \theta_{im} c_{im}}{\partial t} + \frac{\partial \rho s_{im}}{\partial t} = \alpha_s(c_m - c_{im}) \qquad [7b]$$

where $c_m$ and $c_{im}$ are the liquid concentrations in the mobile (macropore) and immobile (matrix) regions (M $L^{-3}$), respectively, $s_{im}$ is the adsorbed concentration in the immobile region (M $M^{-1}$), $D_{ij}$ is the dispersion tensor in the mobile region ($L^2$ $T^{-1}$), and $\alpha_s$ is the solute mass transfer coefficient between the two regions ($T^{-1}$). In this study, we assumed that the immobile water content, $\theta_{im}$, in Eq. [7a] and [7b] was constant during the simulations and that sorption occurred only in the immobile region.

We used a longitudinal dispersivity of 15 cm and a transversal dispersivity of 1 cm for the solute transport simulations. These values are well within the range of dispersivities (5–20 cm) generally found for field-scale transport (Anderson, 1984; Jury and Sposito, 1985; Beven et al., 1993), and are the same as those used by de Vos et al. (1999) in their tile-drained field flow and transport simulations. Also, following Boivin et al. (2005), we assumed linear equilibrium partitioning between the adsorbed and solution concentrations in both Eq. [6] and [7] using laboratory-measured $k_D$ values.

## Numerical Implementation

For each soil profile, a finite element grid was generated using the MeshGen-2D module of HYDRUS-2D (Šimůnek et al., 1999), stratified in accordance with observed soil profile layering (Fig. 2). As an example, the Bouzule-2 silty clay loam soil profile was taken to be 4 m wide (half the spacing between the tile drains) and 1.2 m deep, with the flow domain being divided into three layers and assigned soil hydraulic parameters as described in Table 2. A total of 1237 nodes and 2298 triangular elements was used to discretize the Bouzule-2 transport domain, using relatively fine discretizations near the soil surface and around the tile drain to accommodate higher pressure gradients in those parts of the domain (Fig. 4), and coarser grids elsewhere. The tile drain was specified at a depth of 90 cm along the side of the modeled system.

Discretizations of the Bouzule-1 and the Villey sites were analogous to those in Fig. 4 for Bouzule-2 (grids not further shown here). The transport domain for the Bouzule-1 silt loam system was 6 m wide and 1.2 m deep (Fig. 2). The soil profile at this site was divided into five layers with soil hydraulic properties as listed in Table 2. The flow domain itself was discretized using 1874 nodes and 3494 triangular elements. The sandy loam soil profile of the Villey site was modeled to be 6 m wide and 2.2 m deep, with the soil profile being divided into five layers (Fig. 2) using a total of 1833 nodes and 3465 triangular elements.

Boundary conditions for the simulations included no-flow boundaries on the sides of the modeled systems, atmospheric conditions at the soil surface (daily precipitation and evaporation rates), and free drainage (zero pressure gradients) at the bottom boundary. The free-drainage condition reduces to a zero-flux boundary condition when the saturated conductivity of the bottom layer is made very small or zero. The tile drains were implemented using seepage face boundary conditions, thus implying that the drains functioned only when the surrounding soil was saturated. Root water uptake was calculated from potential transpiration values using the reduction model of Feddes et al. (1978), with model uptake parameters for wheat as compiled previously by Wesseling (1991) in the SWATRE model. Sensitivity analyses with HYDRUS-2D showed that transpiration and root water uptake affected mostly water contents near the soil surface and had little effect on calculated drain discharge rates and bentazone concentrations in the drainage water during the 100-d experimental period.

Preliminary flow simulations starting on 10 Jan. 2002 (~2 mo before the pesticide application) were performed with an initial equilibrium pressure head profile so as to obtain realistic pressure head and water content distributions in the profile at the time of the pesticide application (4 March at Villey and 11 March at the Bouzule sites). The initial solute concentration was assumed zero throughout the profile, except for a 1-cm layer near the soil surface in which the concentration was defined such that the total solute mass in that layer was equal to the applied dose (corresponding to the same 1.2 kg ha$^{-1}$ for all three sites). Simulations in all cases continued for 100 d.

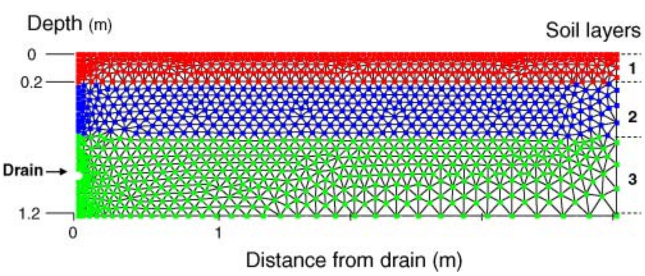


**Fig. 4. Finite element grid for the transport domain representing half the drain spacing of the modeled silty clay (Bouzule-2) site. The grid consisted of 2298 triangular elements and 1237 nodes.**

## RESULTS AND DISCUSSION

Measured and simulated instantaneous and cumulative drain discharge rates are compared in Fig. 5, 6, and 7 for the Villey, Bouzule-1, and Bouzule-2 sites, respectively. These figures also show measured and calculated bentazone concentrations in the drainage water, as well as daily and cumulative amounts of bentazone exported with the drainage water as a percentage of the applied amounts. The same scales were used for similar plots in the three figures to better visualize differences between the sites. Notice that all three sites produced drainage during the experiments, with the Bouzule-1 site (Fig. 6b) producing more drainage than the other two sites. From 10 Mar. to 20 Apr. 2002, the cumulative volume of drain water measured at the Bouzule-1 silt loam site (Fig. 6b) was 521 m$^3$ ha$^{-1}$, compared with volumes of 240 and 175 m$^3$ ha$^{-1}$ recorded at the Villey sandy loam (Fig. 5b) and Bouzule-2 silty clay (Fig. 7b) sites, respectively.

Bentazone concentrations in the drainage water at Bouzule-1 and Bouzule-2 were relatively high, leading to considerable amounts of pesticide being exported from those two sites, especially from Bouzule-1 (Fig. 6e) because of the higher drainage volumes at this site than at Bouzule-2. By comparison, total pesticide export from the Villey site was relatively small, mostly because of lower pesticide concentrations in the drainage water (Fig. 5c and 5e).

### Villey Sandy Loam Site

Recent excavations at this site indicated the presence of a low-permeability marl layer at a depth between 1.8 and 2 m, but no intermediate (mixed) layer between the sandy deposit and the bottom layer. The excavations also showed evidence of oxidation–reduction processes between 1.8- and 2-m depth (L. Florentin, personal communication, 2004), consistent with perched water table conditions. Following Jacquin and Florentin (1980), the $K_s$ of the marl material was set equal to 0.1 cm d$^{-1}$ in the numerical calculations. The HYDRUS-2D simulations for the entire soil profile with the marl layer included correctly produced perched water above the low-conductive marl layer, with the tile drain calculations closely matching the observed field data (Fig. 5a and 5b).

Simulations with the standard ADE model did not lead to any pesticide in the tile drainage water at the Villey site during the experimental time period (Fig. 5c and 5d). Although the Villey sandy loam soil contained a large sand fraction (Table 1), significant amounts of loam, clay, and organic matter were also present, which promoted good soil structure. Hence, we simulated the experiment also with the MIM transport model, assuming $\theta_{im}$ to be the same as $\theta_r$. We used a relatively high value of 0.258 for $\theta_{im}$, consistent with results of recent infiltrometer experiments by Bartoli et al. (2006), which indicated that the residual water contents at this site were much higher than values predicted with the Rosetta pedotransfer functions (Schaap et al., 2001).

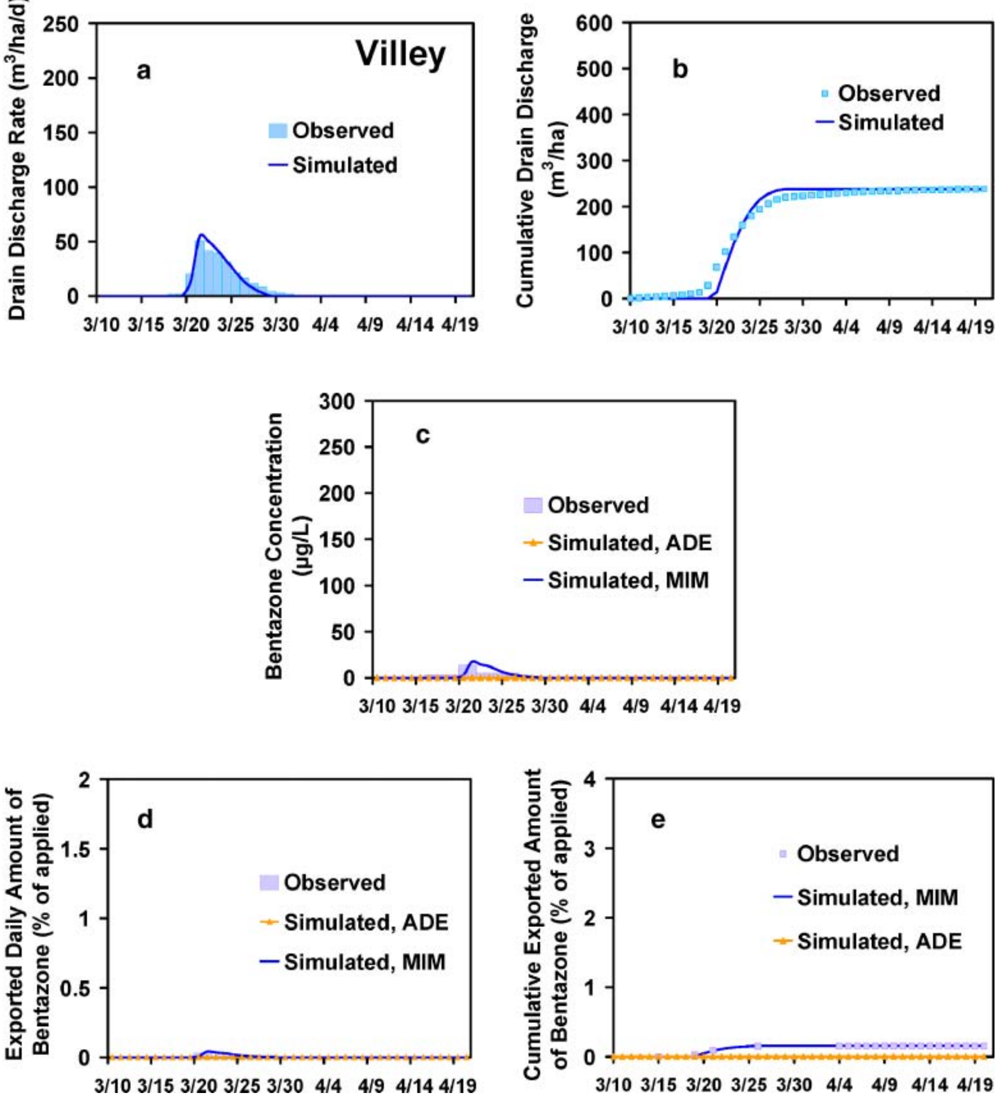


**Fig. 5. Observed and simulated (a) instantaneous and (b) cumulative tile drain discharge rates, (c) bentazone concentrations in the drainage water, (d) daily amounts of bentazone exported with the drainage water, and (e) the cumulative amount of bentazone exported for the Villey sandy loam site. Solute transport simulations were performed with both the advection–dispersion equation (ADE) and the mobile–immobile nonequilibrium transport model (MIM).**

The HYDRUS-2D simulation using the MIM transport model with $\theta_{im} = 0.258$ and a single value of 0.05 $d^{-1}$ for the mass transfer coefficient $\alpha_s$ (visually fitted to the data) produced excellent agreement with the observed concentrations (Fig. 5c), as well as with the amount of pesticide exported with the tile drainage water (Fig. 5d and 5e). The use of the MIM model is qualitatively consistent with previous studies by Boivin et al. (2004) on the time-dependent availability of bentazone. They showed that, immediately after bentazone application, 97% of the applied dose was available using water extraction (0.01 *M* $CaCl_2$), while an additional 0.1% could be removed only with additional methanol extractions. On the other hand, after 7 d only 77% was available with water extraction (0.01 *M* $CaCl_2$) and 19% using subsequent methanol extraction. Boivin et al. (2004) concluded that slow solute diffusion into the soil microporosity may have resulted in entrapment of a significant part of the chemical, which subsequently could be removed only by means of a more effective solvent (methanol).

## Bouzule-1 Silt Loam Site

Simulations for the Bouzule-1 site again showed the key role of the $K_s$ of the bottom layer in determining the amount of drain discharge. A sensitivity analysis (Fig. 6a and 6b) showed that small changes in $K_s$ can cause large variations in both the instantaneous and cumulative tile drainage rates. Excellent results were obtained with a value of 0.1 cm $d^{-1}$ for $K_s$. The only noticeable difference between the simulation and observed data was a slightly larger calculated drain discharge rate immediately after the rainfall event (Fig. 6a). The optimal value of 0.1 cm $d^{-1}$ was similar to a laboratory-measured value reported by Ailliot (1972). The low permeability of the

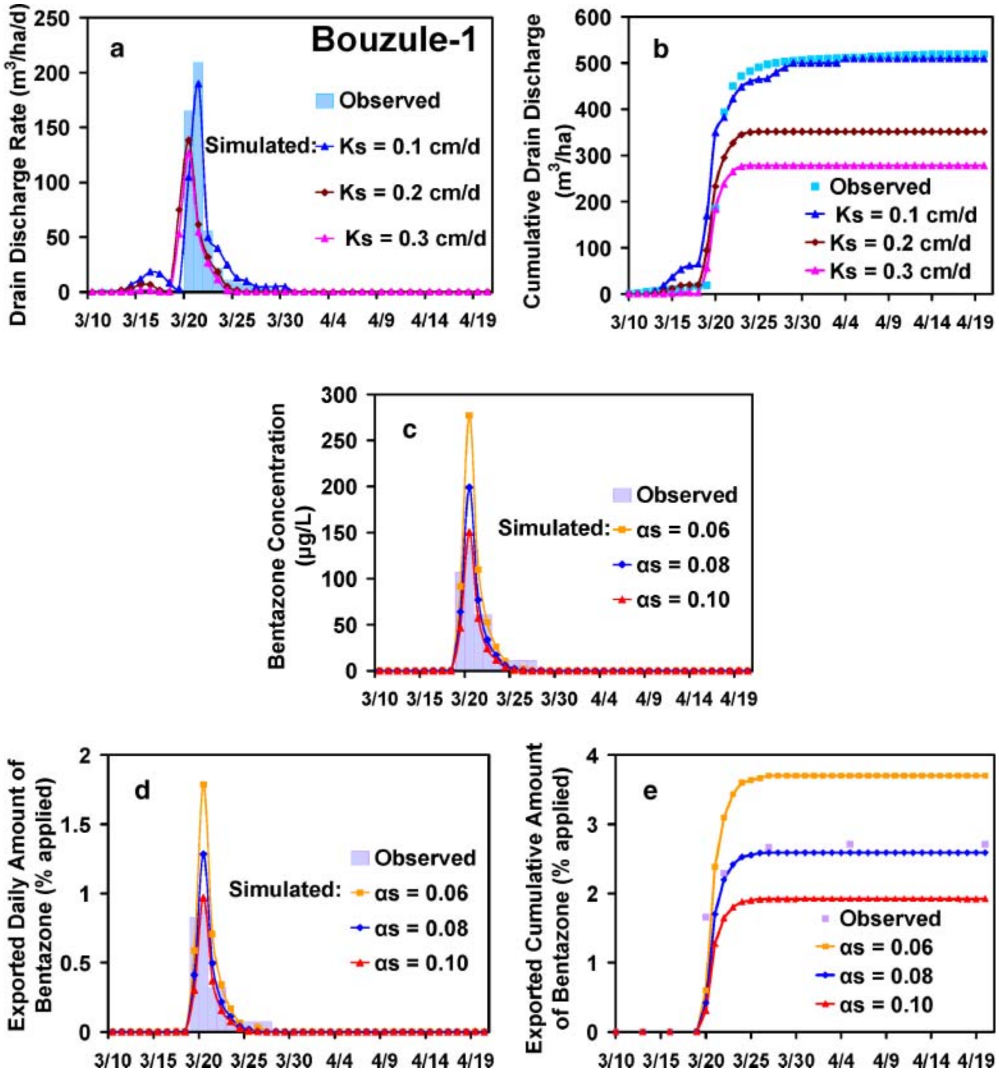


**Fig. 6. Observed and simulated (a) instantaneous and (b) cumulative tile drain discharge rates, (c) bentazone concentrations in the drainage water, (d) daily amounts of bentazone exported with the drainage water, and (e) the cumulative amount of bentazone exported for the Bouzule-1 silt loam site. Drain discharge calculations were carried using three values of the saturated hydraulic conductivity ($K_s$) of the bottom layer 5 (Fig. 2b). Solute transport simulations were performed with the mobile–immobile nonequilibrium transport model (MIM) using three values of the mass transfer coefficient ($\alpha_s$).**

bottom layer explains why this site becomes quickly water saturated during large rain events, and why artificial tile drains are needed in this area, where the average annual precipitation is only ~800 mm (mostly restricted to the fall and winter periods). Previous field studies by Novak et al. (2001) also indicated the presence of a perched water table during part of the year at this site, leading to considerable tile drainage, especially during the winter season. In our case, having no drain discharge in the beginning of the simulation indicated that little or no perched water must have been present at the time of the pesticide application, with the major rainfall event after the bentazone application causing considerable tile drainage flow.

Similarly as for the Villey site, ADE solute transport simulations that considered only equilibrium transport did not produce any pesticide transport into the tile drains at Bouzule-1 (Fig. 6c and 6d). Although we were able to predict some pesticide leaching by increasing the longitudinal dispersivity $D_L$ (results not further shown), the total amount of leached bentazone remained severely underestimated. Good agreement between simulated and observed concentrations could be obtained again with the MIM. Calculated outflow concentrations were found to be very sensitive to the solute mass transfer coefficient $\alpha_s$ in Eq. [6]. A sensitivity analysis (Fig. 6c, 6d, and 6e) revealed good agreement between simulated and observed concentrations and amounts of pesticides exported when $\alpha_s$ was set equal to 0.08 $d^{-1}$, somewhat higher than the optimal value of 0.05 $d^{-1}$ found for the Villey site.

## Bouzule-2 Silty Clay Site

The Bouzule-2 site showed less drainage (175 $m^3$ $ha^{-1}$) than the adjacent Bouzule-1 silt loam site (521 $m^3$ $ha^{-1}$), but higher bentazone concentrations in the drainage water, probably due to preferential flow. Evidence of

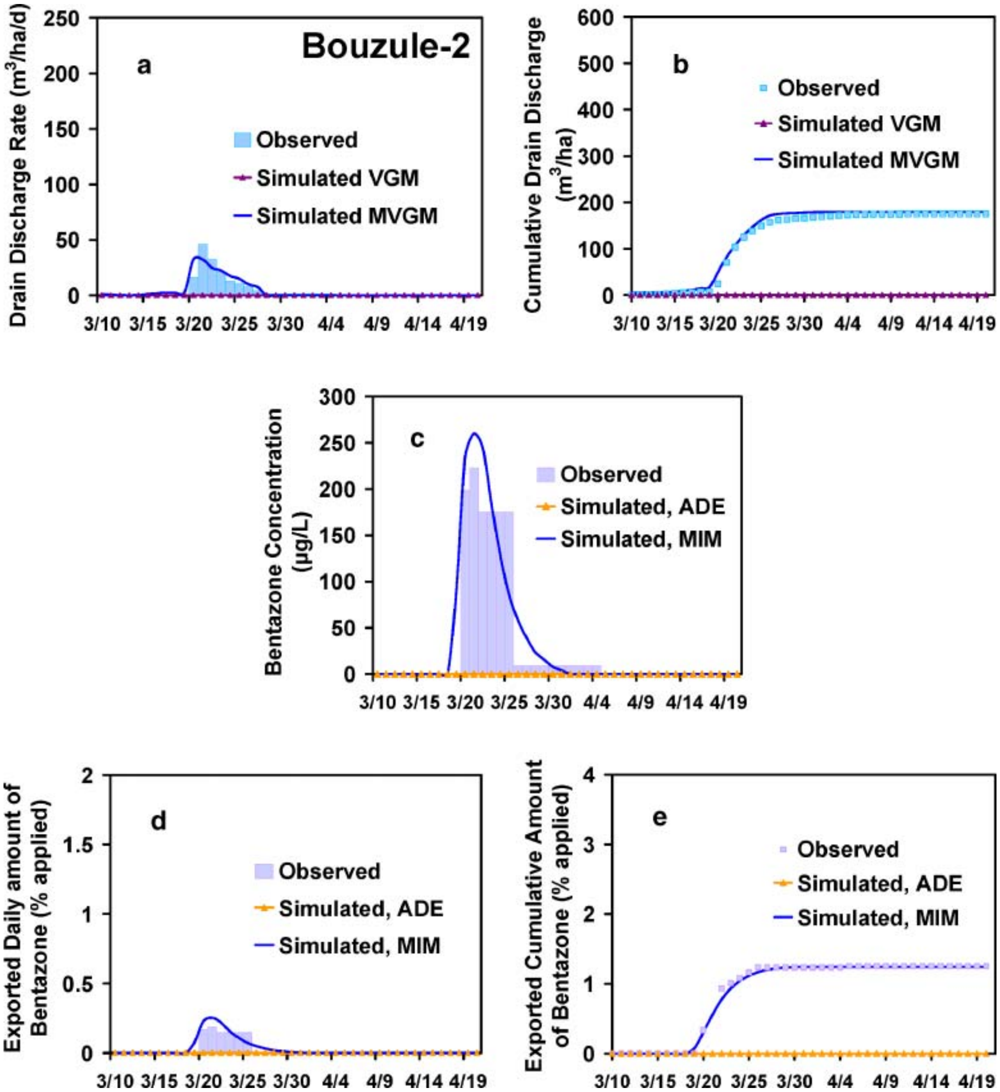


**Fig. 7. Observed and simulated (a) instantaneous and (b) cumulative tile drain discharge rates, using the standard van Genuchten–Mualem (VGM) and the modified van Genuchten–Mualem (MVGM) hydraulic functions; (c) bentazone concentrations in the drainage water; (d) daily amounts of bentazone exported with the drainage water; and (e) the cumulative amount of bentazone exported for the Bouzule-2 silty clay site. Solute transport simulations were performed with both the advection–dispersion equation (ADE) and the mobile–immobile nonequilibrium transport model (MIM).**



preferential flow at this same site was previously provided by Novak et al. (2001, 2003), who observed large amounts of both $Br^-$ and the pesticide metolachlor in the drainage water, especially during the spring and summer seasons. Novak et al. (2003) concluded from the experiments that tile drainage water at Bouzule-2 probably came directly from the soil surface through short-circuiting of much of the soil matrix and rapid leaching of large amounts of pesticides. The $K_s$ values obtained from our laboratory experiments did not account for the influence of small drying cracks (up to 2 mm wide) in especially the surface horizons at this site, and thus substantially underestimated the actual $K_s$ values in the field. The drying cracks at this site were particularly noticeable in the late spring and summer months. Direct field experiments of $K_s$ of the first soil layer (10-cm depth) using a ring infiltrometer showed the importance of these drying cracks. When the infiltration ring was placed on top of surface cracks, the measured infiltration rates increased by factors of 2 to 10 relative to areas without cracks (Bartoli et al., 2006).

Preferential flow at Bouzule-2 could not be simulated using the standard van Genuchten–Mualem hydraulic functions. Predictions in this case severely underestimated observed drain discharge rates (Fig. 7a and 7b). To account for flow through the drying cracks, the composite soil hydraulic functions of Vogel et al. (2000) were used to mimic preferential flow of water and solute (modified van Genuchten–Mualem hydraulic functions). Parameters for these functions (Eq. [4] and [5]) are listed in Table 2. By using higher values for the hydraulic conductivity near saturation ($K_s > K_k$), good agreement was obtained between the simulated and observed drain discharges (Fig. 7a and 7b). Minor differences between the observed and simulated data still occurred at the end of the drainage event, with the simulations producing no more tile drainage while the field data still indicated some drainage.

Using the modified van Genuchten soil hydraulic functions did produce much more realistic simulations of the drain discharge rate at the Bouzule-2 silty clay site. While adjustment of the $K_k$ values of the different soil horizons resulted in a close match with the observed data at this site, it is unlikely that the selected combination of $K_k$ values in our simulations represented a single unique description of the flow process. Please note that we used a trial-and-error approach to obtain the best set of $K_k$ values, rather than the full parameter estimation capabilities of HYDRUS-2D. While we calibrated this parameter in our study, it possibly could be measured also independently using tension infiltrometers, or even estimated from texture using pedotransfer functions (Jarvis et al., 2002).

Similarly as for the Villey and Bouzule-1 sites, the amount of leached pesticide was severely underestimated unless the MIM model was used. As for the other two sites, $\theta_{im}$ was again assumed to be the same as $\theta_r$; however, the mass transfer coefficient $\alpha_s$ was again fitted to the data. A value of 0.027 $d^{-1}$ for $\alpha_s$ produced excellent agreement between measured and simulated results, both for the bentazone concentrations in the tile drainage water (Fig. 7c) and the total amount of bentazone exported with the drainage water. The fitted value of 0.027 $d^{-1}$ for $\alpha_s$ is somewhat lower than the values of 0.08 and 0.05 $d^{-1}$ found for the other two sites. These values are all well within the range of values reported for intermediate-scale and field studies (e.g., Pang and Close, 1999; Maraqa, 2001; Jørgenson et al., 2004), and mostly lower than laboratory studies (van Genuchten and Wierenga, 1976; Maraqa, 2001; Lee et al., 2000). We note that in our study we adopted a single value for $\alpha_s$ for each site as a whole. This approach ignores any dependency of $\alpha_s$ on the water content or the flow velocity, which have been shown to occur in several previous studies (e.g., Nkedi-Kizza et al., 1983; De Smedt and Wierenga, 1984; Maraqa, 2001; Jaynes, 2002).

## CONCLUSIONS

The purpose of this study was to compare the transport of the herbicide bentazone in three contrasting tile-drained cultivated field soils subject to otherwise similar experimental conditions. Observed drain discharge rates and amounts of pesticide exported from the sites were mostly a reflection of the soil textural properties and soil layering at the three sites. Numerical simulations of drain discharge with HYDRUS-2D compared well with the observed drainage data for the relatively homogeneous sandy loam (Villey) and the silt loam (Bouzule-1) soils. The saturated hydraulic conductivity of the bottom layer in both cases was key to correctly predicting the drainage fluxes.

Accurate results could be obtained with the original van Genuchten equations for the Villey and Bouzule-1 sites, but not for the more fine-textured Bouzule-2 silty clay site. Acceptable tile drainage predictions at this site were possible only when the soil hydraulic functions were modified to account for preferential flow through drying cracks near the soil surface. While the selected combination of $K_k$ values in the modified hydraulic properties (Eq. [6]) provided a good description of the drain discharge rates, the values probably were not unique. Hence, we acknowledge a need for further studies that more precisely delineate the exact and possibly time-dependent (seasonal) nature of the preferential flow processes at especially the Bouzule-2 site. More comprehensive long-term data sets may be needed for this purpose, including in situ measured water contents and concentrations.

Simulations of pesticide concentrations in the drainage water were unsuccessful when the equilibrium ADE transport model was used. Much better results were obtained with the nonequilibrium MIM approach, both for the concentrations of the tile drainage water and total amounts of solute being exported with the drainage water. In this study we assumed the immobile water content to be the same as the residual water content, an assumption that appeared very much adequate for our data; however, $\alpha_s$ was found to be a critical parameter that needed to be fitted to the data. Numerical results were very sensitive to the adopted value of $\alpha_s$ (e.g., Fig. 6e), even if we limited this parameter to values well within the range of values previously documented in the literature. This points to the importance of methods to directly measure $\alpha_s$ in the field (e.g., Jaynes, 2002) at spatial and time scales typical of tile drainage experiments.

Our study shows that the use of a limited amount of input data can still lead to acceptable simulations of drain discharge rates and chemical concentrations of the drainage water. Most of the data we used were derived from previous studies at the sites (Table 2), or using reasonable assumptions (e.g., for the dispersivities and the immobile water content). Notable exceptions, again, were the modified hydraulic parameters ($K_k$) to account for preferential flow at the fine-textured Bouzule-2 site, and the mass transfer coefficient ($\alpha_s$) at all three sites. These parameters had to be fitted to the field data. This suggests that future studies should concentrate especially on these two parameters, including their possible time dependency during the year as a result of agricultural management practices and shrink–swell phenomena.

Finally, we note that maximum bentazone concentrations in the drainage water ranged between 13.6 $\mu g\ L^{-1}$ at Villey to 223 $\mu g\ L^{-1}$ at Bouzule-2, while intermediate concentrations were observed at Bouzule-1 (120 $\mu g\ L^{-1}$). These concentrations are significantly higher that the limit of 0.1 $\mu g\ L^{-1}$ set by the European Union for maximum pesticide concentrations in groundwater (Focus Leaching Modelling Workgroup, 1995), and higher than 3 $\mu g\ L^{-1}$ used by the U.S. Environmental Protection Agency for the maximum contaminant level for bentazone (USEPA, 2004). Equally important, the total amount of bentazone exported with the drainage water during our study was very large for two of the three sites. This was especially the case for the Bouzule-1 silt loam site, where 2.7% of the applied amount of bentazone ended up in the tile drains (large volumes of drainage water with relatively high solute concentrations).

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