Simulation of 2,4-d herbicide transport through the unsaturated zone using an analytical model

Lucila Candela[a]; Miguel A. Mariño[b]

[a] Department of Geotechnical Engineering and Geoscience, UPC, 08034-Barcelona, Spain [b] Hydrology Program and Department of Civil and Environmental Engineering, University of California, Davis, CA 95616, USA

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

SIMULATION OF 2,4-D HERBICIDE TRANSPORT THROUGH THE UNSATURATED ZONE USING AN ANALYTICAL MODEL

LUCILA CANDELA[a],* and MIGUEL A. MARIÑO[b]

[a]*Department of Geotechnical Engineering and Geoscience, UPC, Gran Capitán, s/n, 08034-Barcelona, Spain;*
[b]*Hydrology Program and Department of Civil and Environmental Engineering, University of California, Davis, CA 95616, USA*

Pesticide movement through the unsaturated zone of the subsurface environment is a complex process. Agricultural practices, soil properties, and climatic conditions among others, constitute the most important aspects to be considered. To simulate the transport and fate of the herbicide 2,4-D under real agricultural conditions, the Hantush–Mariño (1996) model has been applied. The model is a physically based analytical model that simulates pesticide transport in soils and groundwater. In the unsaturated zone, the model simulates one-dimensional pesticide movement based on the concept of complete mixing, adsorption, volatilization, and degradation. Linear equilibrium liquid–vapor partition is considered based on Henry's law and linear equilibrium adsorption is assumed for sorption and desorption in soil. The simulation model is applied to a study area located in a newly built golf course (Baix Emporda-Gerona, Spain), where 2,4-D is currently applied. Results show that with current agricultural practices, 2,4-D can be still detected at a depth of 2 m at concentrations greater than 0.1 µg/L.

Keywords: 2,4-D herbicide; Simulation; Herbicide transport; Analytical model

INTRODUCTION

Since the early 1980s a great number of pesticides or their breakdown products have been detected in groundwater, many of them at concentrations greater than 0.1 µg/L. The vulnerability of aquifers to pesticide contamination is a long-term and complex process affected by soil physical, (bio)chemical, and hydrogeological properties, climatic conditions, and agricultural practices. Pesticides used for agricultural purposes are leached to the water table through deep percolation of water from infiltrating rainfall and return flow from irrigation.

Because contamination of aquifers by pesticides may take decades before leaching from soil can reach groundwater level, it is not feasible economically or practically to conduct frequent extensive field-scale experiments on pesticide leaching. In order

---

*Corresponding author. Fax: +34-93-4017251. E-mail: lucila.candela@upc.es

to evaluate the potential for pesticide contamination of groundwater, and to predict the fate and transport of residues in soil and groundwater, simulation models are currently used.

Modeling transport of pesticides in soils is not a new undertaking and, in general, transport models vary from complex distributed parameters to simpler lumped-parameter linear-reservoir models [1]. The current work concerns the application of an analytical simulation model to investigate the impact on vulnerability of groundwater to contamination by the herbicide 2,4-D of current agricultural practices on the golf course Serres de Pals (Girona, Spain).

The pesticide selected, 2,4-D (2,4-dichlorophenoxyacetic acid, Bi-Hedonal®), belongs to the group of related synthetic herbicides called chlorophenoxy herbicides, primarily used in agriculture to control weeds in wheat and corn fields and in orchards to prevent fruit from dropping prematurely. Also, 2,4-D has many non-agricultural uses; it is used to control weeds in forests, rangelands/pastures, parks, athletic fields, ponds and lakes, and to clear land for roadways and railway tracks. It has already been detected in groundwater at golf courses in the USA at concentrations greater than $0.1\,\mu g/L$ [2, 3].

SIMULATION MODEL

The Hantush–Mariño [1] model, which is a physically based analytical model suitable for long-term predictions of pesticide concentrations in soils and aquifers, is employed in this study. The soil is divided into a root zone and the intermediate vadose zone, in each of which complete mixing of the pesticide is assumed. The soil model takes into account processes such as leaching, adsorption, (bio)chemical degradation, crop-roots uptake, and volatilization. Linear equilibrium liquid–vapor partition is considered based on Henry's law, and linear equilibrium adsorption is assumed for sorption and desorption in soil. Transport in the aquifer, however, is modeled by a two-dimensional advection–dispersion transport equation. A two-dimensional analytical solution for concentrations in groundwater is obtained by considering leaching through soils, advection, dispersion, degradation, and linear equilibrium adsorption of pesticides in aquifers. Although the model is based on some rigid assumptions (uniform properties in each of the soil zones, steady-state flow, and complete mixing in each zone), it nevertheless predicts concentrations in groundwater analytically, requiring a small set of data, and accounting in a rather simple manner for the complex interactions among the different physical, (bio)chemical, and meteorological processes. For other analytical models describing leached mass fractions of organic compounds, such as pesticides, in soils and flushing of their residues in aquifers, the reader is referred to Hantush *et al.* [4, 5].

Model Description

The simulation model used in this investigation is a one-dimensional, analytical model of reactive transport in the unsaturated zone, developed by Hantush and Mariño [1]. The model actually comprises three sub-models that correspond to: (1) the root zone (upper part of the soil); (2) the intermediate vadose or unsaturated zone (lower soil); and (3) a saturated zone (aquifer). The model uses the assumption of complete mixing in simulating the transport and fate of pesticide residues in the root and

intermediate vadose zones by spatially averaging the related point multiphase-transport partial differential equations over the soil depth. Given the scope of this study, only the sub-model corresponding to the root and vadose zones was considered.

The aforementioned sub-model takes into account processes such as leaching, adsorption, (bio)chemical degradation, crop-roots uptake, and volatilization. Linear equilibrium liquid–vapor partition is considered based on Henry's Law, and linear, equilibrium adsorption is assumed for sorption and desorption of 2,4-D in soil. Water balance in the soil is attained by utilizing rainfall and daily irrigation data. The sub-model allows for various applications of the 2,4-D herbicide during the simulation period.

Volume-averaged 2,4-D concentration for the root and intermediate vadose zones is calculated by expressing the multiphase transport equation [6] in the dissolved phase using equilibrium partitioning and then integrating it over the entire thickness of each soil zone separately. The analytical solution for the transport of the pesticide in the root and intermediate vadose zones is shown next. A detailed description of the model, including all the simplifying assumptions considered, is contained in Hantush and Mariño [1] and Chu et al. [7].

The volume-averaged pesticide concentration in terms of the dissolved phase leaving the root zone after being exposed to volatilization, root uptake, first-order degradation, and linear-equilibrium sorption along the root zone in the case of an instantaneous pesticide application is:

$$C_r(t) = e^{-\beta_r(t-t_0)}C_r(t_0) + \frac{M_0}{\theta_r h R_r}e^{-\beta_r(t-t_0)}, \tag{1}$$

in which

$$\beta_r = \frac{1 + (T_r/\lambda_r \ln 2) + \mu_r)}{T_r} \tag{2}$$

$$T_r = hR_r/(v^*/\theta_r) \tag{3}$$

$$\mu_r = (FS + \sigma_r/h)\lambda_r/(R_r\theta_r) \tag{4}$$

$$\sigma_r = k_r D_g K_H/d \tag{5}$$

$$R_r = 1 + (\rho_{br}K_{dr} + k_r K_H)/\theta_r \tag{6}$$

$$v^* = v - ET_c, \tag{7}$$

where $C_r(t)$ = average solute concentration in the root zone (M/L^3); M_0 = applied pesticide mass per area (M/L^2): λ_r = half-life of the pesticide (T); v = water flux into the root zone (L/T); v^* = net water flux available for deep percolation below the root zone (L/T); h = thickness of the root zone (L); θ_r = volumetric moisture content; R_r = retardation factor; F = transpiration stream concentration factor; S = rate of water uptake by the crop (1/T); k_r = volumetric air content (dimensionless); D_g = soil/gas diffusion coefficient (L^2/T); K_H = dimensionless Henry's constant; d = thickness of an air boundary layer (L); ρ_{br} = bulk density of root zone soil (M/L^3);

K_{dr} = distribution coefficient (L^3/M); ET$_c$ = crop evapotranspiration rate (L/T); and subscript r = root zone index.

Similarly, the solution of the differential equation describing pesticide leaching, first-order reaction, and linear-equilibrium adsorption for an instantaneous application of pesticide in the intermediate vadose zone is:

$$C_u(t) = e^{-\beta_r(t-t_0)} C_u(t_0) + \alpha_u \left(Cr(t_0) + \frac{M_0}{\theta_r h R_r} \right) \cdot \frac{e^{-\beta_r(t-t_0)} - e^{-\beta_r(t-t_0)}}{\beta_u - \beta_r}, \qquad (8)$$

in which

$$\beta_u = \frac{1 + \ln(2)(T_u/\lambda_u)}{T_u} \qquad (9)$$

$$\alpha_u = 1/T_u \qquad (10)$$

$$T_u = HR_u/(v^*/\theta_u) \qquad (11)$$

$$R_u = 1 + (\rho_{bu} K_{du} + k_u K_H)/\theta_u, \qquad (12)$$

where H = thickness of the vadose zone (L) and subscript u = vadose zone index.

EXPERIMENTAL

Study Area and Sampling Site

The study area is a golf course at Serres de Pals in Girona, Northern Spain. The area, which was initially cultivated with paddy rice, has recently been transformed into a golf course. Watering of the area from urban treated wastewater started in June 2000.

The aquifer is of lacustrine detrital origin and is composed of sand, silt, and some clay. The phreatic level is about 1.5–2 m below the soil surface.

Physico-chemical Characterization of Soil Samples

The physico-chemical characterization of the unsaturated zone was made through destructive sampling. Two hollow-stem auger holes were drilled up to 2-m depth and undisturbed soil samples were taken from soil cores at 30-cm intervals to determine physico-chemical parameters. The following parameters for the surface zone, root zone, vadose zone, and aquifer were obtained in the laboratory: bulk density (γ_d), water content (w_i), grain distribution (C_c and U_c), particle density (γ_g), saturated hydraulic conductivity (K_s) and also suction curves at different depths. All parameters were obtained following standard ASTM methods published elsewhere; to calculate suction curves a psychrometric method was used [8]. The retention curve was adjusted to the van Genuchten [9] curve.

Properties of two soil profiles are shown in Table I. Changes in porosity with depth in two boreholes are plotted in Fig. 1, which also shows important changes in surface porosity due to anthropogenic effects for the soil transformation in order to construct the golf course.

TABLE I   Physical and textural characteristics of the vadose zone

| Profile	Depth (m)	Water content (%)	Bulk density (g/cm^3)	Porosity (%)	Saturated hydraulic conductivity (cm/s)	Silt and clay (%)
1	0.0	10.80	1.55	0.42	2.93×10^{-4}	24.84
	0.3	13.88	1.34	0.50	1.93×10^{-5}	42.60
	0.6	8.74	1.48	0.44	1.83×10^{-5}	40.10
	0.9	6.49	1.70	0.36	1.88×10^{-5}	39.13
	1.2	5.92	1.66	0.37	1.01×10^{-6}	29.89
	1.5	12.89	1.57	0.41	1.14×10^{-6}	27.99
	1.8	8.13	1.67	0.37	2.08×10^{-6}	31.59
	2.0	12.92	1.92	0.28	1.23×10^{-6}	44.31
2	0.0	21.47	1.18	0.56	9.14×10^{-6}	54.38
	0.3	10.63	1.34	0.50	1.33×10^{-5}	47.34
	0.6	6.08	1.39	0.48	1.10×10^{-5}	44.32
	0.9	6.89	1.82	0.31	1.21×10^{-5}	43.24
	1.2	7.86	1.79	0.33	3.71×10^{-7}	40.02
	1.5	8.12	1.60	0.40	1.14×10^{-6}	27.99
	1.8	15.33	1.70	0.36	2.41×10^{-6}	31.60
	2.0	17.38	1.90	0.28	6.38×10^{-7}	51.10
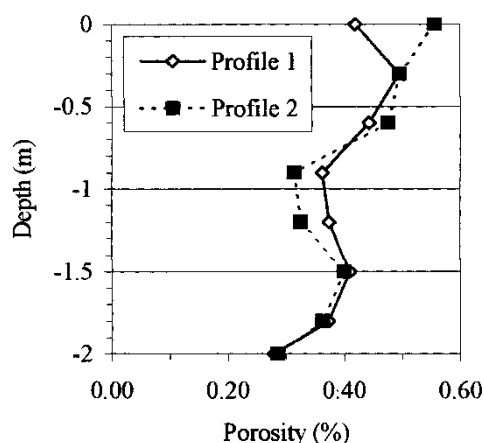
FIGURE 1   Porosity distribution along depth in two profiles.

Batch Sorption Experiments

Batch equilibrium sorption isotherms for 2,4-D in three soil samples at 30, 120, and 180-cm depth were determined at 25°C with a 24-h equilibration period, using procedures described by Brusseau and Rao [10]. Pesticide solutions at concentrations of 0, 100, 200, 300, 400, 500, 700, 1000, and 2000 μg/L were prepared by successive dilutions of stock solutions in 5×10^{-4} M CaCl$_2$ as the electrolyte solution. Soil : water ratio solution was 1 : 4.

Data from the batch adsorption experiments conform to a linear isotherm with K_d values of 1.3, 0.6, and 0.7 for the three depths. The correlation coefficient (R^2) was always greater than 0.93.

MODEL APPLICATION

The Hantush–Mariño model was used to simulate the transport of 2,4-D herbicide through the unsaturated zone of the study area. Recall that pesticide transport in the root zone and vadose zone is modeled using the concept of complete mixing by spatially averaging the related point multiphase-transport partial differential equations over the soil depth. Application of chemical mass is instantaneous.

Chemical properties of the 2,4-D [11] are: half-life $(t_{1/2}) = 24$ days, vapor pressure $= 8 \times 10^{-6}$ (mm of Hg), $K_{oc} = 20$ mg/g, and high water solubility $= 796\,000$ mg/L. Based on the partition coefficient, k_d, 2,4-D herbicide is not expected to be too mobile, with very low persistence because of its short half-life and non-volatility.

The hydrogeologic characteristics of the system, soil properties, and parameters requested by the model are shown in Table II and Fig. 2, which shows a schematic representation of the soil–aquifer system with related geometry used in the simulations. Some necessary parameters were obtained from the literature, and others, estimated according to the study area characteristics, are listed in Table II. In all simulations performed, the boundary between the root and intermediate vadose zones was placed at the maximum root depth (appropriate to the *lolium* variety of grass), and it was assumed to be time-invariant throughout the entire simulation period.

Climatic daily data (precipitation) used for the simulation period correspond to years 2000 and 2001 and have been provided by the meteorologic survey of the area. Average monthly values of the precipitation and irrigation dose provided by the golf course for the simulation period is shown in Table III.

TABLE II   Parameter values used in the simulation model

Parameter	Value
Pesticide	2,4-D
Depth of pesticide application (m)	0.0
Amount of the applied pesticide (kg/ha)	1.8
Diffusion coefficient in water (m^2/day)[a]	0.001
Dimensionless Henry's constant[a]	0.56×10^{-7}
Half-life (day)	24
K_{ow}[a]	2.81
Root zone	
Depth (cm)	20.0
Porosity	0.49
Distribution coefficient (mL/g)	1.3
Bulk density (g/cm^3)	1.35
Field capacity (cm^3/cm^3)[b]	0.338
First-order decay rate (day^{-1})	0.0693
Saturated hydraulic conductivity (cm/day)	1.6
Vadose zone	
Thickness (cm)	200
Porosity	0.32
Distribution coefficient (mL/g)	0.6
Bulk density (g/cm^3)	1.7
First-order decay rate (day^{-1})	0.0231
Saturated hydraulic conductivity (cm/day)	0.08

Pesticide is applied once a year at the beginning of the growing season; [a]data from Ref. [11]; [b]from the suction curve.
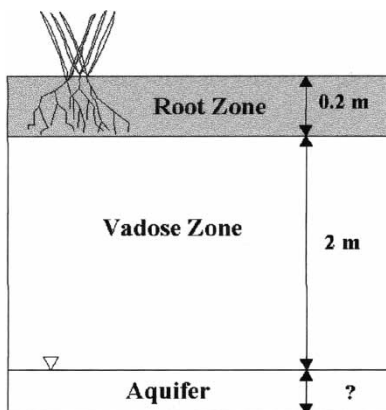
FIGURE 2 Schematic representation of the modeled area.

TABLE III Precipitation and irrigation dose applied during the simulation period

Month	Precipitation (mm)	Irrigation (mm)
2000		
January	44	0
February	4	0
March	29	0
April	59	0
May	19	97
June	55	112
July	44	132
August	7	132
September	52	64
October	58	26
November	17	10
December	125	7
2001		
January	155	11
February	19	19
March	44	51
April	15	103
May	9	103
June	9	165
July	42	168
August	26	156
September	112	56
October	25	18
November	135	19
December	13	7

Mobility of 2,4-D down the vadose zone was monitored in a 100-m^2 plot located in the study area through the simultaneous application of a 2,4-D solution (at a concentration of 1.8 g/L) and NaBr tracer, the latter being used as a chemical tracer of infiltrated water. Concentration of NaBr was 6 mg/L, limited by the grass tolerance to salinity. The pesticide was applied on March 20 (2000) and Br was

TABLE IV   Concentration of 2,4-D in soil samples 15 days after herbicide application

Depth (cm)	2,4-D (mg/L)
0–5	n.d
15–20	n.d
30–35	n.d
45–50	n.d
60–65	0.08
75–80	0.09
90–95	0.12

n.d. not detected.

monitored for 90 days. Results of Br monitoring are not shown here. Fifteen days after herbicide application, undisturbed soil samples at different depth were taken to monitor pesticide content in soil. Results are shown in Table IV.

RESULTS AND DISCUSSION

The simulation period extends from July 1, 2000 to June 30, 2001 and the results based on instantaneous injection of the given pesticide mass are shown in Fig. 3. Simulated soil concentrations correspond to existing agricultural practices and the results are based on the practices that irrigation meets crop evapotranspiration and that the growing season is from March to May. The irrigation demand is currently adjusted to meet the deficit of seasonally averaged precipitation.

Results of the 2,4-D simulation in Fig. 3 show the pesticide distribution through the unsaturated zone at 5, 15, 30, 60, and 90 days after pesticide application. The 2,4-D residues are mostly distributed within a depth from 0 to 1 m below the ground surface. Maximum concentration of pesticide (240 µg/L) in soil appears five days after application at 0.35-m depth, at the vadose zone and close to the root zone. Fifteen days after application, herbicide residues have leached into the vadose zone. Pesticide concentration is still detected after 30 and 90 days with concentrations of 40 µg/L (1 m) and 4 µg/L (2 m), respectively. The peak finally arrived at the interface vadose zone–aquifer after 60 days. However, owing to the high decay rate of the 2,4-D pesticide residues tend to decrease.

Results from the field transport experiment of Table IV show the agreement of results from simulation and real experimental conditions. Although 2,4-D was not detected at the three first sampling depths, experimental data fully agree with the obtained simulated results. Lack of data at the shallowest depths can be attributed to the spatial heterogeneity of transport in the aquifer material.

CONCLUSION

The transport and fate of 2,4-D herbicide through the unsaturated zone in a golf course area was simulated by the Hantush–Mariño model. According to the obtained results, and under the usual agricultural management of the golf course, concentration of 2,4-D after 90 days and at 2-m depth can reach up to 4 µg/L. This value is greater than the
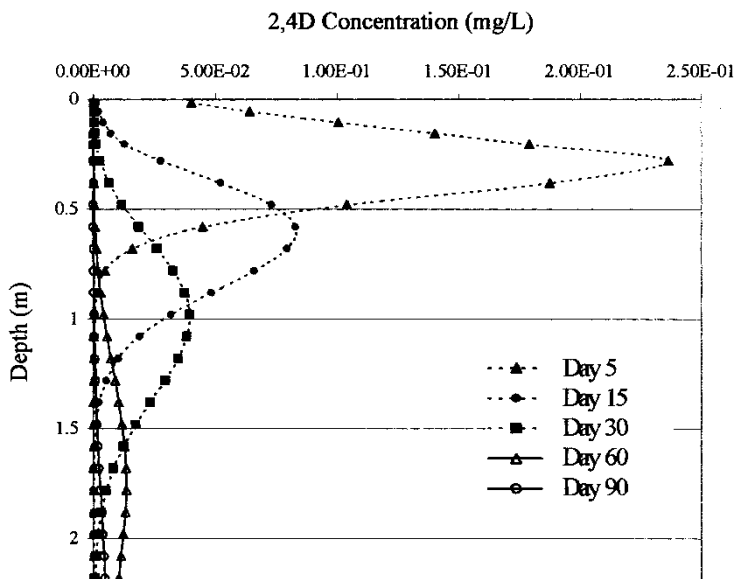
2,4D Concentration (mg/L)

FIGURE 3   Pesticide distribution through the unsaturated zone.

accepted limits for drinking water standards (0.1 μg/L). Under these circumstances, application of the model presented here can be of great help to simulate the changes of agricultural practices necessary in order to avoid groundwater pollution.

Although the model is based on some rigid assumptions (uniform properties in each of the soil zones, steady-state flow, and complete mixing), it nevertheless predicts concentration in the unsaturated zone analytically, requiring a small set of data and accounting in a rather simple manner for the complex interactions among the different physical, (bio)chemical, and meteorological processes. Because it requires less volume of data than a numerical model and provides a quick conclusion that is consistent with the experimental results, it can be used to simulate real-world pesticide transport problems by considering the assumptions used in the derivation of the model.

References

[1] M.M. Hantush and M.A. Mariño, *Environ. Model. Assess.*, **1**, 263–276 (1996).
[2] T. Suziki, H. Kondo, K. Yaguichi, T. Maki and T. Suga, *Environ. Sci. Technol.*, **32**, 920–929 (1998).
[3] S. Cohen, A. Svrjcek, T. Durborow and L. Barnes, *J. Environ. Qual.*, **28**, 798–809 (1999).
[4] M.M. Hantush, M.A. Mariño and M.R. Islam, *J. Hydrol.*, **227**, 66–83 (2000).
[5] M.M. Hantush, R.S. Govindaraju, M.A. Mariño and Z. Zhang, *J. Hydrol.*, **260**, 58–74 (2002).
[6] W.A. Jury, W.F. Spencer and W.J. Farmer, *J. Environ. Qual.*, **12**, 558–564 (1983).
[7] X. Chu, H. Basagaoglu, M.A. Mariño and R.E. Volker, *J. Environ. Eng.*, **126**, 121–129 (2000).
[8] A. Dimos, *Measurement of Soil Suction Using Transistor Psychrometer*. Internal report No IR/91-3, 38 pp. VIC ROADS Co., Adelaide, Australia (1991).
[9] R. Van Genuchten, In: *Calculating the Unsaturated Hydraulic Conductivity with a New Closed-form Analytical Model*. Research Report 78-WR-08. Water Resources Program, 63pp. Dept. of Civil Engineering, Princeton University, Princeton, NJ (1978).
[10] M.L. Brusseau and P.S.C. Rao, *Soil Sci. Soc. Am.*, **27**, 282–302 (1991).
[11] www.http://www.arsusda.gov/acsl/ppdb.html