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Research article

Atrazine movement in corn cultivated soil using HYDRUS-2D: A comparison between real and simulated data

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ABSTRACT

Atrazine is an herbicide that is applied in corn around the world and in sugarcane in Brazil. It is known to be hazardous for animals' health, mobile in the soil, and its analysis is considered expensive and onerous. Solute movement studies are essential to provide information about dangerous molecules movement, which can avoid contamination. While field investigations demand time and financial resources, numerical models are an alternative to describe water and solute distribution in the soil profile. Thus, the objective of this work was to use HYDRUS 2-D model for simulations of atrazine movement in containers packed with tropical soil cultivated with corn and to compare simulated and observed data through statistical parameters. The research was carried out in a greenhouse during 116 days after planting. Atrazine was analyzed in the soil solution at three different depths to validate HYDRUS-2D. Simulations were carried out using hydraulic properties fitted directly to measured retention data and parameters for corn growing and atmospheric characteristics. The mixed procedure analysis indicated that there are differences in atrazine concentration among depths and along time. In general, atrazine concentration is higher at shallow depths and right after application. However, it is possible to find atrazine in deeper soil layers, which might be a concern regarding contamination. RMSE, Willmott and Pearson coefficients indicated a favorable capacity of the model to simulate atrazine concentration on corn cultivation. HYDRUS-2D is a reliable tool to obtain trends in atrazine movement under these experiment's conditions. The uptake parameters, the crop root growth and distribution parameters depend on further specific studies to better describe the relationship between the plant and atrazine and meteorological parameters need to be updated.

1. Introduction

Corn (Zea mays) is an important world crop because it can be used by humans and animal (beef, poultry and swine) as a major food source. This result in 1074.4 million tons corn consumes world-wide annually (FAO, 2017). Approximately 65% of the annual world-wide corn consumption is supplied by these major corn producing countries: United States (320 millions of tons grains), China (241 millions of tons grains), 28-Europe Union (76 millions of tons grains), Brazil (62.5 millions of tons grains). In addition, corn ethanol production is an importance transportation fuel additive in United States accounting for 30% of the U.S. corn produced. It is important to note the material remaining after ethanol production (distiller's grains) is used as an animal feed.

Tools used to increase input use efficiency while improving crop yield are prediction models. These models allow producers to more efficiently use inputs (Ewert et al., 2015) and, also, provide cost-effective predictions resulting from management choices on production as well as environmental consequences (Prata et al., 2003).

Computer modeling has evolved over the years with the advancement of computer hardware and better understanding of physical, chemical and biological processes of the environment. One area of improved prediction is with soil systems. Soil systems are very dynamic and complex systems comprise of many components such as, nutrients, chemical, mineral and biological elements (Islam et. al 2018a, b). Among these elements, there exist important interactions: water and nutrient absorbing, microbiologic transformations, water and nutrients

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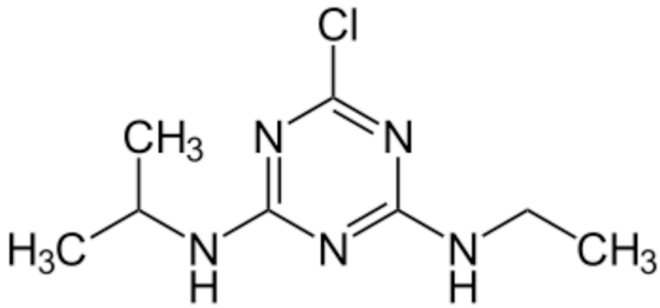

Fig. 1. Atrazine molecular structure (2-cloro-4-2-chloride-4-ethylamino-6-iso-propylamino-striazine).

Table 1
Soil physical and chemical properties.

Properties	Oxisol
Texture class	Sandy loam
Sand (%)	40
Silt (%)	39
Clay (%)	21
Field capacity ($cm^3.cm^{-3}$)	0.236
Wilting point ($cm^3.cm^{-3}$)	0.114
Bulk density ($g.cm^{-3}$)	1.45
pH($CaCl_2$)	5.4
OM ($g.dm^{-3}$)	7
Basis sat (V%)	68
Al sat (m%)	0

leaching, etc. (Vereecken et al., 2016).

Modeling the interactions of these elements and their effects on contaminant transport throughout the soil profile is critical for accurate predictions. As our understanding of these processes improves, models need to reflect these advancements. Thus, it is a necessity to continue updating agricultural models to improve their usefulness (Dourado Neto et al., 1998).

HYDRUS is a software package, which includes several models of water and solute movement through the soil. It uses boundaries conditions to numerically predict soil conditions. Studies have documented the efficacy of HYDRUS (Šimůnek and Hopmans, 2009). HYDRUS is widely used in many industrial and environmental applications, as well as for addressing many agricultural problems (Šimůnek et al., 2016). Examples of existing agricultural applications include irrigation management (Bristow et al., 2002; Dabach et al., 2015), drip and sprinkler irrigation design (Bristow et al., 2002; Gärdeñas et al., 2005; Hanson et al., 2008; Kandelous et al., 2012), studies of root water and nutrient uptake (Šimůnek and Hopmans, 2009; Vrugt et. al 2001a, b).

HYDRUS has been used to model atrazine's fate and transport because studies have shown this pesticide (Fig. 1) can have detrimental impact on the environment, humans and animals (Mendonça et al., 2016; Walters et al., 2014; Lind et al., 2004; Neuman-Lee and Janzen, 2011). Atrazine is used extensively world-wide and is known to be mobile in the soil. This mobility results in atrazine being considered one of the most detected herbicides in European surface waters (Cerejeira et al., 2003) and US (Boyd, 2000). It is reported atrazine affects human health by irritation of eyes and skin and cause effects on central nervous and immune systems (Hayes et al., 2002; Zaya et al., 2011). It is also classified as toxic agent which deregulate the hormonal balance (Friedmann, 2002), and C carcinoma agent, which are potentially carcinogenic to humans (Biradar and Rayburn, 1995). Also, Atrazine has been shown to retard mammal glandules development and induce abortion in lab rats. It can also affect the embryo development in lab rats, even when low exposition levels are used. (Narotsky et al., 2000).

The objective of this work was to evaluate the HYDRUS-2D model for accurately predicting atrazine transport under corn production. To evaluate accuracy, we determined the concentration for atrazine application passing through a tropical soil and compared these values with predicted values generated by the HYDRUS model.

2. Material and methods

2.1. Experimental setup

The research was conducted in a greenhouse managed by the Biosystems Engineering Department of "Luiz de Queiroz" College of Agriculture (ESALQ/USP) and at the Ecotoxicology laboratory owned by Nuclear Energy in Agriculture Center (CENA/USP) between October 26th' 2017 to February 19th' 2018. Both facilities are in Piracicaba-SP with C_{WA} climate as determined by the Köppen classification (22° 43′ 33″ S, 47° 38′ 00″ W, and 511 m of altitude). According to the meteorological station installed inside the greenhouse, average temperature, global radiation, and relative humidity were 24.3 °C; 11.22 MJm^{-2}; 81.11% during the experimental period.

Ten 500-L polyethylene containers (120 cm diameter and 60 cm height) were uniformly packed with a sandy loam soil (Oxisol - Udox) collected in 0–30 cm depth. Packing was done from the bottom to the top using six layers of 10 cm respecting a density 1.45 $g\,cm^{-3}$, which is the natural soil density. The first layer consisting of gravel cover by a geotextile fabric was packed in each container to facilitate drainage and to avoid soil losses in the drain. Three tensiometers, and three ceramic cup extractors were installed at 20, 40 and 60 cm depth.

The corn variety planted was Pioneer® 30F35VYHR Leptra® technology for bugs protection and Roundup ReadyTM. Soil samples were collected to determine initial soil conditions such as selected physical and chemical properties (Table 1). A starter fertilizer was applied to the soil using single superphosphate (100 $kg\,ha^{-1}$), potassium chloride (100 $kg\,ha^{-1}$) e urea (100 $kg\,ha^{-1}$). Potassium and nitrogen were split in 3 phases, 30 $kg\,ha^{-1}$ at rate of 70 $kg\,ha^{-1}$ each one at V4 and V8, according to Fancelli e Dourado Neto (2000).

Atrazine, or Primóleo by Syngenta®, was applied in 11/7/2017 in post-emergence according recommendations to field conditions applying. It was applied in three treatments, (T1) as the provider recommends (240 $mg\,L^{-1}$), (T2) two times (T1) (480 $mg\,L^{-1}$) and (T3) three times (T1) (720 $mg\,L^{-1}$). All the treatments were applied in the same day. The amount applied was 5 $L\,ha^{-1}$ (T1), 10 $L\,ha^{-1}$ (T2) e 15 $L\,ha^{-1}$ (T3) as distributed in a completely randomized experimental design (Fig. 2).

For irrigation management, we used the pressure head of −40kPa (Steduto et al., 2012), as the limit of water stress, corresponding to 0.17cm^3cm^{-3}. When this value was reached, the irrigation started until the water content in the field capacity (0.24 cm^3cm^{-3}). However, 20 mm irrigation depth were applied two days before starting the experiment to homogenize the soil. Then, soil solution samples were collected approximately every other week to measure the actual atrazine concentration in the soil profile. Approximately 24 h following each irrigation, an 80 kPa vacuum was applied to the extraction tubes to collect soil water for analysis.

2.2. Laboratory procedures

Samples were collected every other week and atrazine concentration was analysis using a commercial laboratory (CENA/USP Ecotoxicology Laboratory, Piracicaba-SP, Brazil. Samples were analyzed using liquid chromatography with mass spectrometry (LC-MS/MS) (Agilent Technologies 1200 series with a binary pump equipped and a G1367C automatic sampler). The LC-MS/MS used a C18 Zorbax column (100 mm × 3.0 mm, 3.5 μm) (Agilent Technologies, Santa Clara - CA, United States). The mobile phase was a 40/60 ratio of water to acetonitrile at a constant flow rate of 0.6 $mL\,min^{-1}$. The water phase was comprised of 0.1% formic acid and 5 mmol ammonium formate. The injection volume was 10 μL with a run time of 6 min and the MRM

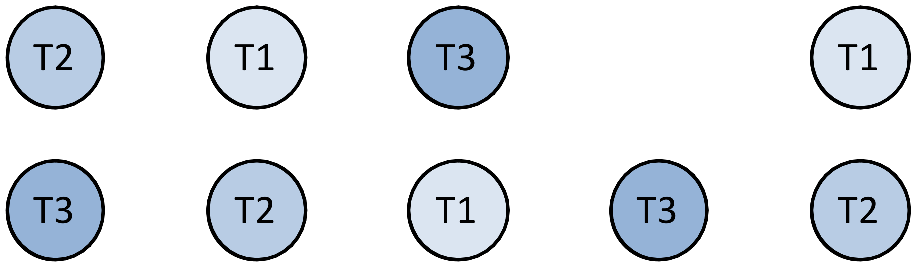

Fig. 2. Completely randomized experimental design divided in three treatments T1, T2, and T3.

mode (Multiple Reactions Monitoring) was used to detect atrazine by the electrospray in positive mode ionization.

To calibrate HYDRUS-2D, breakthrough curves are necessary to obtain atrazine movement parameters. Regarding breakthrough curves, leachate was collected after passing through three laboratory soil columns. The soil columns were glass cylinders (30 cm length and 5 cm diameter) that were filled with soil to a depth of 20 cm and packed to 1.45 g cm^{-3} similar to those measured under field conditions. A 10 mL $CaCl_2$ solution was applied in each column to obtain steady-state conditions. After that, distillated water was applied to leach $CaCl_2$ through the column. Water by itself can be used to condition the soil once the clay existent does not swell.

Once the steady-state was achieved with the distilled water, 500 mL of 14C-atrazine solution (13.62 μg L^{-1}) was applied to each column in 48 h to established atrazine break-through-curves (BTCs). To establish these BTCs, leachate was collected at 12-h interval until the sample contained 10% of the initial atrazine concentration. A 10 mL subsample from each of the collected samples was mixed with scintillation solution. These samples were analyzed using a liquid scintillation spectrometry (LSS) (Packard TR 2500) as described by Mendes et al. (2016). With the estimates of the resident concentration and effluent concentration, displacement parameters for atrazine were obtained for each column using STANMOD model CXTFIT (Toride et al., 1995).

2.3. Atrazine transport

Next, atrazine's transport parameters were determined numerically using equations (1a) and (1b). These simulations were determined using data from the breakthrough curves in the CXTFIT model (Toride et al., 1995) existent on STANMOD described by van Simunek et. al (1999b).

$$\beta R\frac{\partial C_1}{\partial T} + (1-\beta)R\frac{\partial C_2}{\partial T} = \frac{1}{P}\frac{\partial^2 C_1}{\partial x^2} - \frac{\partial C_1}{\partial x} \tag{1a}$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \tag{1b}$$

Where, R is the retardation factor; C_1 is the relative solute concentration in the phase 1 (ML^{-3}); C_2 is the relative solute concentration in the phase 2 (ML^{-3}); T is the relative time (T); P is the Peclet number; x is the relative distance (L); β is the fraction of solute in the mobile region; and ω is the dimensionless mass transfer coefficient.

2.4. HYDRUS-2D simulations

To obtain HYDRUS-2D simulations a set of information is needed regarding the environment where the experiment is located. Thus, information from the soil, corn, atrazine application, irrigation management, geometry of the system, time unit and boundary conditions are explained as follows.

The sprinkler irrigation process was modeled using HYDRUS-2D (Simunek et al., 1999a) based on the following form of the Richards equation for an isotropic soil profile:

$$\frac{\delta\theta(h)}{\delta t} = \frac{\delta}{\delta x}\left(K(h)\frac{\delta h}{\delta x}\right) + \frac{\partial K(h)}{\partial x} - s(h) \tag{2}$$

where θ is the volume water content in the soil ($L^3.L^{-3}$); h is the water head (L); K is the soil hydraulic conductivity ($L.T^{-1}$); t is time (T); s is root water uptake (T^{-1}) as described with the uptake model by Feddes et al. (1978):

$$S(h) = \gamma(h)\beta(r, z)WT_p \tag{3}$$

where $\gamma(h)$ is the soil water stress response function (−); β is the normalized root water uptake distribution (L^{-2}); T_p is the potential transpiration rate (LT^{-1}); and W is the area of the soil surface (L^2) associated with the transpiration process.

The soil hydraulic properties were described using the standard equations of van Genuchten (1980):

$$\theta(\varphi_m) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha|\varphi_m|)^n]^m} \tag{4}$$

$$K(h) = K_s S_e^l[1 - (1 - S_e^{1/m})^n]^2 \tag{5}$$

where θ_r and θ_s are the residual and saturated soil water contents (L^3L^{-3}) respectively, α (L^{-1}), n and m (−) are dimensioless shape parameter of the soil water retention curve, with m = 1-1/n, and S_e is effective saturation given by:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{6}$$

In this study we used soil hydraulic parameters that were either fitted directly to observed retention curve (Fig. 3) using Eq. (4). For the measured hydraulic data, we used undisturbed samples taken from the containers. A total of 9 points were obtained: gravimetric water contents at pressure heads of-10, -20, −40 and −100 cm using a tension table system, and at −300, −500, −1000, −5000 and −15000 cm using the Richards pressure plate approach (Klute, 1980) for 20, 40, and 60 cm (Table 2).

HYDRUS models present a database for root water uptake for different plants based on Wesseling et al. (1991) and Taylor and Ashcroft

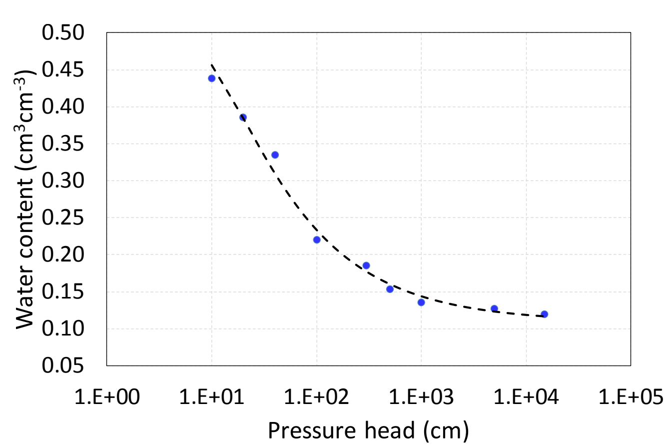

Fig. 3. Observed data fitted to soil water retention curve of the sandy loam soil.

Table 2
Soil hydraulic parameters used in the HYDRUS 2D simulations for retention curve.

depth (cm)	θs (cm^3 cm^{-3})	θr (cm^3 cm^{-3})	α (cm^{-1})	N (−)	Ks cm h^{-1}	l (−)
0–20	0.54497	0.10879	0.09242	1.55771	12.18	0.5
20–40	0.54856	0.11012	0.09451	1.55741	12.17	0.5
40–60	0.54782	0.11245	0.09745	1.55987	12.17	0.5

(1972) and the corn was chosen. The spatial root distribution was described using the model of Vrugt et al. (2001a, b). Regardind geographical positions, the data used were: latitude (22° S); altitude (547 m); Angstrom coefficients (a = 0.26 and b = 0.51) for Piracicaba – SP (Ometto, 1968).

The geometry information was chosen for two dimensions, unity in cm and the initial size was set as a rectangle with a width of 60 cm and a depth of 50 cm. This rectangle was discretized into 1959 two-dimensional elements involving 1035 nodes. Three observation nodes were included at 20, 40, and 60 cm depth in the flow domain to follow simulated atrazine concentration versus time. The observation nodes had similar coordinates as the extractors installed in the containers to allow comparisons of observed and simulated data. It was also determined that the simulations were for water flux, solute transport and water and solute root uptake.

The time unit chosen was days with minimum interval of 0.001 day for model operation. The output time unit was average by day. The hydraulic model used was van Genuchten-Mualem from van Genuchten (1980). The dual-porosity model with two-site sorption in the mobile zone (physical and chemical non-equilibrium) was chosen. The solute parameters and reactions parameters were set as obtained before.

A time-variable flux boundary condition was applied at the up part of the rectangle. During irrigation the sprinkler boundary was held at a constant flux. An atmospheric boundary condition was assumed for the entire soil surface. A no-flow boundary condition was stablished along the left and the right edges of the soil profile, and along part of the container's bottom. A drain was assumed at the container's bottom with the actual drainage being considered. The initial soil water content was 0.23 cm^3cm^{-3} while the initial atrazine concentration was set as 0 μg cm^{-3}.

Potential evapotranspiration was calculated using the Penman-Monteith equation (Allen et. al, 1998) as implemented in the HYDRUS-1D software (Šimůnek et al., 1999a, 1999b). The simulations require daily estimates of potential evapotranspiration and transpiration.

2.5. Statistical analysis

A mixed procedure was done using SAS/STAT to evaluate atrazine concentration considering the three treatments, the three depths and the time. The model was evaluated by statistics analyses, which compare real data to simulated data. The parameters used were Root Mean Square Error (RMSE (eq. (4)), Willmot agreement index (d (eq. (5)), and Pearson correlation coefficient (r (eq. (6)).

$$RMSE = \frac{\sqrt{\sum_{i=1}^{N}(m_i - s_i)^2}}{N} \tag{4}$$

$$d = 1 - \frac{\sum_{i=1}^{N}(m_i - s_i)^2}{\sum_{i=1}^{N}(|s_i - m_a| + |m_i - m_a|)^2} \tag{5}$$

$$r = \frac{\sum_{i=1}^{N}[(m_i - m_a)(s_i - s_a)]}{\sqrt{\sum_{i=1}^{N}[(m_i - m_a)^2]\sum_{i=1}^{N}[(s_i - s_a)^2]}} \tag{6}$$

where, RMSE is root mean square error; s_i is simulated value; N is number of comparisons; d is Willmott agreement index; r is Pearson correlation coefficient; m_a is average observed value; s_a is average simulated value.

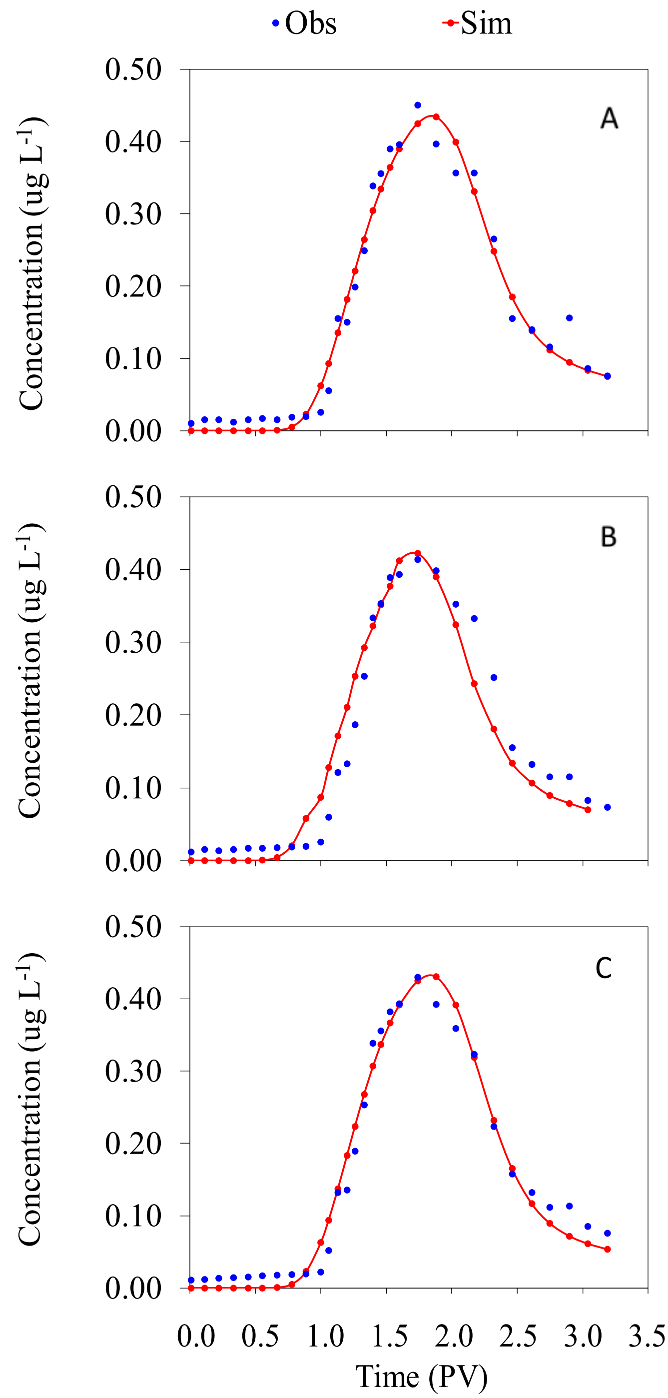

Fig. 4. Atrazine's breakthrough curves obtained for three replicates (column #1 (A), column #2 (B), and column #3 (C)) for tropical soil comparing observed and predicted data.

3. Results

Fig. 4 shows the pulse breakthrough curve for atrazine moving through the soil for each column replicate. The predicted data follows the observed data reasonably well. In the beginning, of all three simulations, predicted data are lower than observed values. Then, both start to increase at 1.0 pore volume, when the values are similar. The concentration peak occurs at 1.7–1.8 pore volume for both predicted

Table 3
Atrazine's movement parameters obtained from three replicates of breakthrough curves (column #1 (A), column #2 (B), and column #3 (C)).

parameter	A	B	C
v (cm h^{-1})	21.80	21.40	21.60
β	0.790	0.830	0.840
ω (h^{-1})	2.420	2.530	2.550
μ	0.500	0.500	0.500

Table 4
Statistical indexes comparing observed and modeled data for three replicates of atrazine's breakthrough curves (column #1 (A), column #2 (B), and column #3 (C)).

index	A	B	C
RMSE (μg L^{-1})	0.0270	0.0312	0.0298
d	0.9906	0.9863	0.9763
r	0.9815	0.9845	0.9848

and observed data on the three replicates which after that they start to decrease forming a shifted sinusoidal form curve. At 2.5 pore volume, the values slightly start to turn into a constant value. The atrazine's movement parameters obtained from the curves above are presented at Table 3. In average, the water velocity (v) through the pores was 21.6 cm h^{-1}, the partition coefficient between the mobile and immobile phases (β) was 0.82, the transfer coefficient (ω) was 2.5 h^{-1}, and the degradation coefficient was 0.5. We subsequently used these values on HYDRUS-2D simulations. The statistical indexes evaluating the model performance for the breakthrough curves are presented in Table 4. In average, the RMSE (ug L^{-1}) was 0.0293. The model accuracy is d = 0.9844, and precision is r = 0.9836. These results show the model works great considering the microenvironment where atrazine moves through the packed soil inside the columns.

After observed and simulated data being obtained, statistical tests (Table 5), show there are significant differences (P-value < 0.0001) among the three treatments along the cycle and depth. Then, it is important to analyze all the data date by date, depth by depth and treatment by treatment. The same test shows that there are differences among treatments (P-value < 0.0001), among depths (P-value < 0.0001), and among days after atrazine application (daaa) (P-value < 0.0001). Besides that, interactions between the treatments and depth (P-value < 0.0001), and between the treatment and the daaa were also significant (P-value < 0.0001). In this case, Fig. 5 is shown to determine where the main significant differences are for observed atrazine's concentration data.

Comparing treatments at the same depth (Fig. 5) shows that all the three treatments are statistically different for every daaa at the 20-cm depth. However, for 40-cm depth the statistical differences start at 35 daaa and go until 56 daaa. At 63 daaa, there are differences between T3 and the other two treatments. From 70 daaa until 84 daaa, there are no statistical differences on the treatments. Last, at 60-cm-depth, the statistical differences start at 35 daaa when T1 and T2 are different from T3. From 42 daaa until 56 daaa, there are significant differences among

Table 5
Mixed procedure for statistical analyses evaluating differences among treatments (trt), depth, and days after atrazine application (daaa).

Effect	DFDen	DFF	p-value
trt	2198414	66.7	< .0001
depth	2198801	96	< .0001
daaa	1019814	239	< .0001
trt*depth	4198137	47.6	< .0001
trt*daaa	2019815	89.24	< .0001
trt*depth*daaa	6019889	13.92	< .0001

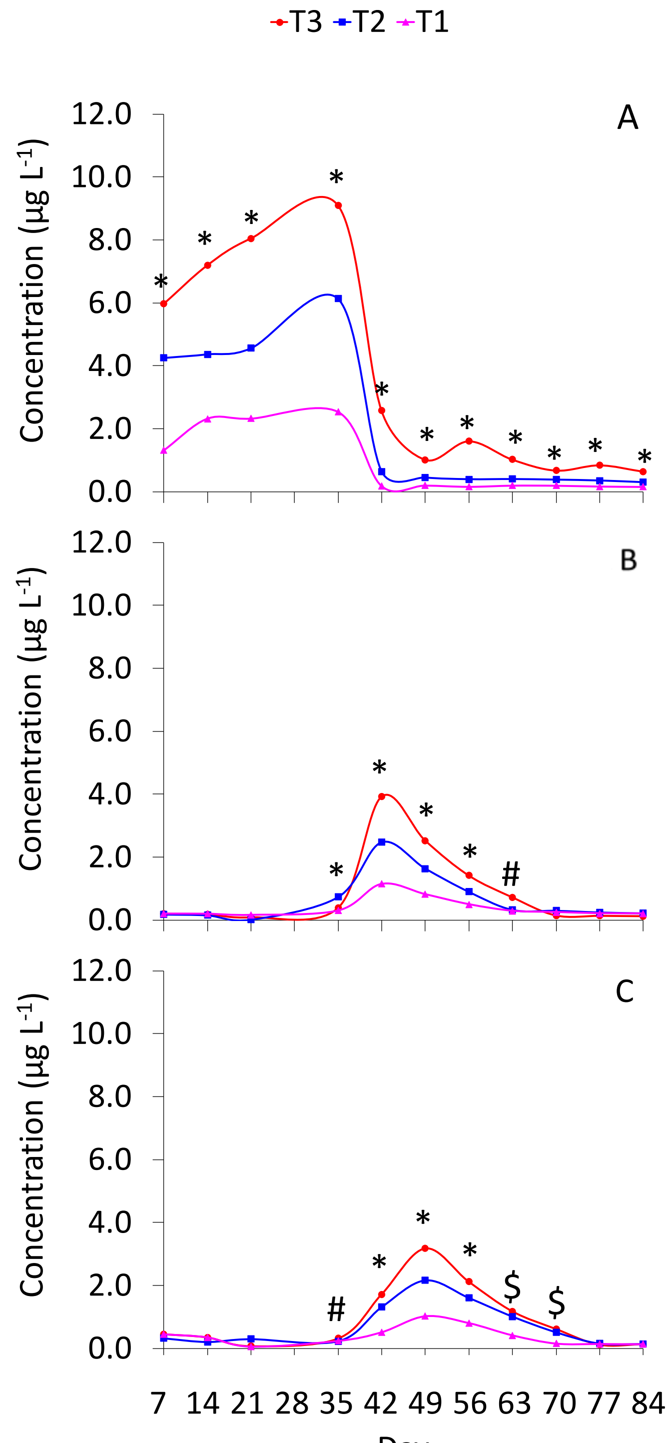

Fig. 5. Observed atrazine's concentration versus days after atrazine application for T1, T2, and T3 at 20 cm (A), 40 cm (B), and 60 cm (C) depth. * - All the treatments are different; # - T3 is different from T2 and T1; $ - T1 is different from T2 and T3.

the three treatments. For 63 and 70 daaa, T1 is considered significantly different from the other two treatments. And, for 77 and 84 daaa there are not significant differences among the treatments anymore.

It is important to highlight the peaks at each depth. At 20-cm depth, the peaks for T3 (~9 μg L^{-1}), T2 (~6 μg L^{-1}), and T1 (~2.5 μg L^{-1}) occur at 35 daaa. At 40-cm depth, the peaks for T3 (~4 μg L^{-1}), T2 (~2.2 μg L^{-1}), and T1 (~1.6 μg L^{-1}) occur at 42 daaa. And, at 60-cm depth, the peaks for T3 (~3.7 μg L^{-1}), T2 (~2 μg L^{-1}), and T1 (~1.5 μg

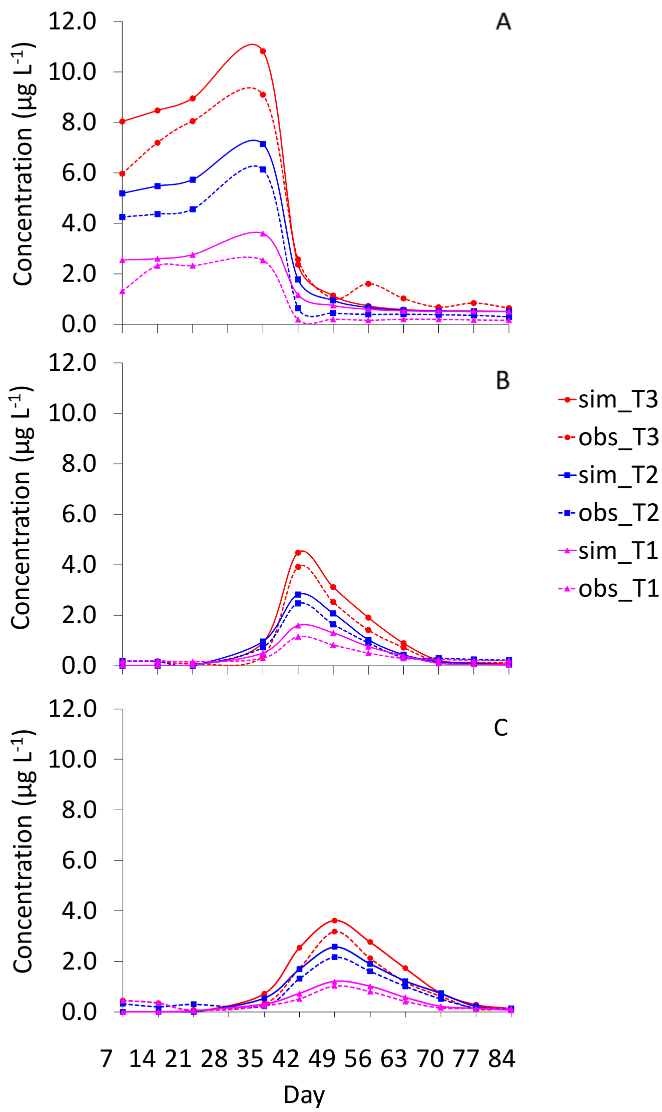

Fig. 6. Observed and simulated data for atrazine concentration (μg L^{-1}) according to days after atrazine application (daaa) for 20 cm (A), 40 cm (B), and 60 cm (C) depths for T1 T2 and T3.

L^{-1}) occur at 49 daaa. Another important characteristic for atrazine in all treatments and all depths is the movement pattern. The atrazine concentration rises after its application (35 daaa) and takes longer to drop to low values, showing the same pattern (shifted sinusoidal curve) obtained in the breakthrough curves.

After analyzing the pattern of atrazine's movement for observed data, Fig. 6 includes the atrazine concentration simulated by HYDRUS-2D for the same period of 84 daaa and under the corn crop condition also simulated by the software. The simulated data is presented as a bold line and the observed data as a dashed line. With this in mind, It is possible to get two major information looking into the figure: first, simulated data follows the pattern described by observed data; second, simulated data overestimates values for atrazine concentration when comparing with observed data.

However, for a better description of this comparison, Table 6 presents the indexes comparing observed and simulated data for atrazine concentration. The RMSE ranges from 0.0350 to 0.2372 μg L^{-1} and shows a pattern where 20-cm depth always has higher values than 40-cm and 60-cm depths no matter the treatment being considered. The Willmott coefficient values range from 0.8953 to 0.9684 and show how accurate the model is. In the same way as RMSE, the accuracy is higher

Table 6
Statistical indexes comparing observed and modeled data for atrazine concentration at three different treatments (T1, T2, and T3) at three different depths (20, 40, and 60 cm).

TRT	Depth (cm)	RMSE (ug L^{-1})	d	R
T1	20	0.1171	0.8981	0.9146
	40	0.0539	0.9629	0.9323
	60	0.0423	0.9684	0.9240
T2	20	0.1877	0.8953	0.9072
	40	0.0612	0.9377	0.9120
	60	0.0532	0.9543	0.9179
T3	20	0.2372	0.8995	0.9057
	40	0.0710	0.9136	0.9112
	60	0.0350	0.9267	0.9177

when the atrazine concentration is lower. The same pattern occurs with the Pearson correlation coefficient, which values range from 0.9057 to 0.9323, and 20-cm depth always presents higher values than 40-cm and 60-cm depths.

4. Discussion

The excellent correlations achieved in this study between the observed data and simulated data confirm that HYDRUS-2D can be effectively used to predict atrazine's movement through the soil in this corn crop condition, and suggest that this assessment methodology should be more broadly applicable. Each of the three model comparison indexes was capable of explaining > 90% of the variation between the observed and simulated data. These results are consistent with previous studies that have compared atrazine's movement through the soil. Persicani (1993) compared five different deterministic models for their ability to predict atrazine leachability towards shallow groundwater. One of these models was HYDRUS-1D. They acquired atrazine's movement parameters from literature () and simulated its breakthrough curves. It was found that, on their conditions, atrazine contaminated the groundwater 6 months after the application, with a major pulse 11 months after application. Pang et al. (2000) used K_{oc} (partition coefficient) and $T_{1/2}$ (half-life) for simulating atrazine's movement. They found that HYDRUS-2D had the best performance simulating atrazine's movement towards the groundwater, and, if the parameters are calibrated, the simulated data are the same as observed data. Kulluru et al. (2010) used Method of Moments to determine atrazine's movement through the soil from breakthrough curves. They found values for D and Kd for different soil textures and also concluded that HYDRUS-1D successfully predicted atrazine's movement through the different soils they tested. Other authors (Prata et al., 2003; Mao and Ren, 2004; Celestino Ladu and Zhang, 2011) also tested atrazine's transport and simulations with either HYDRUS-1D and HYDRUS-2D concluding the same results as the ones cited before.

However, our research was concerned to follow atrazine's movement through a corn crop condition, where we obtained the soil from for breakthrough curves, and a possible comparison between atrazine's concentration *in situ* and atrazine's concentration obtained from HYDRUS-2D. The results obtained from the breakthrough curves show atrazine being mobile through the soil (parameter β closer to 1.0, which indicates more atrazine in the mobile phase of the soil, and water pore velocity around 22 cm h^{-1}). When simulating atrazine's movement through the soil during the corn crop condition, it was expected that atrazine would reach deep layers of the soil, even though corn absorbed soil solution when growing and tasseling.

Fig. 5 shows that the peaks of concentration move with a delay of 7 days through each depth and then it is clear how slow atrazine moves through the soil indicating possible management decisions to avoid groundwater contamination. One best management practice that could be adopted is to maintain the applied concentration around the value of recommended doses, which could avoid major contamination. Another practice is to avoid areas in the soil where there are not weed infestation, what would reduce the amount of pesticide being applied to the field and atrazine only would be used when it is necessary to control the weeds. Fig. 5 also shows there is a time window (from 35 daaa until 70 daaa) at the corn cycle where atrazine movement is problematic regarding a possible contamination. Taking that in consideration, new best management practices need to be considered seeking to avoid the deep atrazine movement. New spacings for corn reducing space for weeds, to speed the corn growth reducing the light availability for weeds, or even changings in the plant structure that could improve the light use by the corn are genetics practices that could be considered in order to avoid atrazine use or at least decrease its amount used.

On another hand, farmers and/or specialists could try to manage the atrazine application according to weather and soil information. It is not easy to think about that once the application is strictly related to the corn planting and the weed growth, however knowing the soil type, the probabilities of rain, the irrigation schedule, the soil moisture, all combined with good decisions also can result in low probability for atrazine contamination.

As found in the observations, in the simulations, atrazine reaches 40–60 cm soil layer and can leach underneath the 60-cm soil layer (Boesten, 2016; De Paula et al., 2016). However, as the root system is not present at this soil depth and there is no way for atrazine being brought to the surface for cycling, it is maintained within sinks in the fine soil particles (silt and clay). It also happens that part of atrazine molecules could have been degraded (Erickson et al., 1989), and part of atrazine molecules could be absorbed by the corn plant (Davis et al., 1965; Roeth and Lavy, 1971; Montgomery and Freed, 1961).

Fig. 6 shows that the model easily tracks atrazine movement through the soil during the crop cycle. It also shows that atrazine moves to a deeper layer where the corn root system does not reach. It means that atrazine will accumulate as the time passes and as the corn season passes. These information leads to the more atrazine applied, the more atrazine will contaminate the subsoil and probably there will be a groundwater contamination in the future. Ackerman (2007) affirmed that atrazine is the pesticide most frequently found in groundwater in the United States and it was also often found in groundwater in Europe when it was used there. Knowing that, it is clear there is a homeopathic dosage of atrazine contaminating the groundwater every crop season. Then, HYDRUS-2D rises as a tool that can provide future information in a range of one, five or even ten years regarding this contamination.

Fig. 6 also shows the model overestimates what happens with the observed data and some explanations can be given. The atrazine's sink parameters should be considered at a real and dynamic corn crop situation where there are the roots liberating exudates, and active microorganisms living at the rhizosphere. Both situations can promote changes at atrazine concentration. Moreover, it needs to be evaluated the atrazine's absorption by the plants. If there is this absorption, a new sink parameter should be estimated. Besides that, the evapotranspiration modeling underestimate water uptake, then more water stays at the arable layer. These parameters need to be corrected. And, finally, root uptake parameters need to be improved because they are old (1991) and nowadays hybrids are different.

To help choosing best management practices and to allow producers finding possible contaminations, HYDRUS-2D seems to be a useful software mostly because it can track atrazine concentration at the soil solution giving a really good idea about the pattern that atrazine has moving through the soil. Atrazine is a potential threat to soil ecosystem and environmental health (Fang et al., 2015; Freeman et al., 2011), thus it is necessary the development, the spreading and the use of models like HYDRUS-2D.

5. Conclusions

The objective of this research was to evaluate HYDRUS-2D model for accurately predict atrazine transport. Within the results and according to statistical indexes, HYDRUS-2D can be considered as a good tool to monitor atrazine's movement in a corn plantation. The model presents high precision and high accuracy when predicting atrazine's movement pattern what means that the atrazine contamination can be followed without analyzing lots of soil samples. It can be used by farmers, specialists, and land-owners to simulate atrazine's fate through the soil and help to decide the best management practices (BMP's) to be considered regarding atrazine application and its contamination to groundwater, streams and water courses. It also can be used by state governments helping to develop public policies regarding atrazine application considering future contaminations in the groundwater and consequently the water is going to be used by the population.

However, the model overestimates the values for atrazine's concentration. What can be considered as model weakness was found at two critical points, the simulation of corn evapotranspiration, the corn growth parameters, and atrazine attached within sinks in the fine soil particles. In order to build a bigger database more researches taking corn in account regarding atrazine movement through the soil need to be done.

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References

Ackerman, F., 2007. The economics of atrazine. Int. J. Occup. Environ. Health 13, 441–449.

Allen, R.G., Pereira, L.S., Ra Es, D., Smith, M., 1998. Crop Evapotranspiration: Guidelines for Computing Crop Water Requirements. FAO, Rome, pp. 300 (FAO – Irrigation and Drainage Paper,56).

Biradar, D.P., Rayburn, A.L., 1995. Chromossomal damage induced by herbicide contamination at concentrations observed in public water supplies. J. Environ. Qual., Madison 24, 1222–1225.

Boesten, J.J.T.I., 2016. Effect of harsh or mild extraction of soil on pesticide leaching to groundwater. J. Environ. Qual. 45, 1320–1328. https://doi.org/10.2134/jeq2015.07.0363.

Boyd, R.A., Apr. 2000. Herbicides and herbicide degradates in shallow groundwater and the Cedar River near a municipal well fiel, Cedar Rapids, Iowa. Amsterdam In: The Science of the Total Environment, vol. 248. pp. 241–253 n. 2-3.

Bristow, K.L., Hopmans, J.W., Cote, C.M., Charlesworth, P.B., Thornburn, P.J., Cook, F.J., 2002. Development of improved water and nutrient management strategies through strategic modeling. In: Proc. 17th WCSS, pp. 14–21 Thailand.

Celestino Ladu, J.L., Zhang, D., 2011. Modeling atrazine transport in soi columns with HYDRUS-1D. Water Sci. Eng. 4 (3), 258–269.

Cerejeira, M.J., P, V., Batista, S., Pereira, T., Valério E Silva, M.J., Silva, A., Ferreira, M., Silva-Fernandes, A.M., March 2003. Pesticides in Portuguese surface and ground waters. Water Res. 37, 1055–1063 fifth ed.

Dabach, C., Shani, U., Lazarovich, N., 2015. Optimal tensiometer placement for high-frequency subsurface drip irrigation management in heterogeneous soils. Agric. Water Manag. 152, 91–98.

Davis, D., Gramlich, J., Funderburk, H., 1965. Atrazine absorption and degradation by corn, cotton, and soybeans. Weeds 13 (3), 252–255. https://doi.org/10.2307/4041040.

De Paula, R.T., de Abreu, A.B.G., de Queiroz, M.E.L.R., Neves, A.A., da Silva, A.A., 2016. Leaching and persistence of ametryn and atrazine in red–yellow latosol. J. Environ. Sci. Health, Part B 51 (2), 90–95. https://doi.org/10.1080/03601234.2015.1092819.

Dourado-Neto, D., Teruel, D.A., Reichardt, K., Nielsen, D.R., Frizzone, J.A., Bacchi, O.O.S., 1998. Principles of crop modeling and simulation: I. Uses of Mathematical Models. In: Agricultural Science. Sci. Agric., vol. 55 Special edition, Piracicaba.

Erickson, L.E., Lee, K.H., Sumner, D.l D., 1989. Degradation of atrazine and related

s-triazines. Crit. Rev. Environ. Contr. 19 (1), 1–14. https://doi.org/10.1080/10643388909388356.
Ewert, F., Rötter, R.P., Bindi, M., Webber, H., Trnka, M., Kersebaum, K.C., Olesen, J.E., van Ittersum, M.K., Janssen, S., Rivington, M., Semenov, M.A., Wallach, D., Porter, J.R., Stewart, D., Verhagen, J., Gaiser, T., Palosuo, T., Tao, F., Nendel, C., Roggero, P.P., Bartošová, L., Asseng, S., 2015. Crop Modeling for integrated assessment of risk to food production from climate change. Environ. Model. Softw 72, 287–303.
Fancelli, A.L. e, Dourado-Neto, D., 2000. Produção de milho. Guaíba: Agropecuária, pp. 360p.
Fang, H., Lian, J.J., Wang, H.F., Cai, L., Yu, Y.L., 2015. Exploring bacterial community structure and function associated with atrazine biodegradation in repeatedly treated soils. J. Hazard Mater. 286, 457–465.
Feddes, R.A., Kowalik, P.J., Zaradny, H., 1978. Simulation of field water use and crop yield. In: Simulation Monograph. Pudoc, Wageningen, The Netherlands, pp. 9–30.
Food and Agriculture organization of the United Nations, 2017. Crop Prospects for 2018. Statistics Division – FAOSTAT.
Freeman, L.E.B., Rusiecki, J.A., Hoppin, J.A., Lubin, J.H., Koutros, S., Andreotti, G., et al., 2011. Atrazine and cancer incidence among pesticide applicators in the agricultural health study (1994–2007). Environ. Health Perspect. 119 (9), 1253–1259.
Friedmann, A.S., 2002. Atrazine inhibition of testosterone production in rat males following peripubertal exposure. Reprod. Toxicol., Limerick 16 (3), 275–279.
Gärdeñas, A.I., Hopmans, J.W., Hanson, B.R., Šimůnek, J., 2005. Two-dimensional modeling of nitrate leaching for various fertirrigation scenarios under micro-irrigation. Agric. Water Manag. 74, 219–242.
Hanson, B.R., Šimůnek, J., Hopmans, J.W., 2008. Leaching with subsurface drip irrigation under saline, shallow-groundwater conditions. Vadose Zone J. 7 (2), 810–818.
Hayes, T.B., Collins, A., Lee, M., Mendoza, M., Noriega, N., Stuart, A.A., et al., 2002. Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses. Proc. Natl. Acad. Sci. U. S. A 99 (8), 5476–5480.
Islam, M.A., Morton, D.W., Johnson, B.B., Mainali, B., Angove, M.J., 2018a. Manganese oxides and their application to metal ion and contaminant removal from wastewater. J. Water Process Eng. 26, 264–280.
Islam, M.A., Morton, D.W., Johnson, B.B., Pramanik, B.K., Mainali, B., Angove, M.J., 2018b. Metal ion and contaminant sorption onto aluminum oxide-based materials: a review and future research. J. Environ. Chem. Eng. 6 (6), 6853–6869.
Kandelous, M.M., Kamai, T., Vrugt, J.A., Šimůnek, J., Hanson, B.R., Hopmans, J.W., 2012. Evaluation of subsurface drip irrigation design and management parameters for alfafa. Agric. Water Manag. 109, 81–93.
Klute, E.A., 1980. Methods of Soil Analysis. Part 1: Physical and Mineralogical Methods. 196. American Society of Agronomy-Soil Science Society of America, Madison, pp. 1358.
Kulluru, P.P., Das, B.S., Panda, R.K., 2010. Evaluation of sorption and leaching potential of malathion and atrazine in agricultural soils of India. Int. J. Environ. Res. 4 (1), 75–90 Winter.
Lind, P.M., Milnes, M.R., Lundberg, R., Bermudez, D., Orberg, J., Guillette Jr., L.J., 2004. Abnormal Bone composition in female juvenile american alligators from a pesticide-polluted lake (Lake Apopka, FL). Environ. Health Perspect. 112 (3), 359–362.
Mao, M., Ren, L., 2004. Simulating non-equilibrium transport of atrazine through saturated soil. Gr. Water 42, 500–508.
Mendes, K.F., Inoue, M.H., Goulart, M.O.G., Pimpinato, R.F., Tornisielo, V.L., 2016. Leaching of a mixture of hexazinone, sulfameturon-methyl, and diuron applied to soils of contrasting textures. Water Air Soil Pollut. 227, 268. https://doi.org/10.1007/s11270-016-2954-4.
Mendonça, J.S., Vieira, L.G., Valdes, S.A.C., Vilca, F.Z., Tornisielo, V.L., Santos, A.L.Q., 2016. Effects of the exposure to atrazine on bone development of *Podocnemis expansa* (Testudines, Podocnemididae). Ecotoxcology 25, 594–600.
Montgomery, M., Freed, V., 1961. The uptake, translocation and metabolism of simazine and atrazine by corn plants. Weeds 9 (2), 231–237. https://doi.org/10.2307/4040410.
Narotsky, M.G., Best, D.S., Guidici, D.L., Cooper, R.L., 2000. Strain comparisons of atrazine-induced pregnancy loss in the rat. Reprod. Toxicol.
Neuman-Lee, L.A., Janzen, F.J., 2011. Atrazine exposure impacts behavior and survivorship of neonatal turtles. Herpetologica 67 (1), 23–30.
Ometto, J.C., 1968. Estudo das relações entre radiação solar global, radiação liquida e insolação. 1968. 64 p. Tese Doutorado (Doutorado em Agronomia) – Escola Superior de Agricultura “Luiz de Queiroz”. Universidade de São Paulo.
Pang, L., Close, M.E., Watt, J.P.C., Vincent, K.W., 2000. Simulation of picloram, atrazine and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. J. Contam. Hydrol. 44, 19–46.
Persicani, D., 1993. Atrazine leaching into groundwater: comparison of five simulation models. Ecological Modeling 70, 239–261.
Prata, F., Lavorenti, A., Vanderborght, J., Burauel, P., Vereecken, H., 2003. Miscible displacement, sorption and desorption of atrazine in a Brazilian oxisol. Vadose Zone J. 2, 728–738. https://doi.org/10.2136/vzj2003.7280.
Roeth, F.W., Lavy, T.L., 1971. Atrazine uptake by sudangrass, sorghum, and corn. Weed Sci. 19 (1), 93–97. JSTOR. www.jstor.org/stable/4041828.
Šimůnek, J., Hopmans, J.W., 2009. Modeling compensated root water and nutrient uptake. Ecological Modeling 220 (4), 505–521.
Šimůnek, J., Šejna, M., van Genuchten, M.T., 1999a. The HYDRUS-2D Software Package for Simulating the Two-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. Version 2.0.
Šimůnek, J., van Genuchten, M.T., Sejna, M., Toride, N., Leij, F.J., 1999b. The STANMOD Computer Software for Evaluating Solute Transport in Porous Media Using Analytical Solutions of Convection-Dispersion Equation. USDA, U.S. Salinity Laboratory, Riverside.
Šimůnek, J., Van Genuchten, M.T.H., Šejna, M., 2016. Development and applications of the HYDRUS and STANMOD softwares packages and related codes. Vadose Zone J. 7 (2), 587–600.
Steduto, P., Hsiao, T.C., Fereres, E., Raes, D., 2012. Crop Yield Response to Water, FAO Irrigation and Drainage Paper 66. Food and Agriculture Organization of the United Nations, Rome.
Taylor, S.A., Ashcroft, G.M., 1972. Physical Edaphology. San Francisco, Freeman, pp. 533.
Toride, N., Leij, F.J., van Genuchten, M.T., 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments: version 2.0. In: Research Report n.137, U.S Salinity Laboratory of Agricultural Research Service. USDA, Riverside, California, pp. 121.
van Genuchten, M.T.H., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. Am. J. 44, 892–898.
Vereecken, H., Schnepf, A., Hopmans, J.W., Javaux, M., Or, D., Roose, T., et al., 2016. Modeling soil processes: review, key challenges and new perspectives. Vadose Zone Journal. Madison 15, 57.
Vrugt, J.A., Hopmans, J.W., Šimůnek, J., 2001a. Calibration of a two-dimensional root water uptake model. Soil Sci. Soc. Am. J. 65 (4), 1027–1037.
Vrugt, J.A., van Wijk, M.T., Hopmans, J.W., Šimůnek, J., 2001b. One-, two-, and three-dimensional root water uptake functions for transient modeling. Water Resour. Res. 37 (10), 2457–2470.
Walters, A.D., Chamberlain, K., Ford, N.B., Placyk-Jr, J.S., 2014. Influence of atrazine on the scalation of Macy's checkered gartersnake, Thamnophis m. marcianus (Baird and Girard, 1853). Bull. Environ. Contam. Toxicol. 92 (1), 1–5.
Wesseling, Z., Elbers, J.A., Kabat, P., van der Broek, Swatre, B.J., 1991. Instructions for Input. Winand Staring Centre, Wageningen.
Zaya, R.M., Amini, Z., Whitaker, A.S., Kohler, S.L., Ide, C.F., 2011. Atrazine exposure affects growth, body condition and liver health in Xenopus laevis tadpoles. Aquat. Toxicol. 104 (3–4), 243–253.