Experimental and numerical study on the leaching of pesticides into the groundwater through a porous medium: Effects of transport parameters

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H I G H L I G H T S

- We have presented a method numerical to approximate the solution of the unsteady linear convection–diffusion–reaction problems of transporting a pesticide through the soil in the unsaturated zone.
- The models we have considered couple the two types of physical non-equilibrium and chemical non-equilibrium.
- The problem will be solved by a numerical approach based on the finite difference method using a FORTRAN program.
- The model allows us to predict the spatial and temporal concentration of pesticides in groundwater.
- The effects of the transport parameters; the dimensionless first order degradation coefficient μ, the Peclet number Pe and the dimensionless mass transfer coefficient w on the evolution of this concentration are presented.

A R T I C L E   I N F O

A B S T R A C T

This study aims to investigate, experimentally and numerically, the pesticide transport through the soil in unsaturated zone. The movement of pesticide is described with one dimensional model. The transport equation incorporates terms accounting for diffusion –convection, adsorption and reaction. The first objective of this work was to identifies the effects of the parameters transport such us; the dimensions first order degradation coefficient (μ), the peclet number (ρ_e) and the dimensionless mass transfer coefficient (w). The evolution of pesticide concentration in function of depth and time was found by using the non-equilibrium transport model. The data obtained show the importance of the adsorbed concentration. The second objective is to find the relation between the concentration and the transport parameters because there is a difficulty of the analytical solution. The solution of the problem was carried out by a numerical approach by using the finite difference method and a Fortran program.

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1. Introduction

After the Second World War, the demographic explosion increased the food needs. This situation was at the origin of an intensification of the world agricultural production. It was accompanied by the development of new pesticides and
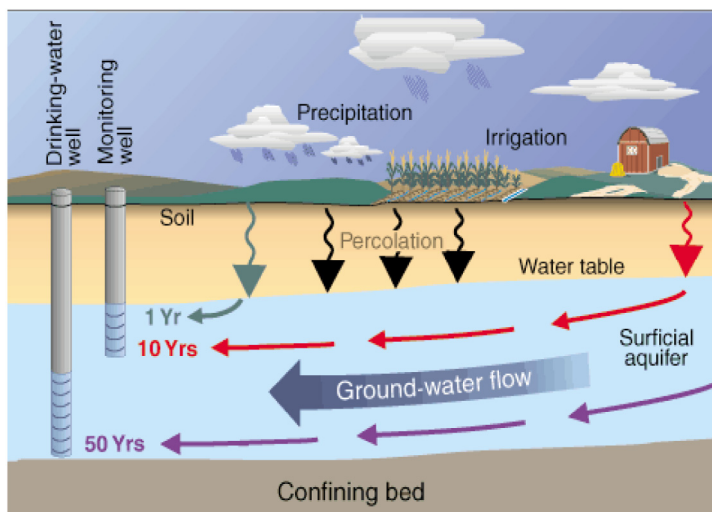
Fig. 1. Synthetic scheme of the mechanisms influencing the dynamics of pesticides in the environment, according to (Manuel et al., 2008; Kathrin et al., 2013).

the increase in their use. The intensive use of chemical products (pesticides) for agriculture is undeniably necessary to eliminate noxious weed; but the remnants of these products contaminate the environment particularly resources such as the groundwater. The presence of such pollutants in water leads to the deterioration of the ecosystems.

The European Standard for the Maximum Allowable Concentration in water intended for human consumption is (0.1 mg/L) to a pesticide (Suziki et al., 1998; Stuart et al., 1999).

The review articles (Markus, 1996; Fereshte and Farid, 2015) collected the literature on sorption and transfer of pollutants in soils. The nowadays preservation of good quality water resources is one of the main environmental concerns. The authors (Mohamed and Miguel, 1996; Lucila and Miguel, 2004; Aude, 2003) presented a model to evaluate the behavior of solutes in soil conditions Many mathematical models have been applied to improve the understanding, management and prediction of the movement of dissolved substances in porous media (Bear, 1979; Lapidus and Amundson, 1952). In the 1970s (Van Genuchten and Wierenga, 1976; Cameron and Klute, 1977) developed the first model of pesticide leaching to estimate leaching of pesticides in groundwater. This model proves that pesticide transformation and sorption are principal pesticide–soil interaction properties in this context. In order to evaluate solute transport for a neutral tracer in one-dimensional steady-state flow, Convection dispersion equation model (CDE) has been used. Several experiments have been conducted, in the laboratory and in nature, to examine the validity of the CDE model for quantifying solute transport in a porous medium (Rao et al., 1980; Li et al., 1994). This model have been changed by the authors (Vanderborght et al., 1997). The model convective lognormal transfer (CLT) has been used to estimate the transport parameters (Assumaning and Chang, 2012; Fereshte, 2015). The non-equilibrium sorption models include the physical non-equilibrium, and the chemical non-equilibrium, respectively, two regions models, or two sites models (Van Genuchten and Wierenga, 1976; Cameron and Klute, 1977). The convection dispersion equation has been broadly used to estimate solute transfer. Reducing the impact of pesticides on the environment requires understanding the processes which are subjected in soils, mainly, the processes of retention, stabilization, as well as their transport. Addressing chemical pollution; requires knowledge of the transport mechanisms of solutes in porous media and the nature of the pesticide (Fig. 1). In our work the multi residues GC 250 (Metribuzin) and LC 250 (Isoproturon) are studied.

Numerical simulations of groundwater flow and chemical transport in subsurface formations play an increasingly important role in the field of environmental engineering. In the context of contaminated soil and groundwater systems, simulations are typically used to (1) determine the basic flow and chemical migration patterns at contaminated sites; (2) analyze, develop, or otherwise optimize remediation strategies for the removal of contaminants; (3) demonstrate compliance with regulatory cleanup standards; and (4) evaluate contaminant travel times and attenuation rates for use in environmental risk analyses (National Research Council, 1990).

With the exception of the kinetics and thermodynamics of the reactivity of each pollutant with the soil and its composites theirs mechanisms can be defined in a similar manner (Aude, 2003). Grass strips have many roles (Maurizio et al., 2010), the main one being to be buffer zones between agricultural plots and streams. These bands effectively limit the amount of pesticides and fertilizer entering the watercourses, moving the spray boom and the fertilizer spreader away from these aquatic environments, limiting surface runoff, and trapping and Degrading excess nutrient resources and plant protection products (Stefan et al., 2007).

Therefore, the models beginning of a general passage, which includes both, transport mechanisms (diffusion and convection) and the sorption operation. The usage of the models simulation environmental are faster and less expensive than

Table 1
Physico-chemical characterization of soil used in this study.

	Depth (cm)	pH	OC (%)	Clay (%)	CEC (meq/100 g)	Surface Area (m^2/g)	CaCO3 (%)	Bulk soil density (g/cm^3)	Soil texture
Soil	(0–25)	8.1	2.6	28	15	110	21	1.4	Loam

experimental methods, and can be regarded as an important instrument in the decision-making (Lucila and Miguel, 2004; Javier and Ljerka, 1999). The advantages of using numerical methods instead of analytical methods allow us to generalize without simplifications of assumptions and changes in physical conditions; limits and initials.

The aims of our research work are to investigate, numerically and experimentally, the transport of pesticide through the soil in the unsaturated zone. The effects of the parameters transport such us; the dimensions first order degradation coefficient (μ), the peclet number (ρ_e) and the dimensionless mass transfer coefficient (w) are estimated. The evolution of pesticide concentration in function of depth and time was found by using the non-equilibrium transport model. The relation between the concentration and parameters of transport by Regression because of the difficulty of the analytical solution has been presented.

The solution of the problem was carried out by a numerical approach by using the finite difference method and a Fortran program.

Our numerical results are proved by some experiences in laboratory of material analysis of products of modern technologies and environmental objects by using soil column with two kinds of herbicides (Isoproturon and Metribuzin).

2. Experimental

We used in this work two kinds of herbicides; Isoproturon and Metribuzin and Russian soil. The deterioration of ecosystems is caused by the discharge of these herbicides to surface water. Bromide was used as nonreactive tracers. We used a solution of Potassium Bromide. The soil was air-dried and passed through a sieve (2 mm). The Table 1 shown the Physico-chemical characterizations of soil sample. The Plexiglass column has 30 cm long and 9 cm inner diameter (Fig. 2). The prepared soil was packed into this column. Bed supports composed of woven fiberglass direct contact with a porous Teflon filter of 25 mm pore size. The column connected with a spraying system comprises of a pulse pump of a constant level, because a steady state is required for the model. The solution was pumped at a flow rate of 0.6 ml/min Fig. 2. The solution used for spraying the column of soil before and after the pulse of pesticides is composed of calcium chloride ($CaCl_2$) (5.10^{-3} moles/L). The solution used during pulse is prepared by Bromide (60 mg/L) and (10 mg/L) of pesticide were dissolved in preceding solution. Three replicates were run for each experiment (see Fig. 3).

The concentrations of Bromide, Isoproturon and Metribuzin in the effluent were analyzed by (HPLC). For the Bromide we used an Allsep A-2 anion column. The mobile phase consisting of Na_2CO_3-$NaHCO_3$ mixture was used, with a flow rate of 2 ml/min for 10 min. Injection volume was 50 μL. The wave length of the detector was set at 194 nm. The detection limit was 0.5 to 1 mg/L. The retention times are 6 min. For both herbicides we used a Nova Pack silica-C18 column. The mobile phase consisting of Methanol–water mixture (60/40) used a flow rate of 1 ml/min for 15 min. Injection volume was 100 μL. The wave length of the detector was set at 240 nm for the Isoproturon and the Metribuzin 298 nm. The detection limit was 1 to 10 μg/L. Their retention times are respectively around 8 and 5 min.

3. Numerical

3.1. Physics and mathematical models

3.1.1. Physics model

Due to its ease of infiltration and its great dissolving power, water is the preferred receptacle for pollutants. It is also the first vector of their propagation in the soil (by infiltration) and the atmosphere (by evaporation). Pollutants are of various kinds: organic (Microorganisms and fermentable organic matter), chemical (fertilizers, pesticides, drugs, hormones, etc.), thermal or radioactive. A study in 2013 (Kathrin et al., 2013) showed that, in France, 10% of bottled water also shows traces of pesticides and medicines, although they are small, which confirms a large-scale contamination of the environment by human activities. Sufficient information on the transport of a solute, such as pesticides, in a porous medium are normally needed for efficient management of soil and groundwater.

3.1.2. Mathematical formulation

The description of the transport, retention and degradation of pesticides can be carried out by different models. We choose in this study the equilibrium and non-equilibrium models which are developed following numerous experimental studies these were developed after a number of experiments or after recognizing the inefficiency of the first type of models (Aude, 2003; Asensio et al., 2007).
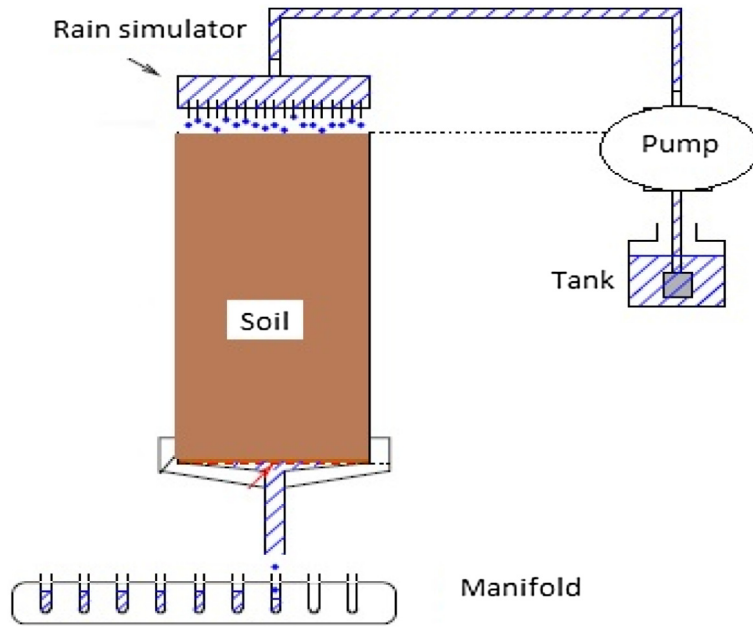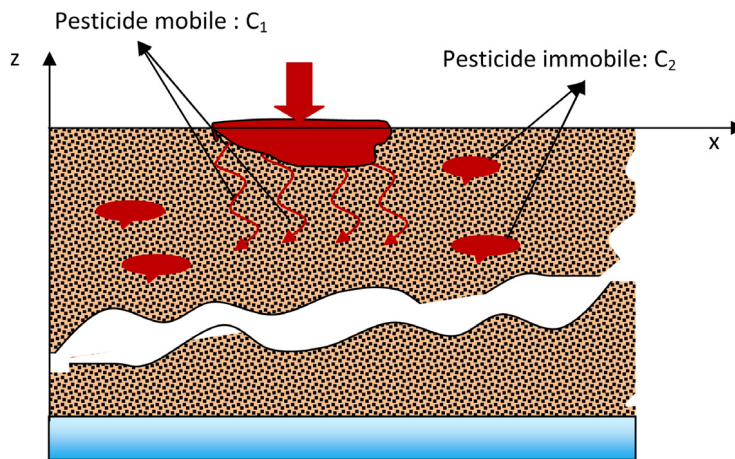
Fig. 2. Schema of a soil column.

Fig. 3. Schematic representation of the transport of pesticide in soil.

3.1.2.1. Equilibrium model. The assumptions of this model, based on the non-dimensional form, are; all the water contained in the soil participates in convective and dispersive transport of the solute and all adsorption sites are assumed to be equivalent. It is expressed by a convective–diffusive equation. The solute adsorption by the solid phase is described with a linear equilibrium isotherm sorption isotherms. Then, during steady state flow in homogeneous porous media, taking into account reactive solute. The governing equations for this equilibrium model may be written as Eq. (1) (Van Genuchten and Wierenga, 1976; Cameron and Klute, 1977).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial Z^2} - v\frac{\partial C}{\partial Z} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} - \mu C \tag{1}$$

Where :C is the liquid phase, S is the solid phase and the relative resident solute concentrations of soil $(g\,cm^{-1})$ are (C, S).
   D is the dispersion coefficient $(cm^2\,h^{-1})$, $v = q/\theta$ average pore velocity of mobile region,
   ρ Bulk soil density $(g\,cm^{-1})$, θ Water content, μ Degradation coefficients (h^{-1}).

Table 2
Dimensionless variables and corresponding physical parameters.

Variables	Physical non-equal.	Chemical non-equal.
T	$\frac{vt}{L}$	$\frac{vt}{L}$
z	$\frac{z}{L}$	$\frac{z}{L}$
C_1	$\frac{C_m}{C_0}$	$\frac{C}{C_0}$
C_2	$\frac{C_{im}}{C_0}$	$\frac{S_2}{(1-f)K_dC_0}$
R	$1 + \rho \frac{K_d}{\theta}$	$1 + \rho \frac{K_d}{\theta}$
Pe	$\frac{v_mL}{D_m}$	$\frac{vL}{D}$
w	$\frac{L}{q\alpha}$	$(1-\beta)\,R\theta\frac{L}{q}K_2$
β	$\frac{\theta_m+f\rho K_d}{\theta+\rho K_d}$	$\frac{\theta+f\rho K_d}{\theta+\rho K_d}$

In the case of equilibrium and linear adsorption, the relation between the parameters S and C is $S = K_dC$ and Eq. (1) can be written in the following form Eq. (2):

$$R\frac{\partial C}{\partial T} - \frac{1}{Pe}\frac{\partial^2 C}{\partial Z^2} + \frac{\partial C}{\partial Z} + \mu C = 0 \tag{2}$$

Where, Z is the dimensionless space, T is the dimensionless time, Pe is the Peclet number and R is the retardation factor.

The Eq. (2) treats, in this order, the time variation of the dissolved and adsorbed concentration, the hydrodynamic diffusion flux, the convective flux and the degradation in the two phases. The equilibrium model predicts symmetric evolution curves (ratio of the sample distribution).

The equilibrium model predicts symmetric evolution curves (ratio of the sample distribution).

Mechanisms non-equilibrium must be considered to explain the Phenomena of preferential flows related with the presence of macrospores. This phenomena show asymmetric curves (Aude, 2003).

As this model cannot predict information on phenomena related to the presence of macrospores, we have been able to account for the mechanisms of the non-equilibrium model to explain the phenomena of preferential fluxes related to the presence of macrospores.

3.1.2.2. Non-equilibrium models. This model involves the coupling of physical and chemical non-equilibrium systems. These models consist of coupling the two types of physical non-equilibrium and chemical, non-equilibrium (Van Genuchten and Wierenga, 1976; Cameron and Klute, 1977).

A numerical model developed by Brusseau et al. (1989) simultaneously taking into account the different sources of non-equilibrium, called MPNE model (Multi Processes Non-Equilibrium). A convection–diffusion model still applies in steady state flow in homogeneous porous media and uniform soil moisture distribution; besides, biotic grading process and abiotic first order are possible. Non-equilibrium models are considered to be caused by physical phenomena such as a preferential transfer, or chemical phenomena such as sorption kinetics (Aude, 2003; Cameron and Klute, 1977).

The environment Porous is divided into 4 sorption domains which operate in parallel:

Two are assigned to the "mobile" region, one having an instant sorption, the other a sorption limited kinetically; two are assigned to the "immobile" region, with instant sorption, and the other with sorption kinetics.

The following, correspond to the equations of the non-equilibrium models (Aude, 2003; Van Genuchten and Wierenga, 1976; Cameron and Klute, 1977; Bouchard et al., 1988):

$$\beta R\frac{\partial C_1}{\partial T} = \frac{1}{Pe}\frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega(C_1 - C_2) - \mu_1 C_1 \tag{3}$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) - \mu_2 C_2 \tag{4}$$

C, R, T, Z, and Pe are the same dimensionless parameters for the equilibrium model, β is the partitioning coefficient between the two kinds of sites, μ_1 and μ_2 are the dimensionless first order degradation coefficients, and w is the dimensionless mass transfer coefficient.

These dimensionless variables and corresponding physical parameters for the non-equilibrium models are presented in Table 2 (Assumaning and Chang, 2012).

The meaning of all the physical parameters is given in Table 3.

3.2. Numerical method

Unsteady linear convection–diffusion–reaction problems unstable include the non-equilibrium model for the leaching of solutes in soils. The transformation of differential equations into algebraic equations can be done by several methods. We choose finite difference method of implicit type using a FORTRAN program (Goncalves da Silva, 2007). We adopt this method

Table 3
Significance of parameters.

Parameter	Physical meaning
L	Soil column length (cm)
θ	Water content $\theta = \theta_m + \theta_{im}$ (cm^3 cm^{-3}) θ_m: mobile phase water content ; θ_{im}: immobile phase water content
q	Darcy flux (cm h^{-1})
$v = q/\theta$	Average pore velocity (cm h^{-1})
C ,S	Resident solute concentration of soil (g cm^{-1}) C-liquid phase, S-solid phase
C_0	initial solute concentration pulse
C_m	resident solute concentration in mobile phase
C_{im}	resident solute concentration in immobile phase
S_2	concentration of solute adsorbed in sites of first-order kinetic
D	Dispersion coefficient (cm^2 h^{-1}) ; Dm dispersion coefficient in mobile region
K	Sorption coefficients (cm^3 g) K_d linear adsorption coefficient ; K_2 kinetic sorption coefficient
ρ	Bulk soil density (g cm^{-1})
α	Coefficient of mass transfer between the two regions (h^{-1})
μ	Degradation coefficients (h^{-1})

to transform the obtained equations in algebraic ones. The following section will solve the equation of the non-equilibrium models. The solution of the system of partial differential equations developed requires the definition of the initial conditions and the boundary conditions of the domain under consideration.

The environment Porous is divided into 4 sorption domains which operate in parallel

- *Initial conditions* At $T = 0$: $C_1 (Z, 0) = 0$; $C_2 (Z, 0) = 0$
- *Boundary conditions*

In this study, we used for the boundary $Z = 0$, two hypotheses:

The First hypothesis assures that the initial concentration of the surface changes exponentially with time. The differential equation describing Kinetic reaction can be written as:

$$\frac{\partial C_1}{\partial T} + \frac{\mu}{R}C_1 = 0 \rightarrow C_1(z = 0, T) = C_0 e^{-\frac{\mu}{R} \cdot T} \tag{5}$$

A second hypothesis corresponds to the Dirichlet condition. This condition assumes that during an injection of a pollutant at the soil surface, it is immediately and constantly subject to the concentration of the pesticide: $C_1(z = 0, T) = 1$.

In the boundary layer at $Z = Zmax$, We suppose a quantity of pollution, imposed on the surface of the soil, reaches a certain depth *Zmax;* this can be translated by a zero concentration gradient at this depth:

$\left.\frac{\partial C_1}{\partial z}\right|_{z=z_{max}} = 0.$

- *Calculation of concentration C_1*

The following approximate procedure is used to obtain the solution C1 (T, Z).
Split the domain *[0, Zmax]* in $(Nz - 1)$ Equal parts of length $\Delta z = \frac{z_{max}}{(Nz-1)}$.

- Constructing the following form: $z(I) = \Delta z.(I - 1)$; $T(k) = \Delta T.(k - 1)$ where
  $I = 1 \rightarrow Nz$ And $K = 1 \rightarrow Nt$; Nz Number of mesh points along the axis Z and $NtNz$ Number of mesh points along the axis of time.
- We choose an arbitrary three-node element of the domain *[0, Zmax]* to define the first and the second derivative, based on the Taylor series:
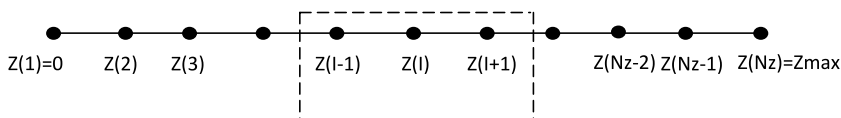
Table 4

The various coefficients of the finite difference method.

$R_{d_{diff}} = \frac{\Delta T}{R\beta Pe \Delta Z^2}$	$R_{C_{CONV}} = \frac{\Delta T}{2R\beta Pe \Delta Z}$	$R_{M_{TR}} = \frac{\Delta T \omega}{R\beta}$	$R_{rea1} = \frac{\Delta T \mu_1}{R\beta}$
$Di_{(I)} = (R_{diff} + R_{conv})$	$Dp_{(I)} = \left(-2R_{d_{diff}} - R_{M_{Tr}} - R_{rea1}\right)$	$Ds_{(I)} = (R_{diff} - R_{conv})$	$V_{(I)} = -C_{1(I)}^K - R_{M_{Tr}} C_{2(I)}^K$

– The first derivative/z : $\left(\frac{dC_1}{dz}\right)_I^t = \frac{C_{1(I+1)}^{t+\Delta t} - C_{1(I-1)}^{t+\Delta t}}{2.\Delta Z}$

– The second derivative/z : $\left(\frac{d^2C_1}{dz^2}\right)_I^t = \frac{C_{1(I-1)}^{t+\Delta t} - 2.C_{1(I)}^{t+\Delta t} + C_{1(I+1)}^{t+\Delta t}}{\Delta z^2}$

– The first derivative/T : $\left(\frac{dC_1}{dT}\right)_I^t = \frac{C_{1(I)}^{t+\Delta t} - C_{1(I)}^t}{\Delta T}$

For solving Eq. (3), we replace the expressions of the temporal and spatial derivatives by using the finite difference method (Goncalves da Silva, 2007).

$$\frac{C_{1I}^{K+1} - C_{1I}^K}{\Delta T} = \frac{1}{R\beta Pe}\left(\frac{C_{1(I-1)}^{K+1} - 2C_{1(I)}^{K+1} + C_{1(I+1)}^{K+1}}{\Delta z^2}\right) - \frac{1}{R\beta}.\left(\frac{C_{1(I+1)}^{K+1} - C_{1(I-1)}^{K+1}}{\Delta z^2}\right) - \frac{\omega}{R\beta}(C_{1I}^{K+1} - C_{2I}^K) - \frac{\mu_1}{R\beta}C_{1I}^{K+1}$$

After arrangement, we obtain the following equation:

$$(R_{diff} + R_{conv})C_{1(I-1)}^{K+1} + \left(-2R_{d_{diff}} - R_{M_{Tr}} - R_{rea1}\right)C_{1I}^{K+1} + (R_{diff} - R_{conv})C_{1(I+1)}^{K+1} = -C_{1(I)}^K - R_{M_{Tr}}C_{2(I)}^K$$

We obtain the following Tri-diagonal system such that K and $(K + 1)$ represent the indices of two Successive times.

$$Di_{(I)}.C_{1(I-1)}^{K+1} + Dp_{(I)}C_{1(I)}^{K+1} + Ds_{(I)}.C_{1(I+1)}^{K+1} = V_{(I)} \tag{6}$$

The Eq. (6) Contains (Nz) Variables with $(N - 2)$ equation, It is valid for all points unless for boundary conditions it means $(Z = 0$ correspond $I = 1)$ and $(Z = Zmax$, correspond $I = Nz)$

Therefore, we must use the formulas of the boundary conditions to complete the system of equations:

For $Z = 0, I = 1$ we have $C_1(z = 0, T) = C_0 e^{-\frac{\mu}{R}T}$

For $Z = Zmax, I = Nz$ on a $\left.\frac{\partial C_1}{\partial z}\right|_{z=z_{max}} = 0 \rightarrow \frac{C_{1(Nz)} - C_{1(Nz-1)}}{\Delta z} = 0$

From these equations we obtain the Tri diagonal system (Goncalves da Silva, 2007). The various coefficients and parameters of this model are grouped in the following ratios (see Table 4).

● *Calculation of concentration C_2*

We used Implicit Euler Method for finding the solution:

$$\frac{\partial C_2}{\partial T} = \frac{C_{2I}^{k+1} - C_{2I}^k}{\Delta T} = \frac{\omega}{(1-\beta)R}(C_{1I}^{k+1} - C_{2I}^{k+1}) - \frac{\mu_2}{(1-\beta)R}C_{2I}^{k+1} \tag{7}$$

$$(1 + \frac{\omega\Delta T}{(1-\beta)R} + \frac{\mu_2\Delta T}{(1-\beta)R})C_{2I}^{k+1} = C_{2I}^k + \frac{\omega\Delta T}{(1-\beta)R}C_{1I}^{k+1} \tag{8}$$

The difficulty of this model lies in the presence of two concentrations C_1 (mobile) and C_2 (immobile) in addition to seven variables: time, depth and five physical and chemical parameters (β, R, Pe, w, μ). The problem is to find a way to present these results. We suggest drawing the curves in the following way:

Concerning the variables of time and depth, we propose the value $T = T_{max}$ and $Z = Z_{max}$ where T_{max} is a value, where the phenomenon is stabilized and Z_{max} is the depth in which the pollutant reaches the water.

3.3. Regression and curve fitting

Regression analysis is a statistical method for modeling relationships between different variables (dependent and independent). A regression is based on the idea that a dependent variable (response) is determined by one or more independent variables (predictors). A regression model is first developed to perform this method on a dataset. Regression analyzes have two main objectives 1) quantify relationships and describe them using measured values and their graphical representation 2) provide predictions.

From a mathematical point of view, there are several regression analyzes: simple, multiple, linear and nonlinear. These models can be very complex because the relationships between variables are not organized and mapped using simple mathematical methods. Regression analyzes are used in very different domains, including science, where the regression model has only one or two predictors.

In this study, we have applied the regression analysis to obtained the relationships between the concentration solute C1 and the two variables Pe (the Peclet number) and w (the dimensionless mass transfer coefficient).
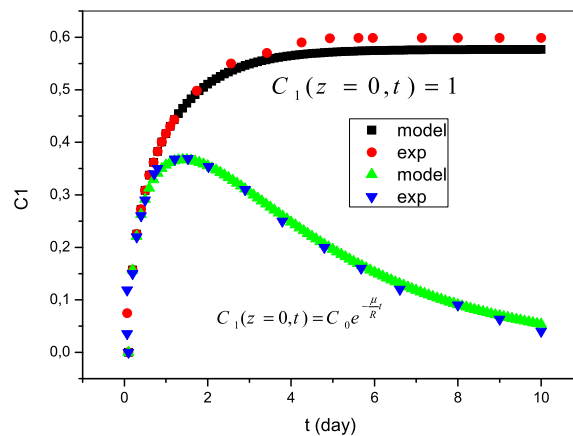
Fig. 4. Evolution of the relative resident solute concentration C_1 at $Z = Z_{max}$ for both hypotheses with non-equilibrium model (symbols continuous line) and experimental (symbols dashed line).

4. Results and discussion

The numerical solution, in one-dimensional homogeneous porous medium, is given discretely in time and in space. The degradation was considered only in the liquid phase. The calculated variables are the concentration of the mobile solute C_1 (mobile) and the immobile concentration C_2.

To clarify the concentration distribution, we needed some results experimental for the execution of the program. The following parameters such us; The Peclet number ($Pe = 10$), the dimensionless first order degradation coefficient and the partitioning coefficient and the dimensionless mass transfer coefficient and the retardation factor are respectively, $\mu_1 = 1.2$, $\mu_2 = 0.3$, $\beta = 0.4$, $w = 4.35$, $R = 5$. The Calculation methods and its theoretical basis are the same that those used in applied in (Aude, 2003; Javier and Ljerka, 1999).

4.1. Comparison between the two hypotheses

The Fig. 4 represents the variation of the relative concentration C_1 versus the time, t, at $Z=Z_{max.}$ for both hypotheses by using the Metribuzin The two hypotheses are the first $C_1(z = 0, t) = C_0 e^{-\frac{\mu}{R}t}$ and the second. $C_1(z = 0, t) = C_0$. For a continuous source (second hypothesis $C_1 (Z = 0, t) = C_0$), after above $t = 4$ days, we observe a saturation due to the pollutant accumulation. This is quite logical because, as time passes, there is a buildup of the pollutant in this section and the concentration kept its value about 0.57. For the first hypothesis, the initial value of the concentration at the surface, C_1 decreases exponentially as a function of time. Over time, the variation of the concentration of the pollutant is carried out in two steps:
- Increased concentration from zero to its maximum value of 0.36 due to accumulation of the pesticide even with small amounts.
- A decrease in the curve due to the decrease of the concentration of the pesticide at the surface ($Z = 0$).

4.2. Comparison of the evolution of concentration for two herbicides

The Comparison of the evolution of concentration for two herbicides, Metribuzin and Isoproturon, as a function of time experimentally and with the non-equilibrium model(Fig. 5);and in function of depth Z only with the non-equilibrium model (Fig. 6), because the difficulty to follow experimentally the evolution of the concentration in all points of column. The solubility of Metribuzin (1.2 g/L) at 20 °C is higher than that of Isoproturon (0.07 g/L), so Metribuzin is more mobile than Isoproturon, also it is an herbicide weakly retained by the soil because the K_{oc} value ($K_{oc} = 0.6$–31.7 L/kg), and for Isoproturon ($K_{oc} = 80$–150 L/kg). Following these properties, the transport of this herbicide is active. Thus these properties facilitate the transport of the Metribuzin herbicide relative to the Isoproturon herbicide; what we see on (Figs. 5 and 6). It is expected that a final concentration of Metribuzin will be greater than that of Isoproturon under the same conditions. This result can be explained by the properties of the two herbicides and the concentration of second herbicide is more important than the concentration of the first herbicide.

4.3. Effect of degradation on concentration

Several physical, chemical and biological forces contribute to the transport of pesticides reaching the soil. However, major role in the degradation of pesticides is due to physical and chemical forces. These forces are acting upon/degrading the
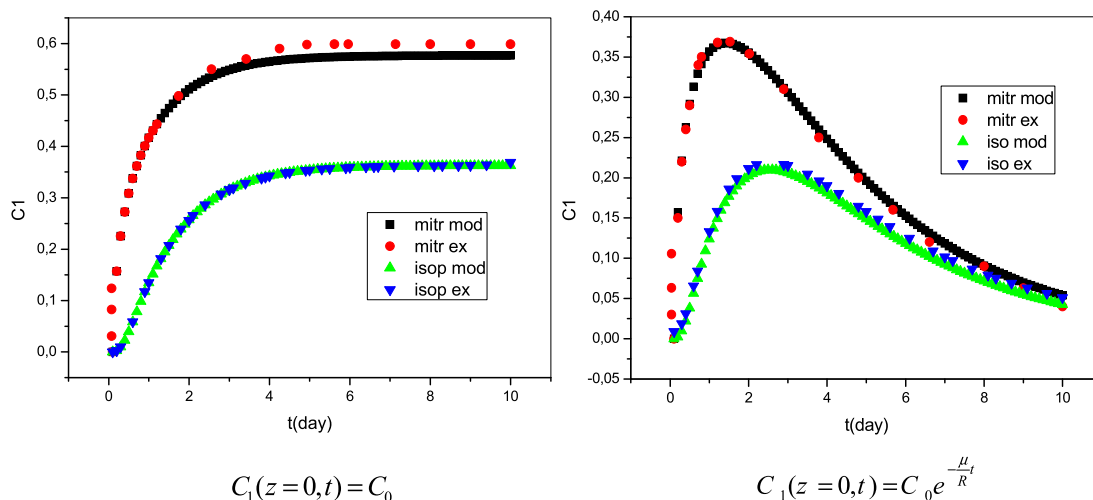
$$C_1(z = 0, t) = C_0 \qquad\qquad C_1(z = 0, t) = C_0 e^{-\frac{\mu}{R}t}$$

Fig. 5. The transient Evolution of the relative resident solute concentration C_1 with no equilibrium model (symbols continuous line,) and experimental (symbols dashed line) for two kind of herbicides Isoproturon(isop) and Metribuzin (Mitr).
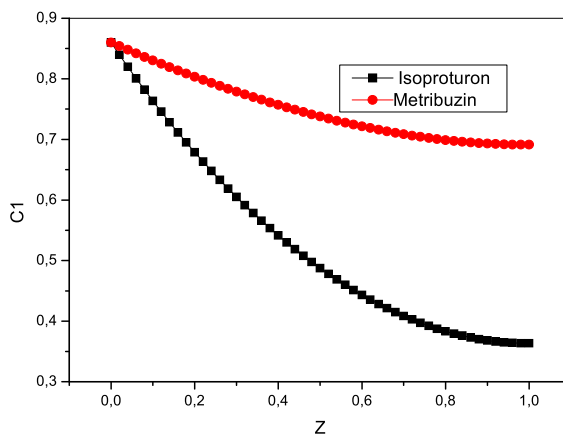

Fig. 6. Evolution of the relative resident solute concentration C_1 as a function of depth Z, for two herbicides: Metribuzin and Isoproturon with the non-equilibrium model and the condition $C_1(z = 0, t) = C_0$.

pesticides to some extent, microorganism's the conversion of pesticides to other toxic compounds is due to the ability of many soil microorganisms to act on pesticides

Formalism Most often used to derive the pesticide concentration over time is kinetics of the first order (Aude, 2003; Asensio et al., 2007). The mathematical models are based on velocity laws. The Fig. 7 shows us that the effect of the reaction is important. We observe this on the curves of the non-equilibrium model and on experimental curves where we used two kind of soil (one sterilized at a temperature of 121 °C for 60 min, the other is the same soil used in all experiments). With reaction, the concentration increases to a value of 0.36; however, without reaction the curves(experimental and model) represent the evolution of the concentration where the maximum value of C_1 is (0.46 experimental and 0.45 models). Then, the concentration is more important when we do not have degradation. The increase of the reaction decreases the presence of pesticide in the groundwater; therefore, these curves show us that the effect of the reaction is important.

4.4. Effect of peclet number on concentration

The Fig. 8(A and B) shows the effect of peclet number on the transient concentration. The different values of peclet chosen are (0.5, 1, 2, 5, 10, 100, and 1000). It is noted that more the value of the peclet number is greater more the concentration of C1 decreases.

It is noted that the higher the value of the peclet number, the greater the concentration of C_1 diminishes. This result can be explained by the increase of the convection phenomenon, because the relation of Peclet is the Convection divided by diffusion. When convection increases, that means an increase of the velocity, which causes the ejection of the pollutant
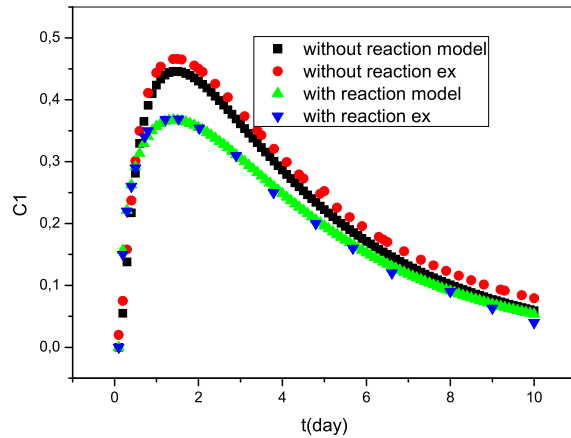
Fig. 7. Transient concentration of the relative resident solute concentration C_1 with none-equilibrium model (symbols continuous line) and experimental (symbols dashed line) with and without reaction.

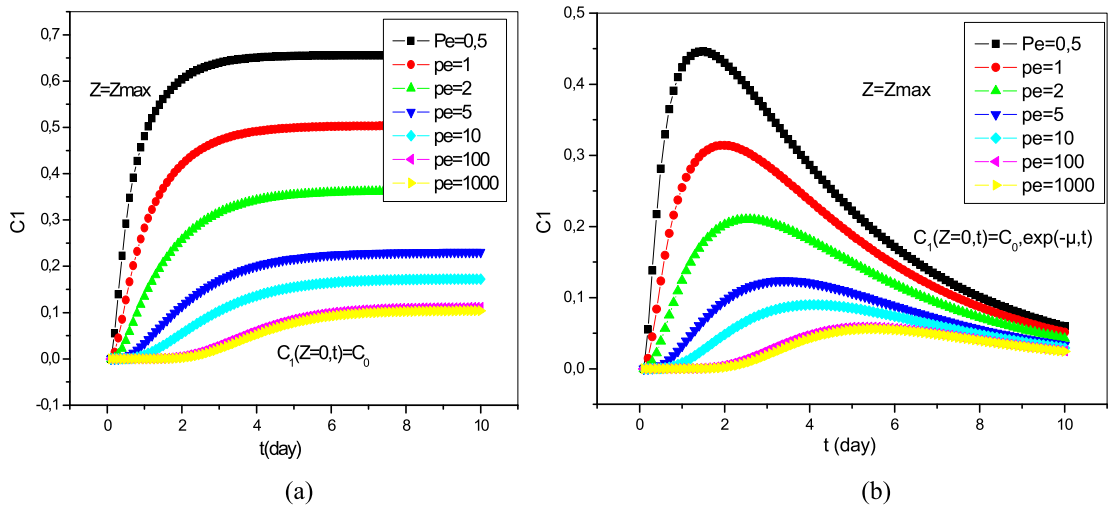(a)   (b)

Fig. 8. Transient concentration C1 for various values of peclet number (Pe).

quickly without accumulation in the column. On the contrary, a little value of velocity leads to an accumulation of pollutant, hence, an increase of the concentration in the column.

There is proportionality between *Pe* and *v* (convection velocities). For values of peclet number in the range (100–1000) we do not observe any change in curves so the effect of peclet number is negligible.

4.5. Effect of the mass transfer coefficient on concentration C_1 and C_2

The evolution of the transient concentration mobile C_1 for different values of the mass transfer coefficient (*w*) is illustrated in (Fig. 9). Note that when *w* increases, the value of the concentration C_1 decreases.

We show in (Fig. 10) the effect of mass transfer coefficient *w* on the concentration immobile C_2. Note that the concentration C_2 increases gradually as *w* increases. These results are logical because *w* is a mass transfer coefficient, which transfers C_1 to C_2.

4.6. Effect of the concentration C_2 on the evolution of the concentration C_1

We tried to choose curves (Figs. 11 and 12)which give us in the same time the variation of *w*, *Pe*, C_1 and C_2 at t_{max} and Z_{max}. By using these curves, we can find the concentration of the pesticide mobile or immobile at any value of *Pe* or *w*, so the curves allow us to predict the concentration of groundwater by pesticides.

The production of the concentration C_2 is made by mass transfer phenomena of the concentration C_1, $\omega (C_1 - C_2)$. If we neglect the reaction of $C_2(\mu_2 = 0)$, the latter cumulates with time until arrival in a value greater than that of C_1, in this case
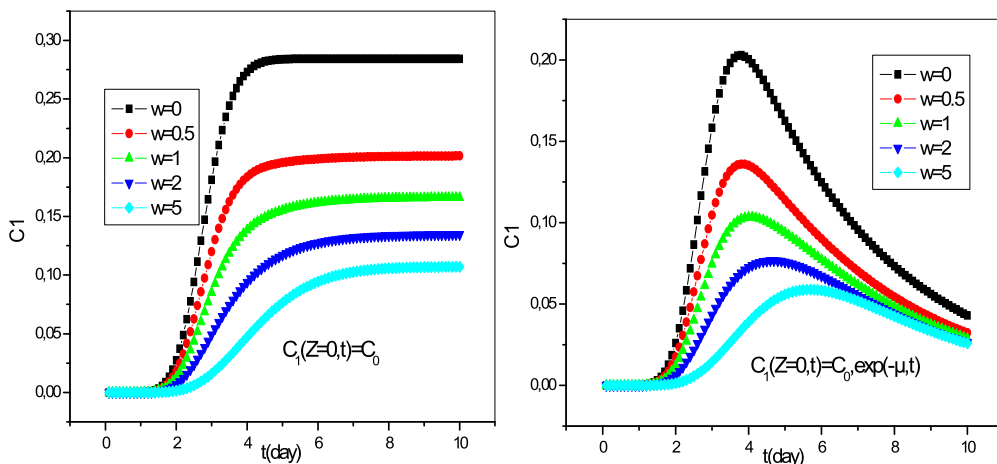
Fig. 9. The evolution of the concentration C_1 in function of the time a differs w at Z_{max}.
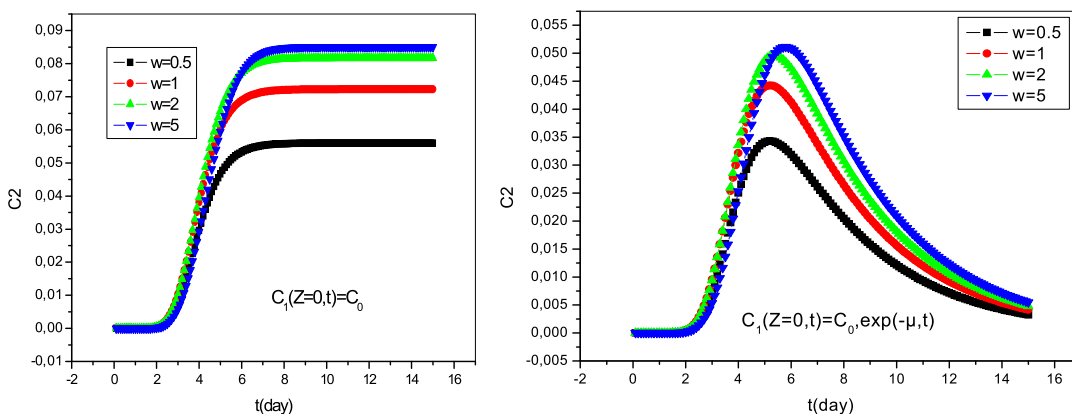

Fig. 10. The evolution of the concentration immobile C_2 in function of time a differs w at Z_{max}.
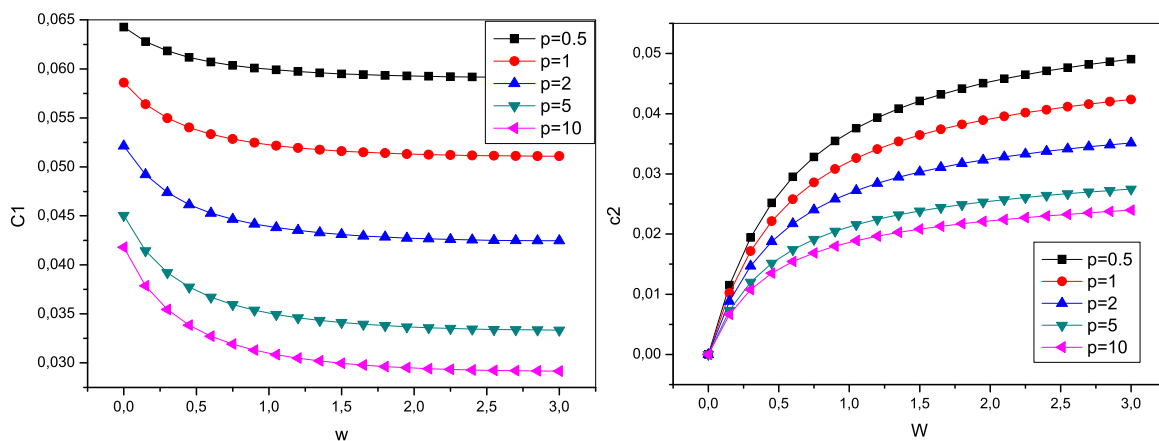

Fig. 11. Variation of the concentration according to w at different Peclet with $\mu_2 = 0.3$ for $C_1(z = 0, t) = C_0 e^{-\frac{\mu}{R}t}$.

we observe in Fig. 12 an inverse transfer (C_2 transfer to C_1), this is why we observe an increase of C_1 and decrease of C_2 but after a while we observe an equilibrium.
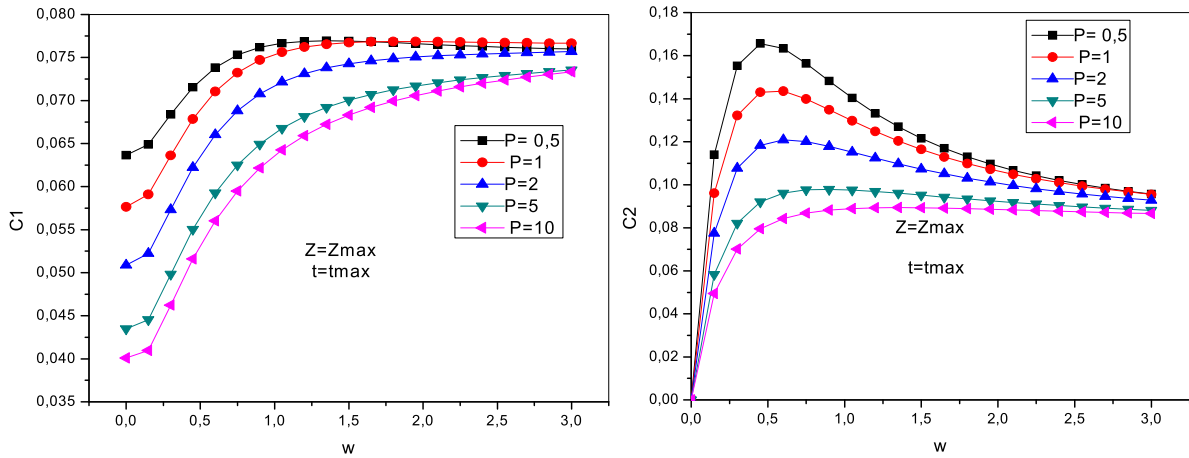
Fig. 12. Variation of the concentration according to w at different Peclet with $\mu_2 = 0$ for $C_1(z = 0, t) = C_0 e^{-\frac{\mu}{R}t}$.

4.7. Regression of two variables

The Peclet number Pe and the dimensionless mass transfer coefficient, w. and C_1 are noted by The following data: $x_{(k)}$, $y_{(k)}$ and $z_{(k)}$ respectively.

The objective is to link the C_1 concentration by two variables Pe and w by a formula of this form: $Z = a1.X^{a2}.Y^{a3} \rightarrow C1 = a1.P^{a2}.w^{a3}$

The equation is linearized by introducing Logarithm on both members of the equation

$$Ln(Z) = Ln(a1) + a2.Ln(X) + a3.Ln(Y)$$

We pose: $Z' = Ln(Z)$, $A1 = Ln(a1)$, $A2 = a_2$, $X' = Ln(X)$, $A_3 = a3$, $Z' = Ln(Z)$
So we have a linear formula: $Z' = A_1 + A_2.X' + A_3.Y'$
By using the least-square method, we can determine the coefficients (A1, A2 and A3).
As these coefficients are found by the resolution of the system obtained (Goncalves da Silva, 2007).
The solution of the system is:

$$A1 = -2.6443, A2 = -0.0561, A3 = 0.124$$
$$a1 = exp(A1) = 0.0711; a2 = -0.0561 ; a3 = 0.124$$

So we found:
$C_1 = a1.P^{a2}.w^{a3} \rightarrow C_1 = 0.0711*P^{-0.0561}*w^{0.124}$ With error 4%
We did the same work for C_2 we found:
$C_2 = a1.P^{a2}.w^{a3} \rightarrow C_2 = 0.113*P^{-0.128}*w^{-0.013}$ With error 7%

5. Conclusion

Mathematical models are means that are often used in studying groundwater systems. Generally, the prediction of the solute transport in a porous media is obtained by the mathematical models. In the order to approximate the solution of the unsteady linear convection–diffusion–reaction problems of transporting a pesticide through the soil in the unsaturated zone a method numerical is presented.

The models we have examined couple the two types of physical non equilibrium and chemical non-equilibrium respectively (two regions) and (two sites). The solution of the problem was carried out by a numerical approach by using the finite difference method and a Fortran program.

The model allows us to predict the spatial and temporal concentration of pesticides in groundwater, and enables us to determine the effects of the transport parameters on the evolution of this concentration. The parameters studied are the dimensionless first order degradation coefficient μ, the Peclet number Pe and the dimensionless mass transfer coefficient w.

Our results proved by some experiences in the laboratory by using soil column with two kinds of herbicides; Isoproturon and Metribuzin. It found the relation between the concentration and parameters of transport by Regression because the difficulty of the analytical solution.

The main noticed and concluded effects are:

- The effect of the degradation on concentration C_1: The concentration is more important when we do not have degradation. The increase of the reaction decreases the presence of pesticide in the groundwater.

- The effect of the Peclet number: It is noted that ; more the value of the number of peclet is large more the concentration of C1 decreases. For values of peclet number in the range (100–1000), the effect of peclet Number is negligible because we do not observe any change in curves.
- The effect of the Mass Transfer Coefficient w on Concentration C_1 and C_2: when w increases the value of the concentration C_1 decreases, and the concentration C_2 increases gradually as w increases.
- The effect of the concentration C_2 on the evolution of the concentration C_1:
  We saw this importance when we make the value of $\mu_2 = 0$.
- A Comparison between two hypotheses, the first hypothesis assures that the initial concentration of the surface changes exponentially with time and the second corresponds to the Dirichlet condition. This condition assumes that during an injection of a pollutant at the soil surface, it is immediately and constantly subject to the concentration of the pesticide.
- After the comparison of the evolution of concentration between two herbicides Isoproturon and Metribuzin, we observe that the result obtained conforms, to the properties of the two herbicides; the concentration of second herbicide is higher than the concentration of the first herbicide.
- A relation between the concentration and parameters of transport by Regression was found.

References

Asensio, M.I., Ayuso, B., Ferragut, L., Sangalli, G., 2007. Numerical methods for modelling leaching of pollutants in soils. Adv. Eng. Softw. 38, 429–438.
Assumaning, G.A., Chang, S.Y., 2012. Use of simulation filters in three-dimensional groundwater contaminant transport modeling. J. Environ. Eng. 138, 1122–1129.
Aude, V., 2003. Impact de l'implantation de bandes enherbées sur le transport d'herbicides: étude sur colonnes de sol non perturbe. In: DEA, Hydrologie, Géostatistique et Géochimie. Université Pierre et Marie Curie, Paris.
Bear, J., 1979. Hydraulics of Groundwater. McGraw-Hill, NewYork.
Bouchard, D.C., Wood, A.L., Campbell, M.L., Nkedi-Kizza, P., Rao, P.S.C., 1988. Sorption nonequilibrium during solute transport. J. Contam. Hydrol. 2, 209–223.
Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1989. Modeling the transport of solutes influenced by multiprocess nonequilibrium. Water Resour. Res. 25, 1971–1988.
Cameron, D.R., Klute, A., 1977. Convective-DisperSive solute t ransport with a combined equilibrium and kinetic adsorption model. Water. Resour. Res 13, 183–188.
Fereshte, H.F., 2015. A review solute transport modeling in soils and hydrodynamic dispersivity. Agricult. Sci. Pract. 3–4, 95–96.
Fereshte, H.F., Farid, E., 2015. A review of uncertainty-based calibration of leach to simulate soil solute transport and water content. Acad. J. Sci. Res. 3 (10), 146–151.
Goncalves da Silva, E., 2007. Méthodes et analyses numériques' Engineering school. 99, Institut Polytechnique de Grenoble.
Javier, M. Gonzalez, Ljerka, U., 1999. Transport of nicosulfuron in soilcolumns. J. Environ. Qual. 28, 101–107.
Kathrin, F., Silvio, C.L., Lawrence, P.W., Martin, E., 2013. Evaluating pesticide degradation in the environment: Blind spotsand emerging opportunities. J. Sci. 341, 752–758.
Lapidus, L., Amundson, N.R., 1952. Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. J. Phys. Chem. 56 (8), 984–988.
Li, L., Barry, D.A., Culligan-Hensley, P.J., Bajracharya, K., 1994. Mass transfer in soils with local stratificationof hydraulic conductivity. Water. Resour. Res. 30, 1891–2000.
Lucila, C., Miguel, A.M., 2004. Simulation of 2, 4-d herbicide transport through the unsaturated zone using an analytical model. Int. J. Environ. Anal. Chem. 84, 123–131.
Manuel, A.E., Eugenio, L.P., Elena, M.C., Jesús, S.G., Juan, C.M., G.R., Luis., 2008. Agricult. Ecosyst. Environ. 123, 247–260.
Markus, F., 1996. Experimental evidence of transport of pesticides through field soils-A review. J. Environ. Qual. 25, 25–45.
Maurizio, B., Matteo, P., Mara, T., Tiziano, T., 2010. Multiple functions of buffer strips in farming areas. Eur. J. Agron. 32, 103–111.
Mohamed, M.H., Miguel, A.M., 1996. An analytical model for the assessment of pesticide exposurelevels in soils and groundwater. Environ. Models Assess 1, 263–276.
National Research Council, 1990. Ground Water Models: Scientific and Regulatory Applications. National Academy Press, Washington, DC.
Rao, P.S.C., Rolston, D.E., Jessup, R.E., Davidson, J.M., 1980. Solute transport in aggregated porous media: Theoretical and experimental evaluation. Soil Sci. Soc. Am. J. 44, 1139–1145.
Stefan, R., Martin, B., Adrian, S., Hans. G, .F., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness, a review. Sci. Total Environ. 384, 1–35.
Stuart, C., Amelia, S., Tom, D., LaJan, B., 1999. Water quality impacts by golf courses. J. Environ. Qual. 28, 798–809.
Suziki, T., Kondo, H., Yaguichi, K., Maki, T., Suga, T., 1998. Estimation of leachability and persistence of pesticides at golf courses from point-source monitoring and model to predict pesticide leaching to groundwater. Environ. Sci. Technol. 32, 920–929.
Van Genuchten, M.T.H., Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media I. Analytical Solutions. Soil Sci. Soc. Am. J. 40, 473–480.
Vanderborght, J., Gonzalez, C., Mallants, M.Vanclooster., D, Feyen, J., 1997. Effects of soil type and water flux on solute transport. Soil Sci. Soc. Am. J. 61, 372–389.