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Numerical Modeling of Glyphosate Transfer to Underground Water: Application to the Djuttitsa Watershed in the Bamboutos Mountain, West-Cameroon

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I. INTRODUCTION

The world population increases at an alarming rate, with about 52% of this population expected to be found in urban areas in 2025. Africa has the highest population growth rate in the world, estimated as 2,55% each year from 2010 to 2015. By 2050, Africa is expected to represent about four quarter of the world's population estimated as 1,3 billion inhabitants (AFD, 2014). Therefore, modern agricultural practices become an important challenge for food security (Abass et al., 2016). To increase food yield, Africa is faced by an excessive usage of pesticides without respect of recommended doses and frequency of application (white and Bunn, 2017). Soil and water pollution are direct consequences of this, with levels more than the authorised levels of 0.1 $\mu g.l^{-1}$ and 0.5 $\mu g.l^{-1}$ for maximal concentration of an individual pesticide and the total of all pesticides in water (Sousa et al., 2018). This shift from normal concentrations can induce severe consequences on population health (cancers, infertility, developmental abnormalities, neurotoxicity) (Huang et al., 2018). Pesticides intoxication is estimated at about 1 to 5 million cases per year in the world, with about 220 000 deaths each year. Developing countries use only 25% of the pesticides produced in the world but they account for 99% of deaths in the world due to pesticides poisoning especially in rural areas. To follow the evolution of pesticides in the soil and evaluate the risk of pollution, researchers have developed some numerical transfer models. However, the use of these models remains difficult in Sub-Saharan Africa due to insufficient data and inability to get some parameters. In this study, we therefore developed a 1D numerical model which was tested to study the glyphosate transfer at the watershed of Djuttitsa in West region of Cameroon. Their validation was done after statistical comparison of concentrations obtained from the model to those from the laboratory.

II. MATERIALS AND METHODS

II.1. Presentation of the study site

For this study, Djuttitsa area was selected due to intensive agriculture with high use of pesticides. Predominant crops cultivated in this area are irish potatoes, cabbages and carottes. It is situated on the southern flank of the Bamboutos mountain in the West Region of Cameroon between latitude 5°24' and 5°45' North, and between longitude 10°2' and 10°40' (Figure 1).

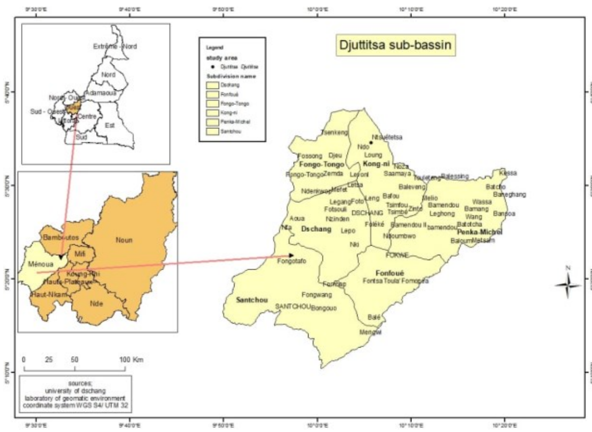

Figure 1: Location of the study site

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2.2 Mathematical modelling

Basic equations which were used by this model are: convection-dispersion equation which controls the transport of pesticides in the soil and Richards equation which controls water flow in the soil.

2.2.1 The convection-dispersion equation

a) Presentation

It is given by the equation (1) and subjected to constraint (2)

$$\begin{cases} \frac{\partial}{\partial t}[R(\theta)C] - \frac{\partial}{\partial z}\left[D(\theta, v)\frac{\partial C}{\partial z}\right] + \frac{\partial}{\partial z}[vC] = 0 \; in \;]0\,,1[\\ C(z,0) = C_0(z) \\ C(0,t) = c(1,t) = 0 \end{cases} \quad (1)$$

$$R(\theta) = 1 + \rho\frac{K_d}{\theta} \quad (2)$$

C = pollutant concentration in the soil in mol. l^{-1}

K_d = transfer coefficient between solid and liquid phase

D = dispersion coefficient

ρ = soil density in $g.cm^{-3}$

Θ = water content in $g.(cm^3)^{-1}$

C_o = Pesticide initial concentration in mol. l^{-1}

b) Resolution using the finite volume method

The mesh admissible of $]0\,,1[$ is defined by a family $(K_i)_{i=1,\ldots N}$, N$\epsilon\mathbb{N}^*$ such that $K_i = \left]z_{i-\frac{1}{2}}, z_{i+\frac{1}{2}}\right[$, and a family $(z_i)_{i=0,\ldots,N+1}$ such that : $z_0 = z_{\frac{1}{2}} = 0 < z_1 < z_{\frac{3}{2}} < \cdots < z_{i-\frac{1}{2}} < z_i < z_{i+\frac{1}{2}} < \cdots < z_N < z_{N+\frac{1}{2}} = z_{N+1} = 1$

with $h_i = mes(K_i) = z_{i+\frac{1}{2}} - z_{i-\frac{1}{2}}$, i=1 , … , N and $\sum_{i=1}^{N} h_i = 1$

$$h_{i+\frac{1}{2}} = z_{i+1} - z_i, i = 0, \ldots, N$$

$$h = max\{h_i\,, i = 1, \ldots, N\}$$

Considering $k \in \mathbb{N}^*$ the time step. Let $t_n = nk$, n$\epsilon\mathbb{N}$ and $C(z_i\,, t_n) = C_i^n$

By integrating equation (3.26) on each control volume K_i of the mesh we have:

$$R_i^n h_i \frac{C_i^{n+1} - C_i^n}{k} - D_i^n\left[\left(C_{i+\frac{1}{2}}^n\right)' - \left(C_{i-\frac{1}{2}}^n\right)'\right] + v\left(C_{i+\frac{1}{2}}^n - C_{i-\frac{1}{2}}^n\right) = 0$$

We choose upwind approximation of $C_{i+\frac{1}{2}}^n$ and $C_{i-\frac{1}{2}}^n$ so that :

$C_{i+\frac{1}{2}}^n = C_i^n$ et $C_{i-\frac{1}{2}}^n = C_{i-1}^n$

Flux approximation.

The flux : $-\left(C_{i+\frac{1}{2}}^n\right)'$ is approximated by : $F_{i+\frac{1}{2}}^n = -\frac{C_{i+1}^n - C_i^n}{h_{i+\frac{1}{2}}}$

The flux : $-\left(C_{i-\frac{1}{2}}^n\right)'$ is approximated by : $F_{i-\frac{1}{2}}^n = -\frac{C_i^n - C_{i-1}^n}{h_{i-\frac{1}{2}}}$

By replacing in the previous scheme, we obtain the numerical scheme for the resolution of the convection-dispersion equation

2.2.2 Richards equation and resolution

a) Presentation

The Richards equation in 1D which governs water movement in the soil is given by equation (3) and subjected to constraints (4) and (5)

$$\begin{cases} C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} - 1\right)\right] \\ h(0,z) = h_{ini}(z) \\ h(t,0) = h_{surf}(z) \\ h(t,Z) = h_{fond}(z) \end{cases} \quad (3)$$

Where K is the hydraulic conductivity: This describes the capacity of the soil to transfer water content for a given quantity of water.

h is the relative pressure compared to the atmospheric pressure of water expressed in water height.

Z is the vertical axis positively oriented toward the down part.

The resolution of Richards equation in a saturated zone needs the knowledge of two others hydrodynamic functions : $C(h) et\, K(h)$

The functions $C(h)\, and\, K(h)$ are defined empirically by :

$$C(h) = \begin{cases} \frac{\theta_s(2-n)}{h_g}\left(\frac{h}{h_g}\right)^{n-1}\left[1 + \left(\frac{h}{h_g}\right)^n\right]^{\frac{2}{n}-2}, & si\; h < 0 \\ 0\;, \quad si & h \geq 0\; (Saturated\; case) \end{cases}$$

$$K(h) = \begin{cases} K_s\left[1 + \left(\frac{h}{h_g}\right)^n\right]^{m\left(\frac{2}{n}-1\right)}\;, & si\; h < 0 \\ K_s\;, & si\; h \geq 0\; (Saturated\; case) \end{cases}$$

These different parameters represent:

θ_s water content at natural saturation,

K_s hydraulic conductivity at saturation,

$m\; and\; n$ parameters related to soil structure,

h_g the inflexion point of the retention curve $h = f(\theta)$ defined by :

$$f(x) = \theta_s\left[1 + \left(\frac{x}{h_g}\right)^n\right]^{\frac{2}{n}-1} \quad (2.4)$$

b) Resolution using the finite volume method

Given $(\zeta_i)_{i=1,\ldots N}$, $N\epsilon\mathbb{N}$ the mesh admissible of the domain $[0\,,1]$. That is $\zeta_i = \left[z_{i-\frac{1}{2}}, z_{i+\frac{1}{2}}\right]$ where the

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family $(z_i)_{i=0,\dots,N+1}$ such that : $z_0 = z_{\frac{1}{2}} = 0 < z_1 < z_{\frac{3}{2}} < \cdots < z_{i-\frac{1}{2}} < z_i < z_{i+\frac{1}{2}} < \cdots < z_N < z_{N+\frac{1}{2}} = z_{N+1} = 1$

With $\delta_i = mes(\zeta_i) = z_{i+\frac{1}{2}} - z_{i-\frac{1}{2}}$, i=1 , … , N and $\sum_{i=1}^{N} \delta_i = 1$

$\delta_{i+\frac{1}{2}} = z_{i+1} - z_i , i = 0 , \dots , N$ $\quad \delta_i^- = z_i - z_{i-\frac{1}{2}}$ and $\delta_i^+ = z_{i+\frac{1}{2}} - z_i$

$$\delta = max\{\delta_i , i = 1 , \dots , N\}$$

Given $(\theta_i^n)_{\substack{n=1,\dots,N \\ i=1,\dots N}}$ discrete unknowns that is $\theta_i^n = \theta(z_i, t_n)$. We integrate equation (3.1) on the control volume ζ_i and we obtain :

$$\int_{\zeta_i} \frac{\partial\theta}{\partial t} dt = \int_{\zeta_i} \frac{\partial}{\partial z}(D(\theta)\frac{\partial\theta}{\partial z})dz - \int_{\zeta_i} \frac{\partial}{\partial z}(D(\theta)dz$$
(2)

(2) becomes : $\int_{\zeta_i} \frac{\theta_i^{n+1} - \theta_i^n}{\Delta t} dt = \left(D(\theta)\frac{\partial\theta}{\partial z}\right)\left(z_{i+\frac{1}{2}}\right) - \left(D(\theta)\frac{\partial\theta}{\partial z}\right)\left(z_{i-\frac{1}{2}}\right) - D(z_{i+\frac{1}{2}}) + D(z_{i-\frac{1}{2}})$

where $\frac{mes(\zeta_i)}{\Delta t}(\theta_{\zeta_i}^{n+1} - \theta_{\zeta_i}^n) = (D\theta_z)\left(z_{i+\frac{1}{2}}\right) - (D\theta_z)\left(z_{i-\frac{1}{2}}\right) - D\left(z_{i+\frac{1}{2}}\right) + D(z_{i-\frac{1}{2}})$

Given $H_{i+\frac{1}{2}}^n$ an approximation of the flux $\left(D(\theta)\frac{\partial\theta}{\partial z}\right)\left(z_{i+\frac{1}{2}}\right)$

We have $H_{i+\frac{1}{2}}^n = D_i^n \frac{\theta_{i+\frac{1}{2}}^n - \theta_i^n}{\delta_i^+}$ on $\zeta_i , i = 1, \dots , N$

and $H_{i+\frac{1}{2}}^n = D_{i+1}^n \frac{\theta_{i+1}^n - \theta_{i+\frac{1}{2}}^n}{\delta_i^-}$ on $\zeta_{i+1} , i = 0, \dots , N - 1$

Where $D_i^n = \frac{1}{\delta_i}\int_{\zeta_i} D(\theta)dz$

with $\theta_{\frac{1}{2}}^1 = \alpha$ et $\theta_{N+\frac{1}{2}}^N = d$

From the principle of continuity of flux, there is an equality between the two flux

where $\theta_{i+\frac{1}{2}}^n = \frac{\theta_{i+1}^n \frac{D_{i+1}^n}{\delta_{i+1}^-} + \theta_i^n \frac{D_i^n}{\delta_i^+}}{\frac{D_{i+1}^n}{\delta_{i+1}^-} + \frac{D_i^n}{\delta_i^+}}$

by replacing $\theta_{i+\frac{1}{2}}^n$ by its value in the relation (4), we have:

$H_{i+\frac{1}{2}}^n = \tau_{i+\frac{1}{2}}^n(\theta_{i+1}^n - \theta_i^n)$ with $\tau_{i+\frac{1}{2}}^n = \frac{D_i^n D_{i+1}^n}{\delta_i^+ D_{i+1}^n + \delta_{i+1}^- D_i^n}$, $i = 1, \dots , N - 1$

We suppose that $\delta_i = \delta$ for all $i = 1, \dots , N$ and z_i the middle of the class ζ_i. We then have, $\delta_i = \frac{\delta}{2}$, $\forall\, i = 1, \dots , N$

where $H_{i+\frac{1}{2}}^n = \frac{2D_i^n D_{i+1}^n}{D_i^n + D_{i++1}^n} \frac{\theta_{i+1}^n - \theta_i^n}{\delta}$

2.3 Determination of pedological parameters

Granulometric analysis were done using the “pipette Robinson” method to determine the soil texture of the area. Water content was determined using the thermogravimetric [11] method as well as the bulk density [12] and absorption coefficient [13]. The hydraulic conductivity was recorded using the permeameter method based on Darcy’s law [14]. The soil organic carbon was determined using the titration method [15].

The percentage of organic matter is determined using equation 6.

% OM =% CO x 1.724. (6)

2.4 Laboratory determination of glyphosate experimental concentrations

At the start, a glyphosate solution of molar mass 360 g/l was used. 100 ml of glyphosate was mixed with 15l of water, giving a ratio of 7 l for 1 l of water. The molar concentration obtained was 14,9x10^{-3} mol/l. The next step was the collection of non-polluted soil samples at the study site. A solution of 50 ml paraquat/glyphosate previously prepared was then introduced in a graduated biuret and the nozzle opened for glyphosate to be distributed in soil samples found in a cylinder under (kodel *et al.*, 2001). The filtrate was collected at 10 min interval for 80 minutes and for each horizon. The experiment was repeated three times for a same horizon and time in order to reduce errors and the average of the 3 experiments was calculated and recorded as the pesticide concentration. The absorbance of the solution was read at wavelength of 258 nm using a UV-visible spectrophotometer.

After obtaining the absorbance values, the Beer-Lambert law was used to deduce corresponding concentrations. The Beer-Lambert law is given as:

A = absorbance $\quad A = \varepsilon l C$ (7)

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L = length of the cuve
ε = Molar extinction coefficient in $\mathrm{L.mol^{-1}cm^{-1}}$
C = Molar concentration of colored substances in $\mathrm{mol.l^{-1}}$

2.5 Statistical analysis

To validate the developed model, four statistical tests were made: The Kolmogorov-Smirnov test to check the normality of the values of the experimental concentrations and those simulated by the model. The t-test was used to compare values of experimental and simulated concentrations for the same horizon and at the same time; the standard mean error (SME) and absolute mean error (AME).

The standard mean error (SME) which quantifies the gap between experimental concentrations and simulated concentrations was calculated using the following formula

$$SME = \sqrt{\frac{1}{n}\left(C_{exp} - C_{sim}\right)^2} \quad (8)$$

The absolute mean (AME or bias) error has been calculated as the ratio between the absolute error (difference between simulated concentrations and experimental concentrations) and the experimental concentration for each horizon.

Horizons(cm)	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100
Clay%	3	5	5	3	7	9	6	3	8	9
Silt%	10	14	8	8	20	19	18	17	11	10
Sand%	87	81	87	89	73	72	76	80	81	81

$$AAE\ (\%) = \frac{C_{sim} - C_{exp}}{C_{exp}} \times 100 \quad (9)$$

Where C_{exp} and C_{sim} are the concentrations measured and estimated respectively. n is the total number of measurement performed.

The Kolmogorov-Smirnov test was used to assess the normality of collected data using SPSS software.

The performance of each horizon was evaluated by calculating the efficiency according to Marin-Benito *et al.,* (2014).

$$\boldsymbol{EF} = 1 - \frac{\sum_{i=1}^{n}(S_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \quad (10)$$

O_i : Observed value
$\bar{O}$: Mean of O_i
S_i : Simulated values
n : Number of observations

The performance of the model was evaluated by calculating the average performance of all horizons.

3- RESULTS

3.1- Numerical resolution of convection-dispersion equation by finite volume method

The resolution of the convection-dispersion equation and Richard's equation in 1D dimension using the finite volume method presented in the methodology lead us to the following numerical solution.

$$\begin{cases} R_i^n h_i \dfrac{C_i^{n+1} - C_i^n}{k} + D_i^n\left(-\dfrac{C_{i+1}^n - C_i^n}{h_{i+\frac{1}{2}}} + \dfrac{C_i^n - C_{i-1}^n}{h_{i-\frac{1}{2}}}\right) + v\left(C_i^n - C_{i-1}^n\right) = 0 \\ \dfrac{mes(\zeta_i)}{\Delta t}\left(\theta_{\zeta_i}^{n+1} - \theta_{\zeta_i}^n\right) = F_{i+\frac{1}{2}}^n - F_{i-\frac{1}{2}}^n \\ C_i^0 = \dfrac{1}{h_i}\displaystyle\int_{K_i} C_0(z)dz\ \forall i = 1, \dots, N \\ C_0^n = C_{N+1}^n = 0 \end{cases}$$

According to [9] the previous numerical scheme is stable and converges towards the solution of continuous problem (1).

3.2 Characteristics of the soil

Results from the granulometric analysis of the soil are presented in Table 1. Based on the USDA textual triangle, these results shows that the soil is a sandy loam soil.

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Table 1: Results of granulometric analysis

(cm)	water content (θ_r)	Saturated water content (θ_s)	Absorption coefficient	Density
0-10	0.77	0.64	1.20	0.35
10-20	0.57	0.52	1.10	0.28
20-30	0.62	0.60	1.04	0.32
30-40	0.38	0.37	1 .03	0.19
40-50	0.45	0.59	0.77	0.26
50-60	0.28	0.50	0.56	0.19
60-70	0.44	0.50	0.88	0.24
70-80	0.51	0.57	0.91	0.28
80-90	0.48	0.58	0.83	0.27
90-100	0.45	0.54	0.78	0.25

Table 2 presents the physico-chemical properties of soil samples used in this study.

Table 2: The physical and chemical properties of soil samples

Depht	Conductivité hydraulique à saturation (K_s) en m/s	CO%	OM%	PH
0-10	$1{,}79\times 10^{-6}$	7,5	12,93	4,8
10-20	$1{,}80\times 10^{-6}$	7,29	12,56	4,2
20-30	$1{,}80\times 10^{-6}$	7,64	13,18	4,3
30-40	$1{,}79\times 10^{-6}$	7,43	12,81	4,5
40-50	$1{,}79\times 10^{-6}$	5,93	10,22	4,7
50-60	$1{,}79\times 10^{-6}$	4,79	8,25	4,7
60-70	$1{,}78\times 10^{-6}$	4,07	7,02	4,9
70-80	$1{,}79\times 10^{-6}$	3,64	6,28	5,2
80-90	$1{,}78\times 10^{-6}$	3,79	6,53	5,4
90-100	$1{,}77\times 10^{-6}$	3,76	6,32	5,1

3.3 Experimental and simulated glyphosate concentrations obtained

a) Experimental concentrations

After polluting the soil samples with glyphosate and collecting the filtrates every 10 minutes. The spectrophotometer analysis gave the concentrations in mol.l^{-1} of glyphosate at each horizon. The result is presented in table 3

Table 3: Experimental concentrations of glyphosate obtained in filtrate (mol.l^{-1})

Time (min)	Horizons (cm)				
	0-10	10-20	20-30	30-40	40-50
10	0,00487	0,00520	0,00367	0,00450	0,00520
20	0,00421	0,00483	0,00331	0,00421	0,00466
30	0,00302	0,00413	0,00290	0,00383	0,00447
40	0,00190	0,00343	0,00225	0,00322	0,00402
50	0,00223	0,00323	0,00176	0,00312	0,00235
60	0,00173	0,00283	0,00163	0,00287	0,00323
70	0,00144	0,00212	0,00134	0,00237	0,00283
80	0,00110	0,00183	0,00103	0,00212	0,00246
Time (min)	Horizon(cm)				
	50-60	60-70	70-80	80-90	90-100
10	0,00603	0,00533	0,00543	0,00520	0,00433
20	0,00563	0,00513	0,00513	0,00503	0,00402
30	0,00513	0,00483	0,00483	0,00473	0,00354
40	0,00488	0,00440	0,00433	0,00383	0,00323
50	0,00467	0,00390	0,00412	0,00412	0,00283
60	0,00412	0,00353	0,00383	0,00277	0,00246
70	0,00390	0,00323	0,00353	0,00235	0,00223
80	0,00323	0,00274	0,00313	0,00223	0,00178

b) Simulated concentrations

Table 4 below presents the simulated values of different concentrations as a function of time

Time (min)	Horizons (cm)				
	0-10	10-20	20-30	30-40	40-50
10	0,00557	0,00537	0,00385	0,00475	0,00555
20	0,00487	0,00511	0,00346	0,00437	0,00505
30	0,00321	0,00453	0,00312	0,00410	0,00483
40	0,00280	0,00408	0,00267	0,00367	0,00420
50	0,00252	0,00355	0,00222	0,00352	0,00367
60	0,00207	0,00313	0,00190	0,00323	0,00340
70	0,00183	0,00242	0,00153	0,00283	0,00307
	0,00153	0,00220	0,00124	0,00245	0,00269

Table 4: Simulated concentrations obtained by the model (mol.l-1)

Time (min)	Horizon(cm)				
	50-60	60-70	70-80	80-90	90-100
10	0,00615	0,00576	0,00585	0,00576	0,00445
20	0,00593	0,00547	0,00557	0,00532	0,00420
30	0,00547	0,00520	0,00517	0,00483	0,00376
40	0,00520	0,00483	0,00487	0,00394	0,00356
50	0,00480	0,00431	0,00454	0,00384	0,00311
60	0,00440	0,00380	0,00417	0,00333	0,00290
70	0,00407	0,00340	0,00370	0,00285	0,00272
80	0,00369	0,00303	0,00340	0,00245	0,00232

Figures 4 to 13 show the simulated and experimental curves of the evolution of paraquat for each horizon of the study area.

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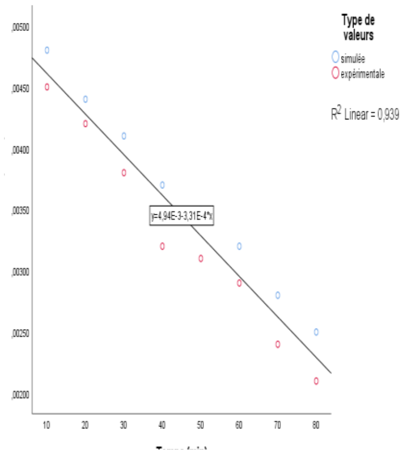

Figure 5: Simulated and experimental curve of the evolution of glyphosate at horizon of 40-50 cm

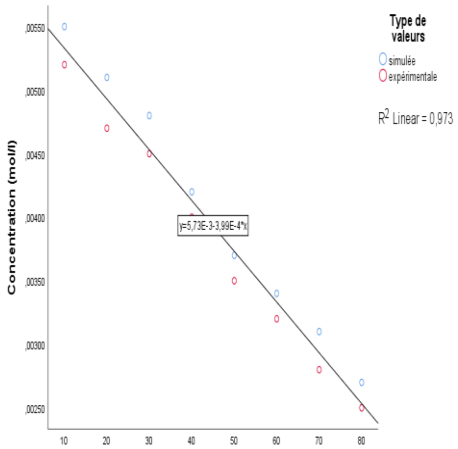

Figure 6: Simulated and experimental curve of the evolution of paraquat at horizon of 50-60 cm

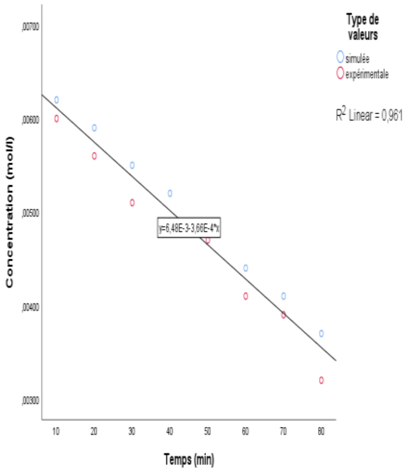

Figure 7: Simulated and experimental curve of the evolution of glyphosate at horizon of 60-70 cm

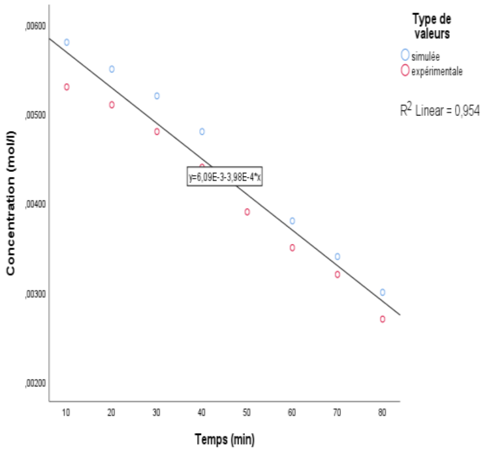

Figure 8: Simulated and experimental curve of the evolution of glyphosate at horizon of 70-80 cm

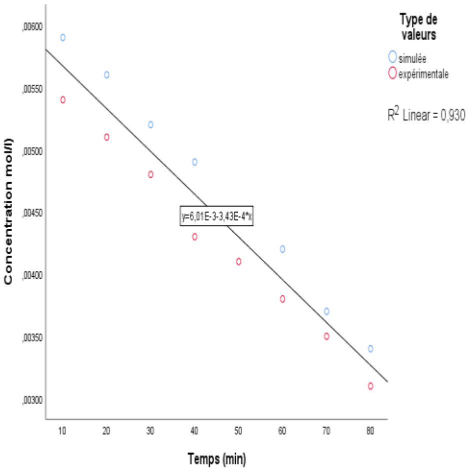

Figure 8: Simulated and experimental curve of the evolution of glyphosate at horizon of 80-90 cm

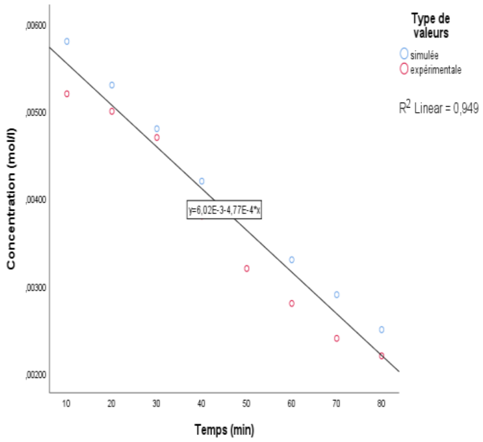

Figure 9: Simulated and experimental curve of the evolution of paraquat at horizon of 90-100 cm

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c) Error chart

Figure 12 shows the mean errors of simulated and experimental concentrations of the evolution of glyphosate.

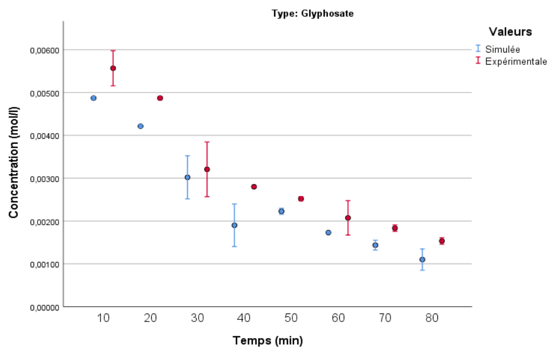

Figure 12: Error chart of simulated and experimental concentrations of glyphosate

3.5 Statistical analysis

The normality test performed was the Kolmogorov test to verify if the data respects the normal law. Results of this test are presented in tables 5 and 6 below for the two cases: simulated and experimental data. Results show that simulated and experimental data respect the normal law at 10% critical value (P≥0.1). So the comparison test (t-test) between simulated and experimental concentrations can be done followed by the test on the difference between the simulated and experimental concentrations. Table 6 presents a summary of results from statistical analysis comparing the differences between the values simulated by the model and those from the laboratory experiment.

Table 5: Kolmogorov-Smirnov test for simulated data

Parameters	Depht (cm)				
	0-10	10-20	20-30	30-40	40-50
Normal Me Parameters	0.0033013	0.0038825	0.0035638	0.0026738	0.0031038
Std.Deviation	0.0013918	0.0012162	0.0088019	0.0004833	0.0014325
Most Extrei Absolute Di	0.162	0.142	0.144	0.144	0.166
Positive	0.162	0.138	0.125	0.109	0.166
Negative	-0.128	-0.142	-0.144	-0.144	-0.138
Test Statistic	0.162	0.142	0.144	0.144	0.166

Parameters				
	60-70	70-80	80-90	90-100
Normal Mean Parameters	0.0033225	0.0030188	0.0028625	0.0026500
Std.Deviation	0.0013975	0.0009326	0.0009874	0.0010670
Most Extreme Differences	0.159	0.146	0.140	0.157
Positive	0.159	0.138	0.140	0.157
Negative	-0.127	-0.146	-0.139	-0.125
Test Statistic	0.159	0.146	0.140	0.157

Table 6: Kolmogorov-Smirnov test for experimental data

Parameters	Horizons (cm)				
	0-10	10-20	20-30	30-40	40-50
Normal Me Parameters	0.0036950	0.0043063	0.0034850	0.0029588	0.0028488
Std.Deviation	0.0012876	0.0011360	0.0014652	0.0005122	0.0011318
Most Extrei Absolute D:	0.164	0.178	0.196	0.195	0.202
Positive	0.164	0.149	0.196	0.150	0.202
Negative	-0.128	-0.178	-0.151	-0.195	-0.139
Test Statistic	0.164	0.178	0.196	0.195	0.202

Parameters	Horizons (cm)				
	50-60	60-70	70-80	80-90	90-100
Normal Me Parameters	0.0028425	0.0028925	0.0032488	0.0032413	0.0032063
Std.Deviation	0.0010630	0.0010961	0.0010727	0.0010012	0.0011432
Most Extrei Absolute D	0.188	0.150	0.130	0.125	0.202
Positive	0.188	0.150	0.127	0.125	0.202
Negative	-0.152	-0.132	-0.130	-0.122	-0.118
Test Statistic	0.188	0.150	0.130	0.125	0.202

Table 7: Values of SME and AME

Clearances	Horizons (cm)				
	0-10	10-20	20-30	30-40	40-50
MAPE(%)	-12,62	-10,88	9,53	-9,41	6,88
RMSE	0,00014	0,00015	0,00020	0,00010	0,00010

Clearances	Horizons (cm)				
	50-60	60-70	70-80	80-90	90-100
MAPE(%)	-18,07	13,82	-6,09	-12,18	-18,29
RMSE	0,00016	0,00015	0,00008	0,00013	0,00020

The t-test which compares the mean values of the simulated and experimental concentrations shows that 4 values have a significant difference at the 10% level ($P \leq 0.1$), 8 have a significant difference at the 5% level (p≤0.05), 63 have a highly significant difference at the 1% level (p≤0.01) and 4 values show a non-significant difference (NS).

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3.6. Performance of the model

The Marin-Benito formula (12) presented above was used to calculate the performance of the model to describe the evolution of the paraquat in the soil. Table 7 below presents the performance of each horizon.

Table 8: Efficiency of the model for each horizon

Depth(cm)	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100
Efficiency	0,95	0,97	0,92	0,98	0,94	0,93	0,97	0,98	0,97	0,94

The performance of the model was evaluated by calculating the average performance of all horizons.

$$E = 0.97$$

4. Graphical interface of the model

Figure 13 shows the graphical interface of the developed model, where the user insert values or required parameters and click on the button « Exe… » to obtain simulated data of different concentrations of pesticides over soil ranges of 10 cm.

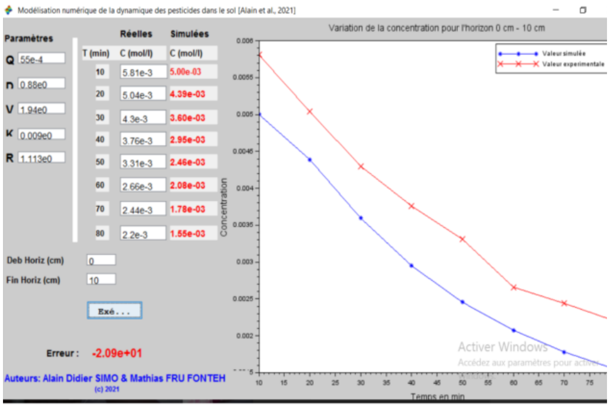

Figure 13: Graphical interface of the model

4. DISCUSSION AND CONCLUSION

Most of the existing models take into account several phenomena such as absorption/desorption, degradation, hypodermic flow and infiltration to describe the transfer of pesticides in soils. This increases the number of parameters and data to be used [7]. The model developed in this study focused on infiltration and the parameters taken into account were the bulk density, the soil/water partition coefficient, the water content and the hydraulic conductivity. The better approximation of the developed model would be due to the discretization technique used, the choice of constant horizons and the dimension of the model. Most of the existing models have been developed with an unstructured mesh that respects the natural stratification of the soil.

The Kolmogorov-Smirnov statistical test performed showed that the simulated and experimental values followed a normal distribution at the 10% threshold with a standard deviation of less than 0.01 in both cases. This shows a homogeneity in the values obtained which would be due to the best experimental measurement conditions and the good quality of the simulated values

Eighty glyphosate concentration values were simulated by the model for each soil horizon and at regular time intervals of 10 min for 80 min and 80 paraquat concentration values were obtained experimentally in the laboratory at the same horizons and at the same times. These 160 values were compared 2 to 2 for the same horizon and at the same time. It results that: 5 had a significant difference at the 10% level ($p \leq 0.1$). 9 have a significant difference at the 5% level ($p \leq 0.05$). 62 have a highly significant difference at the 1 level % ($p \leq 0.01$) and 4 values show a non-significant difference (NS). The best comparison results were obtained for pairs of values where the difference was non-significant (NS) and the worst comparisons were obtained with pairs where the p-value was smallest ($p \leq 0.01$). Non-significant differences were obtained on the 10-20. 40-50 and 70-80 horizons. respectively. after 20. 70. 70 and 80 minutes of flow.

These finding shows that the model used underestimates the values actually obtained in the laboratory, which could be due to the fact that climatic data were not taken into account in the construction of the model. The differences between the experimental values and those simulated by the model increase over time for the same horizon. On the other hand, the average of the deviations shows that it varies from one horizon to another. However, all the mean values of MAE remain very low 30%, a threshold for which a model is considered acceptable [16]. Likewise, the mean standard error (MSE) values are well below unity, further confirming the quality and precision of the used model.

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