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Development of a Simple and Low Cost Mathematical Model to Simulate the Movement of Paraquat in the Soil

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***Abstract*:- Globally, agriculture is evolving into intensive agriculture which is increasingly using pesticides to increase yields. Cameroon as well as other developing countries have not been left behind. The Djuttitsa river basin in the West region of Cameroon, the focus of this study, is an important intensive agricultural area and thus uses a lot of pesticides. The high usage causes pollution of soils and water with potential negative impacts on the environment and human beings. In order to better understand the movement of pollutants in the soil, numerical models are used. Many of the develop models in developed countries are difficult to use in Sub-Saharan Africa due to insufficient data. Therefore, there is a need to develop suitable models for use in this part of the world. In this study, a one dimension (1-D) simple numerical model of the movement of paraquat (pesticide) from the soil surface to a depth of 1 m in the study site was develop. To do this, the depth was segmented into a succession of horizons of 10 cm each, and soil properties was determined. The convection-dispersion equation that governs the transport of pollutants in the soil was solved numerically, by the finite volume method and a Scilab code was written to obtain numerical solutions of the equation followed by simulation using data from the study area. To validate the model, an experiment was carried out in the laboratory where undisturbed soils samples from the study area were polluted with a commercial solution of paraquat previously prepared with a concentration of $5.4x10^{-4}$ $mol.l^{-1}$ and the filtrates were collected every ten minutes and analyzed with a UV-visible spectrophotometer to determine their concentrations. Four statistical tests were done. The Kolmogorov-Smirnov test to ensure that the values of the simulated and experimental concentrations follow a normal law was carried out, the t-test which compares for each horizon and at each instant the values of the simulated and experimental concentrations, then the mean standard error (MSE) and mean absolute error (MAE) which compare the differences between the values of the simulated and experimental concentrations. The efficiency of the model was later calculated using the formula of Marin-Benito by comparing values simulated by the model and those obtained in the laboratory. The efficiency was found to be 97.5%.**

Keywords:- Cameroon, model, convection-dispersion equation, infiltration, pesticides, pollution

I. INTRODUCTION

Water is an invaluable and vital natural resource whose availability has always been a concern. The demand for water has increased over the years due to the increasing population [1]. During the last decade, environmental water quality has greatly deteriorated due to uncontrolled discharge of industrial wastes, high pesticide and fertilizer usage in agriculture as well as poor management of water resources [2]. All these have modified the chemical composition of water making it unsuitable for some desired uses.

Poisoning due to pesticides affects about 1 to 5 million people a year [3]. It is estimated that there are about 220,000 deaths annually in the world due to pesticides [4]. Developing countries use only 25% of the pesticides produced in the world but they account for 99% of the deaths in the world due to pesticides poisoning especially in rural areas most often due to poor handling, usage and storage of pesticides [5]. These deaths arise due to the consumption of water polluted by pesticides with concentrations over the authorized limit of 0.1 $\mu g.l^{-1}$ for each pesticide and 0.5 $\mu g.l^{-1}$ for the total of all pesticides [6].

To appreciate the problem of contaminated water resources due to the use of pesticides in agriculture and evaluate the risks of environmental pollution, mathematical models of the movement of pesticides have been developed. These models can be used to quantitatively evaluate the potential impact of pesticides, by simulating the movement of a given pesticide through air, soil and water. However, these models require data that are most often not available in most developing countries [7]. Hence, there is a need, to develop models for data scarce environments.

II. MATERIALS AND METHODS

A. Presentation of the study area

This study was carried in Djuttitsa situated on the southern flank of the Bamboutos mountain in the Western Region of Cameroon [8] between latitude 5°24’ and 5°45’ North, and between longitude 10°2’ and 10°40’ (Figure 1). This area was selected due to the intensive agricultural activities carried out there, with high use of pesticides. The predominant crops cultivated are irish potatoes, cabbages, carottes, spices and tea [9].

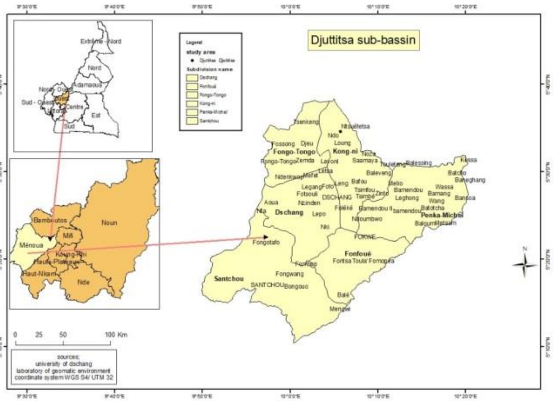

Fig. 1. Location of the study area

In this study, a one dimension (1-D) mathematical model was developed to determine the movement of a pesticide from the soil surface to the depth of 1 m. A depth of 1 m was used because at the study site, after a depth of 1 m, the soil properties were uniform. Paraquat ($C_{12}H_{14}N_2$) a weed killer was selected for use. The 1 m depth was divided into 10 equal horizons of 10 cm each in order to have a constant space step in the mathematical model. The model was developed to simulate the concentration of paraquat at 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm depths as a function of time. In the laboratory, an experiment was setup to determine the concentration of paraquat at the above mentioned depths. The comparison between values of concentrations obtained in the laboratory and those predicted by the model was used to validate the model.

B. Modeling of pollutant movement in the soil using the convection-dispersion equation

1) The convection-dispersion equation

The development of a pesticide transfer numerical model necessitates the resolution of the convection-dispersion equation that controls the transport of pollutants in the soil:

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

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

C = pollutant concentration in the soil in $mol.l^{-1}$
K_d = transfer coefficient between solid and liquid phase
D = dispersion coefficient in $m^2.s^{-1}$
ρ = soil density in $g.cm^{-3}$
ϴ = water content in $g.cm^{-3}$
C_o =the initial concentration in $mol.l^{-1}$

To resolve the equation, the finite volume method was used. The finite volume method is a discretization method that is well suited to the numerical simulation of systems obeying the principle of conservation of matter. This method is locally conservative because it is based on a ‘’balance” approach. A local balance is written on each discretization cell called “control volume”. By the divergence formula, an integral formulation of the fluxes over the boundary of the control volume is then obtained [10] . The fluxes on the boundary are discretized with respect to the discrete unknowns.

To solve the convection-dispersion equation (1), a network of values from $]0\,,1[$ defined by a family: $(K_i)_{i=1,\dots N}$, $N\epsilon\mathbb{N}^*$, $K_i = \left]z_{i-\frac{1}{2}}\,, z_{i+\frac{1}{2}}\right[$ and $(z_i)_{i=0,\dots,N+1}$ so 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 $\sum_{i=1}^{N} h_i = 1$

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

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

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 (1) on each control volume result is

$$R_i^n h_i^n \frac{C_i^{n+1} - C_i^n}{k} - D_i^n\left[\left(C_{i+\frac{1}{2}}^n\right)' - \left(C_{i-\frac{1}{2}}^n\right)'\right] + v\left(C_{i+\frac{1}{2}}^n - C_{i-\frac{1}{2}}^n\right) = 0 \quad (3)$$

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

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

$$F_{i+\frac{1}{2}}^n = -\frac{C_{i+1}^n - C_i^n}{h_{i+\frac{1}{2}}} \quad (4)$$

and the flux: $-\left(C_{i-\frac{1}{2}}^n\right)'$ is approximated by:

$$F_{i-\frac{1}{2}}^n = -\frac{C_i^n - C_{i-1}^n}{h_{i-\frac{1}{2}}} \quad (5)$$

By replacing (4) and (5) in equation (3), the numerical formula is obtained.

To obtain the numerical values of the simulated concentrations of paraquat and to describe its evolution in the different soil horizons of the study site, a scilab code was written and the parameters from the study area were used.

2) Determination of soil parameter

Three cartographic units: bottom, middle and top of the slope of the study were identified. In each unit, three samples were collected using a cylindrical ring with 5.05 cm diameter and 5 cm height with total volume of 100 cm^3 in 9 different plots in the study area.
Granulometric analysis was determined by the ‘’pipette Robinson’’ method [11] to assess the soil texture of the study area. Values of water content were determined by the thermogravimetric method [12] as well as the bulk density[13], absorption coefficient [14] and hydraulic

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conductivity by permeameter method based on Darcy's law[15]. The soil organic carbon of the soil was determined using the titration method [16].
The percentage of organic matter is determined using equation 6.

$$\%OM = \%CO \times 1.724 \quad (6)$$

3) Determination of experimental concentration in the laboratory

A paraquat solution was prepared with similar concentration to that used by farmers in the study area. That is, 75 ml of paraquat 200 mg.l^{-1} in 15 l of water. This gave a concentration of 5ml for 1l, with a molar concentration of 5.4x10^{-4} mol.l^{-1}.
Soil samples were washed with water and the filtrate collected and analyzed under a UV-visible spectrophotometer to ensure the initial absence of paraquat in the soil.
Non polluted soil samples were collected in the study site using cylindrical rings of 10 cm height at different depth: 0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, 90-100 cm.
A burette was used to introduce the paraquat into the soil sample as shown on figure 2.

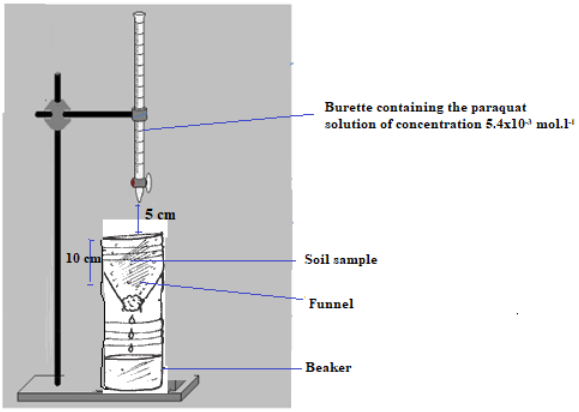

Fig. 2. Experimental setup

The filtrate was collected at 10 minutes interval. The absorbance of the solution was read at wavelength of 268 nm using a UV-visible spectrophotometer. Figure 3 shows the absorption spectra obtained.

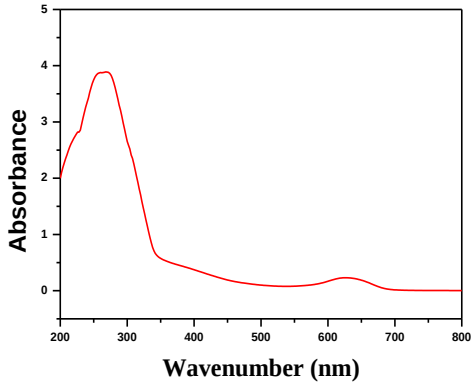

Fig. 3. Absorption spectra

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

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

A = absorbance
L = length of the same cm
ε = Molar extinction coefficient in L. mol^{-1}cm^{-1}
C = Molar concentration of colored substances in mol.l^{-1}

4) Analysis of Result

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 simulated by the model. The t-test was used to compare for the same horizon and at the same time the value of the simulated concentration at the value of the experimental concentration; 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

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

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

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

Where C_{exp} and C_{sim} are the concentrations measured and estimated respectively and n is the total number of measurement performed.
The Kolmogorov-Smirnov test was used to assess the normality of collected data using the SPSS software.
The performance of each horizon was evaluated by calculating the efficiency according to [17].

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

O_i = Observed value in mol.l^{-1}
$\bar{O}$ = Mean of O_i
S_i = Simulated values in mol.l^{-1}
n = Number of observations

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

III. RESULTS AND DISCUSSION

A. Numerical resolution of convection-dispersion equation by finite volume method

The resolution of the convection-dispersion equation in one dimension using the finite volume method presented in the methodology lead us to the following numerical solution.

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$$\begin{cases} R_i^n h_i \dfrac{C_i^{n+1} - C_i^n}{k} + D_i^n \left(- \dfrac{C_{i+1}^n - C_i^n}{h_{i+\frac{1}{2}}} + \dfrac{C_i^n - C_{i-1}^n}{h_{i-\frac{1}{2}}} \right) + v(C_i^n - C_{i-1}^n) = 0 \\ C_i^0 = \dfrac{1}{h_i} \int_{K_i} C_0(z) dz \; \forall i = 1, \dots, N \\ C_0^n = C_{N+1}^n = 0 \qquad \forall n \in \mathbb{N} \end{cases}$$

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

B. *Characteristics of the soil*

Results of 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.

TABLE 1. Results of granulometric analysis

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

The table 2 presents the physico-chemical properties of the soil.

TABLE 2. The physical and chemical properties of the soil

Depht (cm)	Residual water content ($\boldsymbol{\theta_r}$) in $\boldsymbol{g/cm^3}$	Saturated water content ($\boldsymbol{\theta_s}$) in $\boldsymbol{g/cm^3}$	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

Depht	Conductivité hydraulique à saturation ($\boldsymbol{K_s}$) en $\boldsymbol{m/s}$	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

The values of the hydraulic conductivity are not very variable and indicates a rather slow transport of solutes in the study area. The water content is also low and therefore the pesticide will bind more to the soil particles.

C. *Paraquat concentration data obtained*

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

TABLE 3. Experimental concentrations (mol.l-1) obtained in the laboratory

Time (min)	Depht(cm) 0-10	10-20	20-30	30-40	40-50
10	0.00581	0.00578	0.00549	0.00349	0.00458
20	0.00504	0.00543	0.00537	0.00343	0.00410
30	0.00431	0.00515	0.00426	0.00338	0.00362
40	0.00376	0.00483	0.00374	0.00322	0.00288
50	0.00331	0.00393	0.00298	0.00298	0.00225
60	0.00266	0.00345	0.00214	0.00264	0.00198
70	0.00244	0.00299	0.00203	0.00237	0.00176
80	0.00223	0.00289	0.00187	0.00216	0.00162
Time (min)	Depht(cm) 50-60	60-70	70-80	80-90	90-100
10	0.00467	0.00446	0.00467	0.00451	0.00487
20	0.00407	0.00419	0.00439	0.00438	0.00446
30	0.00316	0.00356	0.00399	0.00377	0.00387
40	0.00281	0.00294	0.00357	0.00355	0.00355
50	0.00232	0.00247	0.00290	0.00312	0.00260
60	0.00204	0.00223	0.00263	0.00273	0.00243
70	0.00192	0.00186	0.00207	0.00209	0.00209
80	0.00175	0.00143	0.00177	0.00178	0.00178

These values show that paraquat concentrations obtained in the laboratory decreased over time for each depth. However, these concentrations vary by horizons for the same time. This is due to the variation per horizon of the physical and chemical properties. The higher concentration was obtained at the 0-10 depth after 10 min flow and the smallest was obtained at the 70-80 depth after 80 min.

D. *Numerical simulation*

Figures 4 to 13 show the simulated and experimental curves of the evolution of paraquat for each horizon of the study area. These figures show a decrease in the simulated and experimental concentrations of paraquat over the time. In addition, the simulated curves are below those obtained experimentally, which means that the model underestimates the experimental values.

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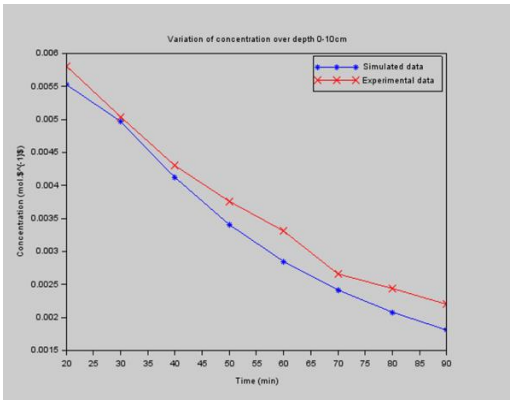

Fig 4. Simulated and experimental curves at horizon 0-10

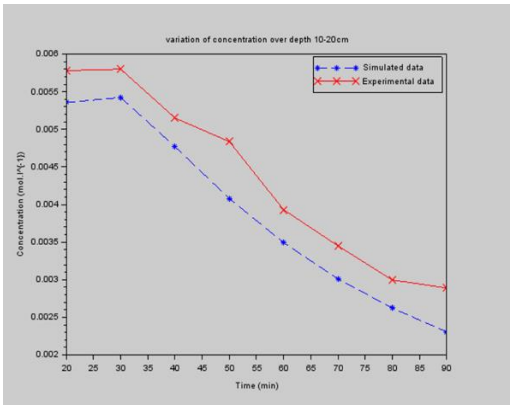

Fig 5. Simulated and experimental curves at horizon 10-20

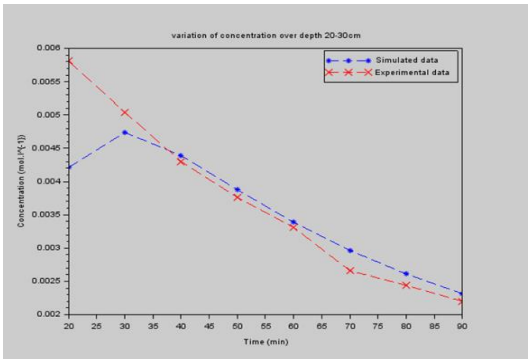

Fig 6. Simulated and experimental curves at horizon 20-30

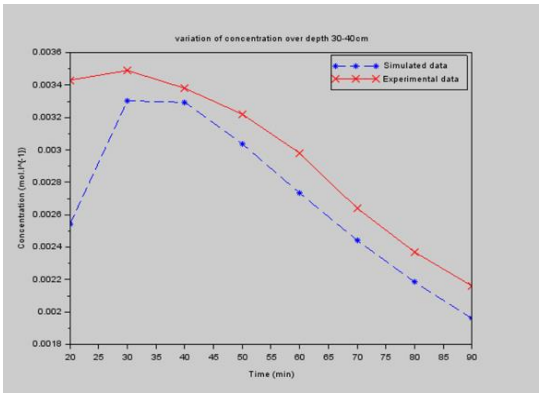

Fig 7. Simulated and experimental curves at horizon 30-40

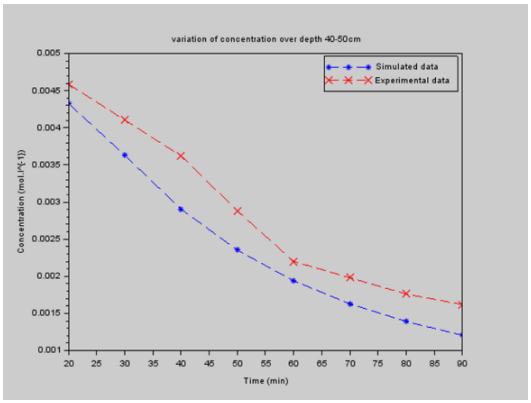

Fig 8. Simulated and experimental curves at horizon 40-50

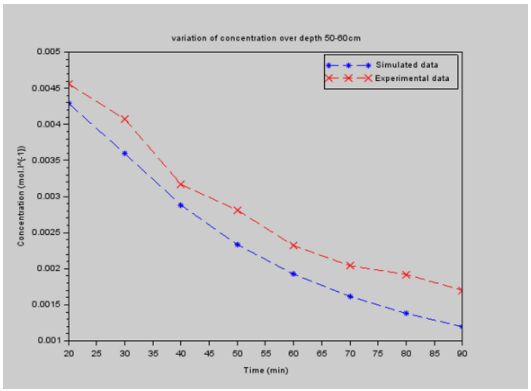

Fig 9. Simulated and experimental curves at horizon 50-60

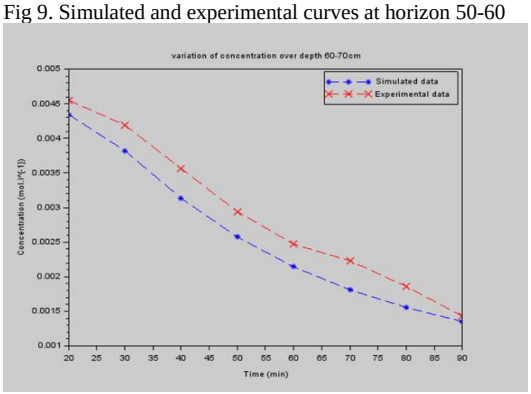

Fig 10. Simulated and experimental curves at horizon 60-70

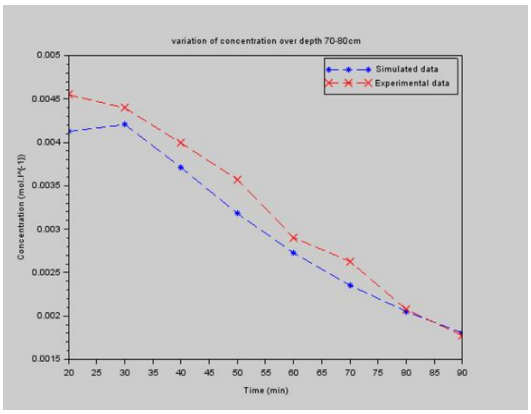

Fig 11. Simulated and experimental curves at horizon 70-80

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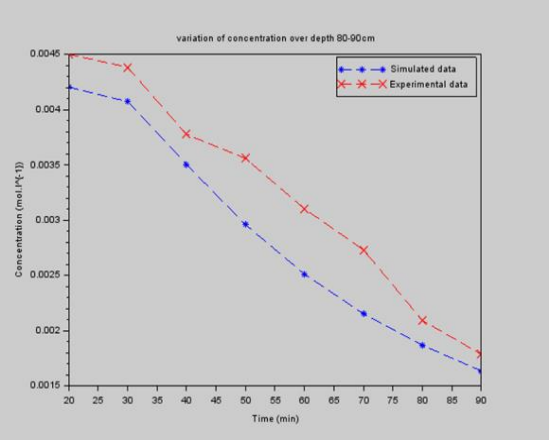

Fig 12. Simulated and experimental curves at horizon 80-90

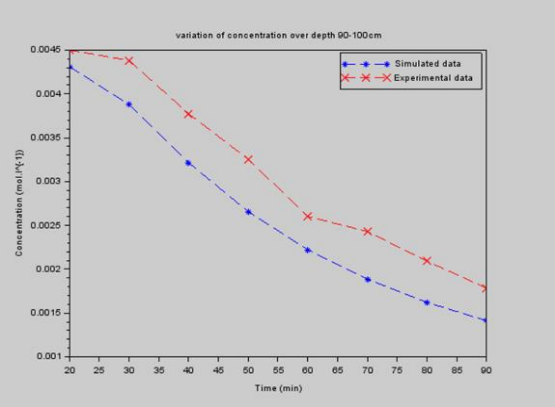

Fig 13. Simulated and experimental curves at horizon 90-100

E. Statistical analysis

1) Normality test

Results of Komogorov normality test are presented in tables 4 and 5 for the two cases: simulated and experimental data

TABLE 4. Kolmogorov test for simulated data

Parameters	Depht (cm)				
	0-10	10-20	20-30	30-40	40-50
Normal Mean Parameters	0.00330 13	0.00388 25	0.00356 38	0.00267 38	0.00310 38
Std.Deviation	0.00139 18	0.00121 62	0.00880 19	0.00048 33	0.00143 25
Most Extreme Differences	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
Asym.Sig.(2-tailed)	0.200[c,d]	0.200[c,d]	0.200[c,d]	0.200[c,d]	0.200[c,d]

Parameters	Depht (cm)				
	50-60	60-70	70-80	80-90	90-100
Normal Mean Parameters	0.00240 00	0.00332 25	0.00301 88	0.00286 25	0.00265 00
Std.Deviation	0.00110 62	0.00139 75	0.00093 26	0.00098 74	0.00106 70
Most Extreme Differences	0.168	0.159	0.146	0.140	0.157
Positive	0.168	0.159	0.138	0.140	0.157
Negative	-0.137	-0.127	-0.146	-0.139	-0.125
Test Statistic	0.168	0.159	0.146	0.140	0.157
Asym.Sig.(2-tailed)	0.200[c,d]	0.200[c,d]	0.200[c,d]	0.200[c,d]	0.200[c,d]

TABLE 5. Kolmogorov test for experimental data

Parameters	Horizons (cm)				
	0-10	10-20	20-30	30-40	40-50
Normal Mean Parameters	0.003695 0	0.004306 3	0.003485 0	0.002958 8	0.002848 8
Std.Deviation	0.001287 6	0.001136 0	0.001465 2	0.000512 2	0.001131 8
Most Extreme Differences	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
Asym.Sig.(2-tailed)	0.200[cd]	0.200[cd]	0.200[cd]	0.200[cd]	0.200[cd]

Parameters	Horizons (cm)				
	50-60	60-70	70-80	80-90	90-100
Normal Mean Parameters	0.0028425	0.002892 5	0.003248 8	0.003241 3	0.003206 3
Std.Deviation	0.001063 0	0.001096 1	0.001072 7	0.001001 2	0.001143 2
Most Extreme Differences	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
Asym.Sig.(2-tailed)	0.200[c,d]	0.200[cd]	0.200[c,d]	0.200[cd]	0.200[cd]

Tables 4 and 5 above show that simulated and experimental data respect the normal law at 10% critical value (P≥0.1). So the comparison test (t-test) simulated and experimental concentrations can be done and the tests on the differences between the simulated and experimental concentrations.

2) Comparison between simulated and experimental data

Table 6 presents summaries of results of statistical tests comparing the differences between the values simulated by the model and the experimental values observed in the laboratory

TABLE 6. Values of SME and AME

TESTS	Depht (cm)				
	0-10	10-20	20-30	30-40	40-50
MAE	-17.8	-10.2	-12.0	-10.0	-10.4
SME	0.00017	0.00012	0.00009	0.00012	0.00014

TESTS	Depht (cm)				
	50-60	60-70	70-80	80-90	90-100
MAE	-5.6	-7.6	-7.8	-7.4	-10.9
MSE	0.00009	0.00012	0.00013	0.00011	0.00011

MAE : Mean Absolute Error (%)
MSE : Mean Standard Error

The values of AME are less than 30% et those of SME less than 1. Moreover, the smallest difference were obtained on depths 20-30 and 50-60 : these are the depth were the simulations were the best. The highest difference was obtained on 0-10.

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The t-test which compares the mean values of the simulated and experimental concentrations shows that 5 values have 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).

3) 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 7. Efficiency of the model for each horizon

Depth (cm)	0-10	10-20	20-30	30-40	40-50
Efficiency	0.96	0.98	0.99	0.98	0.96

Depth (cm)	50-60	60-70	70-80	80-90	90-100
Efficiency	0.99	0.97	0.98	0.98	0.97

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

$$E = 0.975$$

IV. 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. which increases the number of parameters and data [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 then 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 follow 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 paraquat 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 for the same horizon and at the same time. It emerges that: 5 have 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 results were obtained for pairs of values where the difference was insignificant (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.

The finding is 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 development 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 well below 30%, a threshold for which a model is considered acceptable. Likewise, the mean standard error (MSE) values are well below unity. Further confirming the quality and precision of the model used.

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