

Pesticide Chlorpyrifos Loss in Runoff From Andic Soil Potato Fields in Colombia: Comparison of Field Results With Gleams Predictions

EDIER HUMBERTO PEREZ* and MARTHA ISABEL PAEZ†

Department of Chemistry, Cauca University, Cauca, Colombia

Fax: (57)(928)209800 Ext. 2306; Tel: (57)(928)209800

E-mail: ehperetz@unicauca.edu.co

Runoff potential of chlorpyrifos was evaluated in a small scale study under simulated rainfall on a andic soil potato fields. Rainfall events were simulated (80 mm/h × 30 min) a 40 cm × 32 cm field plots with 8, 17, 30 and 40 % slope, 24 h after pesticide application. Sediment amounts and pesticide concentrations in sediment and water were determined in the runoff samples, pesticides residues attached to sediment were extracted by ultrasonification of 40 °C and centrifugation with hexane by GC-ECD with percentages of 94-98 % and residues in aqueous sample was quantified using a solid-phase extraction (SPE) and rotaevaporation in atmosphere of N₂ and GC-ECD, percentages of recuperation were determined between 89-98 %. The observed data in field used to fit sensitivity in the water balance calculus in model GLEAMS. Being observed that the pesticide component of the GLEAMS considers loss by runoff of chlorpyrifos in soil (sediment) and water with modeling efficiency (EF) 0.7 and 0.2, respectively. These data predicted the destiny and behaviour of pesticide in the field in andic soil of high mountain.

Key Words: Runoff, Chlorpyrifos, Andic soil, Behaviour, GLEAMS.

INTRODUCTION

Chlorpyrifos (O,O-diethyl (3,5,6-trichloro-2-pyridyl), phosphorothioate) is a pesticide used in Colombia for the control of *Epitrix* sp, *Agorotis ipsilon*, *Agrotis subterranean* and *Liliomyza ecuadorensis*, applied to the soil before and during the tilling and sowing of potatoes.

The chlorpyrifos can interact with the colloidal material in water systems. Wu and Lair¹, studied the strongly sorption into the Ca-humus complex and is not easy to desorb in order to pass into an aquatic solution, but is easily transported by surface runoff. Understanding the processes that determine the transporting of pesticides from the agricultural fields to the natural water resources is crucial for the safe use

†Department of Chemistry, Valle University, Valle del Cauca, Colombia; Tel: (57)(92)3155251, A.A. 25360, E-mail: mipaezem@gmail.com

of pesticides. Recent studies indicate that the presence of chlorpyrifos suspended in organic matter present in natural water flows is toxic for aquatic organisms Phillipps *et al.*² and Rose *et al.*³ discussed the pesticide-contaminated agricultural runoff.

Finacchiaro and Gennari⁴, showed that the pesticide chlorpyrifos has a strong affinity with sediments, with a Freundlich constant (K_f) of 143, compared with K_f to 65 in soils, meaning that the process of absorption is practically irreversible. Chlorpyrifos is degraded by slow hydrolysis ($< = 0.008 \text{ day}^{-1}$) in acid soils ($\text{pH} < 7$), implying the formation of 3,5,6-trichloro-2-pyridinol (TPC)⁵.

The field studies on surface soil and pesticides runoff were carried out experimentally using rain simulators, the basic characteristics of which are described by Burbenzer⁶, Meyer and Harman^{7,8}, Engel *et al.*⁹ quantify runoff and soil losses by water erosion under different soil tillage systems. Hunsche *et al.*¹⁰ simulated rain events using a laboratory rain simulator. These rainfall simulators simulate the characteristics of natural rain close to the earth, such as: the distribution of the size of the rain drops and the speed and the intensity of the impact. There are three characteristics that determine the surface displacement of rain by runoff.

The GLEAMS model (groundwater loading effects of agricultural management systems) is made up of four components *i.e.*, hydrology, erosion, nutrients and pesticides that function simultaneously. This last component was developed, revised and tested in different environmental conditions by Leonard and Wauchope¹¹, and Leonard *et al.*¹² The pesticide is considered to divide between the soil and the runoff water and the process of adsorption-desorption is simulated in linear and reversible form bearing in mind the adsorption model of Freundlich.

The GLEAMS simulation model is useful for understanding the behaviour for predicting the transportation of pesticides through the profile of the soil and by surface runoff. This model was used by Close *et al.*¹³ to evaluate leaching and runoff in allophanic flooded soils of New Zealand for chlorpyrifos. Chinkuyu *et al.*¹⁴ predicts the pesticide losses in surface runoff from agricultural fields and De Paz *et al.*¹⁵ in Colombian soils with high organic carbon content, low apparent density, high water retention and a high capacity for the adsorption of phosphates and various loads. These characteristics can influence the adsorption of pesticides and facilitate their transport by runoff¹⁶.

The need to adapt models that allow the prediction of the behaviour and destiny of polluting compounds in environmental conditions of humid tropics and high mountain zones, the GLEAMS model was chosen to begin its possible use. This mathematical model interrelates the effects of soil-cultivation-pesticide in the field a surface level and in the soil profile (the root zone), taking into account the movement of water, as well as the physical, chemical and climatic data needed for its implementation at the experimental level.

The GLEAMS model contains the necessary detail to represent and model the runoff, the erosion and the transportation of pesticides. It operates on the field scale

and has been widely used to simulate the transportation of pesticides and is available as free software. In this application of the model a number of curve previously determined to be 95 is used and the highest Koc value calculated at each slope is taken, in order to obtain a simulation which explain the field conditions.

In the study four zones were established with different degrees of slope, each one with three experimental plots in acid andic soils (pH = 4.7) with a high capacity to retain humidity, low temperatures and variable gradient.

EXPERIMENTAL

The experimental site is located in the Calvache region, Cauca, Colombia (76°17.51' W, 2°30.34'N) (Fig. 1). The soil profiles show a deep horizon Ap (more than 30 cm), with low apparent density and structurally stable integrated by micro-aggregates. The region has an average annual rainfall of 1100 mm and average temperature of 10 °C. Twelve plots were marked out in open country without vegetation cover, having naturally occurring slopes of 8, 17, 30 and 40 %. The size of each plot was 40 cm × 32 cm, marked off by a steel tray 10 cm high buried in the ground, to allow the runoff water in the area to be directed. A ditch was dug at the bottom of each plot to collect the runoff water and sediments.

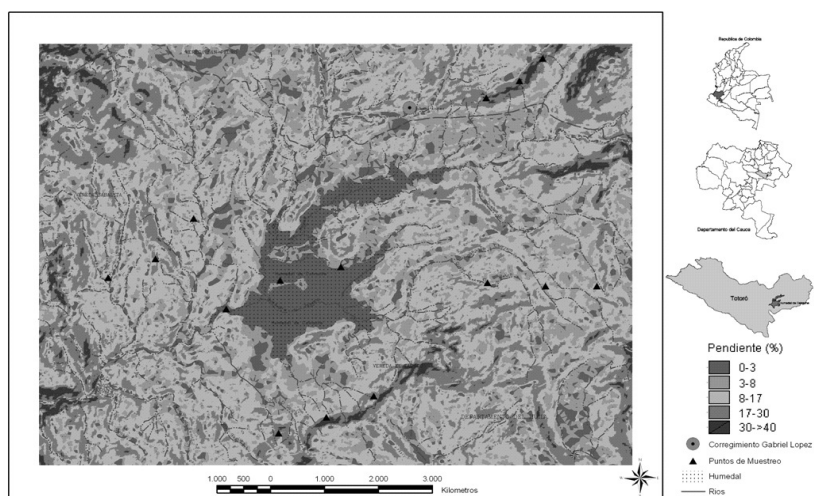


Fig.1. Location of the study zone. Climatology station IDEAM 2602507 Gabriel Lopez, Cauca, Colombia (Latitude 02° 30' N and Longitude 76°17' W), at 3000 meters in elevation

Methodology: The pH of the soil was measured in a ratio 1:2 (w/v), using combined electrodes. The organic carbon is determined by the method of Walkley, the clay content by the method of Bouyucos, the porosity is calculated from the quotient between the apparent density and the real density; specific surface through the retention of ethylene glycol monoethyl ether¹⁷. The speed with which the water

passes through the mixture of soil is calculated with the equation of Darcy Henry, Pla¹⁸ and Eweis *et al.*¹⁹, using the methodology of hydraulic conductivity in saturated soils.

In (Table-1), the main physical-chemical characteristics of the andic soil of the zone are shown, with a high amount of organic matter (OM), high capacity for adsorption and high capacity of anionic and cationic exchange. These characteristics, in combination with a low pH generate a high capacity of adsorption the chemical products and a high retention of phosphates. The soils have a loamy-clay texture, with high porosity and very low hydraulic conductivity.

TABLE-1
PHYSICAL CHARACTERISTICS AND CHEMICAL PROPERTIES OF
THE ANDIC SOIL OF THE ZONE, AT A DEPTH of 0-5 cm, HORIZON Ap

Slope	Plot	pH	OC (%)	Clay (%)	BD (g cm ⁻³)	Porosity (%)	Field capacity (cm cm ⁻¹)	Wilting point (cm cm ⁻¹)	Ksat (m d ⁻¹)	Specific area (m ² g ⁻¹)
8	1	4.65	18.6	19.26	0.54	74.97	52.91	61.28	0.05	408
	2	4.51	19.6	20.90	0.54	76.75	58.30	67.04	0.29	422
	3	4.79	16.4	17.60	0.49	78.87	36.23	46.35	–	415
17	1	4.37	24.1	16.29	0.39	84.23	52.41	62.10	1.75	425
	2	4.76	21.8	20.41	0.43	79.77	44.41	56.89	0.87	474
	3	4.60	21.3	17.33	0.40	81.95	44.61	56.55	1.70	415
30	1	5.07	25.8	21.30	0.47	81.28	62.85	68.95	0.09	374
	2	5.04	19.5	19.39	0.34	82.72	38.13	50.13	–	565
	3	5.09	22.0	12.91	0.42	84.10	63.19	69.93	0.08	396
40	1	5.03	21.5	17.16	0.47	78.19	54.95	69.08	1.07	277
	2	5.22	20.9	18.32	0.45	78.70	60.68	70.04	0.10	496
	3	5.12	21.1	17.74	0.46	78.44	57.82	69.81	0.58	387

BD = Average bulk density, Ksat = Average saturated hydraulic conductivity.

Rain simulator: A portable falling drip type rain simulator described by Pla¹⁸ and Lal²⁰, which has three parts: (i) Adjustable metal legs, used for leveling the base from where the drip is simulated for the precipitation, so that it can be used under different field conditions and different degrees of slope, as well as also allowing it to work in laboratory conditions depending on the case. (ii) The system that makes the drops and controls the intensity of the fall, a process that is held in place by a Marriotte system using hypodermic needles distributed in the form of a spiral. (iii) Trays to mark out the edges of the plots, collection of the runoff and control of splashing.

A wooden frame covered with plastic was used as a barrier against the wind to avoid disturbance. The rain simulator covers an effective area of 1280 cm² and is used in different intensities of rainfall (60, 80 and 100 mm/h) for a period of 0.5 h. Three repetitions with a standard deviation of 10-15 mm/h were recorded. The simulated precipitation of 80 mm/h was selected because it provided the surface runoff necessary for taking samples of the physicochemical conditions of the soil and the climatic conditions of the zone.

Sampling: The data from the simulated precipitation and chemical properties of the soil of each plot are considered, as well as the quantity of chlorpyrifos incubated in the experimental area, the surface runoff collected and measured (mL) and the weighty sediments (g) for extraction.

The surface runoff was collected in 0.5 L bottles installed in the lower part of each plot marked out by the simulator, the bottle being changed every 5 min until 30 min passed, considered enough time for the simulator. The samples of water were maintained at 4 °C until they were analyzed, those of the soil samples (taken at 0-5 cm) and included the samples before and after adding the pesticide they were stored at 0 °C until the analysis of the respective pesticide.

Extraction and determination of chlorpyrifos in water and sediments of the surface runoff: The chlorpyrifos is extracted by agitation of 1.0 g of dry soil with 2 mL of hexane in the 5 mL vial which is subjected to high intensity ultrasound for 0.5 h at 40 °C and then centrifugation at 5000 rpm for 10 min. The extract is evaporated in a vacuum until about 1 mL in a Buchi rotational evaporator, the final residue is dissolved in 100 µL of hexane and is determined by using GC-ECD.

The chlorpyrifos present in the water of the surface runoff is recovered by extraction in solid phase (SPE) through the columns (water, Sep-Pak Plus, 5.0 mL, 0.5 g of absorbent material C-18), extraction with 3 mL of hexane and evaporated in nitrogen atmosphere a 100 µL of hexane, to be determined by GC-ECD.

The chromatographic separation was carried out in a Perkin-Elmer Autosystem XL, predictive ⁶³Ni electron capture detector (ECD) and capillary column DB-5MS (30 m × 0.245 mm), 0.25 µm of film (J and W Scientific). The mobile phase was argon-methane (90:10) at a flow of 1.1 mL/min. The operating parameters are: the column at 200 °C, amount of sample 0.2 µL. The quantification was carried out using the standard internal method used methyl-parathion.

Validation of the method of analysis: To validate the proposed analysis methods a series of control samples were taken (soil and water) prepared by the addition of known quantities of chlorpyrifos. The extractions with hexane were carried out to determine the percentages of recuperation after 4 h for the soils and 2 h for the water, after the addition of the pesticide, so as to be sure of the analytical quality of the data. This validation procedure was used periodically to confirm the extraction method throughout the experiment.

Parameters for the simulation and statistics in the GLEAMS model: The input parameters for the GLEAMS model were: type of soil, topography of the site, volume of runoff, quantity of sediments transported by the precipitations, plots without vegetation cover, quantity of pesticide applied and parameters of transportation by surface runoff. The parameters mentioned were selected to evaluate and estimate the amounts of surface runoff and concentration of pesticide chlorpyrifos in water and sediments supplied by the GLEAMS model and the measured field data. The sum of the quadrants (SSR), coefficient of residual mass (CRM), efficiency of the model (EF) and the normalized average quadratic error (NRMSE) where Pi and

O_i are the values simulated and observed in sample i ; O_m and P_m are the average values of the observed and simulated data.

$$SSR = \sum (P_i - O_i)^2 \quad (1)$$

$$CRM = \frac{\sum (P_i - O_i)}{\sum (O_i)} \quad (2)$$

$$EF = \frac{\sum (O_i - O_m)^2 - \sum (P_i - O_m)^2}{\sum (O_i - O_m)^2} \quad (3)$$

The figures for surface runoff predicted by the GLEAMS model and the figures observed in the field are adjusted through linear regression to quantify the precision of the simulation model. The NRMSE is calculated by:

$$NRMSE = \frac{100}{O_m} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad (4)$$

where n is the number of observations.

RESULTS AND DISCUSSION

The typical chromatograms registered by GC-ECD of the pesticide chlorpyrifos extracted from the soil and water is shown in Fig. 2. These chromatograms were observed free of interference, the limit of detection was $82 \mu\text{g Kg}^{-1}$ in soil and $27 \mu\text{g L}^{-1}$ in water, in the quantification of the curve of the relation of area to chlorpyrifos concentration using methyl-parathion as an internal standard ($R^2 = 0.99$). Considering that the application of the pesticide chlorpyrifos to the soil is 4.0 kg Ha^{-1} , its high adsorption and low solubility (3.0 mg L^{-1}), the sensitivity of the method is high and allows the fate of this pesticide to be followed in the soil, sediments and in the aquatic phase of the surface runoff.

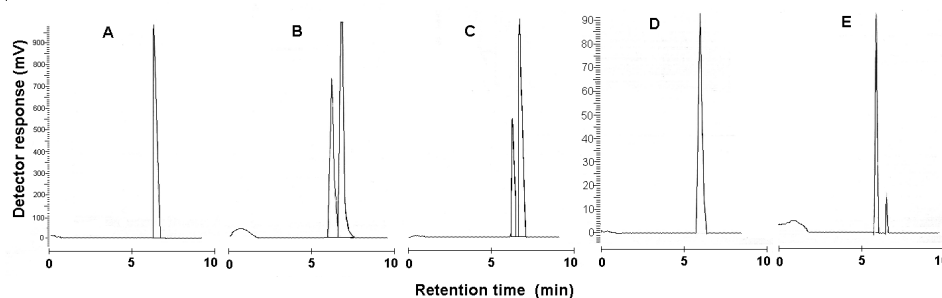


Fig. 2. Chromatograms GC-ECD of chlorpyrifos ($t_R = 6.80 \text{ min}$) and the internal standard methyl parathion ($t_R \text{ min} = 6.50$) in the extracts from the soil and the water. (A) Control of the soil, (B) from soil samples (0-5 cm) before the simulated rain, (C) soil sample (0-5 cm) after the rain, (D) rain control, (E) sample of water from surface runoff collected by the simulated rain

The percentages of recuperation determined during the validation of the analytical method were 97.7 ± 6.7 ($n = 9$) and 99.3 ± 1.0 ($n = 9$), for soil and water samples (for $n = 8$ degrees of freedom and 95 % of confidence t table = 2.306. The t obtained was 1.010 for soil and 1.911 for water), which indicates that the method is reproducible and can be applied to the analysis of residues of chlorpyrifos in samples of soil and water.

Table-2 illustrates the concentration of chlorpyrifos in the soil sample (mg Kg^{-1}) and in water (mg L^{-1}) in the surface runoff collected for each slope of the land where the rain simulator was erected. It was noted that in this type of soil (andic) the concentrations of the pesticide chlorpyrifos in sediments present in the surface runoff show little variability with an increase in the slope, indicating that the amount of pesticide adsorbed in all of the study area ranged between 1.71-3.28 mg kg^{-1} irrespective of the gradient of the site. In the field with slopes of 8-17 % the percentage of organic carbon (OC) shows relationship with the quantity of chlorpyrifos adsorbed into the soil. The potential area of adsorption in the soil makes possible a time that the pesticide is adsorbed into the surface layer its removal in the sediments of the surface runoff to the currents of surface water (Table-1), while the concentration of pesticide in the water of this runoff is low $< 0.20 \mu\text{g L}^{-1}$. This place in evidence once more the possible contamination of the surface water caused in this case by quantities absorbed in the sediment that is swept away.

TABLE-2
CONCENTRATION OF CHLORPYRIFOS IN THE SOIL (0-5 cm) IN THE
in situ SURFACE RUNOFF AND AFTER THE RAIN (80 mm h^{-1} , 30 min),
IN WATER AND SEDIMENT

Slope (%)	Plot	Concentration chlorpyrifos									
		Soil (mg Kg^{-1})			Water runoff ($\text{mg L}^{-1} \times 10^{-3}$)		Sediment runoff ($\text{mg Kg}^{-1} \times 10^{-3}$)		(L Kg^{-1})		
		<i>in situ</i> (a)	After (b)	After rainfall (c)	Measured	Predicted	Measured	Predicted	K_d	K_{oc}	
1	1	0.7	4.02	1.71	0.13	0.135	182.0	188.04	1400	7527	
	8	2	0.4	5.22	2.18	0.12	0.107	189.6	188.03	1580	8061
	3	0.6	4.62	1.70	0.11	0.128	172.4	188.02	1567	9557	
17	1	1.5	4.72	2.04	0.14	0.098	174.4	188.03	1243	5157	
	2	0.8	5.15	1.97	0.11	0.109	192.4	188.03	1749	8023	
	3	1.2	4.94	2.00	0.10	0.111	184.8	188.01	1848	8676	
30	1	1.8	6.61	2.81	0.15	0.078	185.5	188.04	1237	4793	
	2	2.0	6.13	2.59	0.14	0.103	180.7	188.04	1291	6619	
	3	1.9	6.37	2.60	0.13	0.091	190.2	188.03	1463	6650	
40	1	1.0	7.31	3.28	0.20	0.111	185.0	188.03	925	4302	
	2	1.2	4.20	1.77	0.10	0.114	188.7	188.03	1887	9029	
	3	1.1	5.76	2.28	0.14	0.113	190.4	188.03	1360	6445	

(a): 1 h before the application of the pesticide. (b): 24 h after the application of the pesticide and before the rainfall, (c) 1 h after the rain had stopped.

After 24 h, applying the pesticide to the soil and in absence of rain, a decrease in pesticide between 21.4 and 52.3 % is observed, with the lowest percentage of loss seen in soil with 30 % slope (the reason may be the geographic position, wind and light intensity), while in the other soils the lost ranged between 21.4 and 32.5 % (Table-2).

The concentration of pesticide found in soil samples after 1 h of the rainfall is recorded in Table-2, where the retention rate in the first 5 cm of soil was found to be between 16.7 and 30.6 %. Observing the highest retention rate of chlorpyrifos in soils with 30 % slope, a phenomenon attributed to the high concentration of OC, the high capacity of the field and low Ksat (Table-1).

The concentrations of chlorpyrifos found in the sediment of the surface runoff was recorded between 174-192.4 $\mu\text{g Kg}^{-1}$ in all the percentages of the slopes of the land. Briggs *et al.*²¹, report that in the superficial runoff that reaches the roads between 70 and 100 % of the chlorpyrifos applied is washed away, in the first 20 to 40 % of the total surface runoff.

On the other hand at points 1 and 3 with 30 % slope and with high percentages of OC and low Ksat, the lowest values of pesticide absorbed into the ground was found after 1 h of the rain. With these results it is suggested that the variability, mobility, adsorption, disposition and presence of pesticide in the surface runoff of andic soils depend significantly on the organic matter present in the soil²², in a study of the interaction of chlorpyrifos with colloidal matter present in aquatic systems.

Table-2 shows the relationship between the adsorption coefficient $K_d = C_s C_w^{-1}$ (K_d , L Kg^{-1}), of chlorpyrifos present, keeping in mind the balance between the water and the sediment of the surface runoff; C_s is the amount of chlorpyrifos adsorbed into the soil ($\mu\text{g Kg}^{-1}$) y C_w is the quantity of chlorpyrifos in solution ($\mu\text{g L}^{-1}$), $K_{oc} = (K_d \% \text{OC}^{-1}) \times 100$ where the adsorption coefficient is normalized with the OC, the K_{oc} measured for the chlorpyrifos in Andic soil is recorded between 4302-9557 L Kg^{-1} , while the K_{oc} reported and accepted for this pesticide in EXTONET (Toxicology Network), is 6070 L Kg^{-1} . Racke *et al.*⁵ reported a K_{oc} of 8498 L Kg^{-1} . From the above the K_{oc} can not be considered to be the only indicator that describes the interaction between the pesticide and the organic matter present in the soil, similar observations to those found by Oliver *et al.*²³, working in sandy soils.

Fig. 3 shows the results of the process of validation of the surface runoff with slopes from 8 to 40 %, with the surface runoff taken in the field, with the prediction of the model being applicable for all land (Fig. 3E) where a R^2 of 0.6655 is recorded. The best R^2 is recorded on slopes of 8 and 40 % (Fig. 3A and 3D).

It is found that (CRM) and (NRMSE) has the biggest discrepancy between the values observed and predicted by the GLEAMS (Table-3), for the chlorpyrifos present in the surface runoff water, while in the results of the pesticide present in the surface runoff solids the discrepancy is small. In general the model tends to overestimate the total residue present in the sediment and to underestimate the residues of pesticide present in the runoff water (CRM).

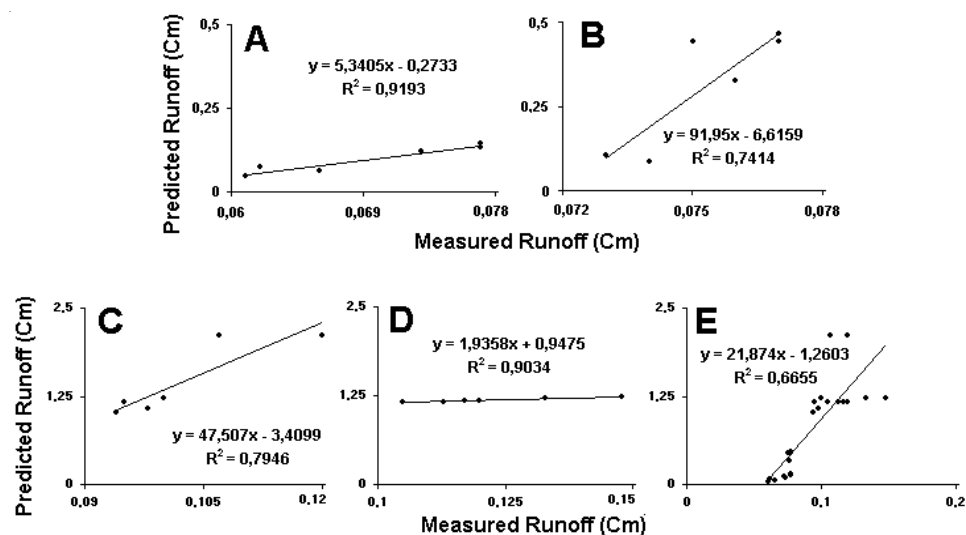


Fig.3. Predicted runoff (cm) and measured runoff and slope 8 % (A)., 17 % (B)., 30 % (C)., 40 % (D) and total field slope (E).

TABLE-3
STATISTICAL ANALYSIS FOR GOODNESS OF FIT GLEAMS
THE CHLORPYRIFOS WATER LOSS (W) AND SEDIMENT (S)
RUNOFF FOR SLOPE AND TOTAL AREA

Slope	Om		Pm		SSR		CRM		EF		NRMSE	
	S	W	S	W	S	W	S	W	S	W	S	W
8 %	181.3	0.12	188.0	0.12	282.9	0.001	0.04	0.03	0.1	-1.3	1.43	48.1
17 %	183.7	0.12	188.0	0.11	75.4	0.001	0.02	-0.09	0.7	0.5	1.14	88.5
30 %	185.5	0.14	188.0	0.09	21.7	0.003	0.01	-0.35	0.6	-37.1	0.86	0.1
40 %	188.0	0.15	188.0	0.11	5.1	0.003	0.00	-0.23	0.9	0.3	0.03	125.7
Total	184.6	0.13	188.0	0.11	588.7	0.017	0.23	-1.73	0.7	0.2	0.99	115.1

The efficiency of the GLEAMS ($EF > 0$) suggests that the model is good for evaluating and predicting the pesticide chlorpyrifos in surface runoff sediments of high mountain andic soils, but is poor in the prediction of the same material in the runoff water.

Fig. 4 shows the variation in the concentration of chlorpyrifos in water and sediments present in the surface runoff of the zone, during the simulation time. For the application of GLEAMS the intensity of rain was estimated only to be 80 mm in one day and 10 °C as the environmental temperature (the average of a normal day in the year in the study zone).

The model reports some predictive results which are variable in the case of the pesticide present in the liquid phase of the surface runoff, while the prediction of the same pesticide in the solid phase is almost constant in all the places regardless of the degree of gradient of the site.

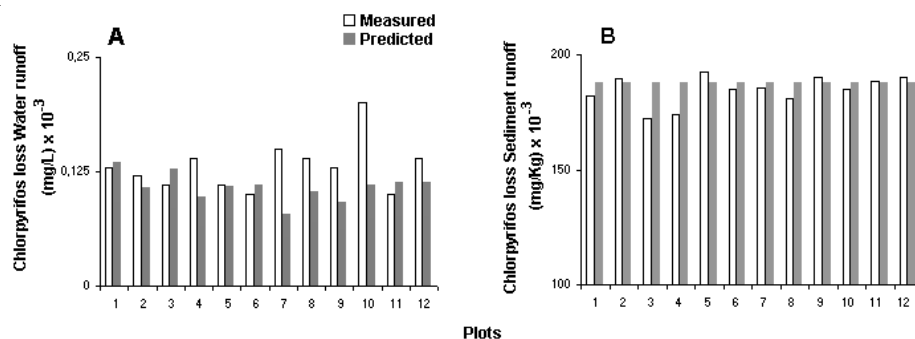


Fig.4. Observed and predicted chlorpyrifos loss by water (A) and sediment (B) runoff for the three experimental plots for slopes of 8 % (1-3), 17 % (4-6), 30 % (7-9) and 40 % (10-12)

Conclusions

According to the results found in this study, it is concluded that close to half of the pesticide chlorpyrifos applied to andic soil is adsorbed in the first five centimeters deep. The loss of pesticide from surface runoff is very strong and rapid if there is rain in the 24 h following the application, especially in the sediment of the surface runoff.

The distribution coefficient (K_d) for adsorption of chlorpyrifos in the country over Andic soils is found to be in the range of 925-1887 L Kg⁻¹.

The understanding of the fundamental interaction between the chlorpyrifos, the organic matter and the clay present in high mountain andic soils is fundamental to knowing the behaviour and final destiny of this pesticide in the sediments of the surface runoff.

The mini rain simulator offers a good alternative for evaluating the processes of the behaviour and of the destiny of the polluting or non-polluting organic compounds that are caused by the surface runoff in zones of difficult access and with security problems. The simulations were achieved in a short time and made possible the results using the GLEAMS model which generated predictive results for processes that in general take months or years. The efficiency of the GLEAMS model to predict the movement and destiny of chlorpyrifos in sediments present in the surface runoff will allow the amplification of the analysis of the behavior of this and other compounds in this type of soil in the future.

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