academicJournals

Vol. 10(3), pp. 108-118, 15 January, 2015
DOI: 10.5897/AJAR2014.8680
Article Number: 17816A449547
ISSN 1991-637X

http://www.academicjournals.org/AJAR

African Journal of Agricultural Research

Full Length Research Paper

A comparison of predicted and measured pesticides concentrations in runoff of cotton farms in Brazil

Isaltino Alves Barbosa[1,3]*, Ricardo Santos Silva Amorim[2] and Eliana Freire Gaspar de Carvalho Dores[1]

[1]Chemistry Department, Mato Grosso Federal University, Postgraduate Program in water resources Cuiabá, Brazil.
[2]Agronomy and Veterinary Medicine Faculty, Mato Grosso Federal University, Cuiabá, Brazil.
[3]Chemistry Department, University of Sao Paulo, São Paulo, Brazil.

Received 11 March, 2014; Accepted 17 December, 2014

The adjustment and evaluation of methods which allow estimation of runoff and the concentration of associated pesticides are important for the development of prognostics studies in agricultural areas, mainly in tropical regions. In this context, this study aimed to adjust a method to estimate the concentration of pesticides in run-off applied to a cotton plantation farm, located in the micro-region of Primavera do Leste – MT (Mato Grosso State) in Central-Western Brazil. The method was based on the association of the model of pesticides concentration in run-off, described by OECD (1999), with the methods of Curve Number (CN) and Water Balance on Soil Surface (BW) to estimate the run-off amount. The pesticides, diuron, alfa and beta endosulfan, metolachlor, were selected based on the frequency and applied amount in cotton crops. Among the studied pesticides, diuron was the one for whom the adjusted method performed better in the studied scenarios, in others words, the best performance of the SFIL for prediction the pesticides concentrations greater than 3 μg L^{-1}. Thus the association of the OECD model to BW or CN performed well to predict the risk of surface waters contamination in cotton crop areas in tropical regions.

Key words: Modeling, contamination, surface waters, solute transport, tropical regions, agricultural areas.

INTRODUCTION

Several authors have reported environmental models as methods to estimate pesticides concentrations in surface or groundwater (Leonard et al., 1987; Berezen et. al., 2005; Swarcewicz and Gregorczyk, 2013; Fantke et al., 2013). The evaluation of a chemical's distribution and fate in the environment is an essential component of a risk assessment procedure (Pinho et al., 2006; Swarcewicz and Gregorczyk, 2013).

Despite the existence of several studies of environmental models application in many countries, in Brazil they are scarce and recent (Plese et al., 2009). Many papers emphasize that in regions of Brazil where agricultural production is intensive, mainly in cotton farms areas, it is necessary to evaluate environmental dynamics of pesticides (Pinho et al., 2004; Please et al., 2009). In this context, environmental models are very useful tools, since their use allows the evaluation of pesticides dissipation in soil. This information can be used to propose measures to mitigate the environmental impacts. In addition, literature indicates that in tropical

*Corresponding author. E-mail: Isaltinoab@gmail.com

Table 1. Description of the chemical and physical characteristics of the monitoring units

Localization	Soil	Management	S%[1]	DP[2] (m)	Clay	Silt	Sand	OC[3]
						g kg^{-1}		%
Chico Nunes small watershed	Yellow latosol	With filter strip of the *Brachiaria decumbens* with width of 10 m (MUS)	3..9	10 × 40	372	108	520	2.00
		Without strip filters *B. decumbens* (MWS)	4..1	10 × 40	461	107	432	3.00
Ilha small watershed	oxisol	Tillage system (MUC)	3..4	3.5 × 11	457	65	478	3.00
		No-tillage system (MUT)	2..9	3.5 × 11	414	95	491	4.27

[1]Slope of the monitoring units. [2]Dimensions of the monitoring units (width × length); [3]Percentage of the organic carbon in the surface layer of the soil (0-20 cm).

regions with cotton industry several pesticides have been detected in surface water and among the innumerous factors that affect pesticides runoff, the agricultural management system is a very important one (Carbo et al., 2008).

Moreover, many studies point out that there is high risk of the environmental contamination of some pesticides, such as, α and β-endosulfan, diuron and metolachlor (Weaver et al., 2012; Kennedy et al., 2001; Barrett and Jaward, 2012). In addition, literature indicates that in tropical regions with cotton industry several pesticides have been detected in surface water and among the innumerous factors that affect pesticides runoff, the agricultural management system is a very important one (Carbo et al., 2008; Casara et al., 2012). Hence, it is necessary to study the influence of the management systems in the dynamics of the pesticides in the environment

The present study, therefore, aimed to adjust a model by combination of the pesticide concentration model, reported by OECD (1999), with Runoff Curve Number (RCN) developed by the USDA Natural Resources Conservation Service (SCS-USDA), and the water balance in soil surface (WB) describe by Pruski et al. (1997) to estimate the concentrations of α- and β-endosulfan, diuron and metolachlor in runoff.

MATERIALS AND METHODS

Investigation area

The experiment consisted of installing four monitoring units in two farms located in the micro-region of Primavera do Leste, Mato Grosso State, Central-Western Brazil, one farm situated near the riverside of Chico Nunes stream and another close to the riverside of Ilha stream, both tributaries of the Mortes River (Table 1).

On the first farm, two units were installed to monitor runoff in cotton cultivated areas. In one of them, one filter strip planted with *Bracchiaria* grass was set up at the low end of the monitoring unit. On the second farm, two runoff monitoring units were installed in areas cultivated with cotton. In one, it was used the tillage system and in the other one, the no-tillage system. In the four units, a runoff collector was installed at the low end. These collectors were formed by a gutter linked to a polyvinyl chloride pipe. The structure of the collector was directed to the lower end of the experimental plot that consisted on a rectangular container (Figure 1), built from galvanized sheet, coated with a filtering system (geotextile blanket). In this container there was a “Geib” type divisor, with nine openings, and in the central opening it was linked to a water tank that stored the runoff volume that had passed by the 1/9 fraction on the Geib aluminum gutter.

Runoff samples were collected at intervals of approximately 15 to 20 days. Water and sediment samples were collected in 1 L amber bottle and plastic bags, respectively. Samples were transported in ice boxes to the laboratory where they were kept under refrigeration (4°C) until analysis.

The collection period, from December 2006 to May 2007, that coincides with the period of heaviest rains in the region and pesticides application. The precipitation rate was obtained by pulse pluviographs installed in each of the monitoring farms.

Water sampling and pesticide analysis

Analysis of pesticides residues by gas chromatography

The residues of alfa and beta endosulfan and metolachlor in the water, were analysed using the method reported by Laabs et al. (2002) that used solid phase extraction with octadecilsylane (C18) cartridge (1000 mg) BakerbondTM, Mallinckrodt Baker, USA, previously conditioned with 10 ml of methanol and 10 ml of water, followed by elution with subsequent portions 10 ml of ethyl acetate, 10 ml of hexane: ethyl acetate (1:1) and 5 ml of hexane. The extract was concentrated in a rotary evaporator to near dryness and so transferred to an autosampler vial with toluene. A gas chromatograph HP-6890 with mass selective detector HP-5973 (Agilent GmbH, Germany), split/splitless injector, automatic sampler and a HP-5MS (5% phenylmethylsiloxane) column (30 m × 250 μm id × 0.25 μm phase thickness) was used for pesticide analysis. Pesticide residues were quantified by GC-MS operated in the selected ion monitoring mode at the following conditions: Injector block temperature: 250°C; carrier gas of helium (99,999% pure), gas flow of 1 ml min^{-1}; split/splitless injector operated in splitless mode; injection volume of 1 ml; oven temperature program with initial temperature of 92°C held for 2.5 min, heating up to 175°C at 15°C min^{-1}; 175°C held for 13 min, heating up to 280°C at 20°C min^{-1}, 280°C held for 9 min; and transfer-line temperature at 290°C. Pesticides were identified by retention time and relative abundance of three major ions from mass spectra of each substance (Table 2). Maximum tolerance for confirmation was specified as 20% of relative ion intensity response.

Analysis of pesticides residues by liquid chromatographic

Diuron residues in water was analysed according to the method

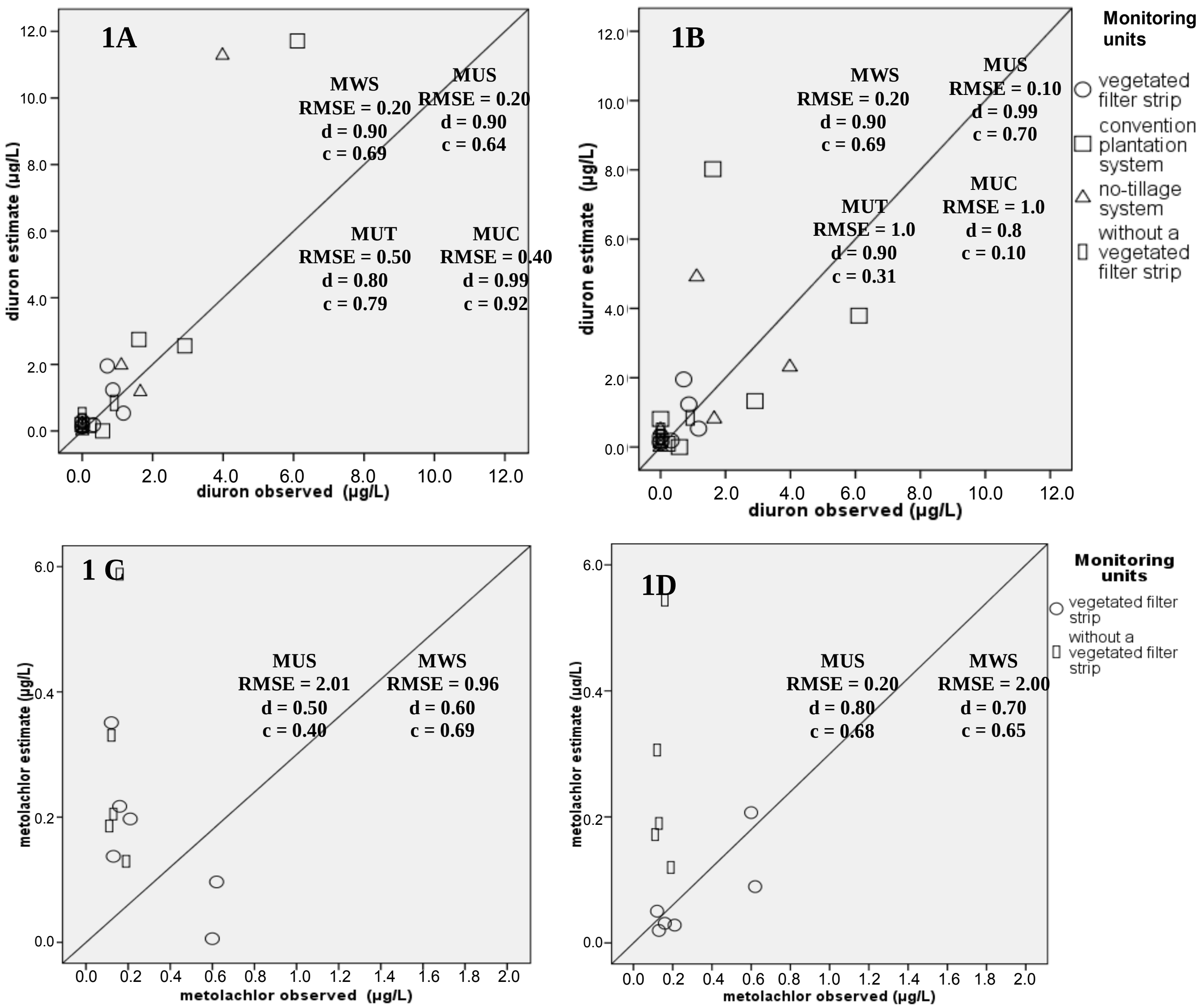

Figure 1. Predicted pesticide concentrations by SFIL Combined with RCN - Runoff *Curve Number (1A and 1C);* Predicted pesticide concentrations by SFIL Combined with WB - water balance in the soil surface (1B and 1D); MUS - Monitoring units with strip filter of the *B.*; MWS - without strip filter of the *B. decumbens*; MUC - Monitoring unit with Conventional system; MUT - Monitoring unit with no-tillage system.

Table 2. Monitoring ions for identification and quantification of the pesticides by GC/EM

Pesticides	Target ion	Fisrt ion	Second ion
Alpha endosulfan	241	238	195
Beta endosulfam	207	195	237
Metolachlor	162	238	240

described by Carbo et al. (2008). Aliquots of 500 ml of the samples were extracted in a SDVB cartridge (Envi-Chrom P, Supelco) previously conditioned with methanol. Then, the cartridge was dried, leaving the vacuum pump on for 30 min. Diuron was eluted with 3 × 5 ml of methanol:acetonitrile 7:3 (v/v) at a flow-rate of about 1 ml min^{-1}. The combined fractions were concentrated in a rotary evaporator (45°C) and the residue was redissolved in 1 ml of acetonitrile, followed by the addition of 50 µl of standard terbuthylazine solution (100 µg ml^{-1}) to the vial.

The analysis was performed with a Varian HPLC system equipped with a 410 autosampler, a 240 quaternary pump and 330 UV diode-array detector linked to a personal computer running the

Table 3. NRCS runoff curve numbers (CN).

Cover type	Treatment	Hydrologic condition	Curve numbers for hydrologic soil group			
			A	B	C	D
Fallow	Bare soil	-	77	86	91	94
	Crop residue cover (CR)	Poor	72	81	88	91
		Good	67	78	85	89
Row crops	Straight row (SR)	Poor	70	79	84	88
		Good	65	75	82	86
	Contoured and terraced (C and T)	Poor	66	74	80	82
		Good	62	71	78	81
Small grain	SR	Poor	65	76	84	88
		Good	63	75	83	87
	SR + CR	Poor	64	75	83	86
		Good	60	72	80	84
	C	Poor	63	74	82	85
		Good	61	73	81	84
	C + CR	Poor	62	73	81	85
		Good	60	72	80	83
	C+T	Poor	61	72	79	82
		Good	59	70	78	81
	C+T+CR	Poor	60	71	78	81
		Good	58	69	77	80
Close seeded or broadcast legumes or rotation meadow	SR	Poor	66	77	85	89
		Good	58	72	81	85
	C	Poor	64	75	83	85
		Good	55	69	78	83
	C+T	Poor	63	73	80	83
		Good	51	67	76	80

Fonte: Iowa Storm water Management Manual, 2008.

software program Varian ProStar, version 5.5 (Varian, USA). The analytical column (250 mm × 4.6 mm I.D.) used here was an Omnisphere 5 µm C_{18}, and the guard column (20 mm × 4.6 mm I.D.) was also an Omnisphere 5 µm C_{18}. For the HPLC analysis, an aliquot (10 µl) was injected into the column and eluted at room temperature at a constant flow-rate of 1 ml min^{-1} under the following conditions.

The analyte was eluted with acetonitrile:water that in the initial composition is 18% acetonitrile, increasing to 40% at 6 min, 80% at 35 min, 90% at 40 min, and 100% acetonitrile at 45 min, when it was kept constant for 3 min and then linearly decreased to the initial analysis conditions in 10 min. The detection and quantification were performed at 230 nm. Diuron was identified by its retention time and identification was confirmed by comparison of its UV spectrum.

Balance water in the soil surface (WB)

The model of the water balance in the soil surface (Equation 1) assumes: uniform precipitation in the study area; soil moisture next to saturation and null evaporation since it is very small during rainfall.

$$ES = PT - I_a - I - e_v \quad (1)$$

ES = runoff, mm; PT = total precipitation, mm; Ia = initial abstractions, mm; I = cumulative infiltration, mm; e_v = evaporation, mm.

The total precipitation (PT) was obtained by rain gauges installed in the experimental areas.

The initial abstractions (surface water until runoff start) depend on interception, depression storage and infiltration before of the runoff. The values of I_a were estimated by RCN (Equation 2), according to the Soil Conservation Service – SCS (1972):

$$I_a = 50,8\left(\frac{100}{CN} - 1\right) \quad (2)$$

CN = Curve Number

The values of CN were obtained by the method described on Soil Conservation Service (1972) (Table 3). According to Pruski et al. (1997), the hydrological conditions, in others words, the soil surface type can be considered:

1. Good condition: grass cover of 75% or more of the area;
2. Fair condition: grass cover of 50 to 75% of the area;
3. Poor condition: grass cover of 50% or less of the area.

The soil cover for the several scenarios of simulation was estimated from the post-emergence days and percentage of plant cover, according to Silva et al. (2004) (Equation 3):

Plant cover (%) = 46.07 ln(post-emergence days) -115.1; R^2 = 0.962 (3)

From Equation (3), at the experimental conditions, it was determined that:

1. Until 36 post-emergence days, 50% of the plant cover, bad condition.
2. From 36 post-emergence days and on, 75% of plant covers, good condition.

The cover type and treatment of surface soil observed in Table 3 for several scenarios of the simulation are briefly described as follows:

(i) The treatment considered in experimental areas was small grain; (ii) The area with butter strip was considered straight row with contoured and terraces and (iii) other experimental areas were considered only contoured.

The soil properties (Table 1) most similar to that of the experimental area were C type: Low infiltration rate when thoroughly moist, layer impediment and with considerable percentage of clay.

The corresponding time for occurrence of the initial abstractions was obtained by the Equation 4:

$$t_{I_a} = \frac{I_a .60}{i_m} \quad (4)$$

t_{Ia} = Time interval between the onset of rain and runoff initiation, min; I_m = Average rainfall intensity, mm; The duration of infiltration was obtained by the Equation 5.

$$t_{inf} = t - t_{I_a} \quad (5)$$

t = Total time of rainfall, min.

The water evapotranspired and evaporated (e_v) during the precipitation was considered negligible, in view of the low vapor pressure.

Runoff curve number (CN)

According to Pruski et al. (2006), the runoff curve number method (Equation 6) is one the most important methods of the estimate the runoff:

$$ES = \frac{(PT - 0,2S)^2}{(PT + 08S)} \quad (6)$$

ES = runoff, mm; PT = = total precipitation, mm; S = infiltration potential, mm (Formula 7).

$$S = \frac{25400}{CN} - 254 \quad (7)$$

CN = Runoff curve numbers (Table 3).

Prediction of pesticide concentrations

The model for the prediction of pesticide concentrations (Equations 8 and 9) was adapted based on the ones described in the Project ''Pesticide Aquatic Risk Indicator" by OECD (1999), and on that reported by Berenzen et al. (2005).

The model assumes that:

1. The rainfall takes place 3 days after pesticides application (OECD, 1999; Berenzen et al., 2005)
2. Due to the fact that the model was calibrated under field conditions, we considered that there was enough time for pesticide equilibration between the solid and liquid phase of the soil.

$$L\%_{runoff} = \frac{ES \; . f . e^{\frac{-3 \ln 2}{t_{1/2}}}}{P} \cdot \frac{100}{1 + K_d} \quad (8)$$

L%runoff = Percentage of application dose that is present in runoff water as a dissolved substance; *ES* = estimated runoff by method WB or CN (mm); f = Correction factor, $f = f_1 . f_2 . f_3$ (modified equation of Beinat and van der Berg, 1996); f_1 = Slope factor: if slope (d)< 20% - $f_1 = 0,02153.d + 0,001423.d^2$; if slope (d)≥ 20% - f_1 = 1; f_2 = Buffer zone factor. f_2 = $0,83^{WZB}$, with WBZ – width of the buffer zone (m); if the buffer zone is not densely covered with plants then the width is set to zero (Berezen et al., 2005) ; f_3 = plant interception factor estimated by Equation (3). (1 - %plant cover/100); *P* = Precipitation amount (mm). DT_{50} = Half-life of active ingredient in soil (days); K_d = Ratio of dissolved to sorbed pesticide concentrations (mL g^{-1}).

The mean pesticide concentration in the runoff was then calculated using Equation (9):

$$P_C = L\%_{runoff} .Pa \frac{1}{ES} \quad (9)$$

P_c = Predicted pesticide concentration (μg L^{-1}); Pa = amount of pesticide applied in the cotton farm in the experimental plot (μg); *ES* = estimated runoff by method WB or CN (mm).

Tables 4 and 5 show the doses of the pesticide applied in the experimental plots under field conditions, in cotton areas cultivated under different management systems: with and without a vegetated filter strip (buffer filter) planted with *Bracchiaria* grass and no-tillage system (direct seeding) and conventional soil preparation.

The physical properties of the pesticides that were used for the prediction in the model are shown in Table 6. They were obtained for tropical soil conditions, aiming to improve the model performance.

RESULTS

Estimated runoff by *curve number* (RCN) and water balance in the soil surface (WB)

The runoff depth estimated by Curve Number (RCN)

Table 4. Doses of the pesticide applied in experimental in cotton groups cultivated with and without a vegetated filter strip

Active ingredient	Dates of the pesticides application	Average dosage per hectare	Pesticides applied in experimental plots (g)
Diuron	01/01/2007	1.0 kg ha^{-1}	32.00
Diuron	01/01/2007	0.8 L ha^{-1}	32.00
Diurom	01/01/2007	0.8 L ha^{-1}	16.00
α-endosulfan	07/02/2007	2 L ha^{-1}	14.70
Β-endosulfan	07/02/2007	2 L ha^{-1}	6.30
α-endosulfan	19/02/2007	2 L ha^{-1}	14.70
β-endosulfan	19/02/2007	2 L ha^{-1}	6.30
Metolachlor	01/01/2007	0.6 L ha^{-1}	23.4

Table 5. Doses of the pesticide applied in experimental in cotton groups cultivated with no-tillage system (direct seeding) and conventional soil preparation

Active ingredient	Dates of the pesticides application	Average dosage per hectare (L ha^{-1})	pesticides applied in experimental plots (g)
Diuron	22/12/2005	0.68	2.9440
		0.26	0.8008
		0.51	0.1963
		0.11	0.42350
		0.08	0.3080
α-endosulfan	31/01/2006	1.50	1.4148
	11/03/2006	2.00	1.8865
	21/03/2006	2.00	1.8865
	27/03/2006	2.00	1.8865
β-endosulfan	31/01/2006	1.50	0.6063
	11/03/2006	2.00	0.8085
	21/03/2006	2.00	0.8085
	27/03/2006	2.00	0.8085

Table 6. Physical properties of the pesticides

Pesticides	Ratio of dissolved to sorbed pesticide concentrations K_d (g mL^{-1})*	Sorption coefficient of active ingredient to organic carbon K_{oc} (g mL^{-1})*	Half-life of active ingredient in soil $t_{1/2}$ (dias)*	Water Solubility S_w (mg.L^{-1})
Diuron	14.3	916.7	15	36.4[d]
α-endosulfan	288	22040	43	0.33[e]
β-endosulfan	405	25961	128	0.32[e]
metolachlor	3.1	198.7	34	5.30[f]

*Tropical soil conditions, values obtained in laboratory; d - Moncada, (2004); e - Fan (2007); f – Rivard (2003).

(Table 7) was higher than the observed values in all units with exception of the monitoring unit with conventional system (MUC). These overestimated values were less significant in the unit with no-tillage system (MUT). As for the Water Balance in the Soil Surface method (WB), an overestimation in runoff was observed for the units with and without filter strip of the *Brachiaria decumbens*. On the other words, for the MUC and MUT units, an underestimation was observed, with a higher runoff depth in the MUC in relation to the MUT unit (Table 7).

Table 7. Observed runoff (R-OBS) and estimated runoff (R-EST) by the prediction methods of Balance water in the soil surface (WB) and Runoff Curve Number (RCN) for the experimental areas

Monitoring units	R-OBS	R-RCN	R-WB
	AR[1]	AR	AR
		mm	
MUS	14.69	286	324.4
MWS	121.58	366	324.4
MUC	319.45	194.7	144.8
MUT	183.07	194.7	86.5

[1]Average runoff; MUS - Monitoring units with strip filter of the *B. decumbens*; MWS - without strip filter of the *B. decumbens*; MUC - Monitoring unit with conventional system; MUT - Monitoring unit with no-tillage system.

Therefore, the WB method represented better the effect of culture systems.

Comparison of the prediction with measured data

In Figure 1A, the relationship between pesticide concentration predicted by the SFIL model associated with RCN or WB and measured diuron concentrations is shown. A greater dispersion of predicted diuron concentrations was observed in the different evaluated scenarios when RCN for runoff prediction was used. In general, there was a predominance of underestimation of diuron concentrations in the monitoring unit with strip filter of the *B. decumbens*, regardless of the methodology used to runoff prediction. It was also observed that there were overestimated and underestimated concentrations for α-endosulfan when the SFIL was combined with RCN or WB (Figure 2). Differently, as for β-endosulfan (Figure 2) an underestimation tendency of the concentration predicted by SFIL for all evaluated scenarios was observed in both methods for runoff prediction. Among the studied pesticides, metolachlor was the pesticide that showed the most overestimation tendency for the concentrations predicted by SFIL combined with RCN or WB (Figure 1C and D).

Statistical analyses

The relationship between predicted pesticides concentrations by SFIL with different methods of runoff prediction (Table 8) or scenarios (Table 9) and measured pesticide concentrations was analyzed using Student's t-test when it was possible to get normal distribution. For the variables that that were not normally distributed, the non-parametric test of Wilcoxon was used. For all statistical analyses the software SPSS 15.0 was used. Moreover, it was evaluated the determination coefficients (R^2) between predicted and observed pesticides concentrations irrespective of methods of runoff prediction or scenarios (Table 10)

No significant differences between observed and predicted pesticide average concentrations by SFIL combined with RCN method for diuron and α-endosulfan were observed (Table 8). In addition, there were no significant differences between predicted pesticide average concentrations by SFIL combined with RCN and WB for metolachlor, α and β endosulfan, however, both of it were statistically different than experimentally observed values (Table 8).

The average concentrations of diuron predicted by SFIL combined with RCN method, with exception of the monitoring unit without strip filters *B. decumbens* (MWS), were not statistically different than experimentally observed values (Table 9). In relation to α-endosulfan, the predicted average concentrations in the monitoring units with and without filter strip of the *B. decumbens* (MUS and MWS) were statistically different, when the SFIL was combined with RCN method. Regarding β-endosulfan, in the MWS and MUC the predicted average concentrations were statistically different when compared to observed concentrations (Table 9).

DISCUSSION

Prediction of runoff

The monitoring units with and without a 10-m filter strip of *B. decumbens* (MUS and MWS) in cotton farm showed overestimation of the runoff by RCN or WB methods, nevertheless in relation the estimated runoff by RCN it was observed lesser values of estimated runoff for MUS when compared with MWS as well as also it was verified to observed runoff (Table 7), probably due to the higher basic infiltration rate (TIB) in the MUS than in the MWS. The presence of roots in the soil provide higher infiltration rate, moreover, the high surface roughness provided by vegetation reduces the runoff velocity, increasing

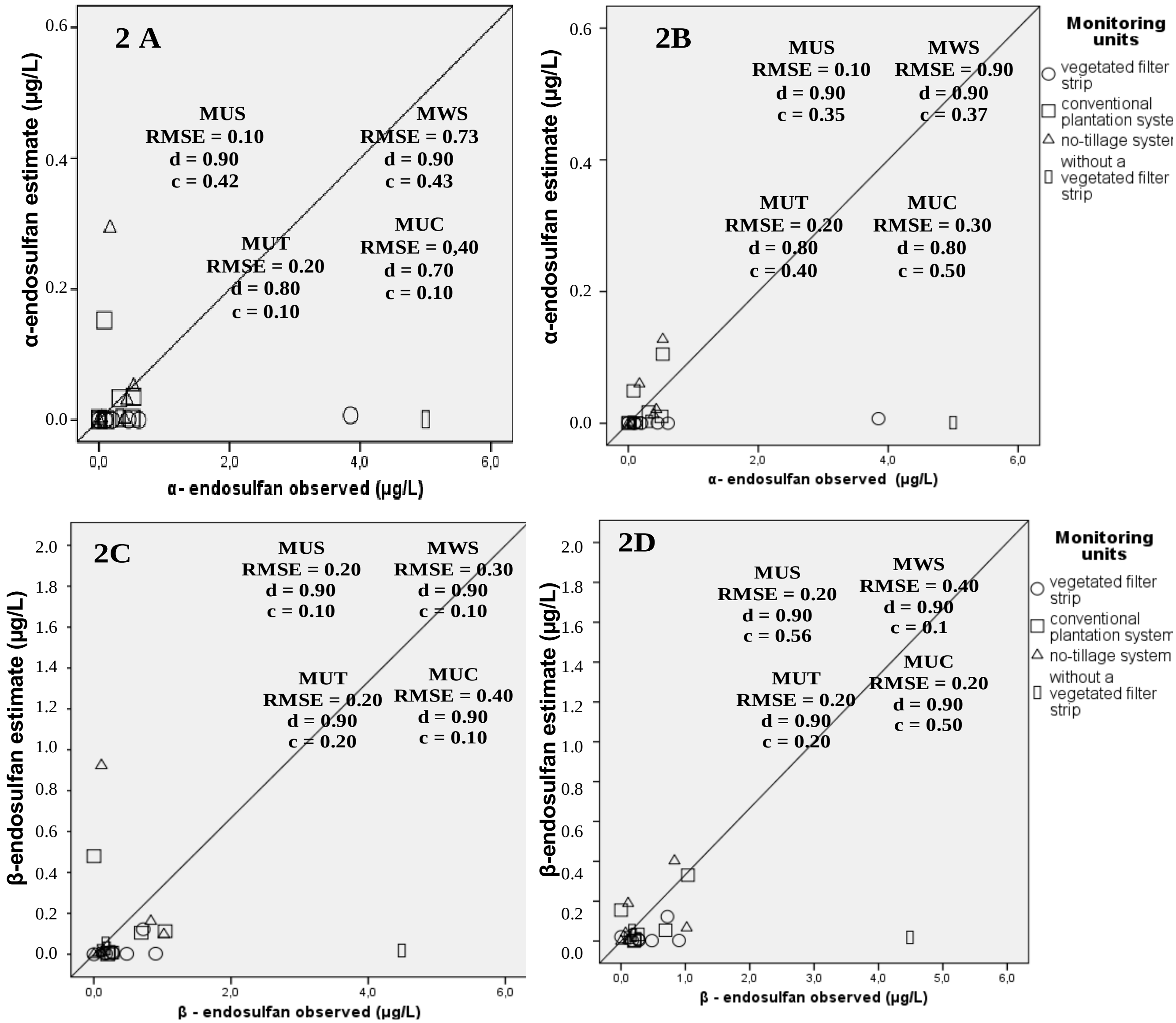

Figure 2. Predicted pesticide concentrations by SFIL Combined with RCN - Runoff *Curve Number (2A and 2C);* Predicted pesticide concentrations by SFIL Combined with WB - water balance in the soil surface (2B and 2D); MUS - Monitoring units with strip filter of the *B. decumbens*; MWS - without strip filter of the *B. decumbens*; MUC - Monitoring unit with Conventional system; MUT - Monitoring unit with no-tillage system.

Table 8. Comparison of the observed and predicted of pesticide concentrations by SFIL

Pesticidas	RCN	WB	OBS
	[1]Average concentrations (μg L^{-1})		
Diuron*	1.218^{A}	1.610^{B}	1.000^{A}
Metolachlor*	2.560^{A}	3.170^{A}	0.260^{B}
α -Endosulfan**	0.176^{AB}	0.259^{A}	0.578^{B}
β -Endosulfan**	0.065^{A}	0.091^{A}	0.523^{B}

[1]Means followed by the same letter in the same line do not differ at 5% probability;* Teste t-Student; ** Teste Wilcoxon; RCN – Runoff *Curve Number;* WB – water balance in the soil surface;OBS – Observed concentrations; MUS - Monitoring units with strip filter of the *B. decumbens*; MWS - without strip filter of the *B. decumbens*; MUC - Monitoring unit with Conventional system; MUT - Monitoring unit with no-tillage system.

Table 9. Comparison of the observed and predicted of pesticide concentrations by SFIL in several scenarios

Pesticides	MUS			MWS			MUC			MUT		
	[1]Average concentrations (µg L^{-1})											
	RCN	WB	OBS	RCN	WB	OBS	RCN	WB	OBS	RCN	WB	OBS
Diuron*	0.640^{A}	0.640^{A}	0.440^{A}	0.410^{A}	0.410^{A}	0.180^{B}	2.340^{A}	2.900^{A}	2.000^{A}	1.440^{A}	2.00^{A}	1.000^{A}
Metolachlor*	0.709^{A}	1.670^{A}	0.306^{B}	0.431^{C}	0.466^{C}	0.210D	nd	nd	nd	nd	nd	nd
α-Endosulfan**	0.004^{A}	0.002^{A}	0.243^{B}	0.023^{B}	0.024^{B}	1.571^{C}	0.372^{A}	0.633^{A}	0.260^{A}	0.305^{A}	0.377^{A}	0.238^{A}
B-Endosulfan**	0.007^{A}	0.003^{A}	0.35^{A}	0.041^{A}	0.041^{A}	0.998^{B}	0.117^{A}	0.199^{A}	0.356^{B}	0.096^{A}	0.118^{A}	0.400^{A}

[1]Means followed by the same letter in the same line do not differ at 5% probability;* Teste t-Student; ** Teste Wilcoxon; RCN – Runoff Curve *Number;* WB – water balance in the soil surface; OBS – Observed concentrations; MUS - Monitoring units with strip filter of the *B. decumbens*; MWS - without strip filter of the *B. decumbens*; MUC - Monitoring unit with Conventional system; MUT - Monitoring unit with no-tillage system.

Table 10. Determination coefficients (linear regression) between predicted and measured pesticide concentrations irrespective of methods of runoff prediction or scenarios

Pesticides	Determination coefficients (R^2)
Diuron	0.6038
α-endosulfan	0.0274
B-endosulfan	0.0040
Metolachlor	0.1081

hydraulic load, consequently providing the higher water infiltration. The predicted runoff by RCN or WB did not consider the different infiltration in the area with filter strip of *B. decumbens.*

Regarding the monitoring units with conventional system (MUC) and no-tillage system (MUT) an overestimation of the runoff was observed, nevertheless, the WB method performed better to describe the effect of the cultivation system in the MUC and MUT. In other words, in the MUC the predicted runoff was greater than in the MUT. This higher runoff values, both estimated and observed of the conventional system compared to no-tillage, is probably due to increasing soil sealing and consequent TIB decreasing caused by this management system (SCHICK et al., 2000).

Measurements of pesticide concentrations

The predicted diuron concentrations observed by SFIL combined with WB method showed Willmott index (d) described by Willmott et al. (1985) ranging from 0.99 to 0.80 (Figure 1A). The Willmott index indicates the degree of accuracy between the observed and predicted values. The Root Mean Square Error ranged from 0.2 to 0.5 (RMSE) (Figure 1A). According to Chung et al. (1999) these values of RMSE (0.2 to 0.5) are considered satisfactory. The performance of the SFIL was evaluated by performance index (c) (Camargo et al., 1997). The values of "c" ranged from medium (0.64) to optimum (0.9) (Figure 1). In relation to predicted diuron concentrations determined by SFIL combined with RCN, the "c" values ranged from 0.1 to 0.7 (Figure1 B) respectively, bad and good performance according to Camargo et al. (1997). The RMSE values were lower than 0.5 for MUS and MWS, however, in the MUC and MUT these values were higher, considered satisfactory and unsatisfactory, according to Chung et al. (1999).

For metolachlor, RMSE ranged from 0.2 to 2.00 (Figure 1C and D) values which are considered satisfactory and unsatisfactory, respectively, according to Chung et al. (1999). Moreover, when SFIL was combined with WB, the model performance can be considered bad (MUS) and good (MWS), but when SFIL was combined with RCN the model performance changed to medium (MUS) and good (MWS).

In addition, considering the mobility and solubility parameters shown in Table 10 according to FAO (2000) and persistence according to IBAMA (1990), it was observed that diuron and metolachlor (Table 11) are the most likely to suffer leaching compared to α- and β-endosulfan. In the SFIL model, leaching was not considered thus the overestimation of the predicted concentrations for these pesticides may be due to absence of leaching calculations by SFIL.

The SFIL model showed the worst performance for α- and β- endosulfan, with "c" values classified as too bad (0.1) and tolerable (0.5) (Figure 2). The RMSE ranged from 0.1 to 0.9 (Figure 2), and the Willmott index showed values close to one.

Table 11. Classification of the pesticides according to physical and chemistry properties

Proposed classification by IBAMA (1990)			
Half-life (days)		Classification	
< 30		Nonpersistent	
30 - 180		Moderately persistent	
180 - 360		Persistent	
> 360		Highly persistent	
Proposed classification by FAO (2000)			
Log K_{OC}	Classification		
<1	Highly mobile	Solubility - S_w (mg.L^{-1})	Classification
1 a 2	Mobile	< 0.1	Insoluble
2 a 3	Moderately mobile	0.1-1.0	Lightly soluble
3 a 4	Lightly mobile	1-10	Moderately soluble
4 a 5	Hardly mobile	10-100	Easily soluble
>5	Immobile	>100	Highly soluble
Pesticides	**Solubility S_w (mg L^{-1})**	**Sorption coefficient of active ingredient to organic carbon Koc (g mL^{-1})**	**Half-life $t_{1/2}$ (days)**
Diuron	Easily soluble	Moderately mobile	Nonpersistent
α-Endosulfan	Lightly soluble	Lightly mobile	Moderately persistent
β -Endosulfan	Lightly soluble	Lightly mobile	Moderately persistent
Metolachlor	Easily soluble	Mobile	Moderately persistent

The Table 10 shows that there was an better relationships (linear regression) between predicted and measured pesticide concentrations for diuron (R^2= 0.6038) than for others pesticides. From above results it can be inferred that the better performace of the SFIL is for high values pesticides concentrations as observed to diuron (Figure 1A and B), corroborates with Berezen et al. (2005) that reported the better performance of the SFIL in estimate concentration above 5 μg L^{-1}.

Conclusions

In summary, the SFIL model showed a good potential of the predict the pesticide concentrations in runoff when combined with the Runoff Curve Number or water balance in the soil surface method, mainly high values of pesticides concentrations as observed to diuron. In addition the SFIL model was efficient in predict the impact of the management systems on the pesticides concentrations in several scenarios, mostly in scenarios where there were strip filters.

Conflict of Interest

The authors have not declared any conflict of interest.

REFERENCES

Barrett K, Jaward FM (2012). A review of endosulfan, dichlorvos, diazinon, and diuron – pesticides used in Jamaica, Int. J. Environ.Health Res. 22:481-499. http://dx.doi.org/10.1080/09603123.2012.667794

Berezen N, Lentzen-Godding A, Probst M, Schulz H, Schulz R, Liess M. A (2005). Comparison of predicted and measured levels of runoff-related pesticide Concentrations in small lowland streams na as landscape level. Chemosphere 58: 683-691. http://dx.doi.org/10.1016/j.chemosphere.2004.05.009

Beinat E, Van der Berg R (1996). EUPHIDS, a decision support system for admission of pesticides. National Institute of Public Health and the Environment, Bilthoven.

Camargo AP, Sentelhas PC (1997). Avaliação do desempenho de diferentes métodos de estimativas de evapotranspiração potencial no Estado de São Paulo, Brasil. Revista Brasileira de Agrometeorologia 5: 89-97.

Carbo L, Souza V, Dores EFGC, Ribeiro ML (2008). Determination of pesticides multiresidues in shallow groundwater in a cotton-growing region of Mato Grosso, J. Braz. Chem. Soc. 19: 1111-1117. http://dx.doi.org/10.1590/S0103-50532008000600009

Chung SW, Gassman PW, Kramer LA, Williams JR, Gu R (1999).Validation of EPIC for Two Watersheds in Southwest. Center for Agricultural and Rural Development Iowa State University Ames, IA, 50011-1070.

Fan S (2007). Endosulfan risk characterization document. Volume III Environmental Fate -Department of Pesticide Regulation Environmental Monitoring Branch,.Sacramento, Califórnia. Available from: <http://www.cdpr.ca.gov.> Accessed on: 05/06/2013.

Fantke P, Wieland P, Wannaz C, Friedrich R, Jolliet O (2013). Dynamics of pesticide uptake into plants: From system functioning to parsimonious modeling. Environmental Modelling & Software 40: 316-324. http://dx.doi.org/10.1016/j.envsoft.2012.09.016

FAO (2000). Food and Agriculture Organization of the United Nations. Assessing soil contamination. Available at: <http//:www.fao.org/docrep/003/X2570E00.htm>. Accessed on 05/ 05/2013.

IBAMA - Brazilian Institute of the Environment (1990). Pesticides manual for evaluation of the ecotoxicity of chemical agents 2:80-90.

Iowa Storm water Management Manual (2008). Available at:

http://www.ctre.iastate.edu/pubs/stormwater/documents/2C-5NRCSTR-55Methodology.pdf Accessed on: 29/06/2013.

Laabs V, Amelung W, Pinto A, Wantzen M, Silva CJ, Zech W (2002). Pesticides in surface water, sediment, and rainfall of the Northeastern Pantanal Basin, Brazil. J. Environ. Q. 31:1636–1648. http://dx.doi.org/10.2134/jeq2002.1636

Kennedy IR, Sanchez-Bayo F, Kimber SW, Hugo L, Ahmad N (2001). Off-Site movement of Endosulfan from irrigated cotton in New South Wales. J. Environ. Q. 30:683–696. http://dx.doi.org/10.2134/jeq2001.303683x

Leonard RA, Knisel WG, Still DA (1987). GLEAMS:Groundwater Loading Effects of Agricultural Management Systems. Transactions of the ASAE. 30:1403-1418. http://dx.doi.org/10.13031/2013.30578

Moncada A (2004). Environmental fate of diuron. Environmental Monitoring Branch Department of Pesticide Regulation 1001 I Street Sacramento, CA 95812-4015. Available from: www.cdpr.ca.gov/docs/emon/pubs/fatememo/diuron.pdf Accessed on: 20/06/ 2013.

OECD (Organisation for Economic Co-operation and Development) (1999). Annex II. Report of the OECD Project Pesticide Aquatic Risk Indicators pp. 28–32. Available at: www.oecd.org/dataoecd/31/36/2078678.pdf Accessed on: 20/05 2013.

Pinho AP, Matos AT, Costa LM, Morris LA, Martinez MA (2006). Modeling of herbicide retention in riparian zones. Rev. Bras. Engenharia Agríc. Ambiental. 10:896-902.

Plese LPM, Silva CL, Foloni LL (2009). Distribution of environmental compartments of herbicides used in the cotton, coffee and citrus culture. Planta Daninha, Viçosa, MG 27:123-132.

Pruski FF, Ferreira PA, Ramos MM, Cecon PR (1997). Model to design level terraces. J. Irrig. Drain. Engineer. 123:8-12. http://dx.doi.org/10.1061/(ASCE)0733-9437(1997)123:1(8)

Pruski FF, Brandão VS, Silva DD da (2006). Escoamento superficial. Viçosa, MG: Editora UFV, 2° ed.

Rivard L (2003). Environmental Monitoring Branch / Department of Pesticide Regulation. Environmental Fate of Metolachlor. California. Available from: http://www.cdpr.ca.gov/docs/empm/pubs/fatememo/metolachlor.pdf Accessed on: 05/05/2013.

Silva AV, Monteiro JEB, Chiavegato EJ, Bernardes MS (2004). Incidence of the solar radiation in plants of cotton in three different rows. Available at: http://www.cnpa.embrapa.br/produtos/algodao/publicacoes/trabalhos_cba5/412.pdf Accessed on: 05/05/2013.

Schick J, Bertol I, Batistela O, Balminot Jr AA (2000). Soil erosion of a clayey inceptisol under different crop and tillage systems: ii. nutrient and organic carbon losses. Rev. Bras. Ciênc. Solo 24:427-436. http://dx.doi.org/10.1590/S0100-06832000000200019

Weaver TB, Ghadiri H, Hulugalle NR, Harden S (2012). Organochlorine pesticides in soil under irrigated cotton farming systems in Vertisols of the Namoi Valley, north-western New South Wales, Australia. Chemosphere 88:336-343. http://dx.doi.org/10.1016/j.chemosphere.2012.03.008

Willmott CJ, Ackleson SG, Davis RE, Feddema JJ, Klink KM, Legates DR, Odonnell J, Rowe CM (1985). Statistics for the evaluation and comparison of models. J. Geophys. Res. Oceans Ottawa 90:8995-9005. http://dx.doi.org/10.1029/JC090iC05p08995

Swarcewicz MK, Gregorczyk A (2013). Atrazine degradation in soil: effects of adjuvants and a comparison of three mathematical models. Pest Manage. Sci. 69(12):1346-1350. doi: 10.1002/ps.3510