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Dynamics of Clomazone Formulations Combined with Sulfentrazone in Sugarcane (*Saccharum* spp.) Straw

Leandro Tropaldi [1], Caio A. Carbonari [2,*], Ivana Paula F. S. de Brito [2], Ana Karollyna A. de Matos [2], Carolina P. de Moraes [2] and Edivaldo D. Velini [2]

[1] Department of Plant Production, College of Agrarian Sciences and Technology, São Paulo State University (UNESP), Dracena 17900-000, SP, Brazil; l.tropaldi@unesp.br

[2] Department of Crop Protection, College of Agricultural Sciences, São Paulo State University (UNESP), Botucatu 18610-034, SP, Brazil; ivana.paula@unesp.br (I.P.F.S.d.B.); ana.karollyna@unesp.br (A.K.A.d.M.); carol.pucci@fca.unesp.br (C.P.d.M.); edivaldo.velini@unesp.br (E.D.V.)

* Correspondence: caio.carbonari@unesp.br; Tel.: +55-14-3880-7223

Abstract: Herbicide formulations can alter the herbicide performance, affecting the application safety and weed control efficiency. Thus, the objective of this work was to compare the dynamics of clomazone herbicide applied single and combined with sulfentrazone on sugarcane (*Saccharum* spp.) straw. Laminated polypropylene containers filled with sugarcane straw (10 t ha^{-1}) were subjected to two clomazone formulations (microencapsulated and conventional formulations; 1200 g ha^{-1}) applied single or combined with sulfentrazone (600 g ha^{-1}) with four replications, and the experiment was duplicated. The application was performed indoors with an automated sprayer. After application, accumulated rainfall depths (0, 5, 10, 20, 50, and 100 mm) on the treated containers were simulated soon after the herbicide applications, and the percolated waters were subsequently collected for herbicide quantification by chromatography and mass spectrometry (LC-MS/MS). The microencapsulated formulation of clomazone applied single or combined with sulfentrazone enabled the recovery of higher quantity of clomazone (>80%), with the advantage that a large percentage remained encapsulated (>70%), thus decreasing losses and increasing the product efficiency. The 30 mm simulated rainfall efficiently carried the clomazone herbicide when its microencapsulated formulation was applied, whereas its conventional formulation required higher rainfall depths (60 mm). Sulfentrazone was easily carried through the sugarcane straw by the rainfall depths when it was combined with clomazone, regardless of the clomazone formulation. The clomazone formulation affect the percolation dynamics of this herbicide through the sugarcane straw.

Keywords: environmental behavior; herbicide; microencapsulation; mulch; *Saccharum* spp.

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1. Introduction

The sugarcane crop is a feedstock to produce sugar, bioethanol and electricity; and is one of the main tropical agricultural crops [1]. Brazil is world's largest sugarcane producer, responsible to produce 654.5 million tons of feedstock in the 2020/21 harvest [2]. In the last harvest, the averages Brazilian yield was 75.9 tons of stalks per hectare, however, in some cultivated fields, more than 100 tons per hectare are also observed [2]. Large ranges of variations in the average sugarcane yield are observed due to the impact of different factors such as, for example, edaphoclimatic conditions, planted varieties and phytosanitary problems such as weed [3]. Therefore, weeds are an important problem in the sugarcane production system, being responsible for causing reductions of up to 80% in yield due to competition; in addition to interfering with other management practices and increasing production costs [4,5].

In Brazil, the Raw Cane Production System is predominant. In this system, the harvest is carried out mechanically without burning and can maintain a thick layer of plant residues on the soil surface, generally greater than 12 ton of straw ha^{-1} [6]; the use of this system has affected and changed the occurrence of weed species and, consequently, their management [6]. The straw layer affects weed germination and emergence and is a barrier that prevents herbicides to reach the soil immediately after application [5,7]. Thus, factors such as the amount and distribution of straw in the soil contribute to a wide range of weed management scenarios [6]. Therefore, the management of weeds in sugarcane is extremely complex and requires attention and knowledge for a satisfactory execution.

A wide diversity of weeds is found in Brazilian sugarcane production fields [8]. Clomazone (2-[(2-chlorophenyl)methyl]-4.4-dimethyl-3-isoxazolidinone) is an herbicide of the isoxazolidinone chemical group; it is a non-ionizable molecule, water-soluble (1100 mg L^{-1} at 25 °C), and mildly volatile, with a vapor pressure of 1.92×10^{-2} Pa (1.44×10^{-4} mm Hg) at 25 °C [9]. Its mechanism of action is the inhibition of the enzyme 1-desoxi-xilulose-5-fosfatase synthase (DOXP) [10,11]. This herbicide is registered for pre-and post-emergence control of monocotyledonous weeds and some eudicotyledonous species in several crops, widely used in sugarcane [8]. However, when herbicides, such as clomazone, are applied on the straw surface, they depend on rainfall events or irrigation to reach the soil [12], and can remain fully exposed to high solar radiation and temperatures before reaching the soil [13]. Studies have shown that the maximum temperature on the straw surface is higher than at of the soil surface [14]; the clomazone volatility can be intensified under these conditions, increasing herbicides losses.

How the use of herbicides for grasses is important for raw cane production system [15]; the use of different formulations or combinations containing clomazone is important, especially when it is necessary to increase the spectrum of weed control [16]. Alternatively, the microencapsulated formulation of clomazone has been recommended for sugarcane crops and can be an alternative to emulsifiable concentrate formulations, due to the lower potential for volatilization and better control performance under less suitable application conditions [17–20].

The combination of herbicides of different action mechanisms and with different characteristics from clomazone, it is also common for sugarcane crops [16], and sulfentrazone ([N-[2.4-dicloro-5-[difluorometil)-4.5-dihidro-3-metil-5-oxo-1H-1.2,4-triazol-1-il]methanesulfonamide) is one of the main herbicides used in combination with clomazone. Sulfentrazone is a weak acid (pKa 6.56) that has solubility in water of 780 mg L^{-1} in pH 7 at 25 °C, coefficient of octanol-water partition of 9.8 (pH 7), and vapor pressure of 1.30×10^{-4} Pa at 25 °C [9]. It has an estimated half-life in the soil of 110 to 280 days, depending on the edaphoclimatic conditions, in addition, the microbiological activity of the soil is responsible for its initial degradation [21,22]. Sulfentrazone is an inhibitor of protoporphyrinogen IX oxidase (PROTOX) and is registered for applications in post-planting sugarcane and pre-emergence of weeds; it has broad spectrum of control, including monocotyledon and eudicotyledon weed species [8], and stands out as an important herbicide in weed control programs for sugarcane crops.

The dynamics of herbicides of different formulations can be altered due to the presence of straw in the production system, combinations of active ingredients, and characteristics of the product themselves [5,23]. Therefore, new formulations, such as microencapsulated formulations, have been developed to minimize the volatilization and photodegradation of more sensitive molecules such as clomazone [19,24,25]. Since, pesticides are subject to several processes of losses in the environment that can reduce the efficiency of the control phytosanitary [26,27] and potentiate the negative effects to not-target organisms and to environments [18], depending on their intensity. Thus, search for technologies that optimize pesticide formulations is essential to improve product characteristics (solubility, chemical and thermal stability and volatilization, for example), in addition to selectivity to crops, and reduce the leaching and toxicity risks to humans and environments [28,29].

Although these herbicides are registered for sugarcane crop, information about the dynamics of their release of herbicides from different formulations after application on straws are scarce. Therefore, more research is needed to advance understanding of the use impact of different formulations on agricultural production systems. Thus, the objective of this work was to compare the dynamics tow formulations of clomazone herbicides when applied single or combined with sulfentrazone on sugarcane straw.

2. Materials and Methods

2.1. Treatments and Experimental Conditions

The experiment was conducted at the Center for Advanced Research in Weed Science (NUPAM) of the College of Agricultural Sciences of the São Paulo State University, in Botucatu, SP, Brazil (22°84′ S; 48°42′ W).

The experiments were implemented in a randomized block design with four treatments and four replications, the experiment was duplicated. The treatments consisted of two clomazone formulations (capsule suspension/microencapsulated-CS and emulsifiable concentrate-EC) applied single or combined with sulfentrazone (suspension concentrated) (Table 1). The percolation of these formulations through the sugarcane straw was evaluated at 20 min after application, with simulation of six rainfall depths (0, 5, 10, 20, 50, and 100 mm).

Table 1. Treatments used in the experiment.

Treatment	Herbicide	Formulation	Commercial Product [1]	Rate (g ha^{-1})
1	Clomazone	capsule suspension (CS)	Gamit 360 CS®	1200
2	Clomazone	emulsifiable concentrate (EC)	Gamit Star®	1200
3	Clomazone + Sulfentrazone	capsule suspension (CS)/suspension concentred (SC)	Gamit 360 CS® + Boral® 500 CS	1200 + 600
4	Clomazone + Sulfentrazone	emulsifiable concentrate (EC) + suspension concentred (SC)	Gamit Star® + Boral® 500 CS	1200 + 600

[1] FMC Agricultural Products, Campinas, SP, Brazil.

Laminated polypropylene containers (4.5-cm diameter) were filled with sugarcane straw (variety RB 86-7515), representing an amount of 10 t ha^{-1}, as described by Araldi et al. [23].

2.2. Herbicide Application and Rainfall Simulation

The herbicides were applied on the straw surface, using a compressed-air stationary sprayer installed in a closed environment, with a spray boom containing four nozzles (XR110.02VS; Teejet®, Wheaton, IL, USA) spaced 0.5 m apart and positioned at a height of 0.5 m from the target surface. The system ran at speed of 3.6 km h^{-1}, with spray volume of 200 L ha^{-1} and constant pressure of 150 kPa. The air temperature and relative humidity at application were 27 °C and 76% respectively.

The plots were composed of plastic containers with an exposure area to application of 168 cm^2, filled with 200 mL of water, and positioned at the same height of the sugarcane straw containers, which were used as reference to detect the quantities of herbicides that were effectively deposited on the targets by the application. After the application, the plots were subjected to rainfall simulation.

The rainfall depths were simulated using the same device described for the application of herbicides, but using another spray boom, which contained eight uniform flat jet nozzles (DG95.05EVS; Teejet®, Wheaton, IL, USA) spaced 0.1 m apart, positioned at a height of 1.4 m from the target, and set to produce a 2.5-mm water depth per passing.

The water that percolated through the straw was collected, measured, and analyzed for clomazone and sulfentrazone herbicide concentrations. After these procedures, a duplicate was carried out, following the same procedures described.

2.3. Herbicide Quantification Procedures

The herbicide contents in the percolated water were determined using samples processed in different forms, according to the formulations used:

(A). Treatments with emulsifiable concentrate (EC) formulation of clomazone: aliquots of 3 mL of samples were subjected to filtering in 0.45 µm PVDF membranes with 13.0-mm diameter (Millex®-HV, Merck Millipore Ltd., Carrigtwohill, Ireland), and transferred to 2-mL amber flasks (Supelco Park Bellefonte, PA, USA) constituting a phase 50:50 methanol:water (v v^{-1}).

(B). Treatments with microencapsulated formulation of clomazone: the samples were analyzed using methodologies for discrimination of quantities of free clomazone in the solution and clomazone maintained in capsules. Aliquots of 2 mL of the solution were filtered in 0.45 µm PVDF membranes with 13.0-mm diameter (Millex®-HV, Merck Millipore Ltd., Carrigtwohill, Ireland) to retain only the herbicide capsules, and the free herbicide was quantified in the filtered solution. Then, 2 mL of methanol was suctioned to the filters used, which were subsequently subjected to ultrasound bath for 30 min, and the resulting filtered solution was transferred to 2-mL amber flasks (Supelco Park Bellefonte, PA, USA), constituting a phase 50:50 methanol:water (v v^{-1}). This procedure removes and makes available all the clomazone present in the capsules.

The active ingredients were identified and quantified by high-performance chromatography combined with mass spectrometry with quadrupole detector in positive electrostatic ionizes mode (HPLC LC/MS/MS 3200 QTrap) (AB Sciex Pte. Ltd., Framingham, MA, USA). A C18 column (Synergi 2.5 µm Hydro-RP 100A, 50 × 4.6 mm × 2.5 µm, Phenomenex, Torrance, CA, USA) was used for the chromatographic separation with elution gradient, combining the mobile phase A (0.5% of acetic acid in water; J.T. Baker) and the mobile phase B (0.5% of acetic acid in methanol; J.T. Baker) in a flux of 0.6 mL min^{-1}, as described in Table 2.

Table 2. Chromatographic conditions used for quantification of solutions.

Parameters	
Analytical column	C18 Synergi 2.5 µ Hydro RP 100 Å
Injection volume	20 µL
Mobile phase (pH 7.0)	Phase A (PA) = 0.5% acetic acid in water Phase B (PB) = 0.5% acetic acid in methanol
Gradient	0–1 min = 50% PB and 50% PA 1–3 min = 95% PB and 5% PA 3–6 min = 95% PB and 5% PA 6–8 min = 30% PB and 70% PA 8–10 min = 30% PB and 70% PA
Flux	0.60 mL min^{-1}
Oven temperature	40 °C

The active ingredients were detected and quantified using specific screening procedures (Multiple Reaction Monitoring) at concentrations equal to or higher than 0.39 ng mL^{-1} (limit of quantification). The retention time was 4.42 min for clomazone, and 4.04 min for sulfentrazone. The clomazone mass was 240.2, and the transitions were 125.1, 89.1, and 99.1; the sulfentrazone mass was 386.95, and the transitions were 110.2, 146.1, and 273.1 (Figure 1). The fragment used for quantification had mass of 125.1 for clomazone, and 110.2 for sulfentrazone. The calibration curve was linear for both molecules, within the range of 0.39 to 100 ng L^{-1}; the linear equations were: $y = 575x + 527$, $r^2 = 0.9993$ for clomazone; and $y = 1.423x + 264$, $r^2 = 0.9987$ for sulfentrazone.

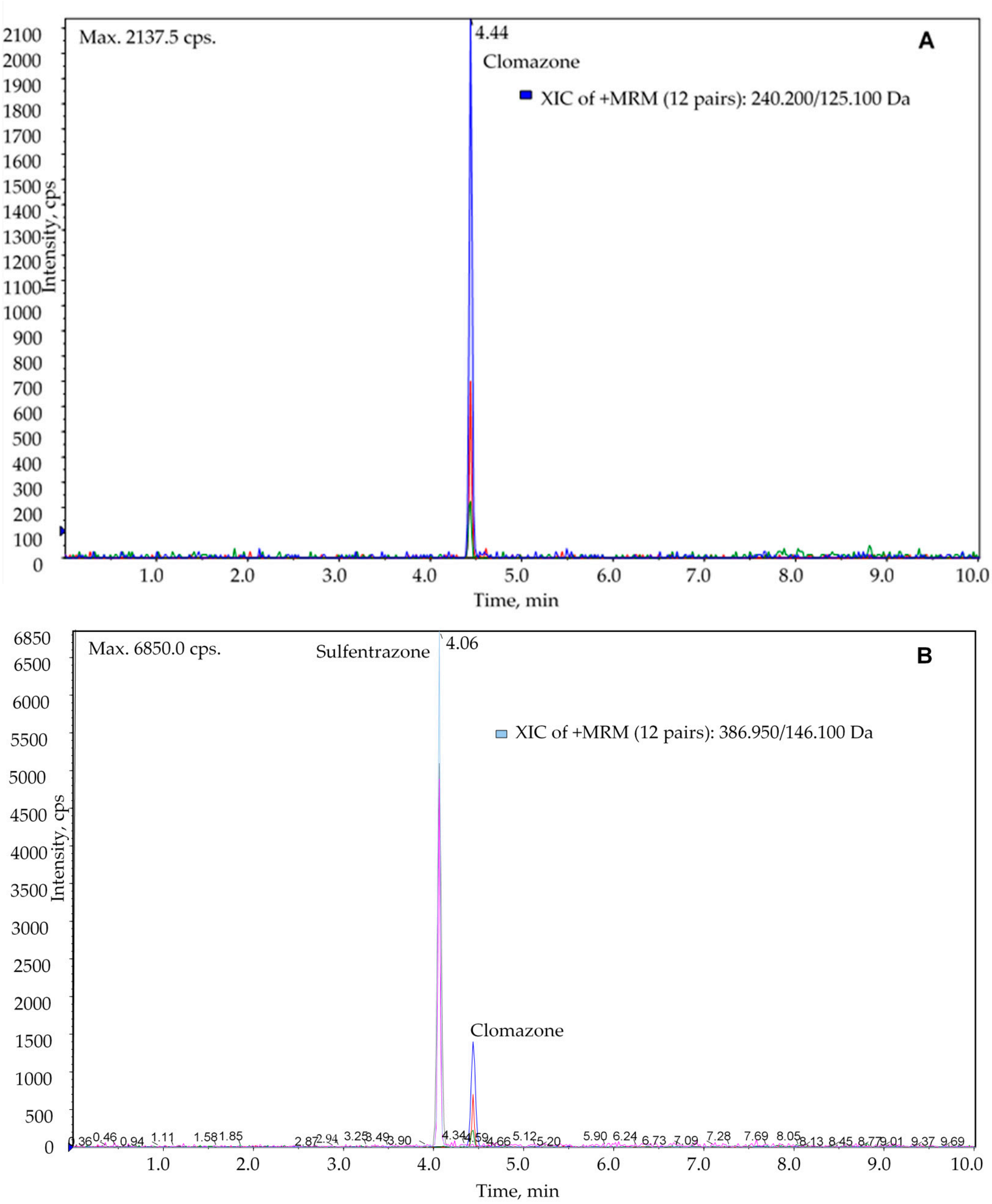

Figure 1. Chromatogram of sample of solutions that percolated the sugarcane straw. Application of clomazone formulations (**A**); application of clomazone formulations combined with sulfentrazone (**B**).

2.4. Data Analysis

The clomazone and sulfentrazone concentrations in the solutions that percolated the sugarcane straw were fitted as a function of the simulated rainfall depths and converted to percentages of the total amount effectively deposited on the straw, as determined by reference containers used as reference during the applications.

The data were subjected to analysis of variance (ANOVA) by the F test at 5% probability, considering the formulations used for each herbicide as treatments, and two blocks (times of conduction of the experiment-duplicated).

The data were also subjected to regression analysis, using the Mitscherlich model as described by Cavenaghi et al. [30]:

$$Y = a\,[1 - 10^{(-c\,(X + b))}] \quad (1)$$

where Y is the amount of clomazone and sulfentrazone recovered from the simulated rainwater (%); a, b, and c are constants in the equation; a is the maximum asymptote of the curve, which corresponds to the maximum recovery of clomazone and sulfentrazone for the total accumulated rainfall; b is the lateral displacement of the curve; c is the concavity of the curve; and x is the amount of rainfall applied (mm). The regression procedure and analysis of variance were performed using the SAS 9.2 program (SAS Institute Inc., Cary, NC, USA).

3. Results and Discussion

The results obtained in the analyses for quantification of clomazone herbicide in the solutions that percolated through the sugarcane straw after the applications of the two herbicide formulations (microencapsulated-CS and emulsifiable concentrate-EC), single or combined with sulfentrazone herbicide, showed high coefficient of determination (R^2) in the analysis of variance and in the Mitscherlich models; the estimates of parameters are presented in Table 3.

Table 3. Estimates of parameters of Mitscherlich models fitted for correlation of quantity of clomazone percolated through sugarcane straw with different simulated rainfall depths (mm), after application of different formulations (single or combined with sulfentrazone).

Treatment	Formulation	Estimates of Parameters				F
		a	*b*	*c*	R^2	
Clomazone	CS [1]	80.355	0.00	0.044	0.999	2288.00 **
	EC [2]	52.511	0.00	0.017	0.994	309.95 **
Clomazone + Sulfentrazone	CS	100.00	0.00	0.047	0.999	2141.11 **
	EC	53.254	0.00	0.019	0.995	375.62 **

[1] CS = capsule suspension; [2] EC = emulsifiable concentrate; ** significant by the F test ($p < 0.01$).

The quantity clomazone found in the reference containers was considered the quantity of herbicide that effectively reached the straw [31]. Therefore, the concentrations of clomazone percolated by the sugarcane straw were presented as a percentage of the total applied. The maximum quantity of clomazone recovered from the EC formulation application was about 52% after the simulated rainfall of 100 mm (Figure 2A,B). There was also no difference between applications with the EC formulation of clomazone single (52.5%) and combined (53.2%) with sulfentrazone. On the other hand, clomazone recovery was higher for the microencapsulated formulation (CS formulation), reaching 80% when applied single, and 100% when combined with sulfentrazone (Figure 2A,B).

The results obtained after the application of different formulations showed that the microencapsulation altered the clomazone dynamics, increasing the quantity of herbicide percolated by sugarcane straw and consequently decreasing the losses. The high percentages of losses (~50% of the rate applied) founded for EC formulation, probably can be related to the high vapor pressure of clomazone, which favors volatilization even in short periods after application, and to the closed environment. Therefore, only part of the applied rate would be available to reach the soil, which can cause a decrease in the residual herbicide effect and compromise the weed control efficiency [19,24].

The presence of straw on the soil surface is a barrier that hinders the passing of solar rays, decreasing the temperature and thermal amplitude of the soil [5]; however, the temperatures in this straw layer are higher than those in the soil [14]. Interception of herbicides by sugar cane straw may be a limiting factor [5]. The surface of the straw cover is a more favorable environment for herbicide lost than the soil or leaf surfaces [31]. Mervosh et al. [32] showed that increases in volatilization are proportional to increases in temperature; thus, losses of clomazone after application of EC formulation on raw cane systems can be intensified.

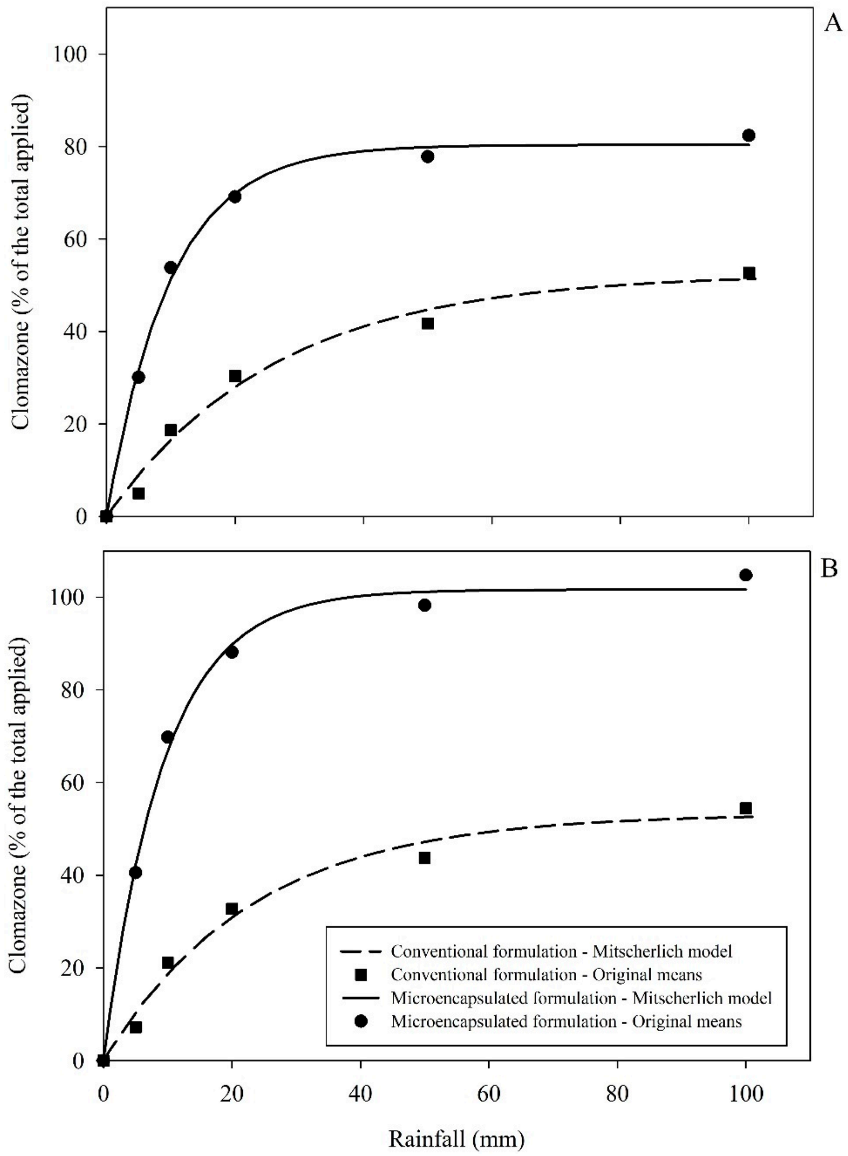

Figure 2. Quantity of clomazone (% of the total applied) percolated through sugarcane straw as a function of different simulated rainfall depths (mm), after application of different formulations. Application of clomazone formulations (**A**); application of clomazone formulations combined with sulfentrazone (**B**).

The potential of contamination of not-target areas and neighboring crops increases after volatilization, and the weed control efficiency can be compromised; thus, technologies are necessary to minimize these losses, increase the safety of the product, decrease risks to the environment, and ensure the control efficiency. A pesticide formulation that allows weed control at low risks and losses is the ideal to be reached, and its encapsulation in polymeric matrix can assist in this search.

Differences in the selectivity among clomazone formulations were reported for different crops [19,33]. A higher selectivity is attributed, in general, to application of microencapsulated formulations of clomazone, which is explained by the slow release of the clomazone molecule [19].

Moreover, the data fitted to the model after application of the microencapsulated formulation of clomazone presented an asymptotic behavior, indicating that the percolation stops to increase as a function of the accumulated rainfall depths; however, this effect was not clear for the EC formulation. The use of the microencapsulated formulation resulted in maximum percolation after an accumulated simulated rainfall of approximately 20 mm, whereas the use of the EC formulation resulted in maximum percolation after an accumulated simulated rainfall of approximately 60 mm. Thus, the microencapsulated formulation of clomazone reached similar percolation percentages to those of the sulfentrazone, which is a standard herbicide regarding mobility in plant straws [31].

Some studies have been conducted on the clomazone dynamics in soils under controlled conditions [32,34,35]; however, information on percolation dynamics of different clomazone formulations in plant straws are scarce.

After application of EC formulation of clomazone on the treatments, only free clomazone molecules were quantified in the solution because of the characteristics of the product; and after the application of the microencapsulated formulation, the solution was analyzed to assess the quantity of free clomazone and the quantity of encapsulated clomazone in the solution. The results obtained in the analysis of the solutions that percolated through the sugarcane straw after application of the microencapsulated formulation showed high coefficient of determination (r^2) in the analysis of variance and fit to the Mitscherlich models; the estimates of parameters are presented in Table 4.

Table 4. Estimates of parameters of Mitscherlich models fitted for the correlation of quantity of clomazone percolated through sugarcane straw with the different simulated rainfall depths (mm), after application of a microencapsulated formulation (single or combined with sulfentrazone).

Treatment	Formulation	Form	Estimates of Parameters				F
			a	*b*	*c*	R^2	
Clomazone	CS [1]	Free [2]	10.062	0.00	0.018	0.992	249.24 **
		Encapsulated [3]	70.898	0.00	0.050	0.999	8633.51 **
Clomazone + Sulfentrazone	CS	Free	11.888	0.00	0.022	0.993	262.15 **
		Encapsulated	88.682	0.00	0.063	0.998	1003.47 **

[1] capsule suspension; [2] out of the capsules and free in the solution; [3] still encapsulated; ** significant by the F test ($p < 0.01$).

The total clomazone recovered after the application of the microencapsulated formulation in absence of sulfentrazone was 80% of the total applied; approximately 12% of the clomazone was free in the solution, and most of it (87%) remained microencapsulated, even after 100 mm of simulated rainfall depth (Figure 3A). These results demonstrate that the release of clomazone form the SC formulation is slow. Therefore, microencapsulation has been used to protect substances sensitive to light, temperature, moisture, and oxygen, by releasing the ingredient active in these formulations under specific conditions and more slowly than EC formulations [17,36]. This could allow the herbicide to be bioavailable for longer periods, increasing its half-life and decreasing the negative effects for non-target organisms and the environment [18].

On the other hand, the comparison between the two formulations evaluated showed that the availability of free clomazone is greater in the EC formulation is higher, as expected; however, this high availability can decrease to values below the effective level depending on the environmental characteristics.

This high percentage of encapsulated clomazone makes the microencapsulated formulation more advantageous than the EC formulation, because the product remains protected by microcapsules that enable a gradual and slower release of the herbicide, increasing its residual period and efficiency, even in dry periods, and also increasing the safety of the application [37,38]. The release of microcapsule contents occurs, in general, by mechanical disturbances, temperature, pH, solubility, biodegradation, and diffusion [38].

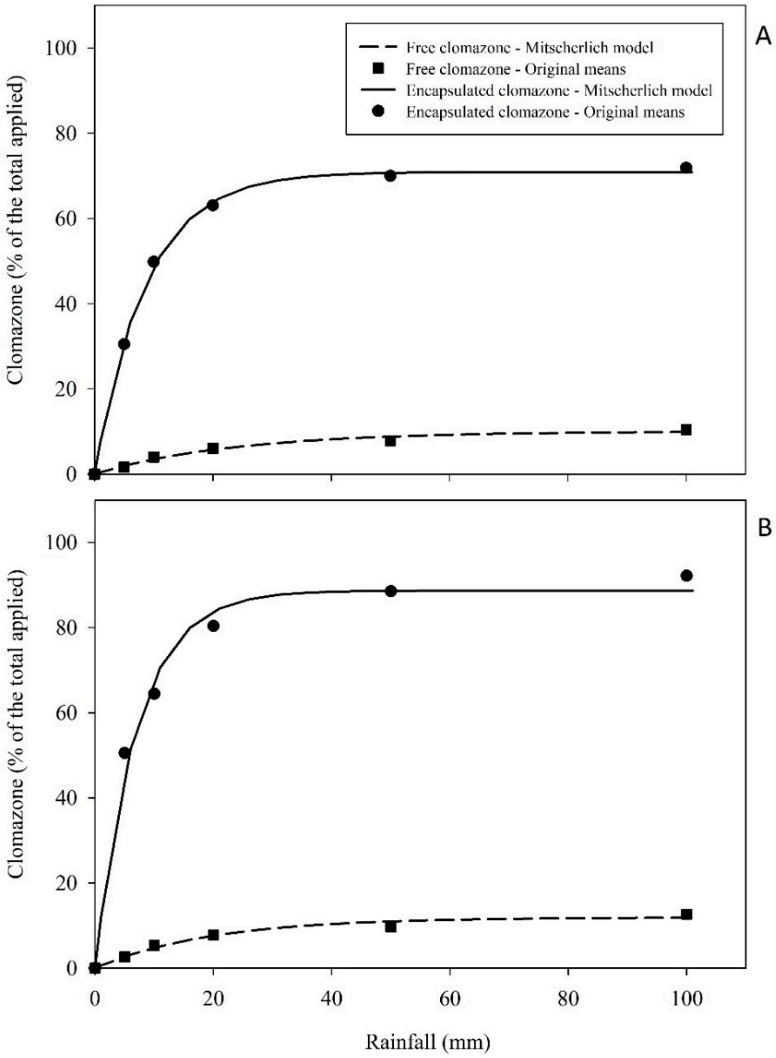

Figure 3. Quantities of free and encapsulated clomazone (% of the total applied) percolated through sugarcane straw as a function of different simulated rainfall depths (mm), after application of the microencapsulated (CS) formulation. Application only of the microencapsulated formulation (**A**); application of microencapsulated (CS) formulation combined with sulfentrazone (**B**).

When clomazone was applied combined with sulfentrazone (formulated as concentrated suspension), more than 90% of the clomazone that reached the straw surface remained encapsulated after 100 mm of simulated rainfall (Figure 3B). This high percolation with the combination of these herbicides is explained by the chemical composition of the formulations used, which can affect the physical-chemical properties of the solution [39,40]. The presence and association with additives can favor or hinder the coverage, interception, and retention of the product by plant straws.

Despite the higher percentages of recovery found with the combination of the herbicides, the proportion between free and encapsulated clomazone found was similar to that found after applying only the microencapsulated formulation of clomazone.

Regarding the quantities of the sulfentrazone herbicide, the quantification analyses also showed high coefficient of determination (R^2) and fit to the Mitscherlich models; the estimates of parameters are presented in Table 5. Considering that the quantities found in the reference containers during the applications are the quantities that effectively reached the straw, the rainfall simulation allowed the recovery of approximately 80% of the total applied (Figure 4).

Table 5. Estimates of parameters of Mitscherlich models fitted for the correlation of quantity of sulfentrazone percolated through sugarcane straw with different simulated rainfall depths (mm), after applications combined with emulsifiable concentrate (EC) formulation or microencapsulated (CS) formulation of clomazone.

Treatment	Formulation	Estimates of Parameters				F
		a	*b*	*c*	R^2	
Sulfentrazone + Clomazone	EC [1]	78.684	0.00	0.048	0.997	859.23 **
Sulfentrazone + Clomazone	CS [2]	80.857	0.00	0.040	0.995	394.87 **

[1] capsule suspension; [2] emulsifiable concentrate; ** significant by the F test ($p < 0.01$).

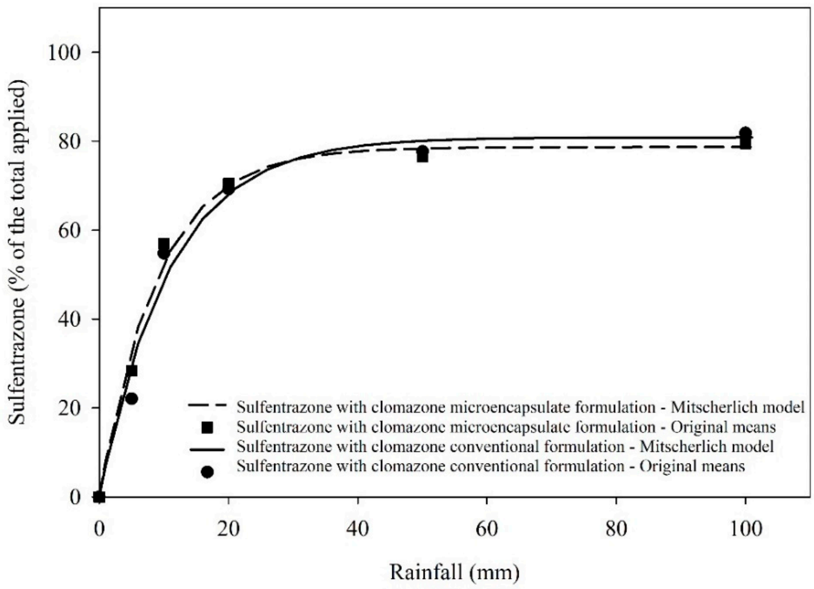

Figure 4. Quantity of sulfentrazone herbicide (% of the total applied) percolated through sugarcane straw as a function of different simulated rainfall depths (mm), after application combined with emulsifiable concentrate formulation (EC) or microencapsulated formulation (CS) of clomazone.

The sulfentrazone with the rainfall water percolated easily through the sugarcane straw, and the quantities presented no significant differences when it was applied combined with the clomazone formulations (EC and CS). Matos [41] evaluated combinations of the herbicides sulfentrazone and diuron and found that the percolation of sulfentrazone was hindered when the products were applied in combination, reaching approximately 69% of the total applied after a 100 mm rainfall depth, whereas the commercial formulation presented recovery of 96.63%. Practically all sulfentrazone applied was percolated through the sugarcane straw after 30 mm of simulated rainfall, presenting an asymptotic behavior, when it was applied in combination with the microencapsulated formulation of clomazone. The sulfentrazone percolation through the sugarcane straw is more intense over the first 20 mm of simulated rainfall depth applied after the application, regardless of the straw volume on the soil surface [32,42,43].

4. Conclusions

The use of the encapsulated formulation of clomazone affected the initial dynamics of the herbicides after its application on sugarcane straw, increasing the quantity of available herbicide after the rainfall simulations, decreasing losses soon after the applications and, thus, affecting the safety of the application and the weed control efficiency. Thus, the knowledge of the dynamics of herbicide release from straw is very important. However, when the first rainfall depth after herbicide application is late, herbicides remain exposed to solar radiation, high temperatures and dew for long period, which can increase losses. Therefore, further research to assess the dynamics of single and/or combined herbicide formulations over time in straw also are still necessary and substantial in advancing efficient and safe weed management in sugarcane.

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