Ciência Rural, Santa Maria, v.54:04, e20230005, 2024 http://doi.org/10.1590/0103-8478cr20230005
ISSNe 1678-4596
CROP PROTECTION

pH and water hardness on the efficiency of auxin mimics herbicides

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ABSTRACT: Carrier water quality is one of the main characteristics for an efficient and safe spraying of pesticides. Overall related to the levels of pH and hardness. The objective was to evaluate the interaction between water pH and storage time of the spray, containing 2,4-D amine, 2,4-D choline and dicamba, on the visible efficacy in *Ipomoea triloba*, *Bidens pilosa*, *Amaranthus viridis*; and water hardness on *I. triloba*. Three studies were carried out in a greenhouse. Study 1 with a 3x5 factorial, which factor A being pH of 2, 6 and 10 and factor B being 0, 2, 6, 24 and 36 hours of application after the mixture. Study 2 was a 3x5 factorial for each herbicide, whith factor A being the levels of pH (2, 6 and 10) and factor B being 0, 6, 12, 24 and 48 hours of application after the mixture. The study 3 is a 3x7 factorial, with factor A being the herbicides and factor B levels of water hardness: 0, 65, 125, 250, 500, 750 and 1000 parts per million. The pH of all solutions remained stable for 48 hours after preparation. However, did not interfere in efficacy of dicamba in *I. triloba*. Also, longer time between preparing the spray with 2,4-D formulations and application caused reduction efficacy on *I. triloba*. Also, the level of water hardness decreased control on *I. triloba*. The pH of carrier water did not affect efficacy of 2,4-D and dicamba on the weeds; however, longer time of the spray application reduce the visible efficacy.
Key words: quality, 2,4-D, dicamba.

Efeitos do pH e da dureza da água na eficiência de herbicidas mimetizadores da auxina

RESUMO: A qualidade da água é uma das principais características para uma aplicação eficiente e segura de pesticidas. De maneira geral, a qualidade da água está relacionada aos níveis de pH e dureza. Assim, o objetivo foi avaliar a interação entre o pH da água e tempo de mistura da calda contendo os herbicidas 2,4-D amina, 2,4-D colina e dicamba, na eficácia visível em *Ipomoea triloba*, *Bidens pilosa*, *Amaranthus viridis*; além dos níveis de dureza da água em *I. triloba*. Três estudos feitos em estufa. Estudo 1 em fatorial 3x5 sendo o fator A pH de 2, 6 e 10 e o fator B 0, 2, 6, 24 e 26 horas da mistura até a aplicação. Estudo 2 em fatorial 3x5 para cada herbicida, sendo o fator A pH de 2, 6 e 10 e o fator B 0, 6, 12, 24 e 48 horas da mistura até a aplicação. Estudo 3 em fatorial 3x7 sendo o fator A os herbicidas e o fator B níveis de dureza da água: 0, 65, 125, 250, 500, 750 e 1000 partes por milhão. O pH manteve-se estável nas 48 horas. Entretanto, não interferiu na eficácia de dicamba em *I. triloba*. Além disso, maior tempo entre o preparo da calda com as formulações de 2,4-D e a aplicação causou redução da eficácia em *I. triloba*. Ainda, a dureza da água diminuiu o controle sobre *I. triloba*. O pH não afetou 2,4-D e dicamba sobre as plantas, entretanto, maior tempo de aplicação reduz a eficácia.
Palavras-chave: qualidade, 2,4-D, dicamba.

INTRODUCTION

Water is the main carrier for spraying pesticides. Therefore, knowing its physical and chemical characteristics is essential for an efficient application. Regarding pesticide application technology, water quality is mainly defined by the levels of hydrogen potential (pH) and hardness (QUEIROZ et al., 2008). Regarding the pH, the scientific scale measures the concentration of free hydrogen and hydroxyl ions, forming acidic and alkaline environments, respectively (NELSON et al., 2017). As for hardness, the measurement scale is obtained in levels of calcium carbonate concentration ($CaCO_3$), expressed in parts per million (ppm), which can be classified as very soft water (< 71.2), soft water (71.2 - 142.4), semi-hard (142.4 - 320.4), hard (320.4 - 534.0) and very hard water (> 534) (QUEIROZ et al., 2008).

The pH of carrier water for the mixture of pesticides may play a very important role in the

Received 01.09.23 Approved 06.20.23 Returned by the author 08.21.23
CR-2023-0005.R1
Editors: Leandro Souza da Silva Arthur Arrobas Martins Barroso

processes of degradation, solubility and efficiency (ROSKAMP et al., 2013b; MUDGE et al., 2010; DEVKOTA & JOHNSON, 2019). Thus, water pH can interfere in the efficiency of pesticides, which can also be affected by the time of spray preparation before the application (RAMOS & DURIGAN, 1999). Besides this, there may be an interaction with the acid-dissociation constant (pKa), which consists in the pH value at which it causes 50% of dissociation and association of each molecule with the environment (NELSON et al., 2017), which can influence in the absorption and translocation of some herbicides. Water hardness can also influence in the absorption and translocation of herbicides, due to reactions between the negative charges of herbicides and positive charges of minerals, generating insolubility or difficulty in the absorption of these compounds (GREEN & HALE, 2005; HALL et al., 2000).

With the launching of new technologies related to herbicide tolerance to the auxin-mimicking mode of action and the continuous search to combine application technology in order to obtain efficiency and also safety in the field, it is of great importance to know the effects of carrier water quality in the application of herbicides. This study hypothesized that the weed control with herbicides 2,4-D amine salt, 2,4-D choline salt and dicamba is reduced with extreme pH values, spray solution storage time and high values of water hardness. Thus, the objective was to evaluate the interaction of different levels of water pH and storage time of the spray containing the herbicides 2,4-D amine salt, 2,4-D choline salt and dicamba in the control of *Ipomoea triloba* L., *Bidens pilosa* L., *Amaranthus viridis* L.; and water hardness levels and their influence in the control of *I. triloba*.

MATERIALS AND METHODS

Three studies were conducted in a greenhouse and in a laboratory at the Federal University of Santa Maria (UFSM), from July 2018 to April 2019. Studies 1 and 2 evaluated the effect of the interaction between carrier water pH and storage time of the spray solution containing herbicides 2,4-D amine, 2,4-D choline and dicamba. Study 3 evaluated the effect of water hardness levels on the efficiency of these herbicides. All experiments used the recommended herbicidal rates (AGROFIT, 2020) used to control *Ipomoea grandifolia* (Dammer) O'Donell, *Bidens pilosa* L., *Amaranthus viridis* L., which are 480 grams (g) of acid equivalent (ae) per hectare (ha)$^{-1}$ of dicamba diglycoamine salt (Atectra, Soluble Liquid, BASF, Germany), 670 g ae ha^{-1} for 2,4-D dimethylamine salt (amine) (U-46 Prime, Soluble Liquid, Nufarm, Australia) and 456 g ae ha^{-1} for 2,4-D choline salt (Enlist Colex-D, Soluble Liquid, Corteva Agriscience, United States). For Study 1, the greenhouse environment had an average temperature of 25 ºC during the day and 20º C during the night, and relative humidity (RH%) set at 90 %. Studies 2 and 3 presented average temperatures of 30 ºC during the day and 25 ºC during the night, also with RH% at 90%. The greenhouse photoperiod was not changed, in study 1 with a 10 hour photoperiod, and in the studies 2 and 3 with a 12 hour photoperiod.

Carrier water pH studies (Studies 1 and 2)

In study 1, the experiment units consisted of trays with a capacity of 5.5 L of soil, containing the species *Ipomoea triloba*, *Bidens pilosa* and *Amaranthus viridis*, arranged in lines side by side, with rows spaced at 8 cm. For study 2, the experiment units consisted of plastic pots with a capacity of 0.3 liters of soil, containing one species per pot. For both studies the herbicides were applied in an automatic application chamber (Model III, DeVries, United States), equipped with nozzles XR 110015 flat-fan tips, calibrated for an application carrier spray volume of 150 L ha^{-1}, working pressure of 0,20 MPa and travel speed of 3.6 km h^{-1}.

Study 1 used a completely randomized design (CRD) with four replications, conducted in a 3x5 factorial scheme, in which factor A consisted of three carrier water pH levels (2, 6 and 10) and factor B consisted of five intervals between the preparation of the spray with the herbicide dicamba and the application, which were: 0, 2, 6, 24 and 36 hours after preparation. To alter the pH of carrier water in both studies, it was used hydrochloric acid (HCl) (Synth, Brazil) for pH acidification and sodium hydroxide (NaOH) (Synth Brasil) for pH alkalinization, and the measurement with a bench pH meter (PG 1800, Gehaka, Brazil). In order to obtain the values, the pH meter was kept immersed in water and kept in constant agitation, with the addition of HCl or NaOH reagents concomitantly until the desired pH was stabilized. Soon after the pH stabilization, the herbicides were mixed with the carrier water and measured again. The application was carried out with weeds that were in the growth stage of 4 true leaves.

Study 2 was conducted in the form of three separate experiments to control *I. triloba* with herbicides 2,4-D amine, 2,4-D choline and dicamba. The design used was the CRD with four replications, similar to the previous study with the 3x5 factorial scheme, factor A being three levels of water pH (2, 6 and 10), and factor B was five different time intervals after the preparation of the herbicide mixture (0, 6, 12, 24 and 48 hours after mixing). The determination of the spray pH and the application followed the procedure described for experiment 1; however, for experiment 2, it was measured a blank solution with pH levels 2 and 10 to measure the variation during the time intervals. During the time the herbicidal solution was keeped in a closed bottle. The plants of *I. triloba* presented 4 expanded leaves at the time of application.

Carrier water hardness study (Study 3)

In study 3, a CRD was used with four replications in a 3x7 factorial scheme. Factor A consisted of different herbicides: 2,4-D amine, 2,4-D choline and dicamba. Factor B consisted of seven levels of water hardness: 0, 65, 125, 250, 500, 750 and 1000 ppm (parts per million) of calcium carbonate (CaCO3). The plants of *Ipomoea triloba* presented 4 expanded leaves at the time of application.

The alteration of water hardness was given by a similar methodology proposed by DEVKOTA & JOHNSON (2016), using a 3:1 mixture of calcium chloride (Dihydrated Calcium Chloride PA, Synth, Brazil) and magnesium sulfate (Magnesium Sulfate 7H2O PA-ACS, Synth, Brazil). Total hardness was measured using the 2340 method (RICE et al., 2020), using colorimetric titration with ethylene diamine tetra-acetic acid (EDTA) (EDTA Disodium Salt 2H2O PA, Synth, Brazil) as a complexant and erythromycin black T (Eriochrome Black -T PA-ACS, Synth, Brazil) as an indicator. Two base solutions were used to measure hardness, one of 1000 ppm of CaCO3 (Calcium carbonate P.A, Neon, Brazil), and the other with distilled water, verifying 0 ppm of hardness by the titration method used in the experiment.

Data analysis

In study 1, visible efficacy was assessed at 7 and 35 days after treatment (DAT) and shoot dry weight (SDW) was measured at 35 DAT. For studies 2 and 3, visible efficacy was assessed at 7, 14 and 21 DAT and SDW was measured at 21 DAT. Visible efficacy was evaluated on a scale through comparison with injuries without herbicide application, in which zero indicates absence of injuries and 100% means the death of plants. In study 2, the pH values of the control solutions were measured at 0, 6, 12, 24 and 48 hours after mixing. In all experiments, after the last visible efficacy assessment, the plants were collected and dried in an oven for 72 hours at 60 ºC. In experiment 3, the SDW reduction in relation to the SDW without herbicide application at 21 DAT was then calculated, expressed as a percentage of dry weight (DW) reduction (%).

In all studies, the variables were subjected to variance analysis, normality (Shapiro-Wilk) and homogeneity (O'Neill-Matthews), both with $P \leq 0.05$. In studies 1 and 2, the levels of factor A were differentiated by calculating the confidence interval of the means and in factor B the complementary analysis was done by linear regression (Equation 1).

$$y = ax + b \qquad (1)$$

where: y = is the response variable (visible efficacy or SDW), x = storage time of the spray in hours, a the intercept and b the slope.

In experiment 3, it was used non-linear logistic regression (Equation 2).

$$y = \frac{a-c}{\left[1+\left(\frac{x}{ED50}\right)\right]^{b}} \qquad (2)$$

where: y = is the response variable (visible efficacy or DW reduction (%)); x = ppm of $CaCO_3$ hardness levels; and, a, ED_{50} and b, the parameters of the equation, where a is the maximum point of the curve, c the minimum point, ED_{50} is the rate that provides a 50% reduction in the response of the variable and b is the slope of the curve. For a better adjustment of the data, parameter c was limited to 0. For statistical analysis and for making the graphs, software R (R CORE TEAM, 2020) and packages ExpDes.pt (FERREIRA et al., 2014), drc (RITZ et al., 2015) and ggplot2 were used. No transformations were necessary to adjust the normality of errors and homogeneity of variances.

RESULTS

In study 1, no interactions were found between carrier water pH levels and the storage time of the spray. However, there was statistical difference between species and the linear regression was significant in all evaluations for the species *I. triloba*. In study 2, some interactions were found between factors for herbicides 2,4-D amine and 2,4-D choline. In study 3, significant interaction was verified for all tested variables in experiment 3 (Figure 6).

Carrier water pH studies (Studies 1 and 2)

About the study 1, At 7 DAT (Figure 1A), it was observed a reduction of sensitivity (%) of *I. tribloba* for dicamba in relation to the other weeds used in the experiment. However, for the linear coefficient parameter *b*, there was a drop in the visible efficacy value to -0.56 for each hour in *A.*

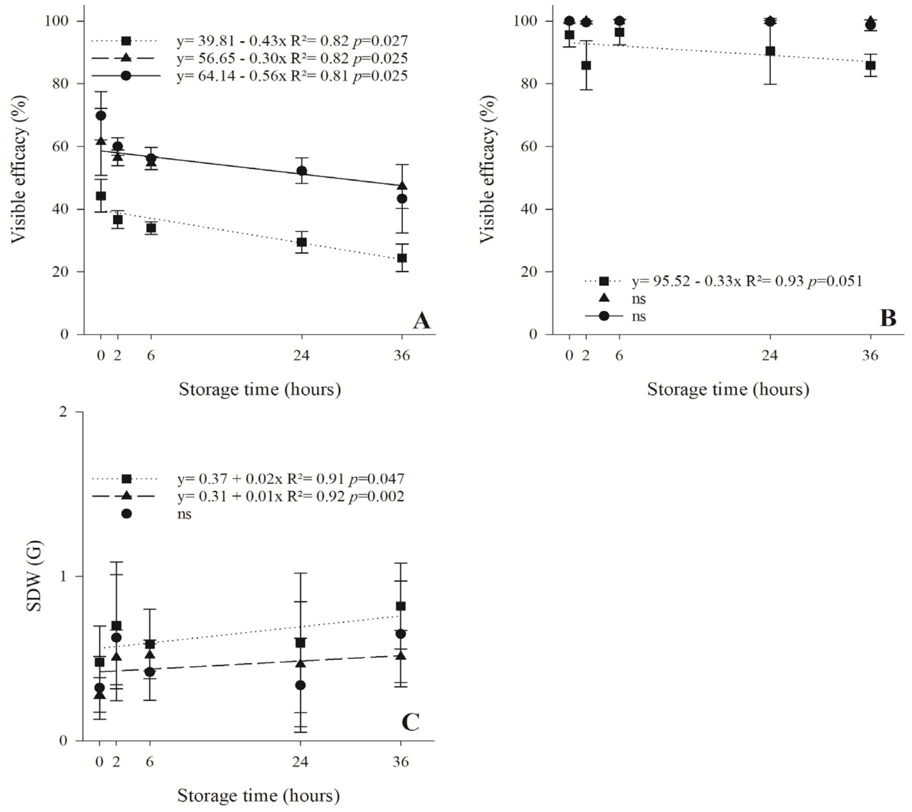

Figure 1 - Dicamba visible efficacy (%) in *Ipomoea triloba* (■), *Bidens pilosa* (▲) and *Amaranthus viridis* (●) of different storage time in hours in the evaluations at 7 (A) and 35 (B) days after application (DAT) and the shoot dry weight (SDW g) at 35 DAT (C). ns = non significant regression. P = *P* value.

viridis, indicating a greater reduction of efficacy with the increasing the storage time of the spray. As for *I. triloba* and *B. pilosa*, the parameter *b* for visible efficacy (%) was set in -0.43 and -0.30, respectively. All the confidence intervals for storage time (H) overlap for *A. viridis* and *B. pilosa,* but do not overlap for *I. triloba.* As for the variable of visible efficacy at 35 DAT (Figure 1B), there was no adjustment for a linear regression for *B. pilosa* and *A. viridis*, since all obtained values reached 100%, expressing that the plants were dead. For *I. triloba*, the parameter *b* was in -0.33, and the intercept was found in 95.52, showing a lack of visible efficacy (%), also with the *p* value of 0,051, pointing to a good adjustment. The confidence interval for *I. triloba* did not overlap with other species when at 2 and 36 hours of storage time.

No regression adjustment also occurred for *A. viridis* in the SDW (Figure 1C), showing no drop in visible efficacy with the spray storage time. Conversely, for *I. triloba* and *B. pilosa,* an adjustment was found, with parameter *b* of 0.02 and 0.01 respectively, showing a reduced visible efficacy (%) to the first weed comparatively with the others plants. But also, all the weeds had this confidence intervals overlap, showing no difference in any storage time interval. Overall, when there was significance for linear regression, there was a decrease in the visible efficacy variable, due to the negative values of parameter *b* of the regression for the visual assessments and positive for the SDW assessment.

In study 2, for the variation of spray solution pH levels over the storage time of the herbicides (Figure 2), when there was no mixture (Figure 2A) the blank solution maintained its values and, in the case of 2,4-D amine (Figure 2B) there was great variation at pH value of 2, reaching a value of 4.9 at 48 hours after mixing. For 2,4-D choline and dicamba (Figures 2C and 2D), there was no

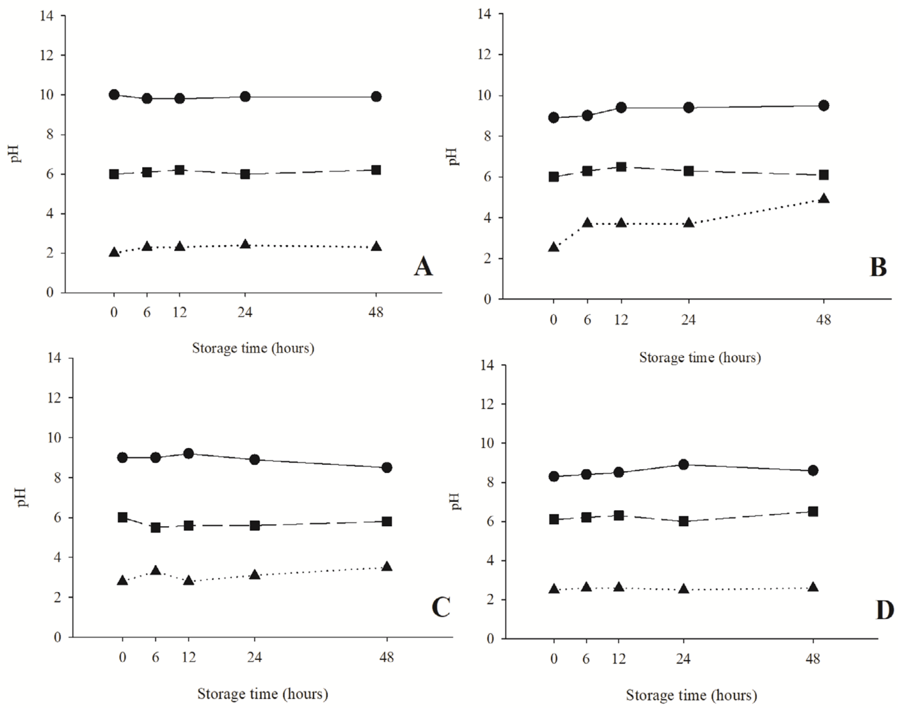

Figure 2 - pH variation measures of carrier water in 2,0 (▲), 6,0 (■) e 10,0 (●), not mixed with herbicide check (A), 2,4-D amine (B), 2,4-D choline (C) and dicamba (D) at different storage time in hours.

significant variation of more than one pH value point, except for a slight decline of pH 10 mixture with 2,4-D choline. According to the methodology mentioned above, the pH alteration was done before adding the herbicide to the spray, that is, the herbicides were not able to change the pH of the spray in relation to its original value, showing a lack of buffering power of the herbicide. For dicamba (Figure 3) there was no statistical interaction between pH x spray storage time. In visible efficacy (%) at 7 DAT (Figure 3A), the parameter *b* was at -0.17, in 14 DAT (Figure 3B) at -0.31 and in SDW (Figure 3D) at 0.005, all those values with a *p* value > 0.01. But for visible efficacy (%) at 21 DAT (Figure 3C) there was no regression adjustment, primarily due to the death of all plants.

There was no interaction for pH and storage time (H) in visible efficacy (%) at 7 DAT (Figure 4A) and SDW (Figure 4D), with the parameter *b* of -0.36 and +0.005, respectively. But an interaction was found for 2,4-D amine at 14 and 21 DAT (Figure 4B and 4C), showing a greater decrease in visible efficacy (%) when at pH 2, wherefore due to the parameter *b* of -0.63, and on other conditions at pH 6 and 10, showing as -0.31 and -0.15, respectively, at 14 DAT. As for confidence intervals, at 0 and 6 hours of storage time, all herbicides overlapped; however, in all pH values at other storage times they did not, appointing that pH 2 has lower visible efficacy (%) effect. At 21 DAT, pH 2 was the only significant regression due to not reaching 100% efficacy at all levels of storage time with a parameter *b* at -0.07, also the confidence intervals for its means did not overlap with the other pH values. For the formulation 2,4-D choline (Figure 5), similarly, a reduction in visible efficacy (%) was found when the herbicidal solution was at pH 2. In the evaluations at 7 DAT (fig 5A), pH 2 showed a parameter *b* value of - 0.64, and the values of 6 and 10, the parameter *b* was in the values of -0.27 and -0.34, respectively, and at pH 2, the confidence intervals did not overlap with pH 6 and 10 when the storage time was at 24 and 48 hours. At 14 DAT (Figure 5B), pH 2 parameter *b* was -0.62 and pH 6 at -0.25, similarly to the 7 DAT values, otherwise the regression was not adjusted for pH 10 values. Also, pH 2 did not show any overlapping at 24 and 48 hours of storage time. Similarly happened at 21 DAT (Figure 5C), with no regression adjustment and interaction between factors. For SDW (Figure 5D), the value of pH 2 parameter *b* was 0.005, of pH 6 was 0.003 and of pH10 was 0.001. Also, due to the overlap of the

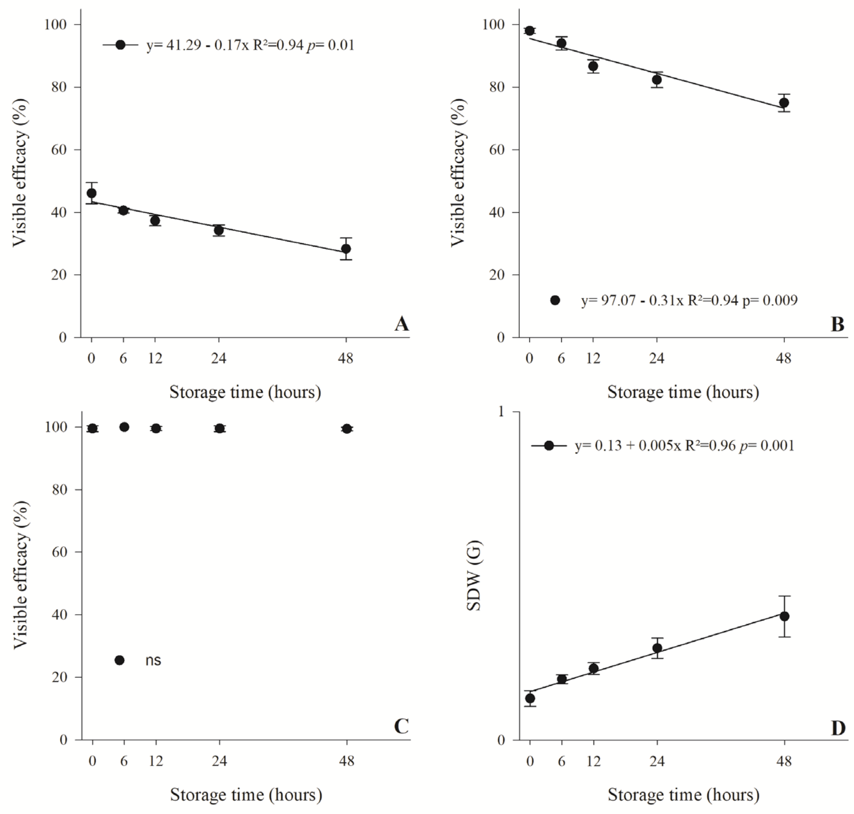

Figure 3 - Dicamba visible efficacy (%) in *Ipomoea triloba* at (%) at 7 (A), 14 (B) e 21 (C) days after treatment (DAT) and Shoot Dry Weight (SDW) g in 21 DAT at storage time in Hours. ns = non significant regression. P = *P* value.

standard error, there was no difference in the SDW at 21 DAT for the treatment at pH 2 and pH 6, but still showing a greater increase in this variable than at pH 10. The lower visible efficacy values mainly in the results with dicamba and 2,4-D amine at 48 hours after the preparation of the spray coincided with the greatest pH variation, reducing in the case of pH 10, or increasing for pH 2.

Carrier water hardness (Study 3)

In the variable of visible efficacy at 7 DAT (Figure 6A), the maximum values found were up to 47 to 52% according to the parameter of the upper limit of the regression. The ED_{50} values varied from 1334.18, 1344.48 and 1524.18, with the lowest value referring to herbicides 2,4-D choline and 2,4-D amine, respectively, which these two formulations of 2,4-D showing similar values. In the evaluation at 14 DAT (Figure 6B), the maximum efficacy ranged from 76 to 89%, significant with a difference between formulations of 2,4-D amine and choline, with values of 84.94 and 76.41, respectively. The ED_{50} value of 2,4-D choline was lower than that for 2,4-D amine (1130.85 and 1266.46, respectively), whereas for dicamba it was at a 5418.68, showing that a larger amount of ppm of $CaCO_3$ is needed to reduce the visible efficacy (%). At 21 DAT (Figure 6C), the values of the upper limit of the curve showed visible efficacy (%) above 95% for *I. triloba*, except for the concentration of 1000 ppm of $CaCO_3$, in which there was a significant decrease in the visible efficacy of 2,4-D choline, with ED_{50} at 1067.34, and also evidenced by the confidence intervals that did not overlap with the other herbicides tested in the experiment. For the DW reduction (%) (Figure 6D), the variable of ED_{50} parameter of dicamba was at 583.94, 2,4-D choline at 935.05 and 2,4-D amine at 840.48, making it possible to claim that water hardness has more effects on dicamba than on other auxin-mimicking herbicides. For the means of each treatment in ppm

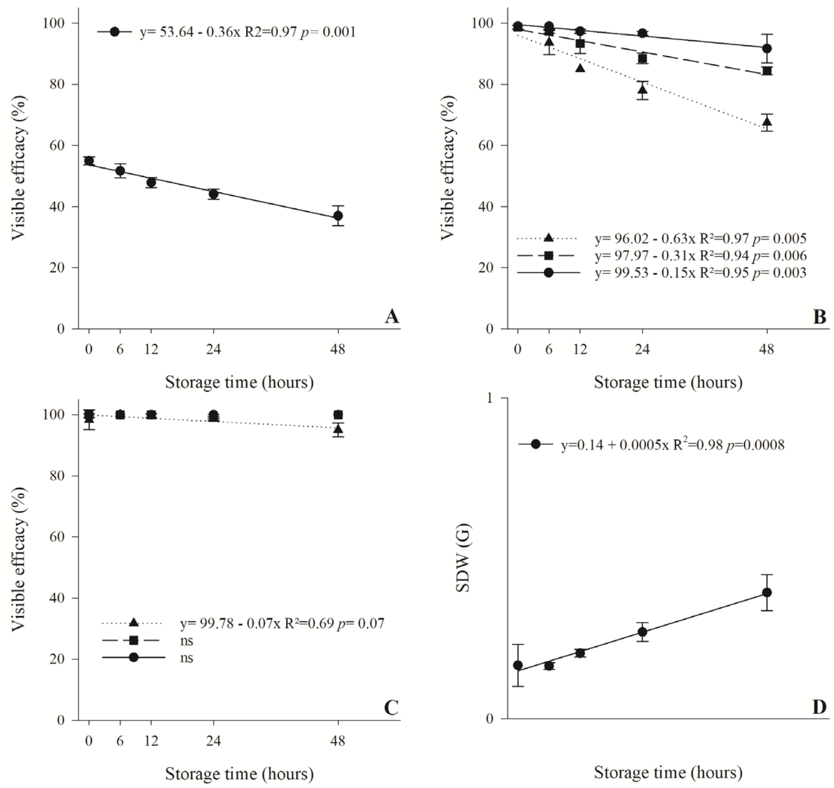

Figure 4 - 2,4-D amine visible efficacy (%) in *Ipomoea triloba* at at 7 (A), 14 (B) e 21 (C) days after treatment (DAT) and Shoot Dry Weight (SDW) g in 21 DAT at different storage time in Hours. In 14 and 21 DAT significant interaction between pH values of 2,0 (▲), 6,0 (■) e 10,0 (●). ns = non significant regression. P = *P* value.

of $CaCO_3$, there was no confidence interval overlap, showing that for this variable the hardness level had no difference on herbicides.

DISCUSSION

Carrier water pH studies

A study showed that the mixture of dicamba with different sources of water, varying the pH, was not able to buffer the values, being extremely variable according to the pH from the source (MUELLER & STECKEL, 2019). A study aiming to compare the influence of three pH values (4, 6.5 and 9) on the control of *Ambrosia trifida* L., *Conyza canadensis* L. and *Amaranthus palmeri* S. Watson, with the use of 2,4-D choline and 2,4-D choline + glyphosate, showed the greatest efficacy on the lowest pH value (4), while there was no statistical difference for the other values (DEVKOTA & JOHNSON, 2019). As for dicamba, which has chemical characteristics similar to the 2,4-D herbicides, it also had reduced efficacy when the pH was neutral or alkaline, to control *Chenopodium album* L. and *A. trifida* (DEVKOTA & JOHNSON, 2020). For a herbicide which also has a weak acid character, but non-systemic, such as saflufenacil, presented a reduction in the efficacy on *C. album* and its solubility in water when it was in an acidic environment (ROSKAMP et al., 2013b). Regarding 4-hydroxyphenylpiruvate dioxygenase herbicides like mesotrione, commonly applied in Brazil, the response for carrier water pH could vary for weed specie. For *C. canadensis* control, the efficacy was higher in 4.0 pH than 9.0 pH (DEVKOTA et al., 2016). Also, this happen for the inhibitor of glutamine synthetase, ammonium glufosinate to control *A. palmerii* and *A. trifida,* (DEVKOTA & JOHNSON, 2016a).

There are few articles in the literature regarding the relationship between storage time before application and efficiency in the use of herbicides. But, it is documented that when more time the herbicide is mixed with its carrier, more will be chances that the

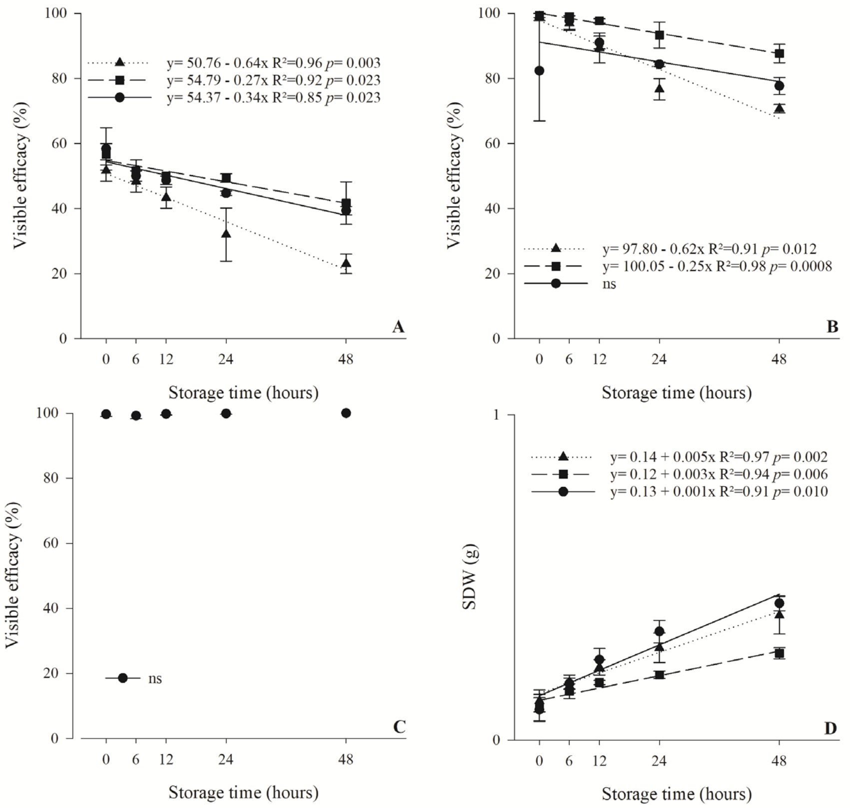

Figure 5 - 2,4-D choline visible efficacy (%) in *Ipomoea triloba* at 7 (A), 14 (B) e 21 (C) days after treatment (DAT) and SDW g in 21 DAT at different storage time in Hours. In 7, 14 and 21 SDW DAT significant interaction between pH values of 2,0 (▲), 6,0 (■) e 10,0 (●). ns = non significant regression. P = *P* value.

molecule will be break or degraded (STEWART et al., 2009). For efficiency, two similar studies reported that the mixture of 2,4-D + glyphosate had reduced control of *Panicum maximum* Jacq., but for two residual herbicides ametrine and diuron, there was no difference in the emergence of weeds (RAMOS & DURIGAN, 1998; RAMOS & DURIGAN, 1999). Also, the use of 2,4-D amine for the control of *Taraxacum officinale* L. with hard water (400 and 600 ppm $CaCO_3$) was not affected by the storage time but can be negative affected by divalent cations (PATTON et al., 2016; SCHORTGEN & PATTON, 2019). In addition, the spray storage time, mixed or not with ammonium sulfate and water with 0 or 1600 ppm of hardness, did not find significant statistical interactions with the control of various dicots and monocots and corn yield (MAHONEY et al., 2014).

These results showed a counterpoint with the results we found. Therefore, the response by storage time in herbicides, varies with a lot of characteristics of compound and the targets weed species (EURE et al., 2013). It was hypothesized that the effect of reducing the efficacy due to the storage time and the pH of carrier water may be related to the process of hydrolysis of the herbicidal molecule. It is known that the effect of flumioxazin for the control of *Hidrylla verticilatta* [Lf] Royle at alkaline pH (> 9) is reduced, which can be explained by the shorter half-life of the active ingredient while in this condition (MUDGE et al., 2010). Thus far, the storage time before herbicide application it is suggested that is more pronounced in auxin mimics herbicides (DARAMOLA et al., 2022). It is necessary to emphasize the difference between the characteristics regarding these herbicides, with 2,4-D and dicamba being a weak acid and flumioxaxin being a non-ionizable herbicide. However, herbicide dicamba has a pKa of 1.96, being lower than that of 2,4-D, which is 2.73 (SENSEMAN, 2007). This fact may explain why there was no difference in visible efficacy between pH values for dicamba, since

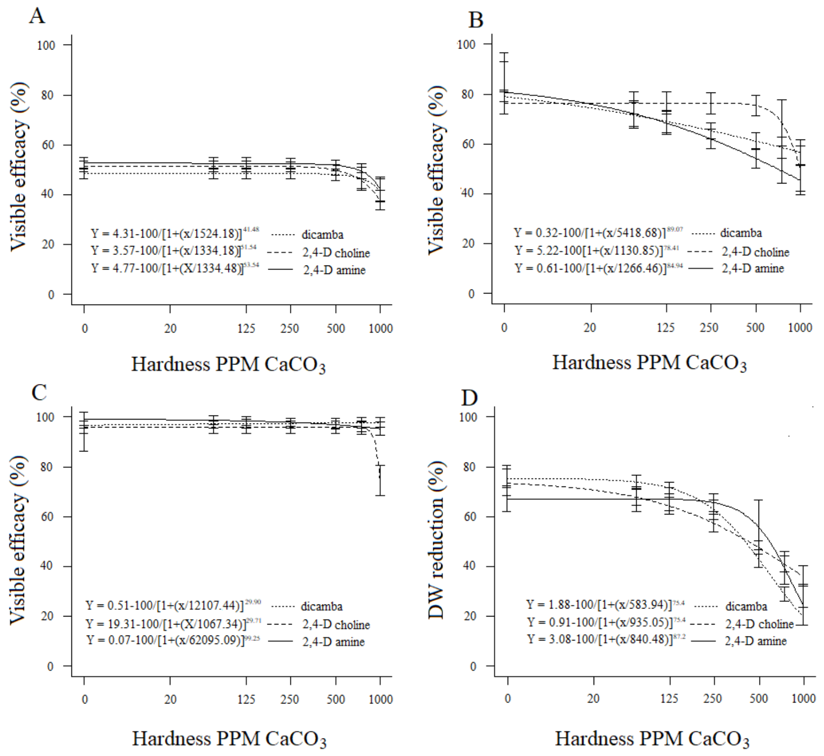

Figure 6 - *Ipomoea triloba* visible efficacy (%) in 7 (A), 14 (B) amd 21 (C) days after treatment (DAT) and dry weight (DW) reduction (%) at seven levels of PPM of calcium carbonate ($CaCO_3$).

the carrier water was always higher than its pKa. Therefore, when happen will facilitate the herbicide diffusion through plant cuticle (GREEN & HALE, 2005). Thus far, the storage time before herbicide application it is suggested that is more pronounced in auxin mimics herbicides (DARAMOLA et al., 2022).

Carrier water hardness

In similar studies evaluating hardness levels for herbicides 2,4-D choline and dicamba + glyphosate, it was generally found that very hard water levels (> 300 ppm $CaCO_3$) reduced the efficacy on *C. canadensis* and *A. trifida*, respectively (DEVKOTA & JOHNSON, 2019; DEVKOTA & JOHNSON, 2020). These results can serve as a counterpoint to the results we have found. The significant interaction evidenced a differentiated response from the herbicides in relation to the level of hardness (ppm $CaCO_3^{-1}$), in addition to the fact that the adjustment in the non-linear regression (Figure 6) showed different responses in the relation herbicide x hardness than those found in the literature, considering that in other studies it was used linear regression for evaluations (DEVKOTA & JOHNSON, 2016a; DEVKOTA & JOHNSON, 2016b; DEVKOTA et al., 2016). Also, analyzing cations that can be found in hard water solutions in 2,4-D and dicamba, an antagonistic effect was found in the efficacy on *Kochia* spp. (NALEWAJA et al., 1991; NALEWAJA & MATYSIAK, 1993). Similarly, when different carrier water volumes were tested, at 80 L ha^{-1} with sodium bicarbonate it can reduce the efficacy on *Kochia* spp. with 2,4-D amine in 45% (NALEWAJA et al., 1993). Sodium bicarbonate also reduce 2,4-D amine effect in various broadleaves weeds control (NALEWAJA et al.,1990) Thus, when hard water antagonism was found, a way to overcome this was the mixing with ammonium sulfate and some other nitrogen-based fertilizers, but only with low rates, as higher rates could not improve the efficacy on *T. officinale* with 2,4-D amine (SCHORTGEN & PATTON, 2021a). Another way to overcome antagonism can be the development of formulations that reduce this effect. In a research that studied these effects, it was found that formulations with emulsifying effects reduce the antagonism caused by 600 ppm of water hardness altered with calcium chloride (SCHORTGEN & PATTON, 2021b). However, in view of the results found in our study, the visible efficacy was not altered at the levels of hardness tested.

For the use of glyphosate, there was no effect of water hardness on the control of important weeds like: (SOLTANI et al., 2011). In addition, when evaluating the control of *Digitaria insularis* Willd with glyphosate at hardness levels between 70 and 430 ppm $CaCO_3$, there was no reduction in the efficiency for the ammonium and potassium salt formulations (CUNHA et al., 2020). Meanwhile, as counterpoint for these studies, some iron, zinc, calcium and magnesium cations can antagonize the glyphosate action to control and reduce weight of wheat (NALEWAJA & MATYSIAK, 1991). Furthermore, cations like manganese affect the control of *C. canadensis* and *C.album*, showing an antagonistic effect in the research of ROSKAMP et al. (2013a). Regarding other herbicides, saflufenacil did not have its effect affected by any level of hardness in the control of *C. album*, whereas for ammonium glufosinate, there was linear reduction in the control of *A. trifida* (DEVKOTA & JOHNSON, 2016a; ROSKAMP et al., 2013a). Also, antagonistic effects of calcium and magnesium was found in the use of aminopyralid, tembotrione, dicamba plus diflufenzopyr, and ammonium glufosinate (ZOLLINGER et al., 2011).

Overall, this study may guide future actions in the area of application technology and must be accompanied. Thus, studies with carrier water quality as a main subject is still scarce. Also, other spray characteristics like temperature and turbidity can reduce herbicide efficiency and the response to pH alteration and hardness are headed by the herbicide character (DARAMOLA et al., 2022). As 2,4-D and dicamba being weak acids herbicides his responses to water pH alterations and hardness level are more pronounced that herbicides that don't have pka or are non-systemic (ZOLLINGER et al., 2011). In addition, it was evident that the storage time of the spray solution plays a role in herbicidal efficiency.

CONCLUSION

The pH value of carrier water did not affect efficacy of 2,4-D and dicamba on *Ipomoea triloba, Bidens pilosa* and *Amaranthus viridis;* however, the longer the storage time of the spray solution, the reduced the visible efficacy (%). The majority of tested pH values of all herbicides remained stable for 48 hours after preparation. The pH of carrier water did not affect the efficiency of dicamba on *I. triloba*. The longer the storage time between preparing the spray with herbicides 2,4-D amine and 2,4-D choline, and applying them, the greater the loss of visible efficacy (%) on *I. triloba*, this loss is more pronounced at an acid pH. It is suggested that the application of herbicides have to be within 12 hours after the preparation of the spray solution, and acid pH levels have potential to decrease herbicide efficacy over storage time. The increase in water hardness levels decreases the visible efficacy of auxin-mimicking herbicides on *I. triloba*.

ACKNOWLEDGEMENTS

We are very thankful to Laboratory of Environment engineering (LEMA) for offering structure to the water hardness alteration. The Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) to concede the author's scholarship. In addition to the Universidade Federal de Santa Maria (UFSM) and the Programa de Pós-graduação em Engenharia Agrícola (PPGEA).

DECLARATION OF CONFLICT OF INTEREST

The author's do not have any conflict and competing of interest.

AUTHORS' CONTRIBUTIONS

Roberto Costa Avila Neto: Conceptualization, Methodology, Software. Geovana Facco Barbieri: Visualization, Investigation, Writing Eduardo Bortolin, Rosana Marzari Thomasi and Eduard Leichtweiss: Investigation and methodology. André da Rosa Ulguim and Adriano Arrué Melo: Data curation, advisory and Writing- Reviewing and Editing.

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