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Physical-chemical properties of spray syrup in tank-mixing multiple pesticides and water sources used in grain farming

Propiedades fisicoquímicas del caldo de pulverización preparado con diferentes plaguicidas y tipos de agua utilizadas durante la producción de granos

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Abstract

This work evaluated physical-chemical properties of spraying syrup formulated with different water types and using or not tank-mixing pesticides. The experimental design was completely randomized in a 4 x 5 factorial scheme (4 water types and 4 pesticide syrups + control, non-sprayed plant) in three sampling times (off-season corn, pre-planting soybean weed control, and soybean season) within one year. Water treatments consisted of deionized, well, river and weir water. Product mixing consisted of herbicide (Glyphosate 925 g a.i. ha^{-1}), herbicide + insecticide (Imidacloprid + beta-cyfluthrin 100+12.5 g a.i. ha^{-1}), herbicide + fungicide (Trifloxystrobin + Prothioconazole 70+60 g a.i. ha^{-1}) and herbicide + insecticide + fungicide. Weir water presented the worst physical quality. Spraying syrup prepared with tank-mixing herbicide, insecticide, and fungicide in various combinations decreased the effectiveness of the pesticide. When associating the three pesticides, less dissolution of the spray syrup and greater risk of syrup incompatibility leads to pesticide ineffectiveness.

Keywords
application technology • water types • plant protection

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RESUMEN

Este trabajo evaluó las propiedades fisicoquímicas del caldo de pulverización formado con diferentes tipos de agua, con y sin utilizar la mezcla de múltiples plaguicidas. El diseño experimental fue completamente aleatorio, los tratamientos se organizaron en un esquema factorial 4x5 (4 tipos de agua y 4 caldos de plaguicidas + 1 sin producto fitosanitario) en tres épocas de muestreo (maíz de segunda zafra, pre-siembra de la soja y durante cultivo de la soja) en un año. Los tipos de agua fueron agua desionizada, agua de pozo, agua de río y agua de laguna, y la mezcla de productos consistió en herbicida (glifosato 925 g i.a. ha^{-1}), herbicida + insecticida (Imidacloprid + beta-cifluthrina 100 + 12.5 g i.a. ha^{-1}), herbicida + fungicida (Trifloxistrobina + Prothioconazole 70+60 g i.a. ha^{-1}), herbicida + insecticida + fungicida. Se encontró relación entre el origen del agua y la mezcla de los plaguicidas, que influenció la calidad del caldo de pulverización. Cuando el agua proviene de lagunas, el caldo presenta la peor calidad física, lo que disminuye el rendimiento del plaguicida. El caldo con el herbicida, insecticida y fungicida mezclados se diluye menos, aumentando el riesgo de incompatibilidad y de ineficacia de los plaguicidas.

Palabras clave
tecnología de aplicación • tipos de agua • protección vegetal

INTRODUCTION

Spraying is widely used in agriculture for plant protection. For pesticide application, a liquid and an active diluted ingredient (phytosanitary product) form a syrup applied towards a target (weed, pest or pathogen) as a homogeneous cloud. The liquid usually used is water, the universal solvent (37). Water quality is essential, as it generally represents around ninety-five per cent of the spray solution. Therefore, chemical and physical elements in water can affect spray quality (18). In this sense, suspended materials such as silt, clay, and organic matter provide a "cloudy" aspect (23).

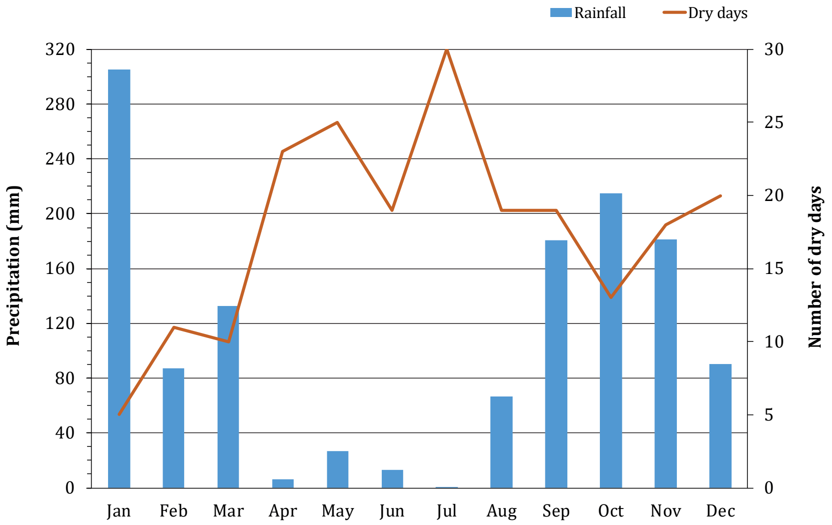
Soil sorption coefficient (Kd) and soil organic carbon-water partition coefficient (Koc) constitute pesticide-related coefficients that reflect pesticide force to be adsorbed to different particles. Pesticides with high Kd or Koc values bind strongly to sediments and organic matter in water, reducing active ingredients in the solution and reducing effectiveness (12). In this sense, several elements can influence application efficiency and effectiveness, such as Calcium, Magnesium, and Iron, free ions in the spray syrup (38). Accordingly, water hardness is a measure of total Calcium and Magnesium in water, reducing. pesticide effectiveness (13). Considering ion content, the pH also influences active ingredient availability in spray syrup. Acid/base ionization constants (pKa or pKb) represent ionization trends in a given pH range, determining syrup ingredient concentrations in the ionizable form directly affecting product effectiveness (12). Waters from rural regions may present dissolved ions or salts. River and weir waters have sediments such as clay and organic matter that can clog nozzles and filters, reducing spray components life (30). Thus, water choice is important for efficient spraying, especially considering water obtained from open reservoirs, such as rivers and weirs (20).

Another factor involved in application quality is product association in the sprayer tank. Products used in Integrated Pest Management or plant protection programs do not have a wide enough spectrum of action to effectively control all crop pests, making it necessary to mix products (21). Thus, farmers adopting this practice, face certain difficulties like product dissolving, foaming, precipitation, and flocculation, among other physical and chemical incompatibilities (15, 16).

Given these facts, this work evaluated spraying syrup physical-chemical properties when formulated with different water qualities and tank-mixing multiple pesticides.

MATERIAL AND METHODS

The experiments were conducted in laboratory and field. Field evaluations were located in the southern State of Mato Grosso do Sul, 22°27'04" latitude S and 55°01'27" longitude W, in Caarapã district, located in the Laguna Carapã city, Brazil. The climate is Monsoon (Am), according to Köppen's classification (3), with dry winters, average annual rainfall of 1500 mm, and average temperature of 22°C (figure 1).



Adapted from National Institute of Meteorology (INMET, https://portal.inmet.gov.br/).

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Figure 1. Monthly rainfall and dry days for the Laguna Carapã, Brazil, 2018.

Figura 1. Lluvias mensuales y días secos para Laguna Carapã, Brasil, 2018.

The soil is an Oxisol, with the chemical properties of a Clay soil (0 to 20 cm) under no-tillage (table 1). Soil sampling was carried out at Santa Lúcia farm, located in Laguna Carapã, Brazil.

Table 1. Chemical soil analysis of the Santa Lúcia farm (0 to 20 cm) in Laguna Carapã, Brazil, 2018.

Tabla 1. Análisis químico del suelo de la granja Santa Lúcia (0 to 20 cm) en Laguna Carapã, Brasil, 2018.

pH	OM	P	S	K	Ca	Mg	Al	H+Al	SB	CEC	V	M
$CaCl_2$	g dm^{-3}	mg dm^{-3}		---------------------- Cmol dm^{-3} ----------------------							---- % ----	
5.2	31.1	18.3	4.4	0.3	6.4	1.4	0.0	4.5	8.1	12.6	64.2	0.0

pH: Hydrogen ion concentration; OM: Soil Organic Matter; P: Phosphorus; S: Sulfur; K: Potassium; Ca: Calcium; Mg: Magnesium; Al: Aluminum; H+Al: Potential Acidity; SB: Sum of Bases; CEC: Cation exchange capacity); V: CEC Base Saturation; M: CEC Aluminum Saturation.

pH: Concentración de iones de Hidrógeno; OM: Materia Orgánica del Suelo; P: Fósforo; S: Azufre; K: Potasio; Ca: Calcio; Mg: Magnesio; Al: Aluminio; H+Al: Acidez potencial; SB: Suma de bases; T: Capacidad de intercambio catiónico; V: Saturación de bases; M: Saturación de Aluminio.

The experimental design was completely randomized, in a 4x5 factorial scheme, with four replications. The treatments combined four water qualities (well, river, weir, and deionized water) and five pesticide tank-mixings (3 associations, one with herbicide and an untreated control). All treatments are described in table 2 (page 135).

Table 2. Treatments combining water quality and pesticide tank-mixing.
Tabla 2. Tratamientos con las combinaciones de tipos de agua y productos fitosanitarios.

Treatment	Description
1	Deionized water
2	Deionized water with herbicide
3	Deionized water with tank-mixing1*
4	Deionized water with tank-mixing2*
5	Deionized water with tank-mixing 3*
6	Well water
7	Well water with herbicide
8	Well water with tank-mixing1
9	Well water with tank-mixing2
10	Well water with tank-mixing3
11	River water
12	River water with herbicide
13	River water with tank-mixing1
14	River water with tank-mixing2
15	River water with tank-mixing3
16	Weir water
17	Weir water with herbicide
18	Water weir with tank-mixing1
19	Water weir with tank-mixing2
20	Water weir with tank-mixing3

* Tank-mixing 1: herbicide + insecticide; tank-mixing 2: herbicide + fungicide; tank-mixing 3: herbicide + insecticide + fungicide.

* Mezcla de tanque1: herbicida + insecticida; mezcla 2: herbicida + fungicida; mezcla 3: herbicida + insecticida + fungicida.

Table 3 describes phytosanitary products used in spray syrups, formulation, dosage, and composition of active ingredients. These pesticides were selected for being the most used in the region.

Table3. Characterization of phytosanitary products.
Tabla 3. Caracterización de productos fitosanitarios.

Trade Name	Composition	Formulation	Function	Dosage (g a.i. ha^{-1})
FOX*	Trifloxystrobin + Prothioconazole	SC	Fungicide	70+60
Roundup*	Glyphosate isopropylamine salt; N-phosphonomethyl glycine	SL	Herbicide	925
CONNECT*	Imidacloprid + beta-cyfluthrin	SC	Insecticide	100+12.5

* AUREO: Soy methyl ester (Adjuvant), 0.25%vv; SL: soluble concentrate; SC: flowable suspension concentrate.

* AUREO: Éster de soja metilado (coadyuvante), 0.25%vv; SL: concentrado soluble; SC: suspensión concentrada.

The experiment was conducted in three sampling periods within a year. The first sampling corresponded to the off-season corn crop analyzed in April 2018. The second sampling was done during the pre-planting soybean weed control, while laboratory analyses were performed in September 2018. The third sampling corresponded to the soybean crop season, and the analyses were conducted in November 2018. All samples were analyzed on sampling date.

Three collecting sites were defined for water sampling, considering the spots where farmers usually obtain water from. These sites correspond to river water (22°26’3.45” S; 55°3’54.26” W), well water (22°27’8.79”S; 55°3’6.74” W), and weir water (22°29’8.42” S; 55°3’32.00” W). In addition, deionized water was used as a standard for comparison. Deionized water was produced by Outletlab equipment. The samples were put in 20 L thermoplastic boxes, labelled, immediately transported to the Physical-Chemical Laboratory, and stored in a refrigerated environment.

The following characteristics determined syrup quality: pH, electrical conductivity, turbidity, total dissolved solids, and total solids.

Water samples were separated into Beckers’s griffin cup type, with a 500 mL capacity. Half the volume (250 mL) was filled with water. Then, pesticides were added, and the container was completely filled with water, constituting the spraying syrup. The syrups were mixed and homogenized manually using a glass stick simulating the sprayer tank. After mixing, 4 repetitions were subdivided. Control treatments (without pesticide) and water types were put in scaled glass containers (beakers) and homogenized. Mineral oil was added only in fungicide treatments. Pesticides were added according to Abnt (2014).

Physical-chemical characteristics of spray syrups associated with phytosanitary products were determined using standard methods (5), while equipment was tested as described in table 4.

Table 4. Methods and equipment used in laboratory analyses.

Tabla 4. Métodos y equipos utilizados en los análisis de laboratorio.

Characteristic	Equipment	Method
Electrical conductivity	Metrohm 712 Conductometer	Electrometric
pH	Metrohm pH meter	Potentiometric
Total dissolved solids	Metrohm 712 Conductometer	Specific conductance
Turbidity	Instrutherm TD 200 Turbidimeters	Nephelometric
Total Solids	Drying chamber	Gravimetric

The physical-chemical data of spraying syrup were submitted to ANOVA, and the means were compared using the Tukey test, at 5% probability, Sisvar software (14).

RESULTS AND DISCUSSION

Significant interactions ($p<0.05$) were found between water qualities and product associations, regardless of sampling time. Total solids showed a significant influence of the tank-mixing multiple pesticides. Treatments with three classes of phytosanitary products (herbicide + insecticide + fungicide) presented the highest content of total solids, regardless of water quality throughout sampling times. The herbicide + fungicide and herbicide + insecticide + fungicide tank-mixing treatment also showed the highest concentration of solids in the off-season corn crop and with well water (table 5, page 137).

Table 5. Water quality and pesticides association for total solids (mg L^{-1}).
Tabla 5. Sólidos totales (mg L^{-1}) considerando las interacciones*entre los tipos de agua y la mezcla de plaguicidas.

Spraying syrup	Water type			
	Deionized	Well	River	Weir
Off-season corn crop$^{(1)}$				
Herbicide + insecticide + fungicide	25981 aA	24435 bA	25914 aA	26360 aA
Herbicide + fungicide	22080 cB	24776 baA	23802 bB	25310 aB
Herbicide + insecticide	21109 cB	22364 baB	21432 cbC	22807 aC
Herbicide	17544 cC	18408 bC	18515 bD	19928 aD
Non-defensive	2 bD	11 bD	58 bE	1380 aE
Pre-planting soybean weed control$^{(2)}$				
Herbicide + insecticide + fungicide	26300 bA	25638 bA	26322 bA	27401 aA
Herbicide + fungicide	21434 aB	19962 cC	20741 bC	21001 baC
Herbicide + insecticide	21215 bB	22070 aB	22198 aB	22366 aB
Herbicide	17544 cC	18408 bD	18515 bD	19928 aD
Non-defensive	2 aD	14 aE	64 aE	574 aE
Season soybean crop$^{(3)}$				
Herbicide + insecticide + fungicide	24012 bA	28652 aA	29124 aA	28604 aA
Herbicide + fungicide	21521 bB	23114 aB	23595 aC	21668 bB
Herbicide + insecticide	19960 dC	22971 bB	25798 aB	21715 cB
Herbicide	17036 cD	19969 bC	20658 baD	20852 aB
Non-defensive	2 bE	83 bD	112 bE	1483 aC

*F-test ($p<0.05$). Coefficient of variation = 2.88$^{(1)}$, 2.10$^{(2)}$ and 2.36$^{(3)}$%. Different lowercase letters in the row and uppercase letters in the column indicate statistical for Tukey test, $p \leq 0.05$.

*Prueba F ($p<0,05$). Coeficiente de variación = 2,88$^{(1)}$, 2,10$^{(2)}$y 2,36$^{(3)}$%. Diferentes letras minúsculas en la fila y mayúscula en la columna indican estadística para la prueba de Tukey, $p \leq 0,05$.

In this sense, product association in the sprayer tank increased total solids, regardless of sampling times and water quality (table 5). When phytosanitary products are mixed in the spray tank, physicochemical interactions given by unknown incompatibilities (two or more mixed chemicals suffer physical-chemical changes) may occur (37). This incompatibility can result in antagonistic effects and consequent reduced effectiveness of pesticides.

In control treatments, the highest total solids were found for weir water in the first and third seasons. However, no interaction was found between water qualities in the second sampling, probably given to absent rain (figure 1, page 134). Similarly, water uptake influenced total solids in the spray syrup, also aggravated by low precipitation during the period. In the second period, all treatments with deionized water presented the lowest values for this variable, statistically differing from the other sources. Regardless of the season, a tendency for increased solids was observed in weir water treatments.

In the driest period, dissolved solids from drag dam and river edges resulted in greater concentration (2) generating greater turbidity. In the wettest period, these solids tended to be in lower concentrations. According to Farias *et al.* (2014), open-air sources, such as rivers and dams, are affected by rainwater and winds, carrying sediments such as clays. However, unlike weirs, rivers do not present still water, and thus, higher loading and dissolution of sediments reduced this water´s total solids values (37).

Solids in the syrup can inactivate glyphosate (20), which is adsorbed onto clay, reducing plant absorption and efficacy (24). Ramos and Durigan (1998) evaluated weir water influence on post-emergent herbicide efficacy. They found that solutions formulated with up to 10 g L^{-1} of soil from the Jaboticabal region containing 56% clay did not interfere with glyphosate efficacy. Brazilian soils are composed of low-activity clay, such as kaolinite.

This means that cloudy water composition also impacts pesticide effectiveness. In tropical regions, such as the one in the present study, a higher concentration of organic matter (OM) in water, with greater effective cation exchange capacity, may result in greater adsorption of pesticides by OM than by clay minerals.

Analysis of total dissolved solids (table 6) showed a precipitating tendency of products with the herbicide treatment, while the treatments with the association of three phytosanitary products (herbicide + insecticide + fungicide) showed lower dissolved solids between mixtures, regardless of water quality and sampling times analyzed, excepting well water at the off-season corn sampling. These results indicate that when different phytosanitary products are associated, a higher content of solids in the sprayer tank may cause clogging of nozzles and filters.

Table 6. Water types and products association for total dissolved solids (mg L^{-1}).
Tabla 6. Sólidos disueltos totales (mg L^{-1}) considerando las interacciones* entre los tipos de agua y la mezcla de plaguicidas.

Spraying syrup	Water type			
	Deionized	Well	River	Weir
Off-season corn(1)				
Herbicide + insecticide + fungicide	6613 cC	6791 bB	6740 bD	7073 aA
Herbicide + fungicide	6874 cbB	6986 aA	6829 cC	6918 bB
Herbicide + insecticide	6644 bC	6958 aA	6986 aB	6969 aB
Herbicide	6955 bA	6981 bA	7090 aA	7085 aA
Non-defensive	2,8 aD	27,0 aC	24,2 aE	12,2 aC
Pre-planting soybean weed control(2)				
Herbicide + insecticide + fungicide	6542 cB	8712 bC	9151 aB	9174 aB
Herbicide + fungicide	6603 cBA	9083 bB	9038 bB	9362 aB
Herbicide + insecticide	6628 cBA	9144 bBA	9078 bB	9266 aB
Herbicide	6758 cA	9283 bA	9347 bA	9687 aA
Non-defensive	3 aC	21 aD	38 aC	26 aC
Season soybean crop(3)				
Herbicide + insecticide + fungicide	6618 bC	6623 bD	6621 bB	6900 aC
Herbicide + fungicide	6702 bCB	7007 aB	6658 bBA	6971 aCB
Herbicide + insecticide	6733 bB	6735 bC	6601 cB	7030 aB
Herbicide	6908 bA	7227 aA	6763 cA	7217 aA
Non-defensive	4 aD	29 aE	49 aC	33 aD

*F-test ($p<0.05$). Coefficient of variation = 0.56(1), 1.44(2) and 1.02(3)%. Different lowercase letters in the row and uppercase letters in the column indicate statistical for Tukey test, $p \leq 0.05$.

*Prueba F ($p<0,05$). Coeficiente de variación = 0,56(1), 1,44(2) y 1.02(3)%. Diferentes letras minúsculas en la fila y mayúscula en la columna indican estadística para la prueba de Tukey, $p \leq 0,05$.

Petter *et al.* (2012) and Pazini *et al.* (2013), evaluating association compatibility of different classes of phytosanitary products, concluded that depending on the added products, the association of more than one type of pesticide can cause physical incompatibility and low dissolution in the spray tank. According to these authors, this incompatibility is due to the type of formulation of phytosanitary products.

The concentrated suspension (SC) formulation is not always stable, and in resting syrup, solid particles can settle (19, 37). When associating phytosanitary products with the same kind of formulation, there is hardly any incompatibility in the syrup. However, this rarely happens in the field. The treatment without any association (herbicide only) showed higher total dissolved solids, due to the high solubility of glyphosate in water (15,700 mg L^{-1} at 25°C and pH 7 - acid) (31), justifying the higher dissolved solid concentration in syrup.

Mean total dissolved solids obtained in the non-defensive treatments were similar between water qualities in the three sampling times (table 6, page 138). Besides, dissolved solids alter water appearance, as turbidity (29). Both insecticide and fungicide increased spray syrup turbidity (table 7).

Table 7. Water types and association of products for syrup turbidity.
Tabla 7. Turbidez del caldo de pulverización considerando las interacciones* entre los tipos de agua y la mezcla de plaguicidas.

Spraying syrup	Water type			
	Deionized	**Well**	**River**	**Weir**
Off-season corn crop(1)				
Herbicide + insecticide + fungicide	5163 dA	8177 cA	8540 bA	9401 aA
Herbicide + fungicide	4597 dB	6847 cB	8052 bB	9073 aB
Herbicide + insecticide	1811 bC	1369 dC	1767 cC	2460 aC
Herbicide	1 bD	6 bD	26 bD	281 aD
Non-defensive	1 bD	6 bD	18 bD	211 aE
Pre-planting soybean weed control(2)				
Herbicide + insecticide + fungicide	5728 aA	3229 bA	3284 bA	5714 aA
Herbicide + fungicide	3490 aB	1885 cB	2444 bB	3606 aB
Herbicide + insecticide	2425 aC	1542 cC	1711 bC	2517 aC
Herbicide	8 bD	2 bD	25 bD	575 aD
Non-defensive	3 bD	1 bD	17 bD	354 aE
Season soybean crop(3)				
Herbicide + insecticide + fungicide	8642 dA	9411 cA	10581 bA	10896 aA
Herbicide + fungicide	4338 dB	4942 cB	8614 bB	9098 aB
Herbicide + insecticide	3389 aC	3460 aC	3509 aC	3539 aC
Herbicide	11 bD	24 bD	37 bD	654 aD
Non-defensive	4 bD	13 bD	28 bD	549 aD

*F-test ($p<0.05$). Coefficient of variation = 0.45(1), 3.81(2) and 2.85(3)%. Different lowercase letters in the row and uppercase letters in the column indicate statistical for Tukey test, $p \leq 0.05$.

*Prueba F (p<0,05). Coeficiente de variación = 0,45(1), 3,81(2) y 2,85(3)%. Diferentes letras minúsculas en la fila y mayúscula en la columna indican estadística para la prueba de Tukey, p ≤ 0,05.

Spray syrups made with weir water, including those treatments without pesticides, were the ones with the highest turbidity values, regardless of product association. As already mentioned, water quality for agricultural spraying is closely related to spray physical quality considered as suspended sediment content. When analyzing waters without pesticides in all sampling periods, higher concentrations of dissolved solids were observed in weir water, representing a greater potential for interaction with pesticides, and consequent less effectiveness.

Treatments with only herbicide did not differ from the treatments without pesticides (water only) regarding turbidity, except for the herbicide treatment with weir water in the first and second sampling times. Considering turbidity may be influenced by product formulation, soluble formulations such as glyphosate, highly soluble in water (4), generate lower turbidity. In contrast, concentrated suspension formulation (fungicide and insecticide) with a milky appearance, increase syrup turbidity (photo, page 140).

When observing mixtures of the herbicide lactofen (Drible® 240 - formulation CE - *emulsifiable concentrate*) with the insecticides Methomy Chlorpyrifos, Cypermethrin, Thiamethoxam/Lambdacialotrine, Teflubenzuron, and Triflumurom, Petter *et al.* (2012) found physical incompatibility in syrups prepared with water, water with pylyrolean acid and water with boric acid. This incompatibility varied between grade 2 (separation after 1 minute, not to be applied) and grade 4 (separation after 10 minutes, apply on continuous agitation), resulting in non-homogeneous mixing, with a decanting tendency. Before, Petter *et al.* (2007) had observed physical-chemical interaction caused by CE with Chlorpyrifos SC (flowable suspension concentrate). According to Theisen and Ruedell (2004), most physical and chemical incompatibilities are observed in mixtures of products with CE formulations and WP (Wettable Powders), EW (emulsion in water) and SC.

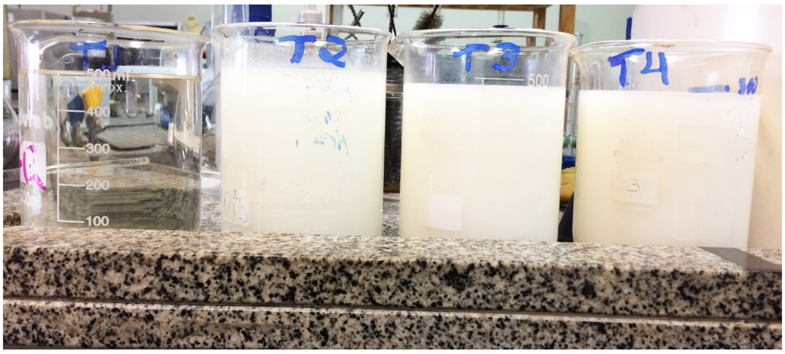

Photo. Turbidimetry of the phytosanitary products in deionized water. T1: Herbicide; T2: Herbicide + Insecticide; T3: Herbicide + Fungicide; T4: Herbicide + Insecticide + Fungicide.

Foto. Turbidimetría de los productos fitosanitarios en agua desionizada. T1: Herbicida; T2: Herbicida + Insecticida; T3: Herbicida + Fungicida; T4: Herbicida + Insecticida + Fungicida.

In this study, product association altered spraying syrup pH (table 8). This variation was lower in the soybean pre-planting weed control sampling. Treatments with phytosanitary products did not differ from each other, except for well water. However, no abrupt change between any treatments occurred, nor did they present alkaline pH (pH> 7), which according to Vuković *et al.* (2013), causes syrup instability for acidic products.

Table 8. Water types and products association for pH of spraying syrup.
Tabla 8. pH del caldo de pulverización considerando las interacciones* entre los tipos de agua y la mezcla de plaguicidas.

Spraying syrup	Water type			
	Deionized	Well	River	Weir
Off-season corn crop$^{(1)}$				
Herbicide + insecticide + fungicide	6.17 cA	6.40 bBA	6.37 bC	6.67 aA
Herbicide + fungicide	6.05 cBA	6.32 bBA	6.55 aB	6.47 aB
Herbicide + insecticide	5.98 cB	6.27 bB	6.52 aB	6.47 aB
Herbicide	6.10 cBA	6.42 bA	6.57 aB	6.45 bB
Non-defensive	6.02 cB	5.65 dC	7.00 aA	6.47 bB
Pre-planting soybean weed control$^{(2)}$				
Herbicide + insecticide + fungicide	6.05 aA	4.67 bB	4.85 bA	4.75 bA
Herbicide + fungicide	6.05 aA	4.80 bBA	4.82 bA	4.72 bA
Herbicide + insecticide	5.97 aA	4.95 bBA	4.87 bA	4.82 bA
Herbicide	6.22 aA	5.05 bA	4.80 bA	4.77 bA
Non-defensive	6.12 aA	4.62 bB	4.77 bA	4.65 bA
Season soybean crop$^{(3)}$				
Herbicide + insecticide + fungicide	6.27 aA	5.65 bA	5.60 bB	5.67 bA
Herbicide + fungicide	6.07 aA	5.65 bA	5.55 bB	5.60 bA
Herbicide + insecticide	6.07 aA	5.55 bBA	5.75 bBA	5.57 bA
Herbicide	6.17 aA	5.80 bA	5.67 bBA	5.75 bA
Non-defensive (control)	6.05 aA	5.25 cB	5.95 baA	5.72 bA

*F-test ($p<0.05$). Coefficient of variation = 1.03$^{(1)}$, 3.34$^{(2)}$ and 2.82$^{(3)}$%. Different lowercase letters in the row and uppercase letters in the column indicate statistical for Tukey test, $p \le 0.05$.

*Prueba F ($p<0,05$). Coeficiente devariación=1,03$^{(1)}$,3,34$^{(2)}$ y 2,82$^{(3)}$ %. Diferentes letras minúsculas en la fila y mayúscula en la columna indican estadística para la prueba de Tukey, $p \le 0,05$.

During pre-plating soybean weed control and soybean crop, no statistical difference between treatments was observed for deionized and well water, *i.e.*, product addition did not influence spray pH (table 8, page 140). Deionized water is pure water that has undergone a process of filtration and total removal of ions like nitrate, Calcium, and Magnesium, among other elements (32). This is considered ideal for spray syrup water, precisely for keeping water quality indicators, such as pH (19). On the other hand, the non-influence of weir water on pH is related to a higher concentration of suspended particles than ions, thus affecting attributes like dissolved solids and solids before affecting pH. For well water, during the three sampling times, an increase in pH was observed after the addition of phytosanitary products, except for the association between herbicide + insecticide + fungicide, in the soybean pre-planting weed control sampling, the driest period. Another relevant fact is that, regardless of sampling time, when glyphosate was added to well water, the highest pH increase was observed. Typically, well waters have high ion concentrations, especially: Ca^{2+}, Mg^{2+}, Na^+, $K^{+,}$ HCO_3^-, $CaSO_4^{2-}$.

Well waters are often classified as hard waters, with high $CaCO_3$ concentrations. Variations in average hardness are related to soil geological nature. Due to high $CaCO_3$ concentration, well water usually reports alkaline pH (7, 36, 39). The use of this hard water may cause ion chelation by glyphosate (34), decreasing efficiency. In addition, given well water alkalinity and glyphosate acid nature, this herbicide is dissociated, losing efficiency (30). Additionally, after mixing phytosanitary products, the resulting syrup may present different pH values. In general, association incompatibility occurs with high syrup pH alteration, leading to degradation of active ingredients and consequent undesirable chemical compounds (37).

Water pH IS The main parameter influencing spray syrup compatibility (11). Ideal pH for plant protection varies among products (37). Pyrethroids insecticides have a pH efficiency of around 4. Carvalho *et al.* (2009) report syrup pH ranging from 4.6 to 5 for glyphosate, while Schilder (2008) mentions 5 to 6. Cunha *et al.* (2017) observed that the combination of Trifloxystrobin + Prothioconazole had pH 7, while with the adjuvant soy methyl ester, achieved pH 5. Most phytosanitary products, in the presence of alkaline pH (>7), decompose rapidly causing in-tank associations instability (17).

Syrup mean electrical conductivities (EC) differed among all treatments (table 9, page 142). Glyphosate highly influenced spray syrup EC. The more acidic the water, the greater the electrical conductivity measured in the syrup after glyphosate addition. According to Amarante Júnior *et al.* (2002), glyphosate is a strong acid with a pH between 2.2 and 5.4, with two dissociations, and a pH 5.5 with three dissociations and an increasing EC.

Evaluating surface tension, pH, and EC of phytosanitary syrup, Cunha *et al.* (2017) demonstrated that glyphosate presented the highest conductivity among tested products using deionized water, evidencing that water addition influences spray syrup EC. In this study, glyphosate EC increased at pH above 6.3. Similarly, with the tank-mixing multiple pesticides, a decrease in syrup EC was observed when compared with the treatment without association, proving that tank-mixing causes chemical interaction between the products (39). Thus, decreasing EC was measured in the three sampling times and with distinct pH ranges between seasons.

Regarding non-defensive treatments, no difference was found between water qualities at any time of analysis. These results differed from those found by Rheinheimer and Souza (2000) and Farias *et al.* (2014) when verifying low EC values in weir water and higher in well water.

Electrical conductivity represents the solution ion concentration that can conduct electricity. Higher conductivity values express higher number of ions in the solution. Thus, the greater the possibility of these ions interacting with agrochemical molecules, the greater the incompatibility of the syrup (8). However, there is no default value for EC, as this characteristic depends on the application volume. According to Vargas *et al.* (1997), smaller application volumes cause less EC influence on herbicides. *i.e.*, decreasing ion proportion concerning pesticide molecules. Considering the same concentration, using an application rate of 1.0 L ha^{-1}, allows lower ion interference (EC) than an application using 30 L ha^{-1} (6).

In this context, this study showed a tendency to increase product dissolution in the spray syrup for no products association and when using high quality water, such as deionized water.

Table 9. Water types and products association for electrical conductivity (µS cm^{-1}).
Tabla 9. Conductividad eléctrica (µS cm^{-1}) considerando las interacciones* entre los tipos de agua y la mezcla de plaguicidas.

Spraying syrup	Water type			
	Deionized	**Well**	**River**	**Weir**
Off-season corn crop$^{(1)}$				
Herbicide + insecticide + fungicide	10020 cB	13200 bC	13865 aB	13900 aB
Herbicide + fungicide	10415 cbA	13762 bB	13695 bB	14185 aB
Herbicide + insecticide	10067 bB	13855 baBA	13755 bB	14040 aB
Herbicide	10537 cA	14065 bA	14162 bA	14677 aA
Non-defensive	4 aC	32 aD	58 aC	40 aC
Pre-planting soybean weed control$^{(2)}$				
Herbicide + insecticide + fungicide	9912 cC	10290 bB	10212 bD	10717 aA
Herbicide + fungicide	10005 cCB	10585 aA	10347 bC	10482 aB
Herbicide + insecticide	10042 cB	10542 aA	10585 aB	10560 aB
Herbicide	10240 cA	10577 bA	10742 aA	10735 aA
Non-defensive	4 aD	41 aC	36 aE	18 aC
Season soybean crop$^{(3)}$				
Herbicide + insecticide + fungicide	10027 bC	10035 bD	10032 bB	10455 aC
Herbicide + fungicide	10155 bCB	10617 aB	10087 bBA	10562 aCB
Herbicide + insecticide	10202 bB	10205 bC	10002 cB	10652 aB
Herbicide	10467 bA	10950 aA	10247 cA	10935 aA
Non-defensive	5 aD	43 aE	74 aC	50 aD

* F-test ($p<0.05$). Coefficient of variation = 1.38$^{(1)}$, 0.76$^{(2)}$ and 1,02$^{(3)}$%. Different lowercase letters in the row and uppercase letters in the column indicate statistical for Tukey test, $p \leq 0.05$.

*Prueba F ($p<0,05$). Coeficiente de variación = 1,38$^{(1)}$, 0,76$^{(2)}$ y 1,02$^{(3)}$%. Diferentes letras minúsculas en la fila y mayúscula en la columna indican estadística para la prueba de Tukey, $p \leq 0,05$.

Phytosanitary product solubility is measured as solubility in water, variable among active ingredients. Glyphosate had the highest water solubility among tested active ingredients by Soares *et al.* (2017). For this reason, correct syrup preparation and association of phytosanitary products in the spray tank, are important (19). However, even following preparation order, treatments associated with tank-mixing multiple pesticides presented worse physical-chemical quality.

CONCLUSIONS

Water from different sources and tank-mixing multiple pesticides affect spraying syrup quality. Weir water presents the worst physical quality among the tested sources. It may decrease pesticide performance.

Spraying syrup prepared with tank-mixing herbicide, insecticide, and fungicide in various combinations increased in the successive cultivation of soybean/corn in the studied area. When the three pesticides are associated, less dissolution of the spray syrup and a greater risk of syrup incompatibility takes place, rising fungicide ineffectiveness.

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