Plant Archives Vol. 20, Supplement 2, 2020 pp. 4046-4050 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

DETECTION OF CLODINAFOP PROPARGYL AND TRIBENURON METHYL RESIDUES IN GRDARASHA AND MAMA JALKA SOILS AT ERBIL PROVINCE, IRAQ

Ismail A. Said[1, 2*] and Dara M.A. Jaff[3]

[1] Plant Production Department, Khabat Technical Institute, Erbil Polytechnic University, Erbil, Iraq
[2] Field Crops Department, College of Agriculture, Salahaddin University, Erbil, Iraq
[3] Biology Department, College of Education, Salahaddin University, Erbil, Iraq.
*Corresponding author: ismail.said@epu.edu.iq

Abstract

Herbicides residue after application is regarded as serious subject in soil pollution and causes damage to the next crops particularly at high doses. Study on the remaining of the herbicides residue is crucially requiring for the environmental consideration and preventive crops damage. After harvest, soil samples are collected in Grdarasha and Mama Jalka soils which previously sprayed by both herbicides at 25% plus recommended dose. The extraction of the soil samples was analyzed by HPLC to detect any residue of either herbicide. The results indicated that all samples are not contained any residue of the level of active ingredients applied. This means of insurance in the fate of any application herbicides is necessary to prevent the next crops damage.

Keywords : Herbicides, Environment, Contamination, Weeds.

Introduction

Environment preservation is one of the aims of the sustainable development. With the modernization of agriculture in the 60's, an enormous use of agrochemicals started and aimed to enhance the crops productivity (Ahmed *et al*., 2017). Herbicides, which are the main element of agrochemicals, have markedly functioned to reduce weeds problem in crop fields; despite of many benefits, its residues after application can contaminate soil, and in crop rotations it might cause damage to sensitive crops (Noshadi *et al*., 2017). The residue can be due to application more rate than recommended or because of indiscriminate use and improper calibration and method of application, there is possibility of residual hazards in soil (Arora *et al*., 2013). So, the fate of such agrochemicals after application has been considered a source of major apprehension (Soliman and Hamza, 2015). However, eventual fate of herbicide in soil relies on number of processes such as volatilization, leaching, runoff and degradation by microbes, chemical processes as well as photodecomposition (Sondhia, 2014). The purpose of this thesis is to determine the residue in soil of most common used herbicides by the farmers in Kurdistan Region-Iraq, which are Clodinafop propargyl and Tribenuron methyl (TBM).

Materials and Methods

Soil Sampling

Soils were sampled at two locations Grdarasha and Mama Jalka where semi-arid and humid regions respectively. The samples were collected in experiment plots previously treated with Clodinafop propargyl and Tribenuron methyl herbicides at %25 plus recommended rate from a depth of 0-30 cm. The soil samples were crushed, ground and sieved through 2mm mesh (Tadeo, 2019).

Table 1: Physical parameters of the study area.

Months	Grdarasha			Mama Jalka		
	Average Air Temperature (^oC)	Average Soil Temperature (^oC) / 10 cm	Rainfall (mm)	Average Air Temperature (^oC)	Average Soil Temperature (^oC) / 10 cm	Rainfall (mm)
January	8.2	8.0	21.1	5.5	3.0	45.0
February	8.1	7.6	6.4	5.5	3.4	40.5
March	13.9	11.8	19.1	10.3	8.0	160.5
April	19.2	16.6	31.7	16.0	14.3	87.5
May	26.6	25.5	3.4	22.7	22.9	25.5
June	31.6	30.7	-	28.8	31.6	-

Table 2 : Some physical and chemical properties of the studied soil (0-30cm)

Locations	Particle Size Distribution			Texture type	pH	EC dSm^{-1}	O.M %	N %	P (ppm)	K (ppm)
	Sand %	Silt %	Clay %							
Grdarasha	15.4	41.6	43	Silty Clay	7.36	0.19	1.33	0.23	1.40	3.4
Mama Jalka	45.71	46.75	7.54	Silty Clay	7.65	0.35	2.06	0.33	3.286	4.00

Residues Extraction

1. The residue of Clodinafon propargyl was extracted according to Sondhia and Mishra (2005) procedure with minor alteration. Twenty g representative soil sample was taken in 250 ml conical flask, and 2 drops of ammonia were added; then mixed properly and kept at room temperature. After 1 h, 100 ml of ethyl acetate was added and extracted twice by shaking on a horizontal shaker for 30 min and filtered through Buchner funnel using water pump. The combined extracts were monitored by oven at 37 ^{o}C to about 2 ml. The residue was dissolved in 50 ml of0.1 N KOH (aqueous) and the contents of the flasks were heated at 60°C on a water bath for half an hour. After cooling, the mixture was neutralized (pH 7) by addition of dilute (I N) HCI. The neutralized mixture was diluted with water (100 ml) and transferred to a 250 ml separatory funnel. The aqueous solution was partitioned with ethyl acetate (3 x 50 ml), and the organic layer was dried on anhydrous Na2SO4; then the solvent was evaporated to dryness by oven at 37 ^{o}C. Final residue was dissolved in acetonitrile (1 ml) for HPLC analysis.
2. Wang *et al*. (2017) method was followed to find residues of Tribenuron methyl. Two gm of every sample was weighed into 10 ml tube and 10 ml of acetone added. The mixture was shaken at high speed for two minutes, and then 1000 mg of Na_2SO_4 was added and shaken for another 2 minutes. The samples were centrifuged at 4000 rpm for 10 minutes, and three ml of the supernatant to 10 ml tube containing 30 mg PSA, 1000 $NaSO_4$ and 200 mg NaCl; then they were shaken for 1 minute and centrifuged for 10 minutes at 4000 rpm. Finally, the samples were filtered and 1 ml of the extract taken for analyzing.

Analytical Technique

The samples were analyzed to find the herbicides residue at Research Center of Zakho University by PerkinElmer Flexar HPLC. The HPLC analytical column was C18 column (4.6 × 300 mm × 5 μm particle size). A 0.1% formic acid in ultrapure water was used as a mobile phase (A) and acetonitrile was used as a mobile phase (B). Separation was performed at a flow rate of 1.0 mL min−1 at 35 °C, a diode array detector in 235 nm. The injection volume was 30 μL. The gradient elution procedure was as follows: 67% B (0–9 min), 67%–75% B (9–10 min), and 75% B (10–18 min).

Results and Discussion

Herbicide residues is regarded a serious fact in crop production which can potentially injure sensitive crops in rotation (Su *et al*. 2017). The chromatograph results show that all samples did not contain any residue of the herbicides (Figure 1&2 B-C), and the data are illustrated in Table-3.

Clodinafop propargyl residue

The residual of clodinafop propargyl was not detected in soil samples at both locations for both varieties after 150 days of the herbicide application, when the soil samples of plus 25% (100g/ha) treatments were analyzed by HPLC technique (Table-3). According to Sondhia and Mishra (2005) results of their work, the residual of this active ingredient was not found after 95 days of spraying; when 240 g/ha of the herbicide was applied. In addition, the results of this study is approximately better to Soliman and Hamza (2015) work, as they concluded that roughly 97% of the clodinafop propargyl was lost by 159 days after application the herbicide. Mir *et al*. (2014) affirm that this chemical is degraded quickly in soil. The breakdown process is occurred by degradation the clodinafop praprgyl to acid derivative-clodinafop as a major metabolite, and it has been found that different concentrations 30, 60 and 120 g/ha of this acid were similar in degradation rates; as all doses were dissipated by 30% and 80% after 5 and 7 days in soil (Sharma *et al*., 2016).

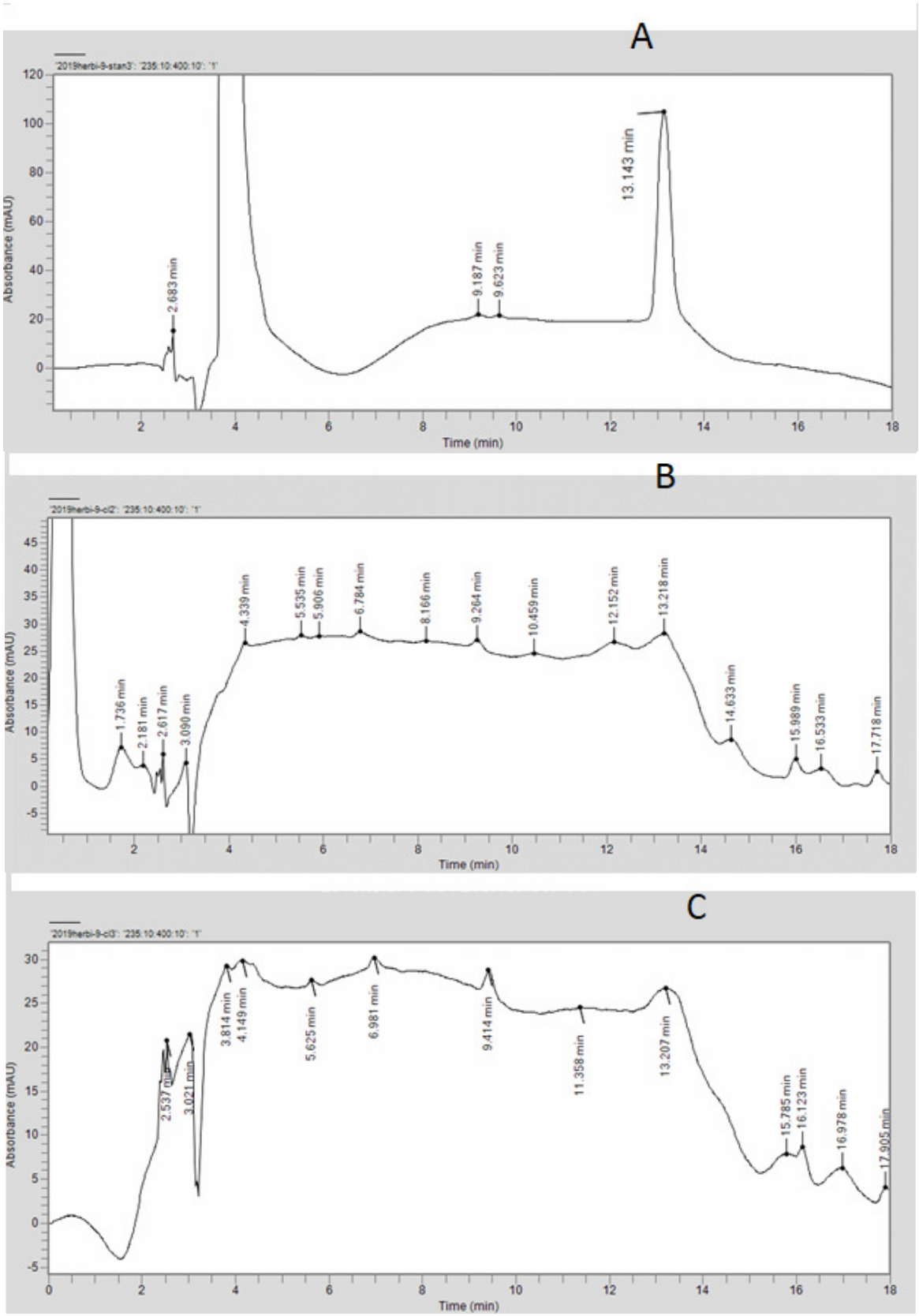

Fig. 1 : Chromatogram of Clodinafop-propargyl standard (A), Colidnafop-propargyl in Simeto plot at Grdarasha (B), Colidnafop-propargyl in Simeto plot at Mama Jalka (C).

Tribenuron methyl residue:

The results of this work found that the residue of this herbicide was not detected in the soil extract of G+25 samples at both locations for Aras and Simeto after 150 days of spray application (Table-3), as the active ingredient is faster degraded than other herbicide according to Wang *et al*. (2017). The result of this work is approximately similar to Soliman and Hamza (2015) study who found that the Tribenuron methyl dosage was lost about 98.67% of its concentration in the soil after 159 days of application. Cessna *et al*. (2017) confirm that the half-life of this active ingredient about 2-10 days; is contrasting Smith (2013) determination who stated that most sulfonylurea herbicides including tribenuron methyl can remain in the soil under field condition for more than one crop year. Furthermore, the fast degradation of the herbicide is possibly due to the predominant hydrolysis reaction of cleavage of the sulfonylurea bridge, as the hydrolysis proceeds through the attack of the neutral bridge carbonyl carbon by water; then releasing carbon dioxide and the herbicidal-inactive

sulfonamide and heterocyclic amine, and they may sometimes undergo further hydrolytic degradation (Sarmah and Sabadie, 2002). On the other hand, rapid increasing of temperatures at both locations after the herbicide application might be a reason to degrade the active ingredient in the soil (Table-2 Climate Condition). Cessna *et al.* (2017) emphasized this conception. The researchers found that rising temperature to 20 ^{o}C resulted more the degradation of tribenuron methyl concentration faster to minimal rate.

Table 3 : Residue results of Clodinafop propargyl and Tribenuron methyl at Grdrasha and Mama Jalka

Treatments	Residues (ppm)	
	Grdarasha	Mama Jalka
Aras Cloditop+25	ND	ND
Aras Granstar+25	ND	ND
Simeto Cloditop+25	ND	ND
Simeto Granstar+25	ND	ND

Note: ND= not detected.

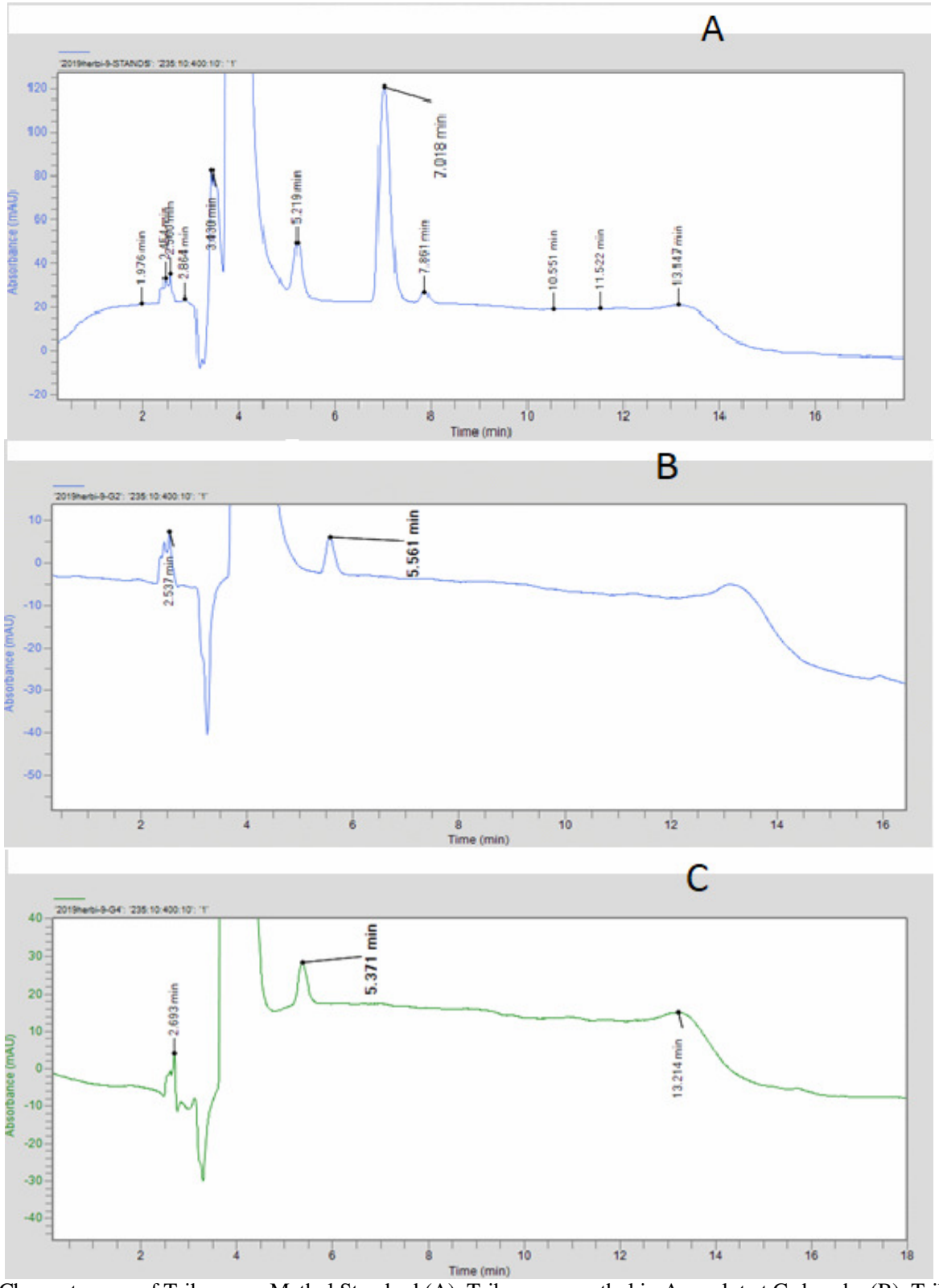

Fig. 2 : Chromatogram of Tribenuron Methyl Standard (A), Tribenuron methyl in Aras plot at Grdarasha (B), Tribenuron methyl in Aras plot at Mama Jalka (C).

Conclusion

Chemical weed control is considered an effective mean to suppress weeds then to increase crops yield; however, applying agrochemical mistakenly, high doses and incorrect time application can affect negatively the environment particularly their residual in soils. So, it is crucially important to confirm the safety uses of herbicides. Furthermore, both herbicides were rapidly degraded in soils at both locations, the residue data analysis reflects the safety of the active ingredients particularly for the next crop growing.

References

Ahmed, I.; Mohammed, O.; Bahgat, M. and Montaser, H. (2017) Biodegradation of Cladinafop Propargyl by *Bacillus sp*. and *Bacillus cereus* Isolated from Field Crop. Am. J. Sci., 13: 72-78.

Arora, A.; Tomar, S.S. and Sondhia, S. (2013). Efficacy of Herbicides on Wheat and their Terminal Residues in Soil, Grain and Straw. Indian J. Weed Sci., 45:109-112.

Cessna, A.J.; Knight, J.D.; Ngombe, D. and Wolf, T.M. (2017). Effect of temperature on the dissipation of seven herbicides in a biobed matrix. Can. J. Soil Sci., 97: 717-731.

Mir, N.A.; Khan, A.; Muneer, M. and Vijayalakhsmi, S. (2014). Photocatalytic Degradation of Trifluralin, Clodinafop-Propargyl and 1,2-Dichloro-4-Nitrobenzene As Determined by Gas Chromatography Coupled with Mass Spectrometry. Chromatogr. Res. Int., 1-9.

Noshadi, M.; Foroutani, A. and Sepaskhah, A. (2017) Analysis of Clodinafop-propargyl Herbicide Transport in Soil Profile under Vetiver Cultivation using HYDRUS-1D and Modified PRZM-3 Models. Toxicology 3: 1-11.

Sarmah, A.K. and Sabadie, J. (2002) Hydrolysis of Sulfonylurea Herbicides in Soils and Aqueous Solutions: A Review. J. Agric. Food Chem., 50: 6253-6265.

Sharma, N.; Sharma, E.; Thakur, N.; Gulati, A.; Joshi, R. and Sharma, V. (2016). Persistence of clodinafop propargyl and its metabolite in soil and wheat crop under north western Himalayan Region. Asian J. Chem. 28: 1493-1497.

Soliman, I.S. and Hamza, A.M. (2015). Effect of Some Herbicides on Wheat Characters and associated Weeds with Respect to Its Residues. Egyptian J. Plant Prot. Res., 3: 29-47.

Sondhia, S. and Mishra, J.S. (2005). Determination of Terminal Residue of Clodinafop propargyl in Soil, Wheat Grains and Straw. Indian J. Weed Sci., 37: 296-297.

Sondhia, S. (2014). Herbicides Residues in Soil, Water, Plants and non-Targeted Organisms and Human Health Implications: An Indian Perspective. Indian J. Weed Sci., 46: 66-85.

Smith, A.E. (2013). A Review of Analytical Methods for Sulfonylurea Herbicides in Soil. Int. J. Environ. Anal. Chem., 59: 97-106.

Su, W.C.; Sun, L.L.; Ge, Y.H.; Wu, R.H.; Xu, H.L. and Lu, C.T. (2017). The Residual Effects of Bensulfuron-Methyl on Growth and Photosynthesis of Soybean and Peanut. Photosynthetica, 55: 1-8.

Tadeo, J.L. (2019). Analysis of Pesticides in Food and Environmental Samples, Boca Raton, Florida, Unites States of America, Taylor and Francis, 43.

Wang, F.; Wang, Z.; Zhang, B. and Zhang, Q. (2017). Degradation and adsorption of tebuconazole and tribenuron-methyl in wheat soil, alone and in combination. Chil. J. Agr. Res., 77: 281-286.