

# Correlation between 2,4-D herbicide residues and soil attributes in southern of Brazil<sup>1</sup>

## Correlação espacial do residual do herbicida 2,4-D com atributos do solo

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**ABSTRACT** - The 2,4-D herbicide is widely used in Brazilian and global agriculture to control weeds. It is potentially toxic to mankind, and one of the herbicides final destinations is the soil. The aim of the study was to determine the spatial correlation of 2,4-D herbicide in soil attributes after 12 months of application. The experiment was conducted in an agricultural area of 5.04 ha in the municipality of Nova Santa Rosa/PR, in 2011 and 2012. Two soil samples collections were performed: collection 1 (09/03/2011) and collection 2 (08/25/2012), both of which were made 12 months after 2,4-D application. The herbicide was applied in a single dose of 1.5 L ha<sup>-1</sup> in 09/2010 and in two doses in 09/2011 (1.0 L ha<sup>-1</sup> or 1.5 L ha<sup>-1</sup> 2,4-D). The correlation between soil attributes and 2,4-D was determined with the use of a spatial correlation matrix. The 2,4-D soil residues varied widely from one location to another in the same area, with points of no detection of the active ingredient. It was not possible to detect differences between 1.0 L ha<sup>-1</sup> and 1.5 L ha<sup>-1</sup> 2,4-D treatments. Several factors may have interfered in the herbicide residues in the soil, including: climate, product characteristics, physical and chemical soil characteristics, soil management, among others. The spatial correlation of the soil attributes and 2,4-D residues in the soil proved to be an important tool to verify one parameter interference over another.

**Key words:** Agrochemicals. Weeds. Spatial distribution.

**RESUMO** - O herbicida 2,4-D é amplamente utilizado na agricultura brasileira e mundial para o controle de plantas espontâneas, sendo potencialmente tóxico ao homem e um dos destinos finais dos herbicidas é o solo. O objetivo do trabalho foi determinar a correlação espacial do herbicida 2,4-D com os atributos do solo após 12 meses de aplicação. O experimento foi desenvolvido em área agrícola de 5,04 ha, do município de Nova Santa Rosa/PR, nos anos de 2011 e 2012. Duas coletas de solo foram realizadas: coleta 1 (03/09/2011) e coleta 2 (25/08/2012), sendo que ambas foram feitas após 12 meses da aplicação de 2,4-D. O herbicida foi aplicado em dose única de 1,5 L ha<sup>-1</sup> em 09/2010 e em duas dosagens em 09/2011 (1,0 L ha<sup>-1</sup> e 1,5 L ha<sup>-1</sup> de 2,4-D). A correlação entre os atributos do solo e o 2,4-D foi determinada com a utilização de matriz de correlação espacial. O residual de 2,4-D no solo variou muito de um local para outro na mesma área, apresentando pontos sem detecção do ingrediente ativo. Não foi possível detectar diferenças entre os tratamentos 1,0 L ha<sup>-1</sup> e 1,5 L ha<sup>-1</sup> de 2,4-D. Diversos fatores podem ter interferido no residual do herbicida no solo, entre eles: o clima, características do produto, características físico-químicas do solo, manejo do solo, entre outros. A correlação espacial dos atributos do solo e do residual de 2,4-D no solo mostrou-se ser uma importante ferramenta para verificar a interferência de um parâmetro sobre o outro.

**Palavras-chave:** Agrotóxico. Plantas espontâneas. Distribuição espacial.

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## INTRODUCTION

Concern about effects caused by agrochemicals on the environment has increased due to its intensive use in agricultural areas (RIBEIRO *et al.*, 2013). In addition, the method of soil tillage can have considerable influence on soil erosion, rain infiltration, runoff and leaching. Associated with this movement of soil and water are agrochemicals, either bound to soil particles or in a soluble form. The contamination of surface waters with silt, pesticides and nutrients have been frequently found to damage these ecosystems (HOLLAND, 2004; URI; ATWOOD; SANABRIA, 1998). Among widely used agrochemicals, herbicides can be mentioned as being one of the most used methods to control weeds.

The 2,4-D (2,4-dichlorophenoxyacetic acid) is one of the widely used herbicide to control broadleaf weed in the Brazilian and world agriculture, which is potentially toxic to humans (BOIVIN *et al.*, 2005), thus it is important to know your behavior in the environment because it has the ground as one of the final destinations.

“The distribution and degradation of herbicides in the soil are dynamic and unique processes for each herbicide-soil relation” (ROCHA *et al.*, 2013). In studies performed by several authors, different 2,4-D herbicide half-life periods were verified in soils, which can remain for days up to months (SILVA; VIVIAN; D’ANTONINO, 2009). For example, 2,4-D + picloram residues can persist in the soil up to 2.5 years (NASCIMENTO; YAMASHITA, 2009), according to soil and climate conditions.

Agrochemicals residues can be found in different environment places, such as in soil (VIEIRA *et al.*, 2009), and its environmental behavior can be influenced by sorption, drift, biological and chemical decomposition, volatilization, leaching and runoff processes (SPADOTTO; GOMES, 2013; VIEIRA *et al.*, 1999), besides these processes interaction (SPADOTTO; GOMES, 2013; VIVIAN *et al.*, 2006). Its behavior in the soil is very complex and results of several factors, such as interaction with soil constituents (SILVA *et al.*, 2013; VIEIRA *et al.*, 1999; VIVIAN *et al.*, 2006).

Among attributes that typically have soil-agrochemicals interaction is soil texture, thus it is very important to have its knowledge before agrochemical application. Clay soils have a greater herbicide molecules sorption potential (SILVA; VIVIAN; D’ANTONINO, 2009). In addition to texture, Vieira *et al.* (1999) argued that organic matter presence also helps in increasing 2,4-D adsorption.

Understand the interaction between herbicides and soil attributes is of fundamental importance in the knowledge of herbicides persistence in the environment. It

is important to know the residual potential of the herbicide into the soil, or soil properties which have correlation with the herbicide 2,4-D. Since it is potentially toxic to humans and can cause negative effects on plants, such as interruption of growth (SILVA *et al.*, 2011). Among other problems, Nascimento and Yamashita (2009) reported that soil contaminated with 2,4-D + picloram caused reduction in emergency, height and toxicity in vegetable crops. To understand which attributes may have more interaction, the study of the spatial correlation between herbicide residues and soil attributes is shown as an important tool for its knowledge.

Usually, georeferenced collected samples are used to know soil attributes spatial distribution. For Cavalcante *et al.* (2007a) and Silva *et al.* (2003), this sampling allows to spatialize chemical attributes with geostatistics use, which determine the correlation between soil attributes and 2,4-D herbicide residues. In assessing the spatial dependence of agronomic attributes, Deutsch and Journel (1998) emphasized that can make use of geostatistics to describe phenomena that fluctuate over time and/or space. Thematic maps are used for displaying the attributes evaluated, however, the interpolation of values is required for those places where the attribute has not been sampled (VILELA; CAETANO, 2009).

The half-life of the herbicide in the soil can also be considered as an interference factor, because herbicide permanence time in the soil is influenced by many factors, such as temperature, precipitation, soil moisture, among others. Authors mention that the half-life of 2,4-D in the soil may vary from seven days up to several years (MCCALL; VRONA; KELLEY, 1981; NASCIMENTO; YAMASHITA, 2009; SILVA; VIVIAN; D’ANTONINO, 2009) and this time is dependent on climate factors, soil management conditions, chemical product characteristics, physico-chemical soil characteristics, among others.

Cavalcante *et al.* (2007a) consider the study of the spatial variability of soil chemical attributes important when the soil is subjected to different managements. The study area has soybeans and corn in rotation systems its main crops, with different NPK formulations for each culture. The system of no-tillage presented significant accumulation of organic matter, phosphorus, potassium and elevation of CEC in relation to the other studied systems, besides the improvement in the chemical conditions of the soil, the organic matter was larger in relation to the natural system.

As the soil is considered a final herbicides reservoir, it is important to determine herbicide residues in it. In this context, the aim of the study was to determine the correlation between 2,4-D herbicide and soil attributes in an agricultural area located in Nova Santa Rosa/PR municipality, 12 months after herbicide application.

## MATERIAL AND METHODS

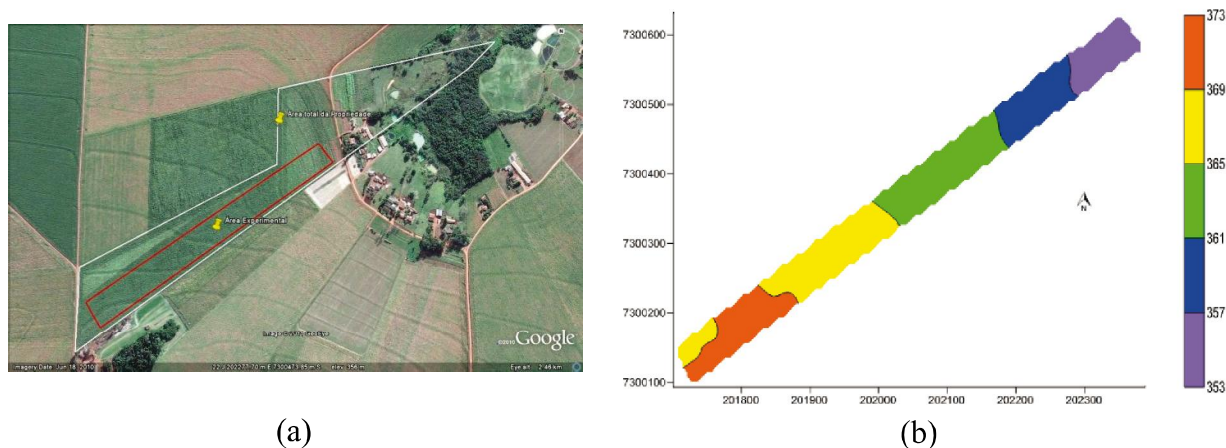
The experiment was conducted at Nova Santa Rosa, western part of Paraná state, in an area of 5.04 ha (800 x 63 m) (Figure 1a) that use no-tillage system with corn and soybeans crop rotation for more than 15 years, with central geographic coordinates of 24°22'54" S and 53°56'14" O (datum WGS-84), and an average altitude of 363 m. The lowest part of the area is located in the northeast region and the highest part in the southwest region (Figure 1b).

The municipality predominant soil is the typical eutrophic RED LATOSOL (EMBRAPA, 2013) and the climate, according to Köppen classification, is Cfa, humid temperate climate with hot summers and infrequent frosts. The monthly precipitation data from 2011 and 2012 were provided by SIMEPAR Technology Institute (Figure 2a).

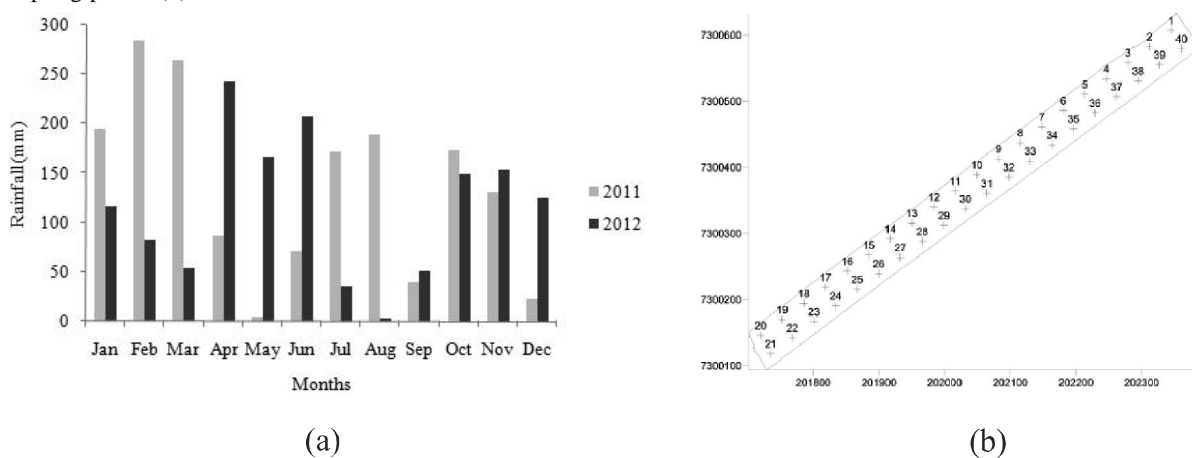
In the experimental area, 40 sampling points (Figure 2b) were georeferenced using the Trimble Geo Explorer XT 2005 Topographic GPS, with post-processed differential correction. The sampling grid was of 40 x 33 m. Forty soil composed samples were collected for each year (2011 and 2012, Tables 1 and 2) using a Dutch auger at depths of 0 to 20 cm. 8 subsamples (Figure 3a) were collected in each of the 40 points and homogenized, removing approximately 300 g of soil from each sample and accommodating it in an identified plastic bag.

Samples 1 (2011) and 2 (2012) were made 12 months after 2,4-D herbicide application. In Sept/2010 a single 1.5 L ha<sup>-1</sup> dose of 2,4-D herbicide (DMA\*806 BR) was applied throughout the area, and 12 months after (09/03/2011), collection 1 was held in the 40 sampling points. In Sep/2011, after collection 1, two herbicide

**Figure 1** - Experimental area image (Google Earth, 2014) (a) and altimetry map (m) (b)



**Figure 2** - Monthly precipitation chart of 2011 and 2012 in Nova Santa Rosa/PR region, in mm (a), and spatial distribution of the sampling points (b)



doses (Figure 3b) were applied: Interval 1, in sampling points 1-20, with a 1.5 L ha<sup>-1</sup> (1.005 g e.a ha<sup>-1</sup>) herbicide dose application; and Interval 2, in sampling points 21-40, with a 1.0 L ha<sup>-1</sup> (670 g e.a. ha<sup>-1</sup>) 2,4-D dose application, and 12 months after herbicide application, collection 2 was performed, in 2012 (08/25/2012) (Figure 3a).

Soil samples for 2,4-D residual analysis were dug, air dried and protected from light for a period of 5 to 7 days, being then sieved with a 1.2 mm mesh and frozen until 2,4-D liquid chromatography (HPLC) determination. For 2,4-D extraction, the following steps proposed by Amarante Junior (2003) and Kashyap *et al.* (2005) were adapted: 1) sieve the soil to 1.2 mm and weigh 5 g; 2) add acidified water with H<sub>2</sub>SO<sub>4</sub> (1 mL, pH=1.0; 9 M) + dichloromethane (15 mL); 3) stay in the ultrasound system for 1 hour; 4) Collect and reserve the extract; 5) add dichloromethane back to the ground (15 mL) for a new extraction; 6) collect the extract along with the previously reserved; 7) Filter the extract by suction with anhydrous sodium sulfate; 8) dry evaporate the solvent on a rotary evaporator up to 1 mL; 9) dry with N<sub>2</sub>; 10) Dissolve the residue in 1 mL methanol, accommodate in Eppendorf and refrigerate until injection on HPLC.

Chromatographic conditions were adapted from Amarante Junior (2003) and Kashyap *et al.* (2005), according to the following conditions: oven temperature: 40 °C; mobile phase flow: 1.0 ml min<sup>-1</sup>; run time: 23.01 min; wavelength used: 225 nm; mobile phase: 60% MilliQ H<sub>2</sub>O and 40% TFA acetonitrile; Sample injection volume 20; μL.

After HPLC 2,4-D herbicide determination in the soil, herbicide frequency detection was verified,

and with Minitab version 16 software, residues classical descriptive analysis was performed. The coefficient of variation (CV) was considered low when CV ≤ 10% (homogeneity); Average when CV was between 10 and 20%; high when CV was between 20 to 30%; and very high when CV > 30% (heteroskedasticity) (PIMENTEL-GOMES, 2009). Asymmetry and kurtosis coefficients were compared with the confidence interval provided by Jones (1969) at 5% probability level. The normal data probability distribution was verified using Kolmogorov-Smirnov and Anderson-Darling tests at a significance level of 5%. Data that presented normality in at least one of the tests were considered normal.

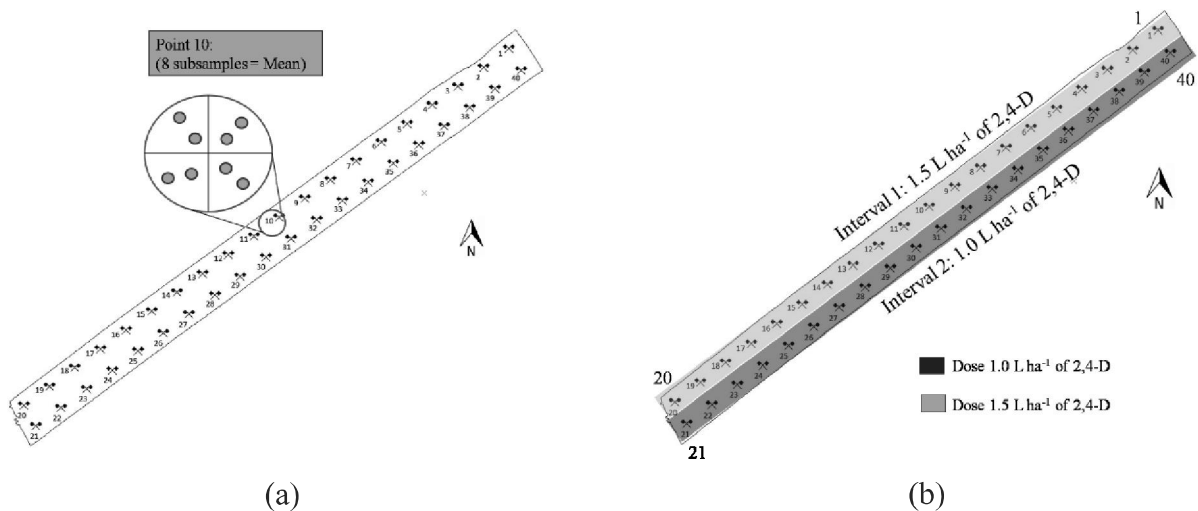
To evaluate herbicide 2,4-D residues spatial distribution, residual thematic maps were generated with Surfer 10 software, using the inverse interpolator of the square of the distance.

The spatial correlation of 2,4-D herbicide residues with soil attributes (Table 1) was calculated using Moran's bivariate spatial autocorrelation statistics Equation 1, (BONHAM; REICH; LEADER, 1995) using the Software for Definition of Management Zones - SDMZ (BAZZI *et al.*, 2013.). The spatial correlation matrix checks at 1% and 5% level and identifies the attributes that influence the yield positively or negatively, and checks whether a sample is correlated spatially (spatial autocorrelation).

$$I_{YZ} = \frac{\sum_{i=1}^n \sum_{j=1}^n W_{ij} * Y_i * Z_j}{W \sqrt{m_1^2 * m_2^2}} \quad (1)$$

where,  $I_{YZ}$  - Degree of association between Y and Z variables, ranging from -1 to 1, as it is followed: positive correlation  $I_{YZ} > 0$  and negative correlation  $I_{YZ} < 0$ ;  $W_{ij}$  -

**Figure 3** - Soil sampling for 2,4-D residual analysis in the soil (a) and herbicide 2,4-D application interval in 2011 and 2012 (b)



correspond to the  $ij$  element of spatial association matrix, calculated by  $W_{ij} = (1/(1 + D_{ij}^2))$ , so that  $D_{ij}$  is the distance between  $i$  and  $j$  points;  $Y_i$  - transformed  $Y$  value at point

$i$ ;  $W$  - the sum of degrees of spatial association, obtained from Matrix  $W_{ij}$ , for  $i \neq j$ ;  $m_Y^2$  - sample variance of variable  $Y$ ;  $m_Z^2$  - sample variance of variable  $Z$ .

**Table 1** - Descriptive statistics of granulometry and soil chemical attributes

Attribute	Min	Mean	Median	Maximum	SD	CV(%)	Kur	Ass	Normal
2011									
% Clay	59.0	68.7	68.5	78.0	4.7	6.9	-0.4 (A)	-0.1 (a)	Yes
% Silt	14.0	21.0	21.0	29.0	3.6	17.3	-0.2 (A)	-0.1 (a)	Yes
% Sand	7.0	10.3	10.0	15.0	1.8	17.9	0.1 (A)	0.2 (a)	Yes
pH in CaCl <sub>2</sub>	4.4	4.8	4.8	5.3	0.2	4.8	-0.6 (A)	0.1 (a)	Yes
Cu (mg dm <sup>-3</sup> )	6.4	12.4	11.7	20.2	3.6	28.7	-0.6 (A)	0.4 (a)	Yes
Zn (mg dm <sup>-3</sup> )	1.0	4.3	3.5	12.9	3.0	69.6	0.5 (A)	1.0 (b)	No
Fe (mg dm <sup>-3</sup> )	14.0	22.1	21.0	33.0	4.6	20.7	-0.3 (A)	0.2 (a)	Yes
Mn (mg dm <sup>-3</sup> )	142.0	259.6	261.5	361.0	42.8	16.5	1.3 (A)	-0.4 (a)	Yes
P (mg dm <sup>-3</sup> )	4.0	15.4	13.1	60.0	10.0	65	9.3 (C)	2.6 (b)	No
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	4.6	6.2	6.2	7.8	0.8	12.6	-0.6 (A)	0.2 (a)	Yes
Ca (cmol <sub>c</sub> dm <sup>-3</sup> )	4.4	6.1	5.9	8.5	1.0	15.8	0.8 (A)	0.8 (b)	Yes
Mg (cmol <sub>c</sub> dm <sup>-3</sup> )	0.8	1.2	1.2	1.8	0.2	17.6	0.5 (A)	0.7 (a)	Yes
Al <sup>3+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0	0.1	0.1	0.4	0.1	118.9	0.6 (A)	1.1 (b)	No
K (cmol <sub>c</sub> dm <sup>-3</sup> )	0.2	0.5	0.4	1.1	0.2	45.8	0.2 (A)	0.9 (b)	Yes
CTC <sub>pH7</sub> (cmol <sub>c</sub> dm <sup>-3</sup> )	11.7	14.0	13.8	17.2	1.1	7.7	1.2 (A)	0.5 (a)	Yes
V%	43.5	55.6	55.4	67.7	6.0	10.8	-0.8 (A)	-0.1 (a)	Yes
MO (g dm <sup>-3</sup> )	20.8	34.5	34.9	53.1	5.6	16.1	2.4 (C)	0.5 (a)	Yes
2012									
pH em CaCl <sub>2</sub>	4.2	4.6	4.6	5.0	0.2	4.4	-0.7 (A)	0.2 (a)	Yes
Cu (mg dm <sup>-3</sup> )	7.4	16.6	16.7	26.7	5.1	30.6	-0.9 (A)	0.1 (a)	Yes
Zn (mg dm <sup>-3</sup> )	2.2	7.6	6.0	31.5	5.7	74.7	8.7 (C)	2.7 (b)	No
Fe (mg dm <sup>-3</sup> )	22.0	33.7	33.0	51.0	6.3	18.7	0.3 (A)	0.4 (a)	Yes
Mn (mg dm <sup>-3</sup> )	186.0	297.8	301.0	394.0	44.4	14.9	0.1 (A)	-0.3 (a)	Yes
P (mg dm <sup>-3</sup> )	9.4	21.9	20.0	51.2	10.5	48.0	0.6 (A)	1.1 (b)	No
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	5.8	7.2	7.2	9.0	0.8	10.9	-0.7 (A)	0.3 (a)	Yes
Ca (cmol <sub>c</sub> dm <sup>-3</sup> )	3.5	4.9	4.6	8.5	1.2	24.1	2.2 (C)	1.5 (b)	No
Mg (cmol <sub>c</sub> dm <sup>-3</sup> )	0.8	1.2	1.2	1.6	0.2	14.3	-0.2 (A)	0.4 (a)	Yes
Al <sup>3+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.0	0.1	0.1	0.5	0.1	81.8	0.1 (A)	0.9 (b)	No
K (cmol <sub>c</sub> dm <sup>-3</sup> )	0.3	0.5	0.5	1.0	0.2	35.1	-0.1 (A)	0.8 (b)	Yes
CTC <sub>pH7</sub> (cmol <sub>c</sub> dm <sup>-3</sup> )	11.8	13.8	13.5	17.1	1.2	8.5	1.3 (A)	1.2 (b)	Yes
V%	35.9	47.7	47.7	63.1	6.5	13.7	-0.2 (A)	0.50 (a)	Yes
MO (g dm <sup>-3</sup> )	22.8	31.7	30.9	39.7	3.9	12.3	0.1 (A)	0.2 (a)	Yes

Min: minimum; Max: maximum; SD - Standard Deviation; CV - Coefficient of Variation; ASS - Symmetry: Symmetric (a); positive asymmetry (b); negative asymmetry (c); KUR - Kurtosis: Mesokurtic (A); Platikurtic (B); Leptokurtic (C). Normal: Normality

## RESULTS AND DISCUSSION

The 2,4-D residues in soil found in 2012 (collection 2) presented a smaller number of points with 2,4-D detection than residues found in soil in 2011, possibly due to the soil being drier in function of low precipitation in the collection 2 period (Figure 2a). This difference in detection points can be better evaluated by the median (Table 2). In 2012, the median was 0  $\mu\text{g kg}^{-1}$ , i.e., herbicide residues were not detected in most sampling sites. Besides the period of hydric stress, other factors that may have interfered with the detection of 2,4-D residues in the soil can be surface runoff, leaching, and the degradation of the active ingredient. For Schaffrath *et al.* (2008), runoffs do not occur evenly, as it runs across preferential paths.

Another factor to consider is soil collection samples depth (0-20 cm), because the herbicide could be displaced by mobility to deeper soil regions. Pinheiro, Moraes and Silva (2011) detected 2,4-D herbicide with the highest frequency (56%) at a depth of 80 to 100 cm, showing mobility according to application time.

According to Malone, Shipitalo and Meek (2004), macropores produce preferential paths. Hence, water runs through empty spaces, carrying pesticides to soil deeper regions. For Pinheiro, Moraes and Silva (2011) this factor may explain concentration differences found for the herbicide.

Vieira *et al.* (1999) consider the soil as one of herbicides final reservoirs. In a study of cucumber plants poisoning, Santos *et al.* (2006) found that the higher the dose of mixed 2,4-D + picloram and the shorter the time after herbicide application, the greater the residual effect in the soil. The average 2,4-D residues in the soil was of 83  $\mu\text{g kg}^{-1}$  in collection 1 (2011) and 92  $\mu\text{g kg}^{-1}$  in collection 2 (2012). In 2012, higher point values than in 2011 were found, despite detection frequency being higher in 2011. In both years, the minimum residual values found were 0  $\mu\text{g kg}^{-1}$  (nd) and the maximum values were of 609  $\mu\text{g kg}^{-1}$  in 2011 (collection 1) and 652  $\mu\text{g kg}^{-1}$  in 2012 (collection 2).

Residues CV found in soil is considered very high (155% and 207%) (Table 2). One of the factors that contributed in having a very high CV is the large number of points without residues detection. The maximum residues

amount of 2,4-D in the soil encountered by Pinheiro, Moraes and Silva (2011) was of 845.5  $\mu\text{g kg}^{-1}$  in the depth of 0 to 20 cm. In Brazil, the CONAMA Resolution No. 357 of March the 17 th 2005 and the CONAMA Resolution No. 396 of April the 3 rd 2008 determine that the acceptable limits of the final 2,4-D residues in water for human consumption are 30  $\mu\text{g L}^{-1}$ .

2,4-D residues in soil in collection 1 presented detection frequency (Table 2) of 40% in points 21 to 40, and of 65% in points 1 to 20. In collection 2 (two 2,4-D doses), herbicide frequency detection (Table 2) was of 40% in points 21 to 40 and of 10% in points 1 to 20. Pinheiro, Moraes and Silva (2011), while evaluating 2,4-D residues in Haplumbrept soil (clayey and medium texture) had also found concentration values variable at the same depth (0-20 cm), with active ingredient detection frequency of 33%. In the same soil class and at the same depth, Pinheiro *et al.* (2009) found a 2,4-D detection frequency of 21% in the soil, i.e., herbicides residues values in soil may vary depending on several factors, including soil characteristics and climatic conditions. An ANOVA could not be made in order to test if there were statistical differences between 1.0  $\text{L ha}^{-1}$  and 1.5  $\text{L ha}^{-1}$  2,4-D treatments because both of samplings presented spatial dependence (Table 3).

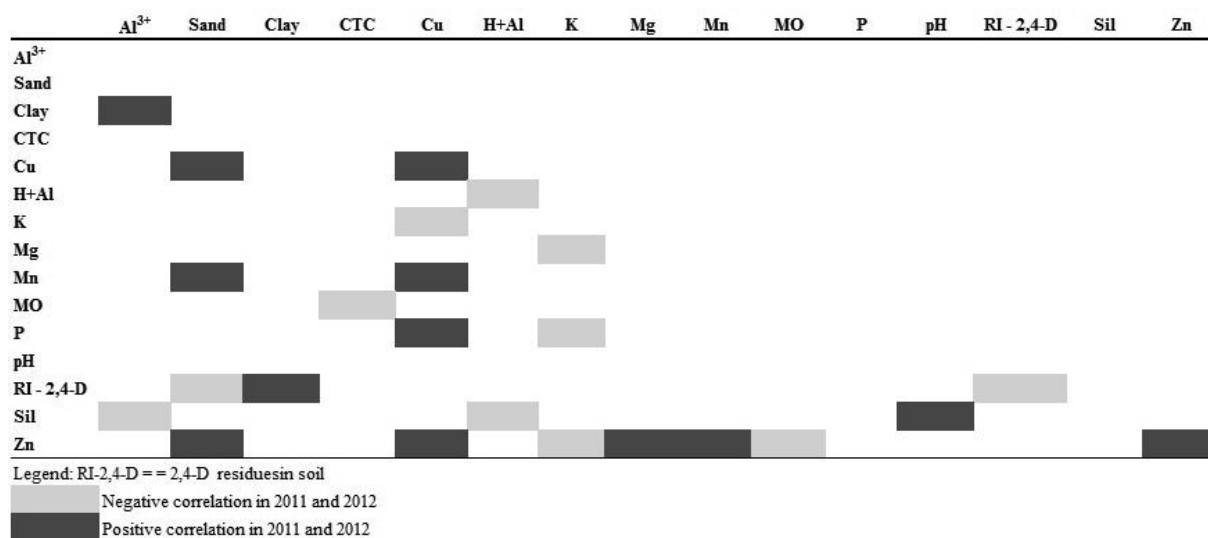
By means of the average and the maximum values of residual 2,4-D was not possible to detect differences between 1.0  $\text{L ha}^{-1}$  and 1.5  $\text{L ha}^{-1}$  2,4-D treatments.

By mapping the spatial distribution of 2,4-D herbicide residues in soil for 2011 (collection 1) (Figure 4a), it was found that most of the experimental area had residual amounts of 2,4-D ranging from 0 (nd) to 122  $\mu\text{g kg}^{-1}$ . However, there was a residual concentration of 2,4-D in the northeastern part of the experimental area, with intervals ranging from 244 to 609  $\mu\text{g kg}^{-1}$ , in the property lower part. According to Spadotto and Gomes (2013), after agrochemicals application, its environment behavior may be influenced by several processes, including transport (drift, volatilization, leaching and runoff), i.e., the 2,4-D applied at the property higher part may have shifted to the lower part by runoff. Schaffrath *et al.* (2008) consider soil as heterogeneous, thus, presenting high soil physical properties spatial variability.

**Table 2** - Detection frequency and descriptive statistics of 2,4-D residues ( $\mu\text{g kg}^{-1}$ ) for the 40 points

Year	Min	Mean	Median	Maximum	SD	CV(%)	Kur	Ass	Normal	Detection Frequency	
										1.0 $\text{L ha}^{-1}$	1.5 $\text{L ha}^{-1}$
										Application Dose...	
2011	0	83	59	609	128	155	7 (C)	2 (b)	No	-	53%
2012	0	92	0	652	191	207	3 (C)	2 (b)	No	40%	10%

Min: minimum; Max: maximum; SD - Standard Deviation; CV - Coefficient of Variation; ASS - Symmetry: Symmetric (a); positive asymmetry (b); negative asymmetry (c); KUR - Kurtosis: Mesokurtic (A); Platikurtic (B); Leptokurtic (C). Normal: Normality

**Table 3** - Correlation matrix of the chemical attributes, texture and 2,4-D herbicide residues in soil for 2011 and 2012

In 2012 (collection 2) (Figure 4b), there were residues concentration on the extreme and central parts of the experimental area, with maximum intervals of residual herbicide ranging 391 to 652  $\mu\text{g kg}^{-1}$  and minimum interval ranging from 0 (na) and 261  $\mu\text{g kg}^{-1}$ , or concentration limits are found in the search. During this period there was a lower precipitation rate (Figure 2a). In the 2,4-D residues difference map (Figure 4c) it is observed that there was an increase in herbicide residues at the extremes and central parts of the experimental area in 2012, although, 12 months before collection 2, a different 2,4-D herbicide application was performed. This spatial variability was commented by Pinheiro, Moraes and Silva (2011), saying that environmental conditions in agricultural areas are dynamic and heterogeneous, influenced by the soil spatial and temporal distribution. Hence, agrochemicals may be lost by degradation, evaporation or organism absorption.

Analyzing the spatial correlation between soil attributes, it was found that many attributes have different correlation coefficients from one year to another, and many attributes have not presented spatial correlation. Table 3 presented the attributes which have in both years, 2011 and 2012, the same behavior. According to Deon (2007) attributes may have different correlation levels from one year to another, probably due to nutritional disorders that may have been induced by improper and excessive fertilization management, among which toxicity and induced deficiency of one nutrient by another.

According to Cavalcante *et al.* (2007b), in the no-tillage system, the V% in depths of 0-10 cm and 10-20 cm, and the pH and Ca in 10-20 cm depths showed a strong spatial dependence. This detected spatial dependence

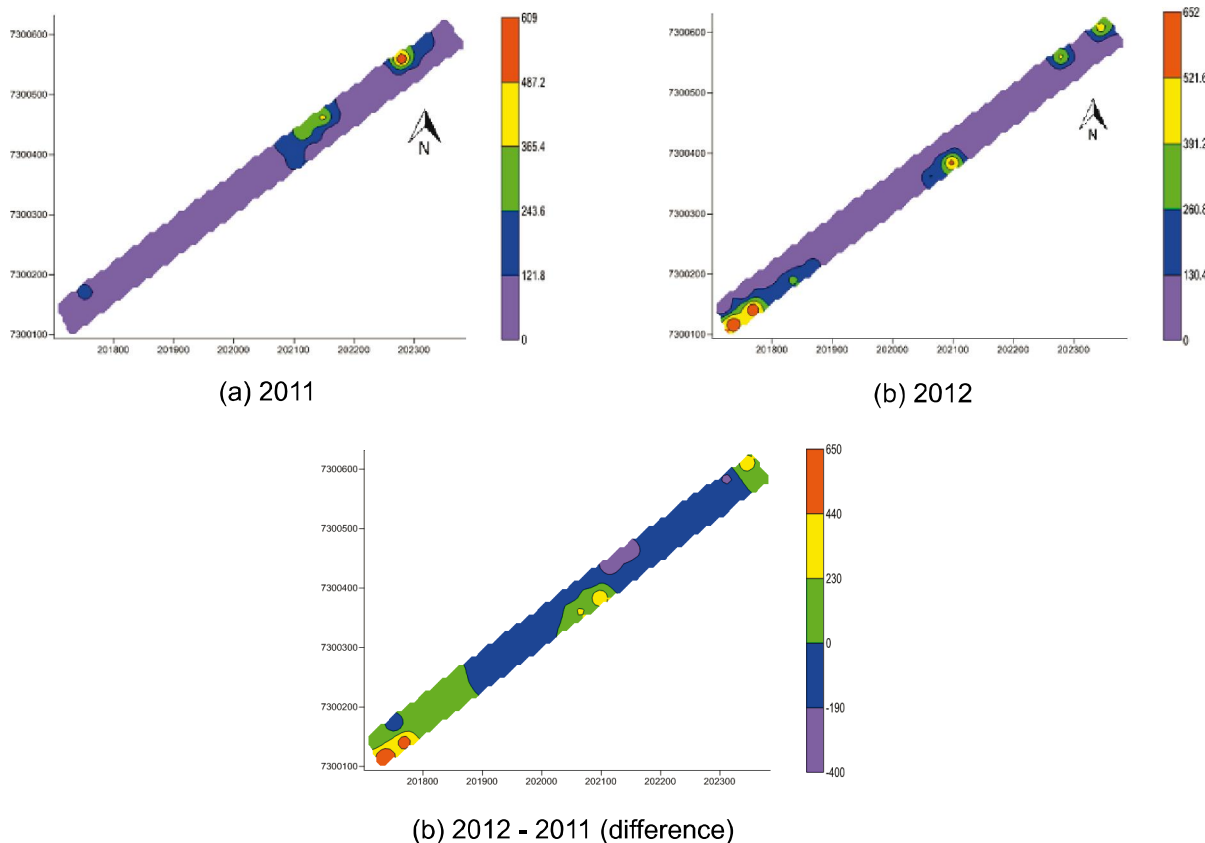
may be derived from any of the soil formation factors, especially source material and relief, while moderate spatial dependence would be derived from soil homogenization that fertilization and liming provided to it. In this study the spatial dependence was found for Cu, Al H +, Zn and 2,4-D soil residues.

Binding of agrochemicals, and other attributes such as Al<sup>3+</sup> + with clay is related to the particle size, then the smaller the particle of the soil is, the higher the reactivity, and clay is the soil reactive fraction, as it is the smallest granulometric fraction of the soil. According to Procopio *et al.* (2009), clay favors 2,4-D adsorption. In accordance with Silva *et al.* (2011) Al<sup>3+</sup> showed positive spatial correlation with the clay content (2011 and 2012). In addition to the particle size, electric charges may also influence the binding, i.e., clays have negative charges and Al<sup>3+</sup> positive charges, thus, it tends to bind. In 2011 and 2012, Al<sup>3+</sup> correlation was negative with silt granulometric content.

Cu spatial correlation was positive with sand, Mn, P, and Zn. Mn showed a positive spatial correlation with sand and Zn. As Mn is an element that was found above the soil necessary limit to plant development (30.0 mg  $\text{dm}^{-3}$ ) (COSTA; OLIVEIRA, 2001), the influence of it on the organic MO was higher. It was also found that the chemical attribute K showed a negative spatial correlation with Cu, Mg, and P, and Mg and had a positive spatial correlation with Zn.

Evaluating 2,4-D residues spatial correlation in the soil, there was a negative correlation with sand and positive with clay, in agreement with Silva, Vivian and D'Antonino (2009), who stated that, with the increase of clay, 2,4-D

**Figure 4** -Spatial distribution of 2,4-D residues ( $\mu\text{g kg}^{-1}$ ) in 2011 (collection 1) (a), 2012 (collection) (b) and residues difference between 2012 and 2011 (c). Map coordinates are in meters (Universal Transverse Mercator - UTM)



residues increase in the soil may occur, as 2,4-D sorption in clay particles is higher, since clay soils normally have a higher herbicides molecules sorption potential, possibly because it is the reactive granulometric fraction of soil. No spatial correlation of 2,4-D herbicide with pH was found, although Johnson, Lavy and Gbur (1995) state that 2,4-D adsorption decreases with pH.

Although the soil MO of the experimental area has not presented spatial correlation with 2,4-D herbicide residues in the soil, this attribute in conjunction with soil texture is one of the main attributes to consider in herbicides choosing and recommended doses, as it can favor an increase in adsorption of 2,4-D to the soil (VIEIRA *et al.*, 1999). In both years, 2,4-D residues present spatial correlation (positive or negative) with at least one granulometric attribute evaluated, demonstrating the importance of knowing soil texture in the selection of the herbicide to be applied in the area. Agreeing with Silva *et al.* (2011), who evaluated 2,4-D residual activity in soybean emergence in soils of different textures and verified that there were residual activity variations due to dosage and time period between soybean planting and

application, presenting a more pronounced effect on plants grown on medium textured soils (20% clay, 4% silt and 76% sand).

With 2,4-D herbicide determination results in the soil in 2011 and 2012 in depths of 0 to 20 cm, it was found that with the time this is a herbicide that may remain in the soil although residues were not detected at certain points of the area. Depending on each soil characteristics, permanence time will be higher or lower, i.e., detection may be related to chemical, physical, and management soil factors.

## CONCLUSIONS

1. In both years it was found only cross-correlation between 2,4-D herbicide and clay and sand;
2. 2,4-D detection in the soil varied greatly from one location to another in the same area, presenting points without the active ingredient detection;
3. It was not possible to detect differences between 1.0 L ha<sup>-1</sup> and 1.5 L ha<sup>-1</sup> 2,4-D treatments;



4. The cross-correlation matrix using the Moran's bivariate spatial autocorrelation statistics proved to be an important tool to verify the interference of one attribute over another. To do so, a chemical and physical soil properties continuous verification must be performed, besides monitoring agrochemicals residual activity, as these can be toxic to plants.

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