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SEÇÃO II - QUÍMICA E MINERALOGIA DO SOLO

GLYPHOSATE BEHAVIOR IN A RHODIC OXISOL UNDER NO-TILL AND CONVENTIONAL AGRICULTURAL SYSTEMS⁽¹⁾

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SUMMARY

The behavior of glyphosate in a Rhodic Oxisol, collected from fields under no-till and conventional management systems in Ponta Grossa, Parana state (Brazil) was investigated. Both agricultural systems had been in production for 23 years. Glyphosate mineralization, soil-bound forms, sorption and desorption kinetics, sorption/desorption batch experiments, and soil glyphosate phytoavailability (to *Panicum maximum*) were determined. The mineralization experiment was set up in a completely randomized design with a 2 x 2 factorial scheme (two management systems and two ¹⁴C radiolabelled positions in the glyphosate), with five replicates. ¹⁴CO₂ evolution was measured in 7-day intervals during 63 days. The glyphosate sorption kinetics was investigated in a batch experiment, employing a glyphosate concentration of 0.84 mg L⁻¹. The equilibration solution was 0.01 mol L⁻¹ CaCl₂ and the equilibration times were 0, 10, 30, 60, 120, 240, and 360 min. Sorption/desorption of glyphosate was also investigated using equilibrium batch experiments. Five different concentrations of the herbicide were used for sorption (0.42, 0.84, 1.68, 3.36, and 6.72 mg L⁻¹) and one concentration for desorption. Glyphosate phytoavailability was analyzed in a 2 x 5 factorial scheme with two management systems and five glyphosate concentrations added to soil (0, 4.2, 8.4, 42.0, and 210.0 µg g⁻¹) in a completely

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randomized design. Phytotoxicity symptoms in *P. maximum* were evaluated for different periods. The soil under both management systems showed high glyphosate sorption, which impeded its desorption and impaired the mineralization in the soil solution. Practically the total amount of the applied glyphosate was quickly sorbed (over 90 % sorbed within 10 min). Glyphosate bound to residues did not have adverse effects on *P. maximum* growth. The mineralization of glyphosate was faster under no-till and aminomethylphosphonic acid was the main glyphosate metabolite.

Index terms: herbicide, sorption, degradation, mineralization, phytotoxicity, *Panicum maximum*.

RESUMO: COMPORTAMENTO DO GLIFOSATO NUM LATOSSOLO VERMELHO SOB PLANTIO DIRETO E CONVENCIONAL

Este trabalho teve por objetivo estudar o comportamento do herbicida glifosato num Latossolo Vermelho argiloso, da região de Ponta Grossa (PR), realizado há 23 anos sob plantio direto e convencional. Para tal, foram instalados quatro experimentos, nos quais foram analisadas a mineralização e a formação de resíduo-ligado, a cinética de sorção e dessorção, a sorção/dessorção e a fitodisponibilidade no solo do glifosato para *Panicum maximum* var. mombaça. O ensaio de mineralização foi realizado em delineamento inteiramente casualizado, em arranjo fatorial (2 x 2), com cinco repetições, sendo os fatores os dois sistemas de cultivo e a posição de marcação radioativa do ^{14}C -glifosato (^{14}C -fosfonometil e ^{14}C -glicina). Foi avaliado o desprendimento de $^{14}\text{CO}_2$, semanalmente, até 63 dias. A cinética de sorção do glifosato foi efetuada seguindo o método "batch", para os dois sistemas de cultivo, utilizando a relação solo: solução de 1: 5 e concentração de glifosato de $0,84 \text{ mg L}^{-1}$. As determinações de radioatividade na solução de equilíbrio foram feitas nos períodos de 0, 10, 30, 60, 120, 240 e 360 min após a aplicação do herbicida. Os tempos utilizados na cinética de dessorção foram de 0, 1, 4, 12, 24, 36, 48, 72 e 96 h. O procedimento utilizado no ensaio de sorção/dessorção foi semelhante ao do estudo de cinética. No entanto, foram utilizadas cinco concentrações do herbicida: 0,42; 0,84; 1,68; 3,36 e $6,72 \text{ mg L}^{-1}$, para a construção das isotermas. Ao final deste ensaio, foram realizadas quatro tentativas de dessorção somente na concentração de $0,84 \text{ mg L}^{-1}$. Por fim, o ensaio de fitodisponibilidade foi realizado em delineamento inteiramente casualizado, arranjado em fatorial 2 (sistemas de cultivo) x 5 (concentrações de glifosato aplicados ao solo: 0, 4,2; 8,4; 42,0 e $210,0 \mu\text{g g}^{-1}$ de solo), sendo feitas avaliações dos sintomas visuais de fitotoxidez no capim mombaça em diferentes períodos de tempo. Para ambos os sistemas de cultivo, o glifosato apresentou elevados coeficientes de sorção, o que impediu sua dessorção e dificultou sua mineralização na solução do solo, visto que a molécula permaneceu como resíduo-ligado. A cinética de sorção do glifosato é instantânea, sendo mínima a concentração sorvida na fase lenta. O glifosato, na forma de resíduo-ligado no solo, não constitui problemas para o *Panicum maximum*, seja sob plantio direto, seja convencional. A mineralização do glifosato é mais rápida no plantio direto e o principal metabólito do glifosato é o ácido amino-metilfosfônico.

Termos de indexação: herbicida, sorção, degradação, mineralização, resíduo-ligado, *Panicum maximum*.

INTRODUCTION

Glyphosate - N[(phosphonomethyl)glycine] (Figure 1) is a non-selective herbicide used on a large scale in Brazil as a desiccant in no-till systems for weed control between rows of perennial crops, in aquatic environments, and for total vegetation control in uncultivated areas, pastures, and sugarcane fields (Rodrigues & Almeida, 1995). In the last two decades,

glyphosate has mainly been used to expand and establish no-till systems in Brazil. It is applied as a post-emergence treatment and is aposymbiotically translocated in plants. It acts by inhibiting the enzyme 5-enolpyruvateshikimate-3-phosphate synthetase (EPSPS), interfering with aromatic amino acid biosynthesis (Roberts et al., 1998). In most cases, glyphosate is not metabolised by plants, enhancing its non-selective activity. Only genetically modified plant species are resistant to this herbicide.

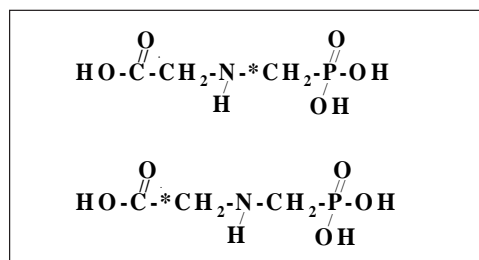


Figure 1. ^{14}C -Glyphosate [n-(phosphonomethyl) glycine]. * Position of ^{14}C .

Glyphosate performance in soils has been studied under different conditions (Glass, 1987; Piccolo et al., 1994, 1996; Maqueda et al., 1998; Jonge et al., 2000). However, only a few studies have dealt with its performance in tropical soils under humid conditions (Cheah et al., 1997; 1998; Prata et al., 2000, 2002).

Although glyphosate has a high water solubility (11.6 g L^{-1}), and a low hydrophobicity ($\log K_{ow} = -4.1$), it strongly sorbs to soil with sorption coefficient values $> 1.000 \text{ L kg}^{-1}$ (Cheah et al., 1997). Several different sorption mechanisms have been proposed for glyphosate depending on the sorbent phase. Miles & Moye (1988) studied the effect of pH and ionic strength on the extraction of glyphosate in not very weathered soils, and clay minerals. They observed an increasing efficiency of extraction in line with an increasing pH and ionic strength of the extracting solution. They suggested electrostatic linkage and hydrogen bonds as the main sorption mechanisms for glyphosate. The electrostatic linkages of glyphosate were also proposed by Nicholls & Evans (1991) for soils with 2:1 clays.

Hydrogen bonds were implicated as the main sorption mechanism for glyphosate in humic substances (HS) (Piccolo et al., 1996). These authors showed that glyphosate sorption to HS is higher the more aliphatic the HS.

Several studies have indicated that soil oxides are the main colloids responsible for sorption of glyphosate in oxidic soils (Hance, 1976; Glass, 1987; Gerritse et al., 1996; Prata et al., 2000; Jonge et al., 2001; Prata et al., 2003). In the same way as the specific adsorption of inorganic phosphates to metallic oxides (Tan, 1993), there is the formation of covalent linkages between the methylphosphonic group of glyphosate and the metal present in the soil oxides (Piccolo et al., 1994; Cheah et al., 1997). The energy involved in this kind of sorption is high, and this mechanism can contribute to the high degree of irreversible sorption of glyphosate in oxidic soils (Prata et al., 2000, 2003).

The bioavailability of pesticide molecules to microorganisms is normally lower when these molecules are sorbed than when they are present in

the soil solution. The pesticide in the soil solution decreases as the sorption energy increases (Steen et al., 1980; Kawamoto & Urano, 1989). Although glyphosate is potentially degradable by microorganisms in the soil solution, as a result of the high sorption rate and the strong soil retention, it can persist in the soil irreversibly sorbed in its original form as a bound-residue, i. e. its high sorption minimizes its degradation.

Glyphosate availability in the soil solution is low, with a dissipation half-life of about 40 days (Rueppel et al., 1977; Roberts et al., 1998). However, mineralization half-lives up to 22.7 years have been reported (Nomura & Hilton, 1977). The most important metabolite of glyphosate in soil is aminomethylphosphonic acid (AMPA) (Rueppel et al., 1977; Roy et al., 1989; Cheah et al., 1998; Roberts et al., 1998). However, AMPA still contains the methylphosphonic group and hence its sorption in soils is still high.

Soil organic matter is considered to be the most important factor controlling herbicide behavior in soil. It affects the sorption as well as the degradation of pesticide molecules in soils (Stvenson, 1994; Hornsby et al., 1995). Therefore, soil management techniques which alter the amount and/or the characteristics of the soil organic matter can indirectly affect the pesticide behavior in the soil.

The aim of this research was to study the glyphosate behavior in a Brazilian Oxisol, which had been cultivated either under no-till or conventional management systems for 23 years. The specific objectives were (a) to evaluate mineralization and soil-bound residue formation, (b) to establish the sorption kinetics, (c) to evaluate the sorption/desorption isotherms with a batch method, and (d) to evaluate the phytoavailability of glyphosate applied to the soil using *Panicum maximum* as a test species.

MATERIALS AND METHODS

Soils

Four separate analyses were conducted to study glyphosate behavior in a loamy Rhodic Oxisol that had been cultivated either under no-till (NT) or conventional (CON) management systems during 23 years.

For all analyses, soil samples were collected from a depth between 0 and 5 cm. The soil was air-dried and passed through a 2 mm mesh sieve. The chemical and granulometric analyses were performed according to Raij & Quaggio (1983) and Camargo et al. (1986), respectively. The soil pH was determined in a soil/0.01 mol L^{-1} CaCl_2 suspension (1:2.5). Soil organic carbon was determined through

oxidation with Cr_2O_7 in acid medium. For determination of the cation exchange capacity (CEC), basic cations (Ca, Mg and K) were extracted with a cation exchange resin (Raij et al., 1986), whereas Al was extracted with 1 mol L^{-1} KCl (Raij & Quaggio, 1983). Concentrations of Al, Ca, and Mg were determined by atomic absorption spectrophotometry and the K concentration by flame spectrophotometry. The P was extracted with an anion exchange resin (Raij et al., 1986) and determined by spectrophotometry. Total Fe (Fe_2O_3) and Al (Al_2O_3) were extracted by 18 mol L^{-1} H_2SO_4 (Jackson, 1969). The predominant clay minerals were identified by X ray diffraction (Jackson, 1969). Chemical and granulometric analyses as well as the mineralogical attributes are shown in table 1.

Mineralization and microbial activity

Glyphosate mineralization was measured using a 2×2 factorial scheme in a completely randomized design with five replicates for each treatment. The factors considered were soil under two management systems and two radiolabelling positions for ^{14}C in glyphosate (^{14}C -phosphonomethyl group and ^{14}C -glycine group) (Figure 1).

The glyphosate concentration (radioactive and technical product) was $4.2 \mu\text{g g}^{-1}$ of soil ($2.52 \text{ kg a.i. ha}^{-1}$ at 5 cm depth and a soil density of 1.2 g cm^{-3}). Radioactivity corresponded to 25.4 and $17.2 \text{ kBq } 100 \text{ g}^{-1}$ for ^{14}C -phosphonomethyl and ^{14}C -glycine glyphosate, respectively. Glyphosate specific activity of ^{14}C -phosphonomethyl was $5.155 \text{ MBq mg}^{-1}$ and the ^{14}C -glycine specific activity was $7.397 \text{ MBq mg}^{-1}$. Both ^{14}C -phosphonomethyl and ^{14}C -glycine glyphosates were produced by International Isotope (Munich, Germany), and their analytical purities were over 97 %.

Glass flasks (500 mL) were filled with 100 g dry soil and mixed with one of the two labeled compounds of glyphosate. The study was conducted over 63 days in darkness and at $25 \pm 2^\circ\text{C}$. The soil moisture was maintained at 60 % of field capacity. The $^{14}\text{CO}_2$ evolved from the decomposed herbicide was collected in 10 mL of 0.2 mol L^{-1} NaOH solution, which was sampled 7, 14, 21, 28, 35, 42, 49, 56, and 63 days after application. Radioactivity was determined using liquid scintillation counting (LSC).

At the end of the incubation period, the soil was extracted by 2 h of shaking with 0.01 mol L^{-1} CaCl_2 solution, repeated twice, and subsequent additional 2 h with "Mehlich-3" extractor solution (Mehlich, 1984). The "Mehlich-3" extractor solution was a mixture of 0.1 mol L^{-1} HCl and 0.03 mol L^{-1} NH_4F . The F^{-1} present in this extractor acts via the complexation of Al^{+3} and Ca^{+2} , allowing the precipitated P to be solubilized and measured (Raij, 1991). This is a type of ligand exchange (F^{-1} for phosphate). It was assumed that the methylphosphonic group of glyphosate would present a behavior comparable to inorganic P in soil.

After extraction, soil samples were oxidized in a biological oxidizer and the radioactivity was measured by LSC.

The radioactivity existing in the soil as well as the cumulative amount of $^{14}\text{CO}_2$ evolved as a function of time were fitted using first order degradation kinetics (Eqs. 1 and 3, respectively) (Sparks, 1989):

$$C = C_0 e^{-k_1 t} \quad \text{Eq. (1)}$$

where C is the percent of radioactivity remaining in the soil at time, t ; C_0 is the entire radioactivity; and k_1 is the velocity constant of ^{14}C -glyphosate mineralization. Using this k_1 value it is possible to calculate the mineralization half-life ($T_{1/2 \text{ min.}}$):

$$T_{1/2 \text{ min.}} = \frac{\ln 2}{k_1} \quad \text{Eq. (2)}$$

In the specific case of glyphosate in oxidic soils, where a major part of the total applied glyphosate undergoes irreversible sorption (bound-residue formation) (Prata et al., 2000, 2003), and considering that this bound-residue form (covalent linkage with metallic soil oxides) is practically unavailable to microorganisms (Steen et al., 1980) because microbial degradation is carried out by bacteria in soil solution (Quinn et al., 1988; Krzysko-Lupicka & Orlik, 1997), we can consider the k_2 value (Eq. 3) as a velocity constant for dissipation. Thus, Eq. (1) can be rewritten as Eq. (3):

$$C_I = C_{0I} (1 - e^{-k_2 t}) \quad \text{Eq. (3)}$$

where C_I is the percentage of $^{14}\text{CO}_2$ evolved and C_{0I} is the maximum cumulative $^{14}\text{CO}_2$ evolved.

Table 1. Chemical characteristics, physical and mineralogical properties of a Brazilian Rhodic Oxisol collected from no-till or conventional management soil system

Management soil system	pH CaCl_2	Organic carbon	P	CEC	Sand	Silt	Clay	Al_2O_3	Fe_2O_3	Clay minerals
No-till	5.2	32.0	89	141.8	460	70	470	158.1	64.7	$\text{K}^{(1)}$; $\text{Gb}^{(2)}$; $\text{HIV}^{(3)}$
Conventional	5.0	25.0	59	123.2	380	60	560	189.7	87.4	K; Gb; HIV

⁽¹⁾ Kaolinite. ⁽²⁾ Gibbsite. ⁽³⁾ Hydroxy interlayer vermiculite.

The dissipation half-life ($T_{1/2dis.}$) refers to the time when 50 % of the total herbicide concentration applied is no longer present in its original form. In the case of glyphosate this corresponds to degradation plus irreversible sorption. This $T_{1/2dis.}$ can be calculated using the following equation:

$$T_{1/2dis.} = \frac{\ln 2}{k_2} \quad \text{Eq. (4)}$$

In parallel to the above investigation, flasks under the same experimental conditions as those of the mineralization test, but using only the technical (non-radioactive) glyphosate were carried out in triplicate, in order to evaluate the microbial activity for each management system over time. Soil microbial activity was evaluated in each flask 0, 15, 30, 45, and 60 days after glyphosate application, using the ^{14}C -glucose method (Freitas et al., 1979). Total $^{14}\text{CO}_2$ evolved from microbial activity was measured by trapping in hydroxylamine and by scintillation counting.

Analysis of variance and Tukey's test ($p < 0.05$) were used to compare the values of total $^{14}\text{CO}_2$ evolved after 63 days and mineralization ($T_{1/2min.}$) and dissipation ($T_{1/2dis.}$) half-life. The software CurveExpert 1.3 was employed to fit the kinetic experiments.

Sorption kinetics

Glyphosate sorption kinetics was studied for both no-till and conventional management systems, using a soil to solution ratio of 1/5 and 0.01 mol L⁻¹ CaCl₂ as the background solution. The applied glyphosate concentration was 0.84 mg L⁻¹ with a radioactivity of 0.233 kBq mL⁻¹. ^{14}C -phosphonomethyl glyphosate was employed in this study as well as in the sorption/desorption study. The soil/solution mixture was shaken in a horizontal shaker (254 g). Solution radioactivity was measured at 0, 10, 30, 60, 120, 240, and 360 min after herbicide application. This study was carried out in triplicate. The soil/solution mixture was centrifuged at 6350 g for 10 min and radioactivity in the supernatant liquid was determined for an aliquot (1 mL) using LSC. The sorbed herbicide was calculated as the difference between the initial and final solution concentrations.

The model of Elovich (Sparks, 1989);

$$\frac{\partial S}{\partial t} = X^{-Y} S \quad \text{Eq. (5)}$$

was fitted to the kinetic data. In this equation, S is the sorbed concentration of glyphosate, t is the equilibration time, and X and Y are specific constants for the experiment.

The analytical solution of this equation is:

$$S = (1/Y) \ln (XY) + (1/Y) \ln t \quad \text{Eq. (6)}$$

The values $[(1/Y) \ln (XY)]$ and $(1/Y)$ represent the total amount sorbed during the initial phase (sorption kinetics in the fast phase) and sorption rate variation as a function of time (kinetics in the slow phase), respectively.

Sorption/desorption

The glyphosate sorption isotherm was determined in a similar manner to the sorption kinetics experiment, with five herbicide concentrations: 0.42, 0.84, 1.68, 3.36 and 6.72 mg L⁻¹ and six replicates. The equilibration time adopted was 2 h. The radioactivity from ^{14}C -phosphonomethyl glyphosate was determined by LSC in aliquots of 1.0 mL. Desorption was performed at a concentration of 0.84 mg L⁻¹. After the sorption step, all the supernatant was decanted and 5 mL of fresh 0.01 mol L⁻¹ CaCl₂ solution was added to the tubes in order to desorb the glyphosate. The tubes were shaken again at 254 g, for 4 h. Afterwards, the tubes were centrifuged at 6350 g for 10 min. Radioactivity in the liquid supernatant was determined for an aliquot (1 mL) using LSC. The procedure was performed 4 times.

Results from the sorption experiment were fitted with the Freundlich equation:

$$S = K_f C_e^N \quad \text{Eq. (7)}$$

where, S is the sorbed herbicide concentration, C_e is the herbicide concentration in the equilibrium solution, K_f is the Freundlich constant, and N is the linearization degree of the isotherm. When the value of N is 1, or $0.9 < N < 1.1$, the Freundlich constant (K_f) can be considered as a partition constant ($K_d = S/C_e$). The values of K_d were normalized for the organic carbon (K_{oc}) (Eq. 8) in order to calculate the GUS index (Eq. 9).

$$K_{oc} = \frac{K_d}{C_{org}} 100 \quad \text{Eq. (8)}$$

Using the dissipation half-life ($T_{1/2dis.}$) and the K_{oc} value, a potential leaching estimate was calculated using the GUS index (Gustafson, 1989):

$$GUS = \ln T_{1/2dis} (4 - \ln K_{oc}) \quad \text{Eq. (9)}$$

Analyses of variance and Tukey's test ($p < 0.05$) were applied to the total amount sorbed, K_{oc} , and K_f values.

Biological test

The biological test was based on the visual inspection of glyphosate phytotoxicity symptoms in *Panicum maximum*. The test plants were grown on soil incubated at different glyphosate concentrations. *P. maximum* was grown in pots with 400 g dry soil collected from both no-till and conventional management systems. Before the start of the

experiment, the soils were initially air-dried and subsequently wetted to 60 % of the field capacity. Afterwards, glyphosate was applied to the soil and the soil was homogenized. Immediately after application, *P. maximum* seeds were sown (10 in each pot) and the plants were maintained in a greenhouse throughout the experiment. The experiment consisted of a 2 x 5 factorial combination (two management systems- NT and CON and 5 glyphosate doses (0, 4.2, 8.4, 42.0, and 210.0 mg kg⁻¹) arranged in a completely randomized block design, with five replicates. The glyphosate doses used were chosen based on the maximum recommended concentration for field conditions (4.2 mg kg⁻¹) up to 50 times that dose (210.0 mg kg⁻¹).

Visual symptoms of phytotoxicity were assessed 3 times and values were assigned in comparison to the control treatment. The scores ranged from 0 (for perfect plants) to 5 (for dead plants) and were assigned by five different people. Average scores were transformed into phytotoxic symptom percentages. Evaluations were performed 7, 14, and 20 days after germination. Plants were then removed from the pots and the soils maintained without water addition for a further 40 days. Sixty-four days after the initial herbicide application, the soil was rewetted to 60 % of the field capacity and new *P. maximum* seeds were sown. No new herbicide application was performed. Subsequently, evaluations of phytotoxic symptoms were obtained 10 and 20 days after seed germination, using the same procedure as described above.

Regression analyses were performed between the percentage of symptoms observed 24 and 84 days after the herbicide application and the glyphosate concentration.

RESULTS AND DISCUSSION

Sixty three days after the application of glyphosate the ¹⁴CO₂ evolved was higher in the no-

till (NT) treatment than in the conventional (CON) management system (Table 2). This may be explained by the greater microbial activity in NT system (Figure 2) and might be related to the greater carbon and P contents found under this management system (Table 1). This observation is supported by the laboratory studies of Rocha (1999), who showed that microbial activity in NT is higher than in CON.

Glyphosate mineralization was dependent on the ¹⁴C labeling position (Table 2). For both soil management systems, mineralization was faster for the molecule with the labeling in the ¹⁴C2-glycine group than for the molecule labeled in the phosphonomethyl group (Table 2). This suggests that the main route of glyphosate mineralization resulted in the formation of the metabolite aminomethylphosphonic acid (AMPA), the main glyphosate transformation product found in soil (Rueppel et al., 1977; Roy et al., 1989; Cheah et al., 1998). However, AMPA still contains the methylphosphonic group, which is involved in covalent linkages with the soil oxides (Gerritse et al., 1996; Prata et al., 2000, 2003). Therefore, its

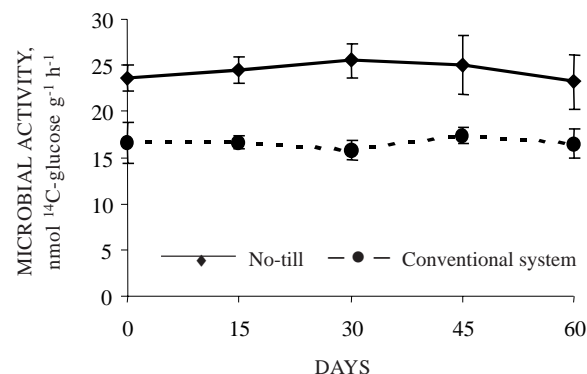


Figure 2. Microbial activity in a Brazilian Rhodic Oxisol under 23 years with no-till and conventional management soil systems. Bars represent standard deviation.

Table 2. ¹⁴CO₂ evolved, mineralization half-life (T_{1/2} min), dissipation half-life (T_{1/2} dis) and extraction of ¹⁴C-glyphosate, radiolabelled at different positions, in a Brazilian Rhodic Oxisol under 23 years of no-till (NT) or conventional management soil system (CON)

Management system	¹⁴ C position	¹⁴ CO ₂ evolved	T _{1/2} min	T _{1/2} dis	Extracted glyphosate
		%	days		%
NT	C – phosphonomethyl	10.8 ± 0.9 b ⁽¹⁾	440.0 ± 39.3 c	14.5 ± 0.8 c	0.00
	C-2 – glycine	17.1 ± 0.8 a	252.6 ± 12.8 d	19.3 ± 2.2 b	0.00
CON	C – phosphonomethyl	5.6 ± 0.2 d	782.1 ± 32.8 a	18.4 ± 2.2 b	0.00
	C-2 – glycine	8.6 ± 0.8 c	539.1 ± 58.4 b	25.8 ± 1.4 a	0.00

⁽¹⁾ Means followed by the same letters are not statistically significantly different according to Tukey's test (p < 0.05).

sorption coefficients may be comparable with those of the parent molecule. Considering that the bound-residues of glyphosate are practically unavailable to microorganisms, the sorption of AMPA may restrict the complete mineralization of glyphosate in the soil.

Since the AMPA formation is the main pathway for glyphosate degradation in soils, the best glyphosate labeling position for mineralization studies must be the phosphonomethyl group. This is supported by the fact that when the labelling position is at the ^{14}C -glycine position, the ^{14}C -AMPA formation is not considered, and the total mineralization of glyphosate may be overestimated. This overestimation does not occur with the labeling position in the ^{14}C -phosphonomethyl group. On the other hand, for dissipation studies it is important to use two glyphosate-labeling positions.

The values for the dissipation half-life ($T_{1/2dis.}$) were lower than those for $T_{1/2min.}$, and ranged between 14.5 and 25.8 days (Table 2). Despite the value of $T_{1/2min.}$, $T_{1/2dis.}$ was faster for ^{14}C -phosphonomethyl glyphosate than for ^{14}C -glycine under both management systems (Table 2). In this case the dissipation half-life considers the degraded fraction of glyphosate as well as the non-extracted fraction (bound-residue fraction). Therefore, although the mineralization is faster when the labeling position is in the phosphonomethyl group, the sorption of ^{14}C is also higher in this case, as discussed above. This can explain the contrasting results for $T_{1/2min.}$ and $T_{1/2dis.}$ (Table 2).

Glyphosate sorption was characterized by a high soil phase affinity, a behavior not expected from the basic chemical data, because it has a high water solubility (11.6 g L^{-1}) and low hydrophobicity ($\log K_{ow} = -4.1$). This strong affinity can be observed in the glyphosate sorption kinetic graphics (Figure 3). Elovich's parameter $[(1/Y)\ln(XY)]$ was equal to 89.9 and 94.2 % for NT and CON, respectively. This suggests that sorption was surface

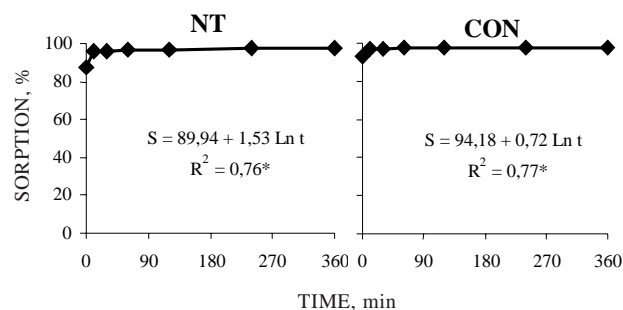


Figure 3. Sorption kinetics of glyphosate and application of the Elovich model to a Brazilian Rhodic Oxisol under 23 years with no-till (NT) or conventional management soil system (CON).

controlled, because there was no slow kinetic phase. Practically the entire amount applied was sorbed during the initial contact time for this soil under both management systems.

Several authors indicated that covalent bonding between the methylphosphonic group and soil metallic oxides is the main retention mechanism of glyphosate in oxidic soils (Hance, 1976; Glass, 1987; Piccolo et al, 1994; Gerritse et al., 1996; Cheah et al., 1997; Prata et al., 2000). This binding presents a high energy, which is in agreement with sorption and desorption data (Table 3).

The proportion of glyphosate sorbed was about 97 % for this soil, for both management systems, and no desorption was observed after four extraction attempts (Table 3). This performance in conjunction with the high K_{f-sor} values (162.9 and 215.7 L kg^{-1} in NT and CON, respectively) suggests sorption by covalent binding. Additional evidence to support the presence of covalent binding was given by the higher sorption rates in CON than in NT (Table 3). For CON, the soil organic carbon content was lower than for NT. The higher carbon content in NT could

Table 3. Sorption and desorption, Freundlich isotherm parameters and GUS index for Glyphosate in a Brazilian Rhodic Oxisol after 23 years under no-till (NT) or conventional management soil system(CON)

Management system	S ⁽¹⁾	D ⁽²⁾	K _{oc}	K _{f-sor} ⁽³⁾	N	R ²	GUS
	%		L kg ⁻¹				
NT	97.2 ± 0.16	0.00 ± 0.0	540.90 ± 8.30	162.9 ± 8.1	0.98	0.99	1.63 ± 0.01
COM	97.9 ± 0.10	0.00 ± 0.0	922.57 ± 41.48	215.7 ± 2.6	0.99	0.99	1.46 ± 0.03
LSD ⁽⁴⁾	0.24	-	54.71	11.00	-	-	-

⁽¹⁾ Glyphosate sorbed. ⁽²⁾ Glyphosate desorbed. ⁽³⁾ Freundlich sorption constant. ⁽⁴⁾ Freundlich desorption constant. ⁽⁴⁾ Calculated by Tukey's test ($p < 0.05$).

contribute to a better protection of oxide surfaces by soil organic matter, which in turn would block these sites for covalent binding. This may likely explain the lower values of K_f -sor in NT, although these values are still very high.

Piccolo et al. (1996) studied glyphosate sorption to humic substances and found lower K_f values than the ones obtained here. Glyphosate sorption to humic substances was attributed to hydrogen bonds.

The low GUS index value (Table 3) suggests that glyphosate is an herbicide with a low leaching potential in this soil under both management systems (Gustafson, 1989). However, this index has limitations and serves only as an indication of the leaching potential. More information concerning glyphosate movement may be obtained from column or lysimeter experiments. Vertical movement of this molecule was observed in sandy soils with an elevated macropore volume. Glyphosate leaching in a Danish soil was observed in undisturbed topsoil columns (Jonge et al., 2000), although sorption was very high [$K_f = 59 \text{ [(mg g}^{-1}) \text{ (mL mg}^{-1})^{-1}]$]. The glyphosate concentration in the percolated column solution varied with solution turbidity, indicating that the molecule was probably leached in its bound-residue form.

For both agricultural systems, phytotoxic symptoms only appeared at concentrations equal to or higher than $42 \mu\text{g g}^{-1}$ (Figure 4). This concentration is equivalent to ten times the maximum dose recommended for field conditions. Only at concentration of $210 \mu\text{g g}^{-1}$ substantial phytotoxicity

problems were noted. There was only a negligible impact of bound glyphosate on crop growth safety, confirming the results from the sorption-desorption experiments, which indicated an extreme glyphosate affinity for the soil solid phase.

CONCLUSIONS

1. The NT system contributed to the acceleration of glyphosate mineralization.
2. The main metabolite resulting from glyphosate degradation was aminomethylphosphonic acid (AMPA).
3. For both the NT and CON systems, glyphosate presented a high sorption rate, which difficult its mineralization. The molecules remained in the soil as bound-residue.
4. The glyphosate sorption kinetics was practically instantaneous.
5. For both agricultural systems, glyphosate phytotoxic symptoms on *P. maximum* only appeared at soil glyphosate concentrations equal to or higher than $42 \mu\text{g g}^{-1}$.

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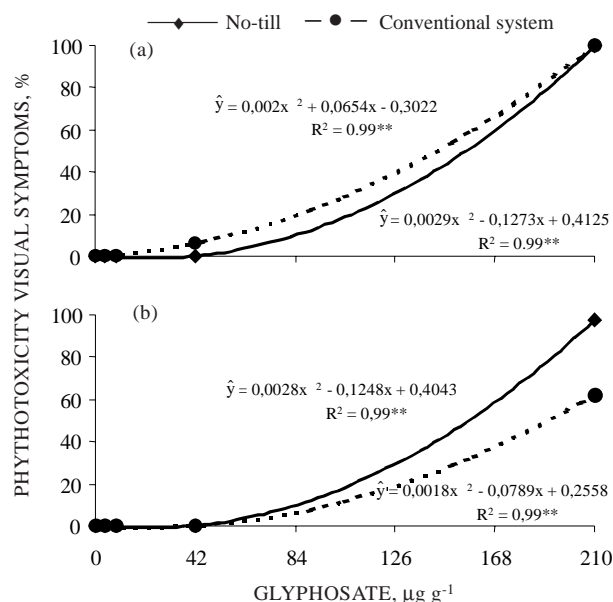


Figure 4. Phytotoxicity symptoms of glyphosate in *Panicum maximum* at 20 days after germination. (a and b: 24 or 84 days after glyphosate soil application, respectively).

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