DIVISÃO 3 - USO E MANEJO DO SOLO

Comissão 3.1 - Fertilidade do solo e nutrição de plantas

EFFECTS OF PIG SLURRY APPLICATION ON SOIL PHYSICAL AND CHEMICAL PROPERTIES AND GLYPHOSATE MOBILITY(1)

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SUMMARY

Pig slurry applied to soil at different rates may affect soil properties and the mobility of chemical compounds within the soil. The purpose of this study was to evaluate the effects of rates of pig slurry application in agricultural areas on soil physical and chemical properties and on the mobility of glyphosate through the soil profile. The study was carried out in the 12th year of an experiment with pig slurry applied at rates of 0 (control), 50, 100 and 200 m^3 ha^{-1} yr^{-1} on a Latossolo Vermelho distrófico (Hapludox) soil. In the control, the quantities of P and K removed by harvested grains were replaced in the next crop cycle. Soil physical properties (bulk density, porosity, texture, and saturated hydraulic conductivity) and chemical properties (organic matter, pH, extractable P, and exchangeable K) were measured. Soil solution samples were collected at depths of 20, 40 and 80 cm using suction lysimeters, and glyphosate concentrations were measured over a 60-day period after slurry application. Soil physical and chemical properties were little affected by the pig slurry applications, but soil pH was reduced and P levels increased in the surface layers. In turn, K levels were increased in sub-surface layers. Glyphosate concentrations tended to decrease over time but were not affected by pig slurry application. The concentrations of glyphosate found in different depths show that the pratice of this application in agricultural soils has the potential for contamination of groundwater, especially when the water table is the surface and heavy rains occur immediately after application.

Index terms: soil fertilization, physical and chemical properties, pollutant transport, pesticide.

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RESUMO: *EFEITOS DE DOSES DE DEJETOS LÍQUIDOS DE SUÍNOS SOBRE OS ATRIBUTOS FÍSICOS E QUÍMICOS DO SOLO E SOBRE A MOBILIDADE DO GLIFOSATO*

Os dejetos líquidos de suínos são aplicados no solo, como fertilizantes, em diferentes doses. Isso pode interferir nos atributos do solo e na mobilidade de espécies químicas. Este trabalho teve por objetivo avaliar a influência das doses de dejeto líquido de suínos aplicadas em áreas agrícolas sobre os atributos químicos e físicos do solo e sobre a mobilidade de glifosato no perfil do solo. O trabalho foi realizado no 12º ano de condução de um experimento, com aplicação de dejeto líquido de suínos em Latossolo Vermelho distrófico, com doses anuais de 0, 50, 100 e 200 m^3 *ha*$^{-1}$ *ano*$^{-1}$*. Na testemunha (dose 0), houve reposição das quantidades de P e K exportados pelos grãos das culturas. Em cada parcela, foi realizada a determinação dos atributos físicos (densidade, porosidade, textura, condutividade hidráulica do solo saturado) e químicos (teor de matéria orgânica, pH, P extraível e K trocável) do solo. Amostras de solução do solo foram coletadas em seu perfil com o uso de lisímetros de sucção, sendo determinadas as concentrações de glifosato durante 60 dias. Os atributos físicos e químicos do solo foram pouco influenciados pelas doses aplicadas de dejeto líquido de suíno; contudo, o pH do solo foi reduzido e os teores de P aumentaram nas camadas superficiais. Por sua vez, os teores de K aumentaram nas camadas subsuperficiais. As concentrações de glifosato apresentaram tendência de diminuir ao longo do tempo e não foram influenciadas pelas doses de dejeto líquido de suínos aplicadas. As concentrações de glifosato encontradas evidenciaram que a prática de aplicação de dejetos de suínos em solos agrícolas tem potencial de contaminação das águas subterrâneas, especialmente quando o lençol freático estiver próximo à superfície e as fortes chuvas ocorrerem após a aplicação do glifosato.*

Termos de indexação: fertilização do solo, atributos físicos e químicos, transporte de poluentes, pesticidas.

INTRODUCTION

Animal production is one of the main activities of Brazilian agriculture, and pig production is an important part (Thiele-Bruhn, 2003). The rearing of pigs in confinement is common in southern Brazil, where the number of production units is decreasing, while the amount of manure produced by the remaining units is increasing (Veiga & Pandolfo, 2010).

Residual waste from pig production has been applied to agricultural areas as a way of minimizing the destruction of natural resources, by avoiding pollutant discharge to water bodies, recycling nutrients and increasing the nutrients given to crops. Different application rates have been used. In some studies, application rates from 20 to 200 m^3 ha^{-1} yr^{-1} were used (Veiga et al., 2008), and a question is whether such levels affect the soil physical and chemical properties and interfere with the transport of chemical compounds through the soil profile.

The accelerated development of agriculture has brought the need for increased use of pesticides, and herbicides are the biggest group of pesticides used, making up half of all such products (Amarante Junior et al., 2002; Cserháti et al., 2004). Of all pesticides sold in Brazil in 2.011, 34 % were herbicides (SINDAG, 2012), including glyphosate [n-(phosphonomethyl) glycine]. Glyphosate is the most sold herbicide in the world because of its efficiency in eliminating an extensive range of weed species (Amarante Junior et al., 2002).

Despite its proven efficiency, there is evidence that it has adverse environmental effects. Glyphosate residues have been found in surface waters (Dores & Freire, 2001; Silva et al., 2003; Queiroz et al., 2011), in groundwater (Sakaliene et al., 2007; Andrade et al., 2011; Britto et al., 2011), and in soil (Prata et al., 2000; Souza et al., 2006).

In most cases, glyphosate is not metabolized by the plant and almost all of its active ingredient enters the soil (Prata et al., 2000). Movement of herbicides through the soil is influenced by the type of organic material, pH, composition and distribution of soil particle size, bulk density, and the size and distribution of soil pores (Rossi et al., 2005). Glyphosate has a half-life ($T_{1/2}$) of 32 days with moderate persistence (Giesy et al., 2000) and, under natural conditions, it is water-soluble, percolating easily through the soil profile with internal drainage water (Veiga et al., 2001; Amarante Junior et al., 2002).

It is therefore important to study how glyphosate moves through soil in solution by mass flux and diffusion (Javaroni et al., 1999). After they have been applied to agricultural areas, herbicides undergo transport processes between environmental sectors by leaching and surface runoff (Queiroz et al., 2011). By leaching, the downward movement of herbicides in the soil profile, molecules move to deeper layers with the potential to degrade groundwater, especially when soil is highly permeable and/or the water table is close to the surface (Inoue et al., 2003). Surface runoff, on the other hand, allows the transport of molecules adsorbed on sediments or in solution, leading to degradation of surface waters (Prata et al., 2000).

Glyphosate is easily adsorbed onto soil colloids and can reach values of 1.188 L kg^{-1} in organic soils (Cheah et al., 1999), being adsorbed into soils even after destruction of the organic matter (Prata et al., 2000). Adsorption of glyphosate is mainly related to the mineral fraction of the soil, especially on Fe and Al oxides and clays, but organic matter also plays a fundamental role in the process (Toni et al., 2006). Once adsorbed, glyphosate tends to persist in the soil for years (Amarante Junior et al., 2002), with the active component remaining as a residue attached to soil colloids (Prata et al., 2000). Thus, knowledge of the soil physico-chemical properties is extremely important in the study of pesticide mobility, as factors including pH and clay and organic matter contents have a significant influence on the determination and recovery of the molecules (Souza et al., 2006).

One of the factors with observed effects on the movement of pesticides in soil is the influence of organic material originating from the application of pig slurry to agricultural areas. Prata & Lavorenti (2000) found that, when organic material is added to soil, herbicide behavior is altered because the added organic material increases sorption capacity in the soil, contributing to greater adsorption and the formation of residues linked to herbicides. Some studies, however, have reported that the herbicides could be desorbed, resulting in further leaching down to groundwater (Correia et al., 2007; Song et al., 2008).

Due to the importance of animal production in Brazilian agriculture, it is essential to evaluate the effects of pig slurry applications on the dynamic of environmental processes. The relation between pesticide use and organic matter introduced by pig slurry application to soil is not yet clear, nor is the influence of soil physical and chemical properties on the way that pesticides move. The purpose of this study is, therefore, to evaluate the influence of pig slurry applied to agricultural areas on soil chemical and physical properties and on the mobility of glyphosate through the soil profile.

MATERIALS AND METHODS

The study was performed in the 12th year of an experiment with continuous pig slurry application and consisted of the analysis of soil samples and soil solution collected in the 2011/2012 crop season at different depths and times after application of pig slurry and glyphosate. Soil chemical and physical properties and glyphosate concentration in the soil solution were measured. Amount of rainfall and its distribution through the course of the sampling period were also recorded in order to analyze glyphosate mobility.

Study area and treatments

The field work was carried out in an agricultural area of the municipality of Campos Novos in the midwestern part of the State of Santa Catarina, in the south of Brazil, located at latitude 27° 22' 59" S, longitude 51° 15' 33" W and 896 m altitude. The soil is a Hapludox, with clayey texture, deep profile, low slope, and high water storage capacity, where the primary vegetation is that of sub-tropical savannah (Embrapa, 2004). The predominant climate is moist sub-tropical with mild summers, classified as Cfb according to Köppen (Pandolfo et al., 2002).The experiment was carried out in a field, managed with crop rotation and no-tillage for more than 10 years, with the following soil properties at the 0.00-0.20 m soil depth: pH(H_2O) of 5.8; 45 g kg^{-1} of soil organic matter (SOM); 0.0, 0.5, 4.7, and 2.9 $cmol_c$ dm^{-3} of exchangeable Al, K, Ca, and Mg, respectively; and 10.0, 10.5, and 1.7 mg dm^{-3} of extractable P, Cu, and Zn (Mehlich-1), respectively.

The treatments applied were annual rates of 0 (control), 50, 100, and 200 m^3 ha^{-1} yr^{-1} of pig slurry (denoted by PS50, PS100, and PS200, respectively). In the control treatment, the amounts of P and K exported by harvested grains were replaced (denoted by RPK). Over the 12 years of experimentation, a three-year crop rotation was used, with the following annual sequence, all sowed by direct drilling: oats (*Avena strigosa* L.) + vetch *(Vicia sativa* L.*)* in autumn, and oats and corn *(Zea mays L.)* in the spring; oats in the autumn and soybean (*Glycine max* L.*)* in the spring; and oats in the autumn and beans *(Phaseolus vulgaris* L.*)* in the spring. The treatments were applied in plots of 5 × 6 m, in a randomized complete block design with three replications.

Annual ratess of pig slurry were applied in two parts, half in the autumn and half in the spring, before sowing of crops. Pig slurry was obtained from an anaerobic lagoon reservoir, in a pig finishing farm located in the municipality of Campos Novos. The average composition of the slurry used in the 24 applications (two applications per year) was 2.36 % dry matter; 7.3 pH(H_2O); 3.86, 0.67, 1.66, 0.38, and 0.41 kg m^{-3} of total N, P, K, Ca, and Mg, respectively; and 24 and 49 g m^{-3} of total Cu and Zn, respectively. The total amounts of organic matter and nutrients applied as pig slurry in the 12 years of experimentation are shown in table 1. The P and K exported by harvested grains were replaced in each control plot before sowing the subsequent summer crop, using superphosphate and potassium chloride as nutrient sources.

In May 2011, the whole area was broadcast seeded with black oats (*Avena strigosa* L.) on residues of soybean, which had been sown with no-tillage and a planter containing a chisel trencher that reached 10 cm depth, in soil that had been cropped in the preceding April. This was followed by weed control by spraying 1.0 kg ha^{-1} of active ingredient of glyphosate

Table 1.Total amount of dry matter from organic matter and nutrients applied through pig slurry over the 12 years of experimentation

Application rate	Dry matter	N	P	K	Ca	Mg
m^3 ha^{-1} yr^{-1}	t ha^{-1}					
50	14.16	2.32	0.40	1.00	0.23	0.25
100	28.32	4.63	0.80	1.99	0.46	0.49
200	57.64	9.26	1.61	3.98	0.91	0.98

on all areas on May 25, 2011, using a backpack sprayer.

Sampling of soil solution

Between May and June 2011, soil water was collected at 1, 3, 7, 15, 30, and 60 days after glyphosate application, to evaluate the presence of glyphosate in the soil solution. Samples were stored in 300 mL polyethylene flasks, which were stored in heat-proof boxes for transport to the laboratory, where they were immediately analyzed.

The soil solution samples were collected by suction lysimeters (Hanna, 2011), which extracted the solution retained in the porous soil matrix at a tension lower than that applied for extraction. The lysimeters were installed in the soil in an orifice opened using a screw-type auger with the same diameter as the porous capsule (Figure 1). Three lysimeters were installed in each plot, with the porous capsules placed at depths from 0.175 to 0.225, 0.375 to 0.425, and 0.775 to 0.825 m, corresponding to sampling at mean depths of 0.20, 0.40, and 0.80 m. Within each plot, the lysimeters were installed 1.0 m from the lower border, with a distance of 0.10 m between them.

Glyphosate analyses

The glyphosate standard used in the analytical procedure was 99.7 % pure, obtained from Sigma-Aldrich®. Samples were filtered using a cellulose acetate membrane with pore-size of 0.45 μm, and glyphosate concentrations were determined using a Dionex® ion exchange chromatograph, model ICS-90, equipped with a conductivity detector, model DS5, following the method described by Queiroz et al. (2011). An analytical column IonPac® AS22 4 × 250 mm, guard column IonPac® AG22 4 × 50 mm, anionic micro-membrane suppressor (AMMS® 300 4 mm), eluent 9.0 mmol L^{-1} Na_2CO_3/2.8 mmol L^{-1} $NaHCO_3$ with flow of 1.2 mL min^{-1}, regenerant 50 mmol L^{-1} H_2SO_4, and injection loop of 250 μL were also used in glyphosate analyses.

Sampling and determination of soil physical and chemical properties.

Soil physical properties were determined in undisturbed samples collected in January 2012 in volumetric rings at the depths of 0.00-0.05, 0.05-0.10, and 0.12-0.17 m. Bulk density, porosity, soil penetration resistance, saturated hydraulic conductivity and aggregate stability of the soil, were determined using methods described by Veiga (2011). Soil chemical properties were determined in samples collected in November 2011 at three points within each plot at the depths of 0.000-0.025, 0.025-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.40, 0.40-0.60, and 0.60-0.80 m. These samples were used to determine pH in water and levels of organic matter, extractable P, and exchangeable K using methods described by Tedesco et al. (1995).

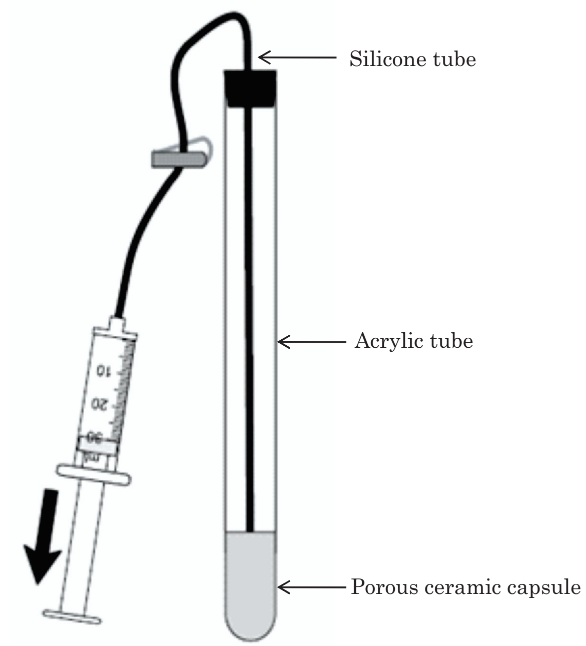

Figure 1. Suction lysimeter used for sampling soil solution.

Statistical analysis

Statistical analysis of the glyphosate concentrations in the soil solution was performed using the “general linear model” procedure (SAS) due to the impossibility of collecting soil solutions in some layers at certain sampling times. The soil property results were analyzed by ANOVA, and the comparison of means (Tukey, p<0.05) was performed when the F test was significant at 5 %. Both analyses were performed for each soil layer individually.

RESULTS AND DISCUSSION

Soil physical properties

For most soil physical properties, no differences were found among treatments (Table 2). However, differences among treatments were observed for water retention in pores less than 50 µm in diameter, saturated hydraulic conductivity, and arithmetic mean diameter of air-dried aggregates (Table 3). Similar results have been reported in other studies comparing physical characteristics of plots to which different rates of pig slurry were applied (Veiga et al., 2008; Arruda et al., 2010; Veiga et al., 2012).

Statistical comparison between soil layers was not possible, so the greatest differences in physical properties are observed within them (Table 2). Bulk density is lower in the 0.00-0.05 m layer, increasing with depth. Similar results were obtained by Arruda et al. (2010), who also examined the effect of pig slurry application on soil physical properties. These authors concluded that the lower density in surface layers could be related to the organic matter introduced when organic residues are applied, which may improve the degree of aggregation and reduce the soil mass by lowering specific density, and may even fill soil pores. As a consequence, lower porosity was found in the 0.00-0.05 and 0.05-0.10 m layers. However, a greater volume of macropores was found in these layers. Similar results were found by Seganfredo (1998), showing that pig slurry application increased macroporosity and reduced soil density.

Malone et al. (2003) reported that the presence of macropores increased water flux through the soil profile, with a consequent increased potential for leaching herbicides into deeper layers (Correia et al.,

Table 2. Physical properties of an Hapludox after twelve years of pig slurry applications, which did not show differences among application rates (averaged across pig slurry treatments)

Layer	Bd	PR_{600}	TP	MA	ME	MI	Sand	Silt	Clay	AMDws	ASI
m	kg dm^{-3}	MPa	m^3 m^{-3}				kg kg^{-1}			mm	
0.00-0.05	0.89	2.00	0.58	0.18	0.10	0.30	28	350	622	2.44	0.86
0.05-0.10	1.00	2.36	0.58	0.16	0.10	0.35	19	316	666	2.36	0.78
0.12-0.17	1.06	3.29	0.61	0.12	0.11	0.35	20	333	648	2.08	0.70
CV (%)	6.2	25.7	4.8	24.6	8.3	8.5	23.7	7.2	3.9	17.6	16.1

BD: Bulk density; PR: soil penetration resistance with water tension at 600 kPa; Pores with Ø < 50 µm (meso- + micropores); TP: total porosity; MA: macropores; ME: mesopores; MI: micropores; AMDws: arithmetic mean diameter of water-stable aggregates; and ASI: aggregate stability index. CV: coefficient of variation.

Table 3. Physical properties of an Hapludox after 12 years of pig slurry applications that showed differences among application rates

Layer	Pig slurry application rate (m^3 ha^{-1} yr^{-1})				
	0/RPK[(1)]	50	100	200	Mean
m	Saturated hydraulic conductivity (cm h^{-1})				
0.00-0.05	105.6 AB	85.0 BC	126.7 A	67.9 C	96.3
0.05-0.10	38.1 A	19.6 A	13.7 A	35.6 A	26.7
0.12-0.17	19.9 A	5.5 A	4.2 A	12.6 A	10.6
Mean	54.5	36.7	48.2	38.7	
	Pores < 50 µm (m^3 m^{-3})				
0.00-0.05	0.419 A	0.387 B	0.418 A	0.393 B	0.404
0.05-0.10	0.439 B	0.449 AB	0.464 A	0.451 AB	0.451
0.12-0.17	0.446 A	0.468 A	0.469 A	0.465 A	0.462
Mean	0.435	0.434	0.450	0.436	
	Arithmetic mean aggregate diameter, air dried (mm)				
0.00-0.05	2.9 AB	2.6 B	2.8 AB	3.1 A	2.8
0.05-0.10	3.2 A	3.0 A	2.9 A	2.9 A	3.0
0.12-0.17	2.9 A	2.9 A	3.1 A	3.1 A	3.0
Mean	3.0	2.8	2.9	3.0	

(1) RPK: replacement of P + K exported as harvested grain. Means of each property that are followed by different letters in the lines are statistically different (Tukey, p<0.05).

2007). This was shown in the present study by increased saturated hydraulic conductivity of the soil (SHC) in the surface layer (Table 1). In contrast, some authors suggest that root growth along cultivation rows gives rise to channels for the preferential flow of water after their decomposition, increasing hydraulic conductivity in surface layers (Singh et al., 2002).

The differences in clay, silt, and sand contents between layers (Table 2) are characteristics of the soil itself, with a moderate increase in clay level with depth. The small inversion in this trend between the two subsurface layers may be related to the clay eluviation-illuviation process, acting between the subsurface and intermediate layers as a result of soil management in a no-till system that would cause no mixing of layers.

The differences in SHC among application rates were found only for the first layer (Table 3). However, there was no clear relationship between application rates and SHC, just a suggestion that SHC was lower at the higher pig slurry application rate. This indicates that other factors influence the variability in SHC among plots and layers. The volume of meso + micropores (pores with Ø < 50 μm) showed the same trend as SHC between application rates (Table 3). For this property, differences were also observed in the second layer sampled, and its values increase up to 100 m^3 ha^{-1} yr^{-1} of pig slurry application and fall at the highest rate of application. Different results were reported by Arruda et al. (2010), who found that pig slurry applications at rates of 50 and 100 m^3 ha^{-1} reduced soil aggregate stability in relation to fertilized control plots, and that there were no changes in other soil physical properties, showing that pig slurry use in agriculture maintained soil physical quality under the conditions studied.

Soil chemical properties

Organic matter was not significantly altered by the treatments (Figure 2a), a result similar to that observed by Muraishi et al. (2011) and Scherer et al. (2010). However, Lourenzi et al. (2011) found different results, with increasing organic matter in deeper soil layers after pig slurry application.

The pig slurry applications caused a reduction in pH in water in the first sampled layer (Figure 2b), which can be explained as biodegradation of the organic matter by producing organic acids, resulting in soil acidification (Andrade et al., 2002). In addition, the ammonia nitrification process gives rise to liquid release of H^+ ions and reduction in soil pH when the nitrate is not absorbed in the same layer as that where the process occurs (Aita et al., 2007). In deeper layers, no significant differences in pH in water were found among the rates of pig slurry application, in agreement with studies in similar soils by Muriashi et al. (2011) and Scherer et al. (2007). They also found no significant changes in other properties related to soil acidity. However, different results were found by Lourenzi et al. (2011) in an Ultisol soil, where an increase in pH in water was found in the surface layer after pig slurry applications.

Extractable phosphorus contents increased with applications of pig slurry up to a depth of 0.05 m (Figure 2c). However, no appreciable migration to deeper layers was observed, even where levels of P were high in the superficial layers, which could be due to the high soil capacity for P adsorption. Similar results were found by Scherer et al. (2007), who looked at the effects of pig slurry applications in a similar Hapludox, also managed in a no-till system, and by Queiroz et al. (2004), who studied the effects of pig slurry application on pastures in an Ultisol soil in the State of Rio Grande do Sul, Brazil. The P added to soil as pig slurry is adsorbed in it at specific exchange sites. When these sites are saturated, P can be leached by water, percolating through the soil profile. Losses of P by leaching or surface runoff, when attached to soil colloids, present a risk of degradation of groundwater and surface waters, respectively (Ceretta et al., 2010). Berwanger et al. (2008) found that pig slurry application at the surface of an Ultisol soil resulted in nutrient loss by surface runoff, while Djodjic et al. (2004) reported nutrient losses by leaching.

There was no significant increase in the level of exchangeable K in the upper soil layer (Figure 2d) probably because the exchange sites for this element were saturated in this layer. However, in lower layers (0.025-0.40 m) exchangeable K increased with an increasing application rate of pig slurry, and this is somewhat at odds with results found by Scherer et al. (2010) in a Cambisol and in an Inceptisol soil in the west of Santa Catarina, Brazil; it is also at odds with results reported by Queiroz et al. (2004) in a Ultisol soil in Rio Grande do Sul, Brazil, where exchangeable K was found to accumulate in the upper soil layers and to decrease in deeper layers after pig slurry application.

Glyphosate mobility

Rainfall was 412 mm during the period in which the soil solution was sampled (Figure 3) and was relatively well distributed over that period. The rainfall was greater than the climatic mean for the region, given by the National Meteorological Institute (INMET, 2012), which is about 240 mm in this period. The higher than average rainfall may have favored the transport of active ingredients by leaching and by surface runoff (Andrade et al., 2011) and, as a consequence, led to contamination of water bodies.

There were differences in glyphosate concentration in the soil solution among sampling times but not among application rates of pig slurry (Table 4, Figure 3). Concerning the concentrations of glyphosate in the water samples collected with lysimeters, the herbicide was found in 43.5 % of the samples analyzed, with mean concentrations from 0.013 to 0.485 mg L^{-1}

(Figure 4). These results are similar to those reported by Peruzzo et al. (2008), Litz et al. (2011), and Queiroz et al. (2011), who had used similar applications of herbicide in soils treated with organic wastes.

At the first sampling time, performed one day after glyphosate application, no rain fell and the mean concentration was 0.06 mg L^{-1}. It is possible that the prevailing conditions did not result in transport

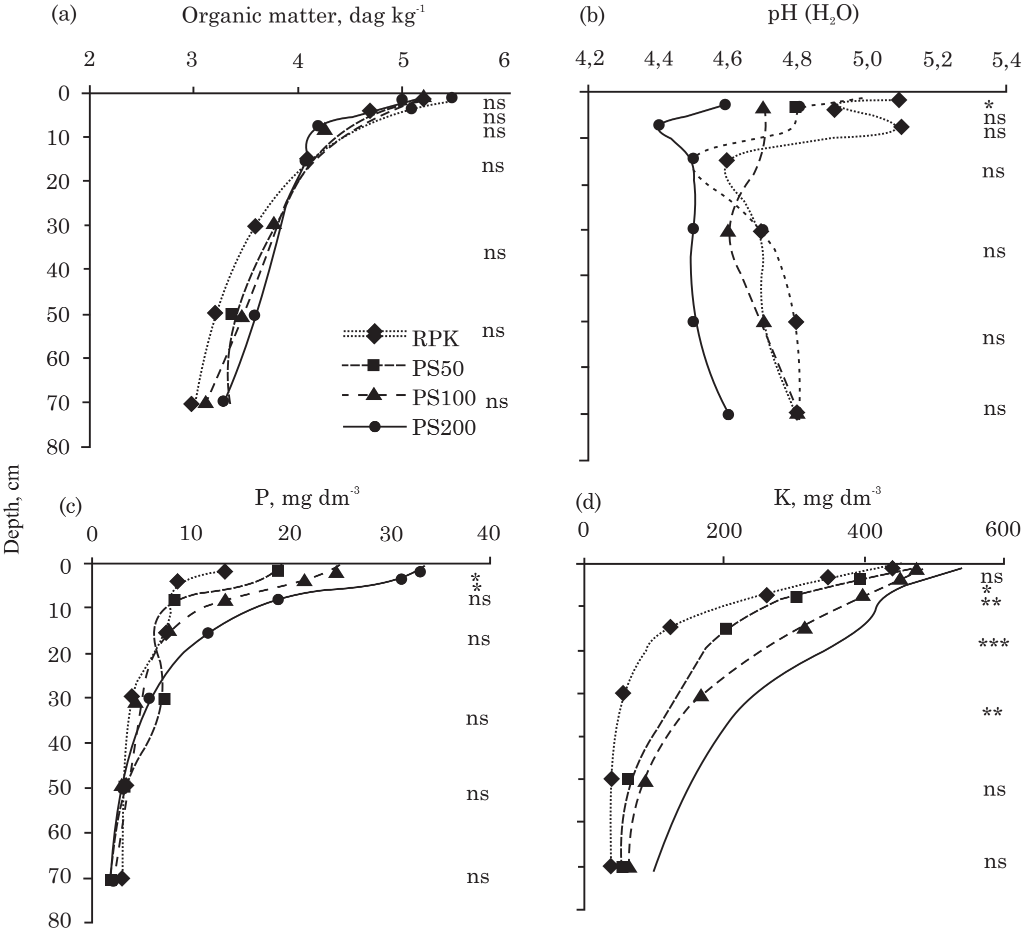

Figure 2. Soil chemical properties throughout the profile of an Hapludox soil in the 12th year of replacement of P + K exported in harvested grain (RPK) and pig slurry applications (PS50, PS100, and PS200); PS50, PS100, and PS200 represent application rates of 50, 100, and 200 m^3 ha^{-1} yr^{-1} of pig slurry, respectively; ns, *, **, and * denote non-significant differences and differences at significance at 5, 1 and 0.1 %, respectively.**

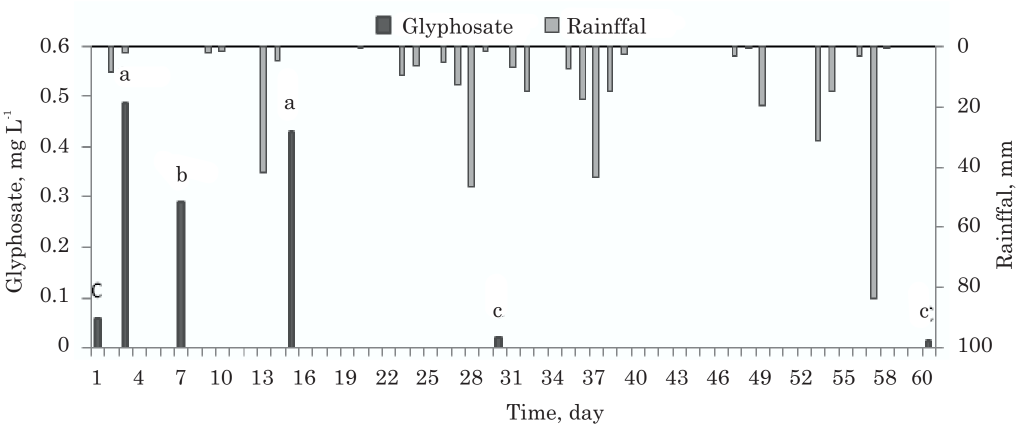

Figure 3. Concentrations of glyphosate and rainfall during the sampling period. Bars identified by different letters are different among themselves (Tukey, p<0.05).

Table 4. Analysis of variance of the glyphosate mobility variable

Source of variation	Degree of freedom	Probability<F	
		Original	Transformed(1)
Pig slurry application rate	3	0.3358	0.2982
Sampling time	5	0.1005	0.0383*
Application rate × time	18	0.2007	0.1990
CV (%)		413	23

(1) $y' = (1 + y)^{1/2}$; * significant difference at 5 %. CV: coefficient of variation.

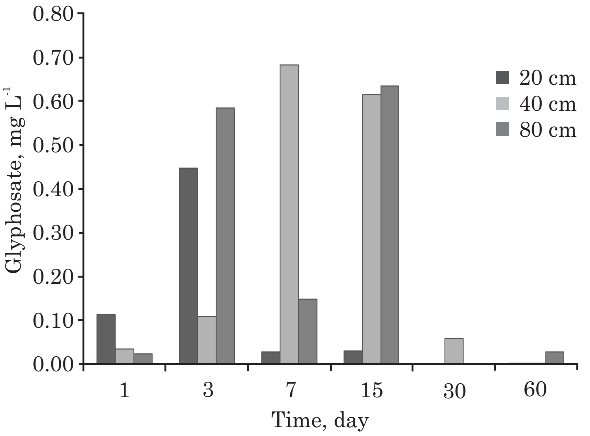

Figure 4. Glyphosate concentrations at different soil depths during the sampling period.

through the soil profile, so that the mean concentration was low. On the other hand, the glyphosate could have been adsorbed to soil constituents or to the particulate organic matter present in the slurry. The addition of dissolved organic matter to soils may promote the leaching of pesticides (Song et al., 2008) since the capacity for phosphate adsorption to organic groups in soil is diminished, giving rise to greater concentration in soil water (Scherer, 1993). Morillo et al. (2002), who studied the effect of pH on glyphosate adsorption in soils, reported that this adsorption diminished as pH increased in the soil water solution. This reduction in adsorption could be a consequence of increasing negative charge at the soil surface because of reduction in pH in water, thus causing a lower electrostatic attraction, reducing its adsorption (Toni et al., 2006).

The high levels of P and amount of soil organic matter (SOM) (Figure 2) may have resulted in glyphosate adsorption since the herbicide molecules interact with SOM and the slurry applied, thus generating linked residues mobilized in the soil (Veiga et al., 2001). This phenomenon of adsorption to soil constituents does not rule out the possibility that, as time passes, the herbicide returns to solution by desorption, making it available for leaching processes (Correia et al., 2007). This mechanism was probably responsible for increasing glyphosate concentration observed three days after application, when it reached 0.485 mg L^{-1}, probably because of high rainfall which preceded sample collection, which would favor its migration through soil in solution (Figure 3). Seven days after application, the concentration was 0.289 mg L^{-1}, which can be explained by the fact that, even after a dry spell, glyphosate continued to be leached by water percolating through the soil profile. Fifteen days after application, mean concentration increased again to 0.430 mg L^{-1}, which is associated with the high rainfall in the 48 h before sampling (47 mm), which contributed to the desorption of glyphosate and its transport through the soil profile. Thirty days after application, glyphosate concentration fell to 0.022 mg L^{-1} and to 0.013 mg L^{-1} after 60 days, which may be associated with degradation of the ingredient by microbial action in the period from the time of application, as was also observed by Newton et al. (1994).

The analysis of glyphosate concentrations at the mean sampled depths of 20, 40, and 80 cm shows the movement of glyphosate through the soil profile during the sampling period (Figure 4). On the 1st day after application, concentration was higher in the 1st layer relative to the 3rd, with values of 0.115 and 0.026 mg L^{-1}, respectively. This demonstrates that glyphosate moved from the surface layer, where it was applied, down to a depth of about 0.80 m, or, alternatively, this level may be a residue from an earlier application, six months before. Glyphosate residues have been found in other studies at depths of 0.15 m (Newton et al., 1994), 0.30 m (Veiga et al., 2001), 0.40 m (Litz et al., 2011) and 1.00 m (Queiroz et al., 2011).

The glyphosate concentrations in the soil solution of the 1st layer increased up to the 3rd day after application, decreasing afterwards to a value of 0.0044 mg L^{-1} 60 days after application (Figure 4). One possible explanation for this is that, in addition to herbicide mobility, greater microbial activity in the surface layer leads to glyphosate degradation in this layer (Veiga et al., 2001). At the mean depth of 0.40 m, concentrations increased up to the 7th day after application, reaching a maximum concentration of 0.6857 mg L^{-1}, and decreased to a final concentration of 0.0045 mg L^{-1}. Then in the 3rd layer, maximum concentration of 0.6375 mg L^{-1} was found in the soil solution sampled 15 days after application, showing a time-lag before the greatest concentration of the molecule was found, this lag being determined by the internal rate of soil water percolation, which in a non-saturated medium is usually very slow (Hillel, 1998).

No statistical differences were found among the pig slurry application rates, among the layers sampled, nor interaction between application rates and layers (Table 4). This shows that the effects of the factors studied on glyphosate mobility are low. Even when concentrations were transformed, there were no differences among sampling times. This confirms the observation given above that glyphosate concentrations vary over time, particularly as a result of biological degradation of the molecule within the soil.

CONCLUSIONS

1. Pig slurry application did not alter most of the physical and chemical soil properties studied, maintaining the original physical and chemical soil quality.

2. Application rates of pig slurry do not affect the mobility of glyphosate in the soil profile.

3. The glyphosate rapidly reached a depth of 80 cm in the soil and showed a tendency to decline over the monitoring period.

4. The concentrations determined for glyphosate in different depths show that its application on farmland has the potential to degrade ground water, especially when heavy rains occur immediately after application.

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