Glyphosate dynamics in a soil under conventional and no-till systems during a soybean growing season

C. Germán Soracco[a,b], Rafael Villarreal[a,b], Luis Alberto Lozano[a,b,*], Santiago Vittori[c], Esteban M. Melani[d], Damián J.G. Marino[b,c]

[a] Facultad de Ciencias Agrarias y Forestales, UNLP, Calles 60 y 119, CC 31, 1900 La Plata, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina
[c] Centro de Investigaciones del Medio Ambiente, Facultad de Ciencias Exactas, UNLP, Calles 47 y 115, 1900 La Plata, Argentina
[d] Instituto Nacional de Tecnología Agropecuaria, Agencia de Extensión Rural Chascomús, Mitre 202, Chascomús, Buenos Aires, Argentina

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ABSTRACT

Glyphosate (GLY) is a non-selective herbicide, heavily used world-wide in agriculture, especially under no-tillage (NT) management. The objectives of this work were i - to determine the temporal and vertical variation of GLY and its main metabolite (AMPA) levels during the soybean cycle in a soil under NT and conventional tillage (CT); ii - to determine the relationship of GLY and AMPA levels variation with different soil properties; and iii - to compare initial and final GLY and AMPA levels in the soil during a crop cycle to infer possible accumulation. GLY and AMPA contents were determined in the A horizon (0–40 cm) of a loam soil from Argentinian Pampas Region, in different dates during soybean crop cycle. Soil physical and chemical properties were also determined. GLY and AMPA were detected in all sampling dates in both treatments (GLY and AMPA contents in the soil ranged between 5.7 and 98.5 $\mu g \cdot kg^{-1}$; and 6.6 and 1686.0 $\mu g \cdot kg^{-1}$, respectively). GLY was strongly retained in the top soil in most of the sampling dates for both treatments (> 80% of total GLY was found in the topsoil - 20 cm). CT treatment showed higher GLY temporal variation, favored by higher values of saturated hydraulic conductivity (K_0), total macroporosity (θ_{ma}) and effective macroporosity (ε_{ma}), especially when strong precipitation occurred near the application. GLY vertical transport under NT seemed to be limited by low values of K_0, θ_{ma}, and ε_{ma}. The temporal variation of GLY vertical transport was explained by the temporal variation of the studied soil physical and hydraulic properties. Total extracted GLY accumulated, with an increment between the last and the first sampling date of 54% and 82% during the crop cycle for NT and CT, respectively.

1. Introduction

Glyphosate (N-[phosphonomethyl] glycine) (GLY) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. Since its introduction in 1974, GLY became a widely used herbicide, especially under no tillage (NT) management systems. In Argentina three-quarters of agricultural land is cultivated with transgenic crops (soybean, maize and cotton) (Aparicio et al., 2013). Additionally, around 90% of agricultural lands in Argentina are under NT (AAPRESID, 2015), where chemical control is the most common practice for weed control, during cultivation and fallow periods. Around 200 million L of GLY are applied every year in Argentina, being the most commonly used herbicide in the country (Aparicio et al., 2013).

Several studies reported the presence of GLY and its main metabolite aminomethyl phosphonic acid (AMPA) at different depths along the

soil profile (Veiga et al., 2001; Kjær et al., 2005; Candela et al., 2010; Aparicio et al., 2013; Lupi et al., 2015). Also its presence was reported in surface water near to application areas (Vereecken, 2005; Peruzzo et al., 2008; Coupe et al., 2012; Sanchís et al., 2012; Etchegoyen et al., 2017).

Several factors can influence the fate of GLY in the soil. Some of these factors are intrinsic properties of the herbicide (e.g. molecular structure, solubility, and persistence), while other factors correspond to soil properties as clay fraction, organic carbon (OC), pore connectivity, cation exchange capacity (CEC) and pH (Okada et al., 2016). GLY is a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups) which allows a strong adsorption to soil minerals. This may results in a low mobility of GLY in the soil (Vereecken, 2005; Borggaard and Gimsing, 2008). GLY adsorption is positively related to soil CEC and clay content and negatively related with soil pH (Zhao et al., 2009; Paradelo et al., 2015; Okada et al., 2016). On the other

hand, GLY high water solubility can lead to lixiviation, especially when high precipitation occurs near application (Veiga et al., 2001). Additionally, inorganic phosphate competes strongly for the same adsorption sites, increasing GLY mobility in soil (Prata et al., 2005; Sasal et al., 2015; Okada et al., 2016). Degradation of GLY in soils is mainly due to microbial activity and chemical decomposition. Its degradation can occur rapidly in the soil; with reported half-lives from 1 to 174 days and is generally considered moderately persistent in soil (Mamy, 2004). However, the adsorption process can make the herbicide more persistent (Veiga et al., 2001). Some authors mentioned that greater persistence of pesticides was attributed to their greater retention in soil surface with high OC content (Mazzoncini et al., 1998; Zablotowicz et al., 2000). This results in GLY accumulation, due to a decrease in availability for degrading microorganisms (Aslam et al., 2015). Additionally, some authors mentioned that GLY and AMPA can accumulates in soil or rivers bottom sediments (Aparicio et al., 2013; Imfeld et al., 2013; Napoli et al., 2016). Primost et al. (2017) mentioned that GLY and AMPA can behave as "pseudo-persistent" pollutants due to high GLY applications rates in the field. In contrast, other authors mentioned that the risk of GLY and AMPA accumulation is very low (Yang et al., 2015).

However, the prediction of GLY and AMPA mobility considering only adsorption capacity is not quite correct, because the soil is a highly complex medium involving many interacting processes (Bergström et al., 2011). In this sense, some authors emphasized that in order to study solute transport in soil it is necessary to take into account the top soil physical and hydraulic properties, such as pore size distribution (PoSD) and hydraulic conductivity (K) (Gjettermann et al., 2000; Kjær et al., 2011; Larsbo et al., 2014). Candela et al. (2007), from miscible displacement experiments, found that sorption is a process dependent on the pore-water velocity and residence time of soil solution. Several laboratory and lysimeter studies indicated that GLY is transported by preferential flow in structured soils (Vereecken, 2005). De Jonge et al. (2000) concluded that GLY leaching was due to preferential transport through macropores. Kjær et al. (2005) reported no leaching of GLY and AMPA in sandy soils with low macroporosity, and the opposite for structured clayey soils with high macroporosity. Borggaard and Gimsing (2008), mentioned that soil with high macroporosity may increase the leaching risk, but only when a large precipitation occurs close to the application. In addition, several authors mentioned that in soils without continuous macropores, GLY lixiviation is not possible (De Jonge et al., 2000; Fomsgaard et al., 2003; Stone and Wilson, 2006). Iversen et al. (2011) mentioned that K is a good proxy variable for the risk of preferential solute leaching. Larsbo et al. (2014) mentioned that K could be used to estimate preferential transport under field conditions. These authors found that soils with small macroporosity and low K exhibited a greater degree of preferential transport. However, there is few information in the literature about K influence on GLY and AMPA vertical transport.

Pore size distribution and pore connectivity are affected by tillage practices, and therefore they may also affect flow and solute transport (Lipiec et al., 2006). The replacement of conventional tillage (CT) by NT at local scale, generally resulted in lower infiltration rates, reported by several authors in a wide range of soil textures in Argentinean Pampas region (Ferreras et al., 2000; Sasal et al., 2006; Álvarez et al., 2009; Soracco et al., 2010; Lozano et al., 2013), especially in silty soils with platy structure development. This kind of structure can exhibit a pattern of soil porosity with a preferential horizontal orientation, affecting water entry into the soil profile (Lozano et al., 2013), and therefore solutes fate.

Some studies from different regions analyzed the relationship between solute transport and tillage system. Jarvis et al. (2007) reported that NT system promotes the formation of continuous macropores favoring preferential flow of water and solutes, while CT usually results in uniform flow and transport in the uppermost disturbed layer, generating a barrier for macropore preferential flow. Larsbo et al. (2009)

studied different herbicides' migration in undisturbed soil columns in clayey and silty-clay soils under NT and CT. These authors observed higher levels of lixiviation under NT, due to a higher macropore connectivity. In the other hand, Gjettermann et al. (2000) studied GLY lixiviation in a sandy loam soil, finding significantly higher leached levels in the recently tilled soil. Okada et al. (2014) compared the effects of long-term tillage in different soils on solute transport. These authors found that in clayey soils the solute dispersion was higher under NT. In the other hand, several authors did not found significant differences in GLY and AMPA content at different depths between NT and CT (Fomsgaard et al., 2003; Rampazzo et al., 2013).

In Argentina few studies have been reported at local and regional scales about GLY and AMPA behavior in agricultural soils (Lupi et al., 2015). Peruzzo et al. (2008) found an increase of GLY and AMPA levels in silty loam Argiudolls under NT after its application, especially when large precipitation occurred. Okada et al. (2016) analyzed the soil management influence on GLY dynamics using undisturbed soil columns in laboratory from silty loam and silty clay loams soils. These authors did not found a significant difference between NT and CT systems. In both managements 80% of GLY remained in the first 5 cm top soil. Lupi et al. (2015) studied in the Argentina South Pampa Region GLY and AMPA levels at different depths before and after application in two agricultural soybean fields. They mentioned that most of the herbicide was retained in the upper 10 cm of soil profile. However, although GLY and AMPA concentrations diminished drastically along the soil profile, both compounds were found even at 35 cm of depth.

There are few studies, especially in Argentina, following the evolution of GLY and AMPA levels in the soil during the crop cycle under different tillage systems, and the dependence with physical, chemical and hydraulic properties. The joint study of GLY and AMPA temporal and vertical dynamics, and temporal variation of soil physical, chemical and hydraulic properties, would allow us to better understand the influence of tillage systems on GLY transport, and the contamination hazard.

We hypothesized that: i - the level of GLY and AMPA in the soil profile presents higher temporal and vertical variation during the crop cycle under CT as compared with NT; ii - temporal and vertical dynamics of GLY and AMPA are related with soil hydraulic properties; and iii - the processes involved in GLY and AMPA levels balances lead to accumulation during the crop cycle.

The objectives of this work were: i - to determine the temporal and vertical variation of GLY and AMPA levels during the soybean cycle in a soil under NT and CT; ii - to determine the relationship of GLY and AMPA levels variation with different soil properties; and iii - to compare initial and final GLY and AMPA levels in the soil during a crop cycle to infer possible accumulation.

2. Materials and methods

2.1. Site, treatments and sampling dates

The experiment was carried out near the city of Chascomús, Argentina (located at 35°44′37.61″ south and 58°03′10.22″ west). The soil was classified as a fine, illitic, thermic abruptic Argiudoll (Soil Survey Staff, 2006), Luvic Phaeozem (IUSS Working Group WRB, 2007). The climate in the region is temperate without freezing and thaw process. The mean annual precipitation is 946 mm. Precipitation was recorded during the experiment period (June 2015–August 2016).

Before the treatments were applied, the plots were under CT and with the same crop rotation for > 20 years. In the year 2000 an experimental design with complete randomized blocks with two treatments (plots of 30 m wide and 50 m long for each treatment) was applied: a) no tillage (NT), in which only a narrow (0.05 m) strip of the soil was drilled to deposit crop seeds, b) conventional tillage (CT) in which the soil was ploughed (disc plough + tooth harrow) at 0.20 m depth, and later smoothed using the tooth harrow each year in October,

Table 1

Soil sampling determinations during the studied period: June 12th 2015 (after maize harvest) to determine the initial GLY and AMPA content, October 5th 2015 (one week before seeding), December 9th 2015, January 15th 2016, March 31th 2016 and one month after harvest in August 4th 2016; GLY applications: September 5th (1.6 kg·ha^{-1} active ingredient, before the CT plough), November 26th (1.6 kg·ha^{-1} active ingredient) and December 19th (1.6 kg·ha^{-1} active ingredient), all in 2015.

Date	Soybean growth stage	GLY applications	GLY and AMPA content	Texture, pH, OC, CEC	K(h), PoSD, ε_{ma}
June 2015	–		x	x	x
September 2015	–	x			
October 2015	–		x		x
November 2015	Seeding	x			
December 2015	V2	x	x	x	x
January 2016	R1		x		
March 2016	R5		x		x
August 2016	–		x	x	x

GLY, glyphosate; AMPA, aminomethyl phosphonic acid; OC, organic carbon content; CEC, cation exchange capacity; K(h), hydraulic conductivity at different tensions; PoSD, pore size distribution; ε_{ma}, effective macroporosity.

just before summer crop seeding. The crop over the last 4 years was GLY-resistant (GR) maize. Three applications per year of GLY-based herbicide were used over the last 20 years. The experiment was carried-out during a GR soybean crop cycle.

During the studied period, three applications of glyphosate Roundup® UltraMax were carried out (1.6 kg·ha^{-1} active ingredient) on September 5th (before the CT plough), November 26th and December 19th, all in 2015. The preparation of the soil under CT was carried out in September 30th, 2015. The soybean seeding was carried out in November 20th, 2015. Soil sampling for GLY, AMPA and different soil properties determinations are detailed in Table 1.

2.2. Soil general characterization

Topsoil was sampled at four different depths: 0–10 cm, 10–20 cm, 20–30 cm and 30–40 cm for pH, organic carbon (OC) and CEC determinations. Soil texture was determined according to Gee and Bauder (1986), soil pH was determined with an electrode with 1:2.5 soil–water relation. Walkley and Black (1934) method was used for organic carbon determination. Cation-exchange capacity (pH 7 ammonium acetate 1 N) and Ca, Mg, Na and K contents were determined following Chapman (1965).

2.3. Soil physical properties

2.3.1. Soil hydraulic conductivity

Hydraulic conductivity (K) at different tensions (h) was measured in the field in both treatments. Tension disc infiltrometer (Perroux and White, 1988) with a base radius of 6.25 cm, was used in order to determine steady-state infiltration rate. Five replicates were carried out for each treatment and date. Infiltration measurements were conducted in five randomly selected sites of each plot, avoiding rows and recently trafficked areas. To consider only the effects of tillage on soil water infiltration, crop residues were removed from the soil surface. To ensure good hydraulic contact between the device and the soil, the surface was flattened with a spatula and a thin dry sand layer was spread on it. Infiltration runs were performed at two values of soil water pressure head, h (namely, −3 and 0 cm, applied in this order and at the same place). This sequence of supply water pressure heads was adopted, because a descending order may cause hysteresis, with progressive

drainage occurring close to the disc while wetting continues at the infiltration front (Jarvis and Messing, 1995). Flow monitoring continued until steady-state flow, which was achieved around 1.5 h for each tension. The soil hydraulic conductivity, K, at the different soil water pressure heads, h (i.e., K_3, and K_0) were thus calculated from the cumulative water infiltration using the multiple-head method (Ankeny et al., 1991). The values of K_3 were used to obtain the water-conducting macroporosity, and will not be discussed as a response variable.

2.3.2. Water-conducting macroporosity

The classical capillary rise equation allows us to approximate the maximum water-filled pore size, r, [L] at a specific h [L]:

$$r = \frac{2\sigma \cos(\alpha)}{\rho g \, |h|} \tag{1}$$

where σ is the surface tension of water [MT^{-2}], α is the contact angle between water and the pore wall (assumed to be zero), ρ is the density of water [ML^{-3}], and g is the acceleration due to gravity [LT^{-2}].

We assume that the equivalent pores with radii smaller than r calculated from Eq. (1) are full of water and are responsible for all the flux of water under a given water pressure head, and that the equivalent pores with radii larger than the value calculated from Eq. (1) are not contributing to the water flux.

According to Watson and Luxmoore (1986), the water-conducting porosity due to pores between two radii r_a and r_b ($r_a \le r_b$), θ (r_a,r_b) (assuming pore radius equals to the minimum pore radius), resulting in a difference in total soil water flux or hydraulic conductivity ΔK (r_a,r_b), is:

$$\varepsilon(a,b) = \frac{8\eta \Delta K(r_a, \, r_b)}{\rho g (r_a)^2} \tag{2}$$

Since r_a is the minimum equivalent pore radius in the range, ε (r_a,r_b) is an estimation of the maximum water-conducting porosity, because pore radius (r_a) appears in the denominator of Eq. (2). Implicitly assumed in Eq. (2) is a unit hydraulic gradient, i.e. steady-state conditions during infiltration.

According to Eq. (1), infiltration at water pressure head of −3 cm will exclude pores with equivalent diameters > 1 mm. In our study we defined as water-conducting big macropores (ε_{ma}) as those pores draining at h > −3 cm (equivalent r > 0.5 mm).

2.3.3. Pore size distribution

Undisturbed soil samples (5 cm height, 5 cm diameter, 98 cm^3) were collected from the first 10 cm of each treatment, avoiding rows and visible wheel tracks. Eight replicates from each treatment and date were collected (the total number of samples was 80). The samples were covered with plastic caps to protect the soil from mechanical disturbances and evaporation.

The samples were brought to different tensions (−50 cm and −100 cm water column) at which pores with equivalent diameters larger than 60 μm and 30 μm, respectively, drain in a sand box apparatus. Pore fractions corresponding to macropores (θ_{ma}, diameter > 60 μm), mesopores (θ_{me}, 30 μm < diameter < 60 μm), and micropores (θ_{mi}, diameter < 30 μm) were calculated as the ratio between the amount of water retained in those pores (1 g = 1 cm^3) and the sample volume (Danielson and Sutherland, 1986).

2.4. Glyphosate and AMPA quantification

In order to determine glyphosate and AMPA contents, the first 40 cm of soil was sampled and divided in four layers: layer 1 (0–10 cm), layer 2 (10–20 cm), layer 3 (20–30 cm) and layer 4 (30–40 cm). Three composite samples (each one containing 10 subsamples taken from sites randomly selected) were obtained from each treatment. All samples were stored at −18 °C until analysis.

Glyphosate and AMPA quantification were carried out according to

Aparicio et al. (2013). Briefly, the samples (5 g of soil) were fortified with 250 μL of 10 μg mL^{-1} stock solution of isotope-labeled glyphosate (1,2-^{13}C, ^{15}N-GLY), respectively to determine matrix effects and recovery. The samples were extracted with 25 mL of extracting solution (0.1 M of KH$_2$PO$_4$). The samples were sonicated and then centrifuged to separate the suspended material. Aliquot of 2 mL was taken from the supernatant was adjusted to pH = 9 with 40 mM borate buffer and then derivatized with 2 mL of a solution composed of 1 mg mL^{-1} of 9-fluorenylmethylchloroformate (FMOC-CL) in acetonitrile. It was left to rest overnight in darkness at room temperature. Standard curves in the range 0–0.2 μg g^{-1} were prepared for GLY and AMPA and processed identically as the samples. The samples were filtered through a 0.22 μm nylon filter and were injected into the HPLC MS system. According Meyer et al. (2009), selected ion monitoring in the negative ionization mode was applied. For both GLY and AMPA soil concentrations analyses showed linear behavior, with a correlation coefficient > 0.99. The analytical recoveries were over 95%. The limit of detection (LD) was 0.001 μg g^{-1}, both for AMPA and glyphosate and the limit of quantification (LQ) was 0.003 μg g^{-1}, both for AMPA and glyphosate, according SANCO 2016. The results were expressed as μg of GLY or AMPA per kg of dry soil. In order to determine the relationship between GLY content and different physical properties, and if GLY accumulation occurred along the soil profile, soil AMPA content was expressed on a GLY mass equivalent basis and added to the GLY content to obtain the total extracted GLY (TEG), following Coupe et al. (2012).

2.5. Statistical analysis

In order to determine the effect of treatment, sampling date, and sampling depth on GLY and AMPA contents, three way ANOVAs were carried out (Sokal and Rohlf, 1995). For soil physical properties two way ANOVAs were carried out with treatment and sampling dates as factors. Fisher's least significant difference (LSD) test (Sokal and Rohlf, 1995) was used to compare the means. Correlation analyses were used to assess the relationship among TEG content and different soil physical properties. For all analysis the significance was determined at p = 0.05.

3. Results

3.1. Soil general characterization

The mean particle size distribution of the studied soil was constant along the sampled depths and dates for both treatments with mean values of 25% clay, 41.5% silt, and 33.5% sand (loam). OC content, CEC, changeable cations and pH did not varied significantly along the crop cycle. Mean values of OC, CEC, changeable cations and pH for the different studied depths are shown in Table 2. A decrease in OC content with depth was observed for both treatments. The highest OC content was found under NT in the upper 10 cm of soil. Exchangeable cations and CEC showed a similar behavior than OC, decreasing with soil depth

in NT. Under CT, the CEC was constant in the first 20 cm, and decreased with depth from 20 cm. This can be attributed to the homogenization of first 20 cm due to tillage practice. Soil pH was similar between treatments and increased slightly with depth. These results are in agreement with Lupi et al. (2015), who reported that OC, and CEC decrease with depth, while pH is almost constant in the topsoil.

3.2. Soil physical properties

The values of soil physical properties K_0, ε_{ma}, θ_{ma}, θ_{me}, θ_{mi}, and TP for different sampling dates for both tillage treatments are shown in Fig. 1. From two-way ANOVAs the interaction between factors was significant only for θ_{ma} and θ_{mi} (p < 0.05). TP and θ_{me} did not differ significantly between tillage treatments and sampling dates (Fig. 1b and d). In the other hand, K_0 showed no significant difference between treatments during the fallow periods (June 2015 and August 2016), while this variable was significantly higher under CT during the growing season from October 2015 to March 2016 (Fig. 1e), especially after the tillage (October 2015). The values of ε_{ma} and θ_{ma} showed a similar behavior as compared with K_0, except in March 2016 when no significant differences between treatments were observed for θ_{ma} (Fig. 1a and f). The values of θ_{mi} followed the opposite trend as compared with θ_{ma} in both treatments (Fig. 1c), with significantly higher values under NT during the growing season. Different temporal variations were observed between the treatments. Under NT, K_0, ε_{ma} and θ_{ma} decreased in the first fallow period (June 2015–October 2015), increasing during the growing season and decreased again at the end of the crop cycle (Fig. 1a, e and f). Under CT, K_0, ε_{ma} and θ_{ma} remained constant during the vegetative period, and decreased towards the end of the cycle in August 2016 (Fig. 1a, e and f). As mentioned before, under both treatments, TP and θ_{me} did not vary during the studied period.

3.3. Temporal variation of glyphosate and AMPA levels in the soil during the crop cycle

Soil GLY and AMPA content for different treatments, sampling dates and depths are shown in Fig. 2. From ANOVA test, a significant interaction between the factors treatment, sampling date and depth was found (Tables 3 and 4).

Overall, > 60% of GLY and 80% of AMPA content along the studied soil profile for all sampling dates was found between 0 and 20 cm. GLY contents in the first sampling date ranged between 5.66 and 61.71 μg kg^{-1} depending on soil depth. Highest levels were found in layer 1 for both treatments, and decreased with depth (Fig. 2b and c, June 2015). Under NT 60% of GLY was found in the layer 1, while under CT, this value was 47%. AMPA levels in the first sampling date ranged between 19.21 and 895.99 μg kg^{-1}, following the same behavior than GLY. Under NT, 80% was retained in layer 1, and 15% in layer 2, while under CT the levels of AMPA were 56% in layer 1 and 34% in layer 2 (Fig. 2d and e, June 2015).

Table 2
Chemical properties for the studied soil for different depths and treatments (mean values ± standard deviation of three sampling dates) (NT: no tillage, CT: conventional tillage).

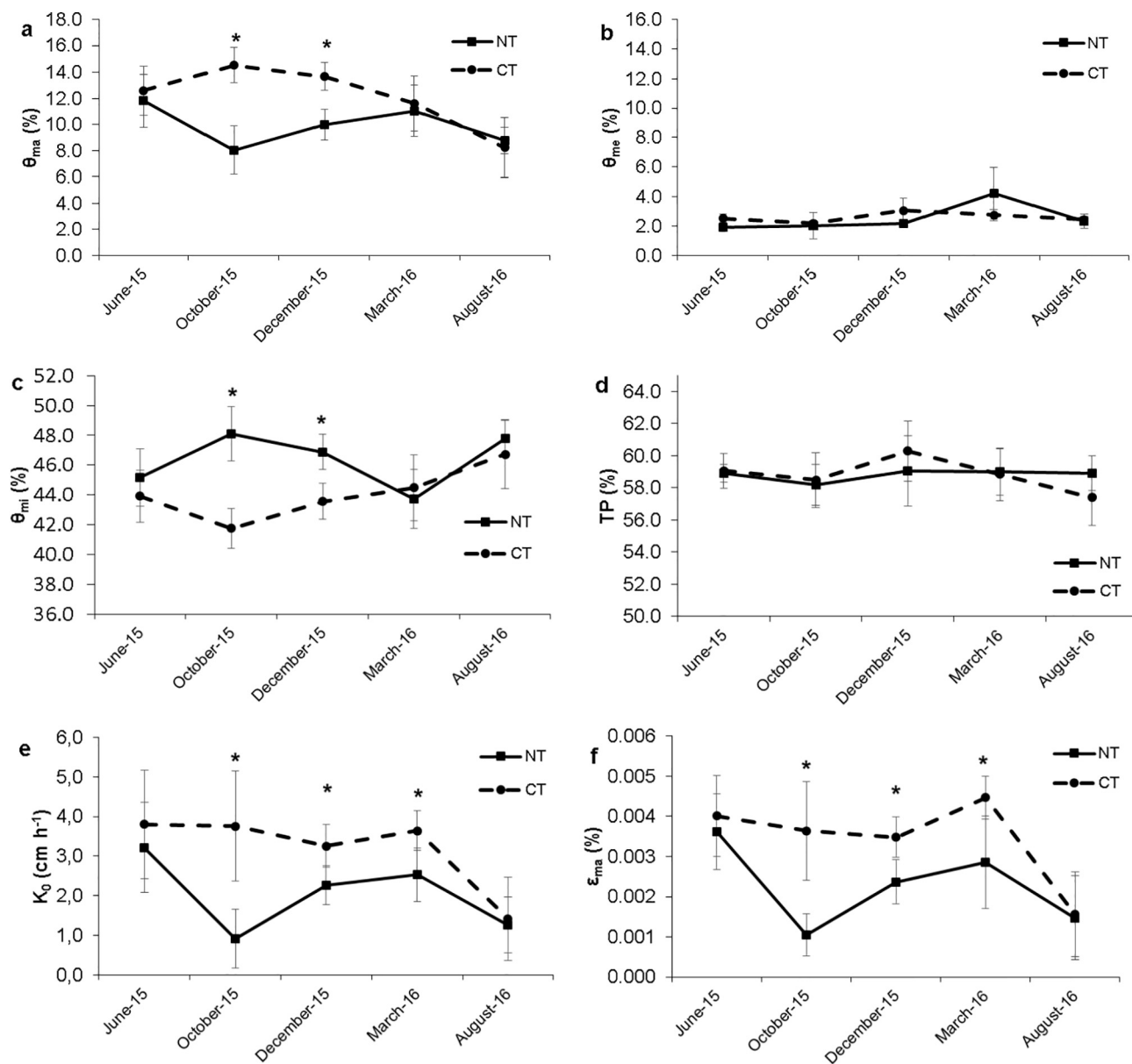| Treatment	Depth (cm)	OC (%)	Exchangeable cations (meq 100 g^{-1})					pH
			CEC	Ca	Mg	Na	K	
NT	0–10	3.5 ± 0.2	22.3 ± 1.5	12.10 ± 1.9	1.30 ± 0.8	0.38 ± 0.5	1.78 ± 1	5.6 ± 0.06
	10–20	3.0 ± 0.2	18.2 ± 1.2	11.30 ± 1.3	1.00 ± 1.1	0.29 ± 0.4	1.28 ± 1.1	5.5 ± 0.15
	20–30	1.9 ± 0.3	16.1 ± 1.4	10.60 ± 1.3	0.20 ± 1.3	0.29 ± 0.4	1.05 ± 1.2	5.9 ± 0.08
	30–40	0.9 ± 0.2	13.7 ± 1.5	7.90 ± 1.4	0.50 ± 1.5	0.27 ± 0.3	1.27 ± 1	6.1 ± 0.10
CT	0–10	3.2 ± 0.2	20.2 ± 1.5	10.00 ± 1.2	0.50 ± 0.1	0.15 ± 0.01	1.71 ± 1	5.6 ± 0.06
	10–20	2.9 ± 0.1	20.9 ± 1.5	10.90 ± 1.1	2.50 ± 0.1	0.27 ± 0.1	0.99 ± 1.1	5.6 ± 0.10
	20–30	2.1 ± 0.1	17.6 ± 1.1	9.60 ± 0.9	3.10 ± 0.1	0.15 ± 0.3	0.34 ± 1	5.9 ± 0.06
	30–40	1.5 ± 0.1	17.7 ± 0.9	11.00 ± 1.0	1.40 ± 0.1	0.17 ± 0.1	0.42 ± 1	6.1 ± 0.02

OC, organic carbon content; CEC, cation exchange capacity.

Fig. 1. Soil physical properties: a) macroporosity (θ_{ma}), b) mesoporosity (θ_{me}), c) microporosity (θ_{mi}), d) total porosity (TP), e) saturated hydraulic conductivity (K_0), and effective macroporosity (ε_{ma}); evaluated during the crop cycle, for different treatments (NT: no tillage, CT: conventional tillage). * means significant difference between treatments for pointed sampling date (p < 0.05).

In the sampling of October 2015, after first GLY application, the GLY contents in layer 1 remained constant under NT and decreased under CT. For the rest of depths, GLY was detected below of the LQ (Fig. 2b and c, October 2015). Under NT and CT, AMPA contents decreased between layer 1 and 3, and increased in layer 4 (Fig. 2d and e, October 2015).

Between October and December 2015, post second application, GLY content increased in all depths under both treatments. The values of GLY ranged between 7.45 and 105.06 µg kg^{-1}. As observed in previous sampling date, the highest values were observed in layer 1 and > 60% of GLY was retained at this depth for both treatments (Fig. 2b and c, December 2015). AMPA levels increased in all depths as compared with previous sampling date, except in layer 4. However, > 70% of AMPA was retained in layer 1 under both treatments (Fig. 2d and e, October 2015).

In January 2016, after the third application, total GLY content along the soil profile showed different behavior between treatments. Under NT, GLY content along the 40 cm remained constant and varied in the different layers, increasing in layer 4 and decreasing in layer 1 (Fig. 2b, January 2016). Under CT, total GLY along the soil profile decreased significantly, showing lixiviation process to deeper soil layers (Fig. 2c, January 16). Furthermore, GLY content decreased in layer 1 and increased in layer 3 as compared with the previous sampling date, showing vertical transport under CT. Similar behavior was observed for AMPA content (Fig. 2d and e).

Although there was not any application, in March 2016, GLY contents increased in layer 1 under NT (Fig. 2b, March 2016) and in layer 2 under CT (Fig. 2c, March 2016). Total GLY along the 40 cm soil profile were no significant different between treatments. AMPA contents increased for both treatments between layer 1 and 3, especially under NT in layer 1. NT showed higher GLY and AMPA contents in layer 1 (Fig. 2d, March 2016). As was observed for previous sampling date, NT showed higher retention of GLY and AMPA in the top soil (69% and 75% respectively), while under CT an increment was observed in layer 2 (57% and 30% of GLY and AMPA, respectively).

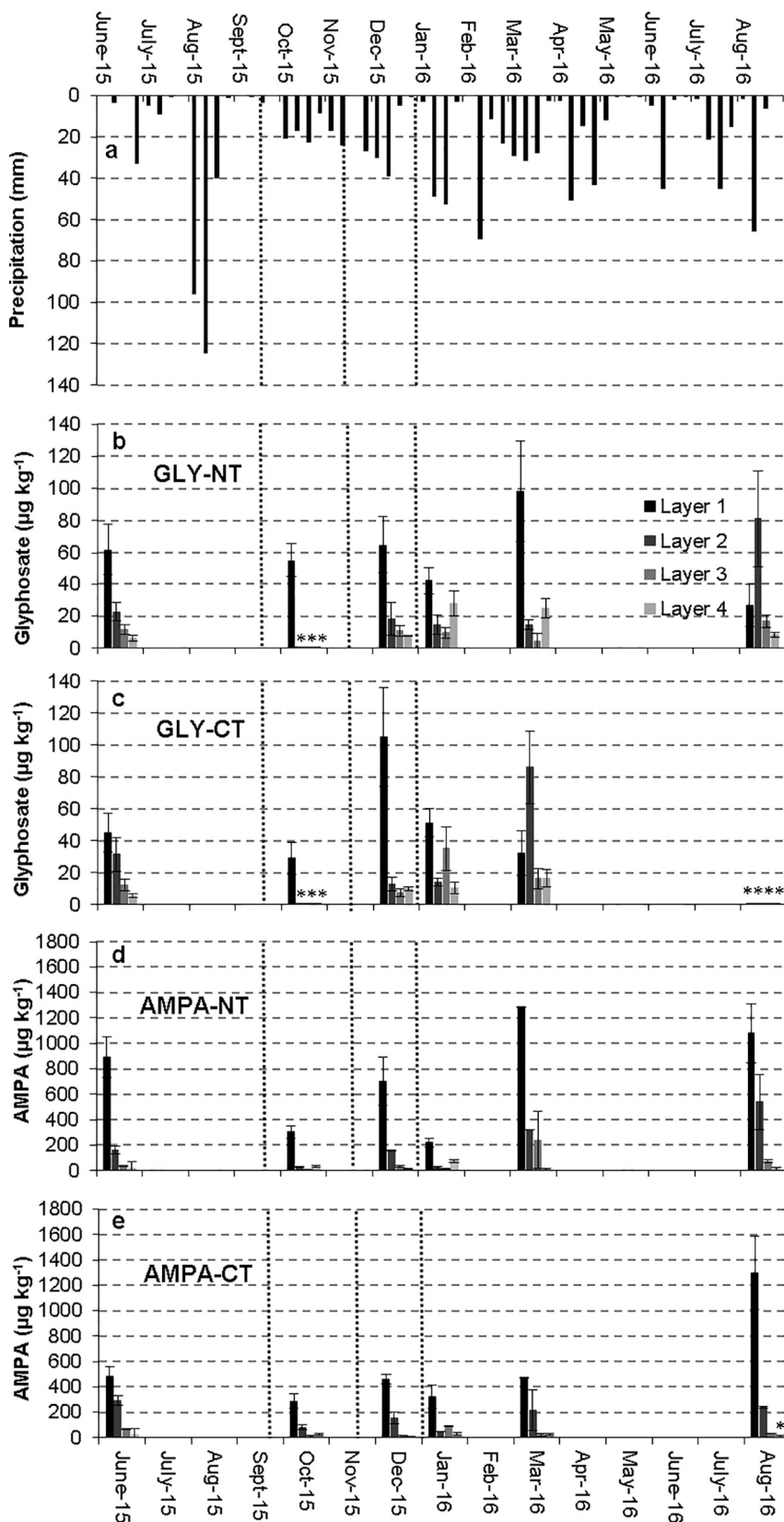In August 2016, after soybean harvest, NT treatment showed the

Fig. 2. Precipitation (mm) (a), and glyphosate (GLY) and AMPA contents (µg kg^{-1} of soil) for: no-tillage treatment (NT) and conventional tillage (CT), at different soil depths (layer 1 (0–10 cm), layer 2 (10–20 cm), layer 3 (20–30 cm) and layer 4 (30–40 cm)) and sampling dates (b, c, d, e), during the crop cycle. Dot vertical lines indicate GLY applications. *GLY was detected under the limit of quantification (LQ).

Table 3

Three-way ANOVA of the effects of treatment (no tillage, conventional tillage), sampling date (June 2015, October 2015, December 2015, January 2016, March 2016, August 2016), and sampling depth (0–10, 10–20, 20–30 and 30–40 cm) on glyphosate levels. Two- and three-way interaction terms were incorporated. Tests for significance of factors were based on the Type III sums of squares.

Source of variation	df	Sum of squares	Mean square	F	p
Mean effects					
A: treatment	1	1038.13	1038.13	3.14	ns
B: sampling date	5	11,184.8	2236.96	6.76	**
C: depth	3	44,921.5	14,973.8	45.23	**
Interactions					
AB	5	6077.67	1215.53	3.67	*
AC	3	2043.69	681.231	2.06	ns
BC	15	25,832.9	1722.19	5.20	**
ABC	15	20,768.3	1384.55	4.18	**
Error	96	31,778.5	331.026		
Corrected total	143	143,645			

df: degrees of freedom. F values and significance levels are shown. ns, $p > 0.05$.
* $p < 0.01$.
** $p < 0.0001$.

Table 4

Three-way ANOVA of the effects of treatment (no tillage, conventional tillage), sampling date (June 2015, October 2015, December 2015, January 2016, March 2016, August 2016), and sampling depth (0–10, 10–20, 20–30 and 30–40 cm) on AMPA levels. Two- and three-way interaction terms were incorporated. Tests for significance of factors were based on the Type III sums of squares.

Source of variation	df	Sum of squares	Mean square	F	p
Mean effects					
A: treatment	1	152,438	152,438	23.49	*
B: sampling date	5	$1.8298E^6$	365,959	56.40	*
C: depth	3	$9.10113E^6$	$3.03371E^6$	467.55	*
Interactions					
AB	5	380,256	76,051.1	11.72	*
AC	3	199,093	66,364.2	10.23	*
BC	15	$2.48099E^6$	165,399.	25.49	*
ABC	15	965,771	64,384.8	9.92	*
Error	96	622,900	6488.54		
Corrected total	143	$1.57324E^7$			

df: degrees of freedom. F values and significance levels are shown. ns, $p > 0.05$.
* $p < 0.0001$.

same values of total GLY content along the soil profile compared with the previous sampling date. However, in layer 1 GLY content decreased and increased in layer 2 and 3, showing that vertical transport occurred (Fig. 2b, August 2016). Under CT, GLY was under the LQ for all depths (Fig. 2c, August 2016). AMPA contents decreased in layer 1 and increased in layer 2 under NT (Fig. 2d, August 2016). Under CT, AMPA content increased in layer 1 and decreased in layer 4 (Fig. 2e, August 2016).

In order to determine the influence of different physical properties on GLY and AMPA vertical transport, correlation analyses were carried-out between TEG content in layer 1 and its corresponding physical properties values to each treatment and sampling date (the TEG content in January 2016 was excluded because there was no physical properties determination). Negative relationships with K_0 (r = −0.76, p = 0.030), ε_{ma} (r: −0.74, p = 0.028) and θ_{ma} (r = −0.82, p = 0.013) were observed.

3.4. GLY soil accumulation during the soybean crop cycle

TEG values along the studied soil profile for initial (June 2015) and final (August 2016) dates were calculated and expressed as total active ingredient mass per hectare using soil bulk density for the corresponding sampling date for the conversion. The mean values were: NT: 1.96 and CT: 1.53 kg ha^{-1} in June 2015; and NT: 3.02 and CT:

2.8 kg ha^{-1} in August 2016. This implies a significant increment of 54% and 82% during the crop cycle for NT and CT, respectively. In layer 1, TEG increments during the crop cycle were 0.27 and 1.21 mg kg^{-1} for NT and CT respectively.

4. Discussion

4.1. Soil physical properties

Higher values of K_0, ε_{ma} and θ_{ma} under CT during the crop cycle can be attributed to the loosening produced by tillage, also reported by several authors (Angulo-Jaramillo et al., 1997; Strudley et al., 2008; Villarreal et al., 2017). Increasing values of these soil properties under NT during the vegetative period agree with Schwen et al. (2011) who mentioned that K_0 and ε_{ma} increase in spring and summer due to higher biological activity and root growth. Moreover, these results are in agreement with several reports from the Pampas region, that show that tillage effects on soil pore system configuration do not persist after harvest (Sasal et al., 2006; Soracco et al., 2010; Villarreal et al., 2017). The decrease of K_0, ε_{ma} and θ_{ma} values in both treatments after harvest can be attributed to high traffic intensity associated to the harvest operations, which have been shown to damage soil structure (Soracco et al., 2012).

4.2. Temporal variation of glyphosate and AMPA levels in the soil and their relationship with soil properties

In general, GLY and AMPA values were similar to those reported by different authors in different regions of Argentinian Pampas (Aparicio et al., 2013; Lupi et al., 2015; Primost et al., 2017) and from other regions (Sprankle et al., 1975; Roy et al., 1989; Newton et al., 1994; Mamy et al., 2016). The results presented above showed that GLY and AMPA are strongly retained in the top soil. This GLY and AMPA retention observed during the entire crop cycle can be attributed to the high OC content and CEC values in the soil surface observed for both treatments during the studied period (Lupi et al., 2015; Okada et al., 2016). However, GLY and AMPA vertical transport was observed depending on different factors such as precipitation events near the application and soil physical properties. Correlation analyses indicate that higher values of K_0, ε_{ma} and θ_{ma} may lead to lower retention of GLY and AMPA in the top soil, favoring vertical transport to deeper soil layers during the crop cycle. This is in agreement with several authors who reported that GLY leaching was due to preferential transport through macropores (De Jonge et al., 2000; Kjær et al., 2005; Stone and Wilson, 2006; Kjær et al., 2011). In the other hand our results are in disagreement with some authors who mentioned that high values of K_0 limit solute transport by preferential flow (Ghafoor et al., 2013; Larsbo et al., 2014).

In this sense, the strong GLY decrease during the fallow period under NT and CT, observed in October 2015 between layer 2 and 4, can be attributed to high precipitation recorded between the sampling of June and the first GLY application in September 2015 (311 mm) (Fig. 2a, October 2015). Some authors reported that GLY can migrate after rain events to deeper soil layers (Peruzzo et al., 2008). In addition, weeds probably intercepted the September application and subsequently a low GLY proportion reached the soil.

The GLY and AMPA content increase between layer 2 and 4 under both treatments, observed in December 2015, can be attributed to a significant precipitation event the day after application (38 mm) (Borggaard and Gimsing, 2008; Peruzzo et al., 2008). The vertical transport may have been favored by greater K_0, θ_{ma} and ε_{ma} values as compared with previous sampling date (Fig. 1a, e and f). These results support the idea that the presence of macropores may increase GLY and AMPA lixiviation especially when high precipitation occurs shortly after the application.

Constant and lower values of GLY under NT and CT, respectively, in

January 2016 as compared with previous sampling date, mean that the third GLY application did not produce an increase on GLY levels in the soil. This is probably due to herbicide interception by the soybean crop and weeds (Landry et al., 2005; Peruzzo et al., 2008). However, the redistribution of GLY to deeper soil layers under NT, can be attributed to high precipitations registered between GLY application and this sampling date (Fig. 2a), together with high values of K_0, θ_{ma} and ε_{ma}, as mentioned before. The vertical transport in January 2016 was more pronounced under CT treatment, which presented higher values of K_0, θ_{ma} and ε_{ma} as compared with NT (Fig. 1a, e and f). This may facilitate vertical transport but only at tillage depth (0–20 cm) (Jarvis, 2007).

During the studied crop cycle, soybean was affected by *Nezara viridula* in the vegetative period, producing strong defoliation. GLY increase in layer 1 and 2 under NT and CT, respectively, observed between January and March 2016 can be attributed to the release of retained herbicide in soybean and weeds residues (Arregui et al., 2004; Rampoldi et al., 2011; Mamy et al., 2016). Under CT the degradation of vegetal residues was followed by lixiviation favored by high values of K_0 and ε_{ma} (Fig. 1e and f, March 2016). As mentioned for the previous sampling date, it seems that the tillage depth limits GLY lixiviation. Another explanation for this is the occurrence of GLY translocation from the leaves to the soil via roots exudation (Laitinen et al., 2007). These authors found between 8 and 12% of applied GLY in soil samples, 45 days after the application, and pointed out that GLY translocation via roots exudation is rapid. However, to test these two alternatives exceeds the objectives of this work. AMPA content increased for both treatments in layers 1 and 2, showing higher increment under NT in the first 10 cm. This is in agreement with other authors who mentioned higher pesticides persistence in soils with high OC content (Mazzoncini et al., 1998; Zablotowicz et al., 2000). In addition, it has been demonstrated that, after herbicide uptake, translocation to all parts of soybean plants occurs and AMPA is the main product of GLY metabolism in leaves (Arregui et al., 2004).

After harvest, the decline of GLY under the LQ for all depths under CT, can be attributed to degradation process after soybean harvest, reflected in higher AMPA contents as compared with previous sampling date. Some authors mentioned that GLY degradation is significantly higher under CT as compared with conservational systems (Cassigneul et al., 2016). These authors mentioned that the formation of different metabolites, as AMPA, is greater in bared soil.

4.3. GLY soil accumulation during the soybean crop cycle

Results presented above, confirm the idea that GLY and AMPA accumulate in the soil. This is in agreement with previous reports that mention that high adsorption of GLY and AMPA can reduce their degradation (Veiga et al., 2001; Okada, 2014). Another possible explanation for this accumulation is that the time between GLY applications is less than GLY and AMPA DT_{90} (time required for 90% of the initially applied compound to disappear from the soil) that has been reported to be between 40 and 280 days, and 23 and 958 days, respectively (Laitinen et al., 2006). Initial TEG values were around half of the yearly application dose (4.8 kg ha^{-1} per year) showing a previous accumulation. This process was clearly evidenced with the final TEG values, showing that a great proportion of the applied GLY can reach and pseudo-persist in the soil. This is in agreement with Primost et al. (2017) who found a positive correlation between measured GLY concentration in soil and the total number of previous applications, with an increment of 1 mg of GLY per kg of soil every five applications in the first 5 cm of the soil. In the present study, TEG increments in layer 1 were 0.27 and 1.21 mg kg^{-1} for NT and CT respectively, in agreement with the previous report. Also, these authors emphasized that this is not only an environmental matter, but also a productive issue. Higher increment of TEG during the crop cycle under CT may be attributed to differences in soil moisture between treatments. CT treatment showed lower values of soil water content as compared with NT, during all the

crop cycle (data non-shown). Recent studies reported that glyphosate and AMPA dissipation is significantly slower in dry soils (Bento et al., 2016). Further studies about GLY content evolution in soils during longer periods will allow to better understand this process.

5. Conclusions

Glyphosate and AMPA contents during the crop cycle present higher temporal and vertical variation in CT than in NT. Vertical transport is increased when precipitation events occur shortly after the application.

Vertical transport during the crop cycle depends on the temporal variation of hydraulic properties. High values of K_0, θ_{ma} and ε_{ma} increase glyphosate and AMPA lixiviation. To our knowledge this is the first work that includes these variables to this contaminant analysis in our country and shows that soil physical and hydraulic properties are important in order to determine glyphosate and AMPA environmental fate.

During the studied crop cycle and under real field conditions, it was observed that high rates of GLY application lead to accumulation in the soil profile under CT and NT systems, implying a serious potential risk of soil pollution.

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