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Dynamics of glyphosate and AMPA in the soil surface layer of glyphosate-resistant crop cultivations in the loess Pampas of Argentina

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Abstract

This study investigates the dynamics of glyphosate and AMPA in the soil surface layer of two fields growing glyphosate-resistant crops in the loess Pampas of Córdoba Province, Argentina. Glyphosate decay and AMPA formation/decay were studied after a single application, using decay kinetic models. Furthermore, glyphosate and AMPA concentrations were investigated in runoff to evaluate their off-site risk. During a 2.5-month study, cultivations of glyphosate-resistant soybean and maize received an application of 1.0 and 0.81 kg a.e. ha^{-1}, respectively, of Roundup UltraMax©. Topsoil samples (0-1, 1-2 cm) were

collected weekly (including before application) and analysed for glyphosate, AMPA and soil moisture (SM) contents. Runoff was collected from runoff plots (3 m^2) and weirs after 2 erosive rainfall events, and analysed for glyphosate and AMPA contents (water, eroded-sediment). Under both cultivations, background residues in soil before application were 0.27-0.42 mg kg^{-1} for glyphosate and 1.3-1.7 mg kg^{-1} for AMPA. In the soybean area, the single-first-order (SFO) model performed best for glyphosate decay. In the maize area, the bi-phasic Hockey-Stick (HS) model performed best for glyphosate decay, due to an abrupt change in SM regimes after high rainfall. Glyphosate half-life and DT_{90} were 6.0 and 19.8 days, respectively, in the soybean area, and 11.1 and 15.4 days, respectively, in the maize area. In the soybean area, 24% of the glyphosate was degraded to AMPA. In the maize area, it was only 5%. AMPA half-life and DT_{90} were 54.7 and 182 days, respectively, in the soybean area, and 71.0 and 236 days, respectively, in the maize area. Glyphosate and AMPA contents were 1.1-17.5 times higher in water-eroded sediment than in soil. We conclude that AMPA persists and may accumulate in soil, whereas both glyphosate and AMPA are prone to off-site transport with water erosion, representing a contamination risk for surface waters and adjacent fields.

Keywords: Glyphosate, Aminomethylphosphonic acid (AMPA), Field dissipation kinetics, Sediment transport, Genetically modified crops (GM crops)

Capsule

Glyphosate and AMPA dynamics in the soil surface layer of cultivation areas from the loess Pampas of Argentina show high risk of AMPA accumulation, while water erosion represents a high risk for their transport to off-target areas.

1. Introduction

The use of glyphosate-based herbicides in Argentina has increased dramatically since the introduction of glyphosate-resistant (GR) crops in 1996, being the most used pesticide in the country (Trigo, 2011; Aparicio et al., 2013). By 2012, 197 000 tonnes of glyphosate-based herbicides were applied, approximately 10 times more than in 1996, mostly in chemical fallows (47%), and soybean (42%) and maize cultivations (9%) (Trigo, 2011; KleffmannGroup, 2014). Nevertheless, only recently more attention is being paid to the impacts and fate of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in the country.

Glyphosate is considered to decay fast in soil, with some reported half-lives (DT_{50}) <5 days and DT_{90}<10 days (i.e., the time required for 50% (DT_{50}) and 90% (DT_{90}) of a compound to disappear from soil) (Al-Rajab and Schiavon, 2010; Yang et al., 2015a; Bento et al., 2016). However, glyphosate was also found to persist in soil for longer periods of time, namely when adverse soil/climate conditions are present (e.g. dry soil, low temperatures) (Heinonen-Tanski, 1989; Schroll et al., 2006; Bento et al., 2016), or in soils with strong adsorption capacity (Al-Rajab and Schiavon, 2010). Some studies have reported bi-phasic decay behaviour for glyphosate, i.e. a fast initial decay rate – associated with the dissolved phase –, followed by a slower decay rate – associated with its strongly bound phase, apparently not bioavailable (Eberbach, 1998; Al-Rajab and Schiavon, 2010; Bento et al., 2016). AMPA displays similar behaviour in terms of sorption and degradation (Feng and Thompson, 1990; Simonsen et al., 2008; Bento et al., 2016). However, AMPA is found to have longer half-lives than its parent (Simonsen et al., 2008; Yang et al., 2015a; Bento et al., 2016). Considering that glyphosate and AMPA may persist in soil for long periods and the high glyphosate application frequency and rates in agricultural fields (Benbrook, 2016), there is a risk of accumulation in topsoil.

Several authors stated that glyphosate and AMPA are unlikely to reach areas outside the targeted agricultural fields, mostly due to their strong capacity to adsorb to soil particles (Feng and Thompson, 1990; Kjaer et al., 2003; Al-Rajab et al., 2008; Duke and Powles, 2008). However, glyphosate and AMPA remaining in the topsoil are prone to off-site transport during water erosion events (Todorovic et al., 2014; Yang et al., 2015a; Yang et al., 2015b). Shipitalo et al. (2008), for example, reported glyphosate and AMPA concentrations in runoff water up to 182 and 31 μg L^{-1}, respectively, in Appalachian watersheds (USA). Two studies in different parts of Buenos Aires province, in Argentina, reported the occurrence of glyphosate and AMPA in surface water, suspended sediment and sediment from stream beddings (Peruzzo et al., 2008; Aparicio et al., 2013). Considering that the loess Pampas of Argentina are prone to water erosion (Apezteguía et al., 2009), the off-site transport risk of glyphosate and AMPA with eroded soil is high. However, studies on their transport with water erosion in the country are still lacking.

This study aims to investigate the dynamics of glyphosate and AMPA in the soil surface layer of fields cultivated with GR soybeans and GR maize, both under long-term application of glyphosate-based herbicides, in Córdoba province, Argentina. Focus was given to the role of the decay processes of glyphosate and to the formation/decay of AMPA, taking into account the background contents as a consequence of long-term applications. Furthermore, the concentration of these compounds in runoff water and water-eroded sediment was studied to evaluate their off-site risks.

2. Materials and methods

2.1 Study site

2.1.1 General characteristics

This study was performed in a farmland of Córdoba province, Argentina, located in a Piedmont area where the Pampas begin to slope upwards to meet the Sierras Chicas. It belongs to the climate region of the dry Pampas, with a predominant temperate climate, characterized by hot and humid summers and cold and dry winters. Mean annual precipitation is 846 mm, with 80% of the rainfall occurring between October and March. The mean annual temperature is 16.7°C, with a mean annual minimum of 11.2°C (absolute minimum: -7.6°C) and mean annual maximum of 24.3°C (absolute maximum: 42.4°C). Soil types are Mollisols on loess. The agricultural areas under study are dedicated to the cultivation of GR soybean and maize for >15 years according to a soybean-maize rotation plan under no-tillage systems. Glyphosate-based herbicides have been applied for >15 years, since GR crops were adopted. For at least the last 5 years, glyphosate-based herbicides have been applied 3-5 times a year with a ground boom sprayer, at application rates varying between 0.8 and 1.5 kg a.e. ha^{-1}.

2.1.2 Specific characteristics

This study was performed between 28-11-2014 and 10-2-2015 in two agricultural areas cultivated with GR soybean (*Glycine max* (L.) Merr.) and GR maize (*Zea mays* L.), respectively. Soybeans were cultivated in 220 ha with an average slope of 1.8%, while the maize was cultivated in 93 ha with an average slope of 1.7%. The soil was partially covered with stubble from the last harvested crop. The soybean was sown on 11/12-10-2014 and harvested in March 2015. The maize was sown between 28-11 and 1-12-2014 and harvested in July 2015. During sowing, nitrogen fertilizer (urea) was applied in the maize

field. Soil varied from loam (soybean) to clayey loam (maize). Soil properties from both cultivation areas are presented in Table 1. Temperature and rainfall data during the study period are presented in Fig. S1 (supplementary material).

Due to serious water erosion problems in the past, both cultivation areas have soil bunds, i.e. small terraces or ridges 20-30 cm high and 3-5 m wide, made of soil, and used as a soil and water conservation measure to reduce runoff and soil erosion. The soil bunds (60-70 m apart) were built along the contour lines and are discharging into grass channels running through the lowest points in each cultivation area. These channels divide the cultivation areas into small catchments, whereas the soil bunds divide these catchments into sub-catchments. This study was performed in one of the small catchments per cultivation area. The soybean catchment is 35 ha, whereas the maize catchment is 50 ha.

2.1.3 Glyphosate application

Before the study period began, glyphosate was last applied on 12-10-2014 in the soybean area and on 30-10-2014 in the maize area. In both cases, the applied rate was 0.97 kg a.e. ha^{-1} of Roundup full® II (Monsanto, Argentina), mixed with other pesticides.

During the study period, glyphosate was applied once, using the granular commercial formulation Roundup UltraMax© (Monsanto, Argentina). The application rates were 1.0 and 0.81 kg a.e. ha^{-1} in the soybean (on 2-12-2014) and maize (on 26-12-2014) cultivations, respectively. The granular formulation was prepared in water with a commercial formulation of SpeedWet® (SpeedAgro, Argentina), an ethoxylated nonylphenol-based coadjuvant, and applied as a solution mixture with the herbicide Latium® (Monsanto, Argentina) and the insecticide Intrepid® (Dow AgroSciences, Argentina) in the soybean area, and the herbicide Dual Gold® (Syngenta, Argentina) in the maize area.

2.2 Soil sampling for glyphosate decay and AMPA formation/decay

To determine the glyphosate and AMPA contents in the soil surface layer and to investigate their decay behaviour, 6 composite soil samples (5:1) per cultivation area were collected weekly (before and after glyphosate application) in the defined catchments (see section 2.1.2). These composite samples were collected in 3 sub-catchments (delineated by the soil bunds): 3 at a depth of 0-1 cm and 3 at a depth of 1-2 cm. The latter were only collected from beginning of January 2015. Each composite sample per depth was collected from each sub-catchment. The samples were collected randomly from bare patches of the soil using a metal ring, put into plastic bags and stored at -20°C until analysis.

Soil moisture was also monitored weekly at 0-5 cm depth in each cultivation area to investigate its role on the decay rate of glyphosate and AMPA. For this, samples (in triplicate) were collected on the same days as those for glyphosate and AMPA, using a 100cc metal ring. It was determined by weight difference before and after drying at 105°C.

2.3 Off-site glyphosate and AMPA transport with runoff

To investigate the transport of glyphosate and AMPA with runoff during water erosion events, 3 plots and 3 weirs (sub-catchment scale) were installed in each cultivation area. The plots (Fig. 1A) were 3x1 m with the outlet at the lowest point, connected to a 200-L barrel. They were delineated by metal sheets driven 10 cm deep into the soil and retaining a height of 20 cm above the soil surface. Each plot was installed in the middle of a sub-catchment (see section 2.1.2), halfway between the soil bunds. The weirs were located at the outlet of 3 of the sub-catchments, where the surface runoff discharges into the grass channel. Each weir (Fig. 1B) consisted of a metal sheet of 140x10 cm, hammered 9 cm deep into the ground, with a crest of 1 cm above the soil surface. The spillway had a width of 120 cm and was enclosed by a 30 cm high metal sheet at either side, driven 10 cm into the soil. Runoff spilling

over the crest was sampled by using two 20-cm wide collectors. Each collector was connected to a 200-L barrel by a PVC hose (diameter: 51 mm). Installation of the plots and weirs was finished on 28-11-2014 in the soybean area and on 9-12-2014 in the maize area.

Three erosion-inducing rainfall events occurred during the study period: on 6-01-2015 (69.7 mm), 12-01-2015 (54.7 mm) and 9-02-2015 (56.0 mm). However, due to miscommunication with the farmer, runoff samples of the events of January were collected together. Due to problems with the barrels during the rainfall events (some have floated, while others have overflowed), it was not possible to quantify the erosion rates and related glyphosate and AMPA transport. The runoff in each barrel was stirred until a homogenous mix was observed. Then, two 1-L bottles of sample were collected (one for OM content and another for glyphosate and AMPA analysis). At the laboratory, the eroded sediment were separated from the runoff water by filtration, using paper filters of 8-µm pore size. For OM, the eroded sediment were analysed using the loss-by-ignition method. For glyphosate and AMPA analysis, the runoff water and eroded sediment samples were stored at -20°C until analysis.

2.4 Glyphosate and AMPA analysis

Glyphosate and AMPA were analysed by HPLC-ESI-MS/MS, using an XBridge™ Shield RP C18 column 100x2.1 mm, 3.5 µm particle size and an Aquity UPLC I-Class coupled to a Micromass Ultima triple-quadrupole MS (Waters, The Netherlands). The extraction (with potassium hydroxide (KOH), at a 1:5 ratio) and derivatisation (with FMOC-Cl (9-fluorenylmethoxycarbonyl chloride)) methods, chemicals used, as well as the method validation, MS parameters and quality control were as described by Yang et al. (2015b) and Bento et al. (2016). A sample batch was accepted when recoveries of the quality control were between 70-120%. The limits of quantification (LOQ) of the method for both glyphosate and AMPA in soil and in water are 0.05 mg kg^{-1} and 10 µg L^{-1}, respectively. The limits of

detection (LOD) of the method for glyphosate and AMPA in soil are 0.02 and 0.03 mg kg^{-1}, respectively. The LODs of the method for glyphosate and AMPA in water are 5.8 and 8.4 µg L^{-1}, respectively.

2.5 Data analysis

To study the field decay kinetics of glyphosate and AMPA in soil, we used ModelMaker 4.0 (A.P. Benson). For this purpose, the data were converted to percentage of applied glyphosate. The guidance document of FOCUS (2006) was followed to determine and select the models that best describe glyphosate decay and AMPA formation/decay in the upper soil layer (0-1 cm) of each cultivation area. The day of glyphosate application was considered as time zero. No sampling was possible to be performed on the application dates. Therefore, the theoretical glyphosate content in the soil immediately after application was calculated by:

$$C_0 = C_p + \left(\frac{a \cdot 100}{d \cdot \rho_b}\right) \quad (1)$$

where C_0 is the initial glyphosate content (mg kg^{-1}); C_p is the glyphosate content measured prior to the application (mg kg^{-1}) assuming that no decay occurred between the last sampling date and the application date, a is the application rate of glyphosate (kg a.e. ha^{-1}), d is the soil sampling depth (m) and ρ_b is the soil bulk density (kg m^{-3}).

Four models were tested to describe the glyphosate decay kinetics: a single first-order model (SFO, eq. 2); and three bi-phasic models – the First-Order-Multi-Compartment model (FOMC, eq. 3), the Hockey-Stick model (HS, eqs. 4.1 and 4.2) and the Double-First-Order-in-Parallel model (DFOP, eq. 5).

SFO: $$C = C_0 \cdot e^{-k \cdot t} \quad (2)$$

FOMC: $C = \frac{C_0}{\left(\frac{t}{\beta}+1\right)^{\alpha}}$ (3)

HS: $C = C_0 \cdot e^{-k_1 \cdot t}$ for $t \leq t_b$ (4.1)

$C = C_0 \cdot e^{-k_1 \cdot t_b} \cdot e^{-k_2 \cdot (t-t_b)}$ for $t > t_b$ (4.2)

DFOP: $C = C_0 \cdot (g \cdot e^{-k_1 \cdot t} + (1-g) \cdot e^{-k_2 \cdot t})$ (5)

where C is the glyphosate content (%) at time t (days), C_0 is the glyphosate content (%) at t=0, k, k_1 and k_2 are decay rate constants (day^{-1}), α is a shape parameter determined by the coefficient of variation of rate constant values (-), β is a location parameter (-), t_b is the time (days) at which the rate constant changes from k_1 to k_2, and g (-) is the fraction of C_0 in the compartment with rate constant k_1.

To determine the formation/decay kinetics of AMPA, the SFO model was used. The AMPA formation kinetics was described by the fraction of glyphosate that decayed to AMPA (*ffA*).

For each model, the glyphosate decay parameters were optimised first; C_0 of glyphosate was fixed to 100% in all models. Next, the AMPA formation and decay parameters were optimised. C_0 of AMPA was fixed to its content (in %) observed in each field at the last sampling date before glyphosate application; it was assumed that no decay occurred during this period. Then, both glyphosate and AMPA parameters were optimised together. For both fields, all four models were executed for glyphosate and the model with the best fit was selected based on the indicators recommended by FOCUS (2006) (visual assessment of curve fits and residual plots, χ^2 model errors, t-test). The half-life (DT_{50}) and DT_{90} of both compounds were calculated based on the selected best fit model, according to the specific equations presented by FOCUS (2006). Only the results obtained for the selected best model of glyphosate are presented in this study.

To test for significant differences ($p<0.05$) of glyphosate and AMPA contents in the soil between sampling dates per cultivation area and per soil depth, a one-way ANOVA followed

by Tukey or Dunnett's T3 post-hoc tests was performed. For significant differences ($p<0.05$) of glyphosate and AMPA contents in the soil between soil depths per cultivation area and date, an independent-samples T-test was performed. For significant differences ($p<0.05$) of AMPA contents in the soil between cultivation areas per soil depth, an independent-samples T-test was performed. The datasets were verified for their normality and equality of variances, and an ln-transformation was performed whenever these assumptions were violated. Statistics were performed using SPSS 22. Results of the statistical tests can be consulted in supplementary material (Table S1), together with the glyphosate and AMPA contents (in mg kg^{-1}) in soil at both sampling depths per sampling date and per cultivation area.

3. Results

3.1 Temperature, rainfall and SM content

During the study period, the average temperature was 22.5±2.9°C (Fig. S1). Total precipitation was 358.2 mm, with 81% of the rainfall occurring in January (54%) and the first 10 days of February (27%) (Figs. 2-3, S1). The SM content from both cultivation areas at 0-5 cm depth remained below the soil wilting point (soybean: 21% w/w; maize: 19% w/w) until 6-01-2015. The lowest SM content was measured on 6-01-2015, right before the first erosive rainfall event (Figs. 2-3; Table S1). Thereafter, SM in the maize cultivation area increased 1.3 times, on average, being above soil wilting point and quite stable (Fig. 3; Table S1). In the soybean field, the SM content showed alternating high and low values (Fig. 2, Table S1).

3.2 Glyphosate decay and AMPA formation/decay

Glyphosate and AMPA were detected in all soil samples from both cultivation areas, before and after glyphosate application (Figs. 2-3; Table S1). Although, in both cultivation areas, the last glyphosate application was about 2 months before the one applied during the study period, glyphosate and AMPA were still detected in the 0-1 cm soil layer in a range of 0.27-0.42 mg kg^{-1} for glyphosate and 1.3-1.7 mg kg^{-1} for AMPA (Figs. 2-3; Table S1). No significant differences of glyphosate contents were obtained between the sampling dates before application (soybean: 28-11-2014; maize: 9 to 22-12-2014) and the last sampling date (9-2-2015) (Figs. 2-3; Table S1). Thus, this indicates that, for a similar time period of about 2 months after glyphosate application (i.e. before (October) and after (December) the study period began), glyphosate content in soil decreased to comparable levels in both cultivation areas. Glyphosate and AMPA contents were always significantly higher at 0-1 cm soil depth than at 1-2 cm (Figs. 2-3; Table S1). AMPA contents in the soybean area were significantly higher than those in the maize area, for both soil depths.

Based on the glyphosate application rates, the expected average glyphosate content in the soil immediately after application (day 0) at 0-1 cm soil depth was 10.9 and 7.2 mg kg^{-1} in the soybean and maize cultivation areas, respectively. Comparing these with the glyphosate content obtained in the first sampling date after application, a decrease of 45.0% (7 days after) in the soybean area, and of 48.6% (11 days after) in the maize area was observed (Figs. 2-3; Table S1). Nevertheless, a high variation on glyphosate content in the first sampling date after application was observed in the soybean area (Fig. 2). This is likely a consequence of the variability on litter cover and crop growth observed in this cultivation area, which certainly affected the glyphosate reaching the soil during application.

Soybean cultivation area

The SFO model resulted in the best fit for glyphosate decay in the soybean area (Fig. 2). However, although this model presented the lowest χ^2 error value describing the glyphosate decay, it was still very high (47.2%; Table 2). Therefore, the simulated glyphosate behaviour only represents a tendency. The high χ^2 error is the result of the great variation of measured glyphosate contents between replicates in the first sampling date, and the underestimation by the model of the latter sampling values. Glyphosate DT_{50} and DT_{90} estimated by this model were 6.0 and 19.8 days, respectively.

AMPA initial content on the day of application was fixed at 24% of the applied glyphosate, which corresponds to its last measured soil content prior to glyphosate application. The SFO model fit for AMPA was well described, with a χ^2 error below the 15% threshold (Table 2). According to the model estimations, only 24% of the applied glyphosate degraded to AMPA (Table 2), and its decay occurred quite slowly during the study period (Fig. 2, Table 2). As a result, AMPA DT_{50} and DT_{90} estimated by the model were 54.7 and 182 days, respectively.

Maize cultivation area

In the maize area, the decay of glyphosate showed a particular behaviour. The HS model, with a decay rate change (t_b) occurring 11 days after glyphosate application, provided the best fit (Fig. 3). In the 11 days between application and the first sampling, glyphosate content decreased slowly (k_1 = 0.06 day^{-1}) compared to the rapid decay observed in the subsequent period (k_2 = 0.37 $days^{-1}$) (Table 2, Fig. 3). This change coincided with the start of a period of heavy rainfall, beginning in the evening of 6-01-2015, which in turn marked a shift on the SM regime observed in this cultivation area (Fig. 3). Results from the t-test for the HS parameters and the χ^2 error were satisfactory (Table 2). Glyphosate DT_{50} and DT_{90} estimated by this model were 11.1 and 15.4 days, respectively.

The initial AMPA content was fixed at 19% of the applied glyphosate, corresponding to its last measured soil concentration prior to glyphosate application. The SFO model performed reasonably well for AMPA, with a χ^2 error below the 15% threshold and a good visual fit (Table 2, Fig. 3). The lack of perceived formation and decay of AMPA is noticeable, with a model estimation of only 5% of the applied glyphosate degrading into AMPA. AMPA DT_{50} and DT_{90} estimated by the model were 71.0 and 236 days, respectively. Notwithstanding, these values need to be interpreted with care since the t-test of the estimated parameters were only significant at $p<0.1$.

Comparison between both cultivation areas

When comparing both cultivation areas, we see that glyphosate DT_{50} is nearly twice as long in the maize area than in the soybean area. Indeed, the decay rate described by k_1 (HS; maize) is half of that described by k (SFO; soybean) (Table 2). However, the second phase decay rate described by k_2 (HS model; Table 2) in the maize area is 3 times higher than that of the soybean area. Although a longer DT_{50} for glyphosate was observed in the maize area, its persistence was lower than in the soybean area (i.e., a shorter DT_{90} in the maize area). This lower persistence in the maize area was due to the faster glyphosate decay induced by heavy rainfall and higher SM content 11 days after glyphosate application. According to the models results, the degradation of glyphosate to AMPA was nearly 5 times higher in the soybean area than in the maize area (Table 2). The decay of AMPA, however, was similar in both cultivation areas (Table 2), although AMPA persisted longer in the maize area.

3.3 Glyphosate and AMPA contents in eroded sediment and runoff water

Although not all plots and weirs yielded runoff during the water erosion events, glyphosate and AMPA were detected in all collected sediment samples (Table 3). The highest

glyphosate and AMPA contents were detected in the maize area during the water-erosive events of 6/12-01-2015 (11-17 days after glyphosate application), with ranges between 4.2 and 10.9 mg kg^{-1} (Table 3). These contents were 1.1 to 8.3 times higher than those obtained in the parent soil at the same time (Table 3). In fact, glyphosate and AMPA contents were always higher in the eroded sediment than in the parent soil, except for AMPA in the plots of the soybean area (Table 3). The highest sediment/soil ratios were obtained for glyphosate (maize: 16.4; soybean: 17.5) at the sub-catchment scale (weirs) in the erosive rainfall event of 9-02-2015, which occurred 45 (maize) and 69 (soybean) days after glyphosate application (Table 3). This occurred despite the already relatively low glyphosate content observed in the soil surface layer (0-1 cm) when this rainfall event took place (Table 3). In nearly all cases, sediment/soil ratios were higher at the sub-catchment scale than at the plot scale (Table 3). Glyphosate and AMPA contents were unrelated with the transported OM (linear regression: $R^2_{glyphosate} = 0.08$; $R^2_{AMPA} = 0.15$).

Our results show that glyphosate was only detected in 3 runoff water samples and AMPA in only 1 (Table 3). For these runoff water samples, the estimated solid/water distribution coefficients (K_d) were 50.1-446 L Kg^{-1} for glyphosate and 476 L Kg^{-1} for AMPA (Table 3). The low number of runoff water samples detecting glyphosate and AMPA and the high K_d values indicate the higher affinity of these compounds to be transported adsorbed to eroded sediment. The low number of runoff water detections do not allow for a proper comparison between cultivation areas. Nevertheless, the K_d results observed in the maize area for the erosive rainfall events of January at the catchment level show similar and strong adsorption affinity to sediment between glyphosate and AMPA (Table 3). Maximum glyphosate and AMPA concentrations detected in runoff water were 35.4 and 11.3 µg L^{-1}, respectively. In the maize area, glyphosate and AMPA were only detected in the runoff water at the sub-catchment scale and for the erosive rainfall events of January 2015 (Table 3). In the soybean area, glyphosate was detected at the plot and sub-catchment scales, but only in the runoff

water from the erosive rainfall event of 9-02-2015 (Table 3). AMPA was not detected in runoff water for all erosive rainfall events occurring in the soybean area (Table 3).

4. Discussion

Studies pertaining to the environmental fate of glyphosate and AMPA in Argentina have focussed mostly on their occurrence in soil and surface waters (Peruzzo et al., 2008; Aparicio et al., 2013; Lupi et al., 2015; Ronco et al., 2016; Pérez et al., 2017; Primost et al., 2017). No field studies under real-world agricultural management activities were found on the dynamics of glyphosate and AMPA in the soil surface layer in which the role of their decay processes and loss by runoff were both investigated.

4.1 Glyphosate dynamics in the soil surface layer of agribusiness fields

Despite the great geographical proximity (approx. 1 km apart) between the two cultivation areas studied here, differences on glyphosate decay and persistence were observed. Since glyphosate and AMPA decay mostly by microbial activity (Bento et al., 2016), factors such as temperature, SM and soil properties strongly influence the microbial breakdown (Eberbach, 1998; Schroll et al., 2006; Bento et al., 2016). Consequently, glyphosate and AMPA persistence varies greatly between, as well as within, geographical areas (EU, 2002; Silva et al., 2018). Nevertheless, due to the soil sampling method used (random, but in bare patches), decay and persistence differences observed between the soybean and maize areas are not expected to be related to soil cover differences nor to differences between glyphosate spraying interceptions by soil residue cover. Soil erosion and runoff may have played a role though – although we could not quantify losses by erosion and runoff water in both cultivation areas (see section 2.3 for reasons), field observations suggest that higher erosion rates and runoff volumes occurred in the maize area. Moreover, glyphosate

interception by maize residues in the soybean area may have resulted in glyphosate wash-off from the cover residues and consequent direct transport with runoff water to the outlet of the catchment. These factors certainly influenced glyphosate decay. More studies in the region under these agricultural management conditions are needed to confirm this.

As shown in our study, glyphosate followed a first-order decay kinetic model (SFO) in the soybean area, whereas it followed a bi-phasic decay kinetic model (HS) in the maize area. However, as referred in section 0 for the soybean area, the SFO fit shows only a tendency due to the uncertainty resulting from the very high χ^2 error. The consistent model underestimation observed for the soybean area in the later stages of the decay process suggests that a bi-phasic model should have been applied instead. This has also been suggested elsewhere (Eberbach, 1998; Bento et al., 2016). However, higher χ^2 errors for the bi-phasic models were obtained. Moreover, the estimated parameters for the bi-phasic models were not significantly different from zero by the t-test ($p<0.05$), as it is required. Therefore, the SFO model was still the best fit for the soybean area.

In the maize area, the decay rate was affected by an abrupt change in the SM regime after heavy rainfall. Although the same amount of rain occurred in both cultivation areas, this shift from dry to wet conditions in a steady basis was only observed in the maize area, as opposed to the alternating low and high SM contents observed in the soybean area. Residue soil cover differences between the cultivation areas could not explain the behavioural difference in SM – a higher soil cover would be expected to maintain SM for longer periods, however the opposite was observed between the cultivation areas, i.e. soil cover was higher in the soybean area (with maize residues) than in the maize area (with soybean residues). We could not find a plausible explanation for this behavioural difference between cultivation areas. This shift from a dry to a wet phase in the maize area resulted in an increase of the glyphosate decay rate by a factor of six. Only the HS model performed satisfactorily under these conditions. This model has also performed best in a study on glyphosate decay in

water (Maqueda et al., 2017), as well as in another study on the decay of the herbicide isoproturon in soil (Díez and Barrado, 2010). In these studies, however, the HS model was applied similarly to other bi-phasic models, i.e. to represent an initial rapid decay followed by a lower decay rate. The reverse, as observed in our study, was not found in any other study. One should be aware though that the HS model result obtained for the maize area represents a particular case of a shift in SM conditions, and not a typical bi-phasic behaviour resulting from a lower decay rate at a later stage of the degradation process of a pollutant due to chemical properties.

The DT_{50} of 6.0 days in the loam loess soil of the soybean area was comparable to that of 6-9 days obtained under laboratory conditions in other agricultural soils (Eberbach, 1998; Simonsen et al., 2008). However, it was longer than the 3.5 days found in a Chinese loess soil under field conditions (Yang et al., 2015a). In the maize area, which was a clayey loam loess soil, the DT_{50} was 11.1 days. As referred previously, the HS model is bi-phasic, using two decay rates (k_1, k_2). If we consider each phase separately, we could calculate the theoretical half-life values to be 11.5 days if dry conditions would remain, which is only slightly longer than the actual estimated DT_{50}, and 1.9 days if wet conditions would have been present from the start. Schroll et al. (2006) studied the effect of SM on the dissipation of glyphosate, and found a linear (positive) correlation between SM and glyphosate decay. A similar correlation was found by Bento et al. (2016). Therefore, the distinct change in the decay rates in the maize area can largely be attributed to the increase in SM after the heavy rainfall event of 6-01-2015. Additionally, the occurrence of erosive rainfall events also contributed to the loss of glyphosate and AMPA from the soil surface layer through surface transport with runoff. Leaching is believed to have had a minor contribution on glyphosate and AMPA losses from the soil surface layer, since their contents were significantly lower at 1-2 cm soil depth compared to those at 0-1 cm soil depth. Moreover, glyphosate contents were relatively low (close to LOQ for most of the sampling periods) at a 1-2 cm soil depth

and quite stable over time. The high tendency for glyphosate to remain adsorbed to soil particles at the very topsoil surface layer and its low propensity to leach to deeper soil layers has also been demonstrated elsewhere (Kjaer et al., 2003; Al-Rajab et al., 2008; Yang et al., 2015a; Yang et al., 2015b).

4.2 AMPA dynamics in the soil surface layer of agribusiness fields

Similar to glyphosate, differences on AMPA persistence were observed between the cultivation areas studied. This confirms that site-specific external factors (e.g. SM, soil properties, microbial diversity) can vary greatly, affecting the decay behaviour and persistence of these compounds.

High AMPA background residues were found in the soil surface layer (0-1 cm) of both cultivation areas before glyphosate application (1.3-1.7 mg kg^{-1}). These high background residues suggest that AMPA is accumulating in soil. Aparicio et al. (2013) also found AMPA residues ranging between 0.30-2.3 mg kg^{-1} in cultivation areas of the province of Buenos Aires, in Argentina. Primost et al. (2017) reported much higher AMPA residues when compared to those in our study: an average AMPA content of 4.2 mg kg^{-1}, with the highest content reported in the literature of 38.9 mg kg^{-1}, in soils “under real-world agricultural management practices” (comparable to the management practices of our study site), in the Pampas of Entre Ríos province, Argentina. These authors also stated that, “under current practices, (glyphosate) application rates are higher than dissipation rates” and that glyphosate and AMPA are to be considered “pseudo-persistent” compounds (Primost et al., 2017). Our maximum AMPA background residues (1.7 mg kg^{-1}) are, however, slightly lower than the 1.9 mg kg^{-1} reported by Silva et al. (2018) for agricultural topsoils from the European Union.

The decay rate of AMPA is considerably lower than that of glyphosate, resulting in longer DT_{50} and DT_{90} in both cultivation areas. The longer persistence of AMPA compared to glyphosate has also been reported elsewhere (Bergstroem et al., 2011; Yang et al., 2015a; Bento et al., 2016). Notwithstanding, The DT_{50} of 54.7 and 71.0 days obtained in our study were larger than the 23-35 days found under field conditions in a Chinese loess soil (Yang et al., 2015a). A low decay rate suggests that AMPA may accumulate in soil and may persist in higher quantities than glyphosate. In our study, glyphosate peaked in the period shortly after application, decreasing significantly thereafter. AMPA, on the other hand, remained almost constant during the study period and at higher concentrations than glyphosate, suggesting that AMPA is accumulating in these cultivation areas. Nevertheless, the formation rate of AMPA was also low. According to the models results, only 24% of the decayed glyphosate appeared as AMPA in the soybean area, while in the maize area its formation was negligible. Bento et al. (2016) found higher formation rates of AMPA (37-48%) in a laboratory experiment with loess soil at 30°C. Besides degrading to AMPA, glyphosate has a second known degradation pathway to sarcosine (Borggaard and Gimsing, 2008). It is expected that, in this study, glyphosate degraded primarily to sarcosine, particularly in the maize area. If so, the high AMPA soil content in the maize area is most probably a residue of earlier glyphosate applications that is extremely slowly decaying. There is no clear explanation to why glyphosate degraded to AMPA before, but not so distinctly after this application in both cultivation areas. One possible reason may be the formulation of glyphosate that was applied. The granular properties of Roundup UltraMax® may have caused a preference for the sarcosine degradation pathway. On the other hand, the microorganisms responsible to degrade glyphosate to AMPA may have been affected by some external factor, which would explain this shift in degradation pathways. It is particularly unclear why the formation of AMPA was nearly negligible in the maize area compared to the soybean area. A possible explanation is the use of Dual Gold®, a herbicide applied in the

mix for the maize area, which is known to impact microbial communities adversely (Joly et al., 2012). Another possible reason is the use of nitrogen fertilizer in the maize area; it could have affected the soil microbial community in a way that may have resulted in the shift of the glyphosate degradation pathway. According to Nivelle et al. (2017), nitrogen fertilization decreases soil enzyme activities. However, no studies were found relating the effect of Dual Gold® or nitrogen fertilizer to glyphosate degrading microorganisms and consequent glyphosate degradation pathways. Further investigations under controlled conditions are needed to better understand this phenomenon.

4.3 Glyphosate and AMPA contents in eroded soil and runoff water

Our results show higher glyphosate and AMPA contents in eroded sediment than in runoff water. This is in accordance with findings from elsewhere (Yang et al., 2015a; Yang et al., 2015b; Bento et al., 2018). In fact, glyphosate was only detected in 3 runoff water samples and AMPA in 1. For those runoff water samples >LOD, the maximum glyphosate and AMPA concentrations detected were 35.4 and 11.3 µg L^{-1}, respectively. In the eroded sediment, the maximum glyphosate and AMPA contents obtained were 10.9 and 8.3 mg kg^{-1}, respectively. These values are higher than the maximum of 0.56 mg kg^{-1} of glyphosate and 0.21 mg kg^{-1} of AMPA in suspended sediment found in various streams in Buenos Aires Province (Aparicio et al., 2013) or the 0.58 mg kg^{-1} of glyphosate and 0.48 mg kg^{-1} of AMPA in suspended sediment in waterways of Entre Ríos Province (Primost et al., 2017), both studies in the Pampas of Argentina. It is important to refer though that our results in eroded sediment are not affected by a dilution factor, as they were in the above mentioned studies. Our measurements were performed to suspended sediment collected from runoff samples originating directly from the studied cultivation areas.

Glyphosate and AMPA contents were higher in the eroded sediment than their content in the parent soil for all cases, except for the plots in the soybean area. This is in accordance with the findings of Yang et al. (2015a). This result can be explained by the fact that surface transport occurred mostly in the form of sheet erosion. In this type of erosion, only the upper few millimetres of soil are transported (Whiting et al., 2001), which contain the highest glyphosate and AMPA contents (Rampazzo et al., 2013; Yang et al., 2015a; Yang et al., 2015b).

Glyphosate and AMPA contents were higher in the eroded sediment obtained at the sub-catchment scale (weirs) than those at the plot scale. Among these results were some particular high ratios, namely the glyphosate ratio found at the sub-catchment scale in both cultivation areas in the erosive event of 9-02-2015. This is likely a product of glyphosate-rich sediment accumulation in front of the weirs during previous rainfall events. Glyphosate and AMPA strongly adsorb to clay and fine silt particles (Bento et al., 2017; Bento et al., 2018). Glyphosate-rich suspended sediment is the last type of sediment to be deposited at the end of a water erosion event, leading to an accumulation of such sediment at the lowest point of a catchment (Bento et al., 2018). The soil samples were collected in the middle of the cultivation areas and are unlikely to take this effect into account. Some authors found that glyphosate transport is particularly high during erosion events that occur shortly after application (Screpanti et al., 2005; Todorovic et al., 2014). From our sediment/soil ratios obtained at the catchment scale, this was not particularly obvious.

4.4 Limitations of the study

A great limitation of this study has been the short duration of the experiment. Therefore, the presented results should be seen as year-specific and as a preliminary assessment of the dynamics of glyphosate and AMPA in agribusiness cultivation areas of the pampean loess

soils of Argentina. Moreover, the decay models results cannot be generalized to other years. Decay studies taking into account multiple years will give a better insight of the normal decay behaviour of glyphosate and AMPA in these soils, as well as their behaviour when more extreme conditions are observed. The short duration of the study did also not allow to correct the problems faced with the barrels, in order to obtain reliable field data on the transport (load) of glyphosate and AMPA with water-erosion. Moreover, it couldn't be estimated if the floating and overflowing of the barrels could have affected the sediment concentration and/or particle size. Sediment concentration should not affect the presented glyphosate and AMPA contents in eroded sediment, but particle size could have affected, since glyphosate and AMPA tend to adsorb more strongly to clay and fine silt particles (Bento et al., 2017; Bento et al., 2018). Consequently, (long-term) field studies on the transport of glyphosate and AMPA with water erosion in agribusiness cultivation areas, particularly in the Argentinean environment, are still lacking.

5. Conclusions

From this study we conclude that decay is the dominant process describing glyphosate dynamics, and SM content is a very important factor influencing the decay rate. AMPA dynamics, on the other hand, didn't show a clear pattern in our study. The high background residues of AMPA before glyphosate application suggest that AMPA may accumulate in soil, particularly in cultivation areas with repeated glyphosate applications. Nevertheless, long-term (>1 year) decay studies under current-use agricultural management activities are recommended to confirm this. The great variability in the decay behaviour and persistence of glyphosate and AMPA observed in our study indicates the need to perform site-specific decay studies.

From the high glyphosate and AMPA contents obtained in eroded sediment we also conclude that water erosion represents a great risk of glyphosate and AMPA contamination of surface water bodies and adjacent fields. This is particularly true when erosive rainfall events occur in the form of sheet erosion.

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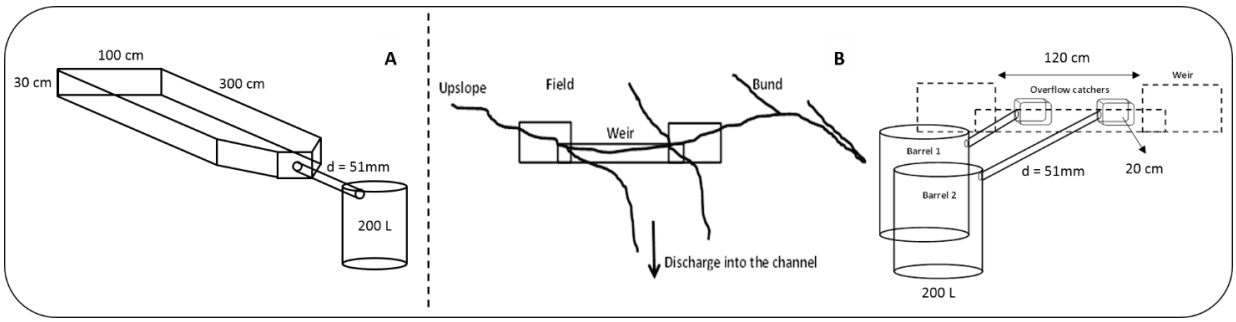

Figure 1: Schematic representation of the plots (A) and weirs (B).

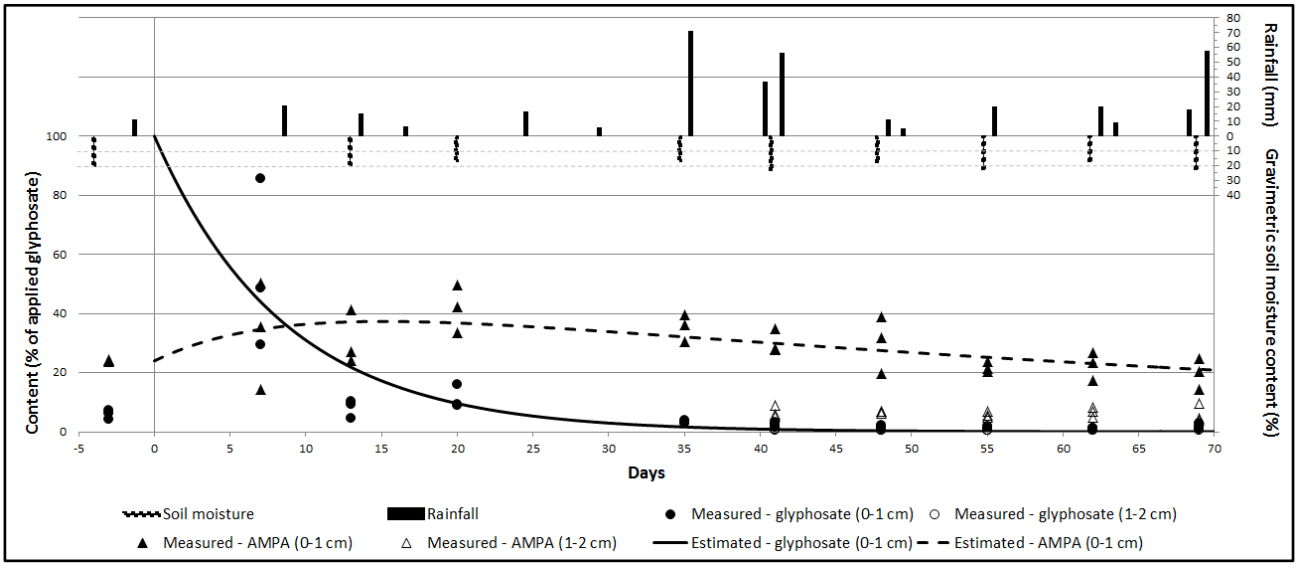

Figure 2: Glyphosate and AMPA residues at 0-1 and 1-2 cm soil depth, their decay behaviour in the top 1 cm soil, and rainfall and soil moisture contents under GR soybean. Day of glyphosate application (t = 0) was 2-12-2014. AMPA results were converted to equivalent mass of glyphosate.

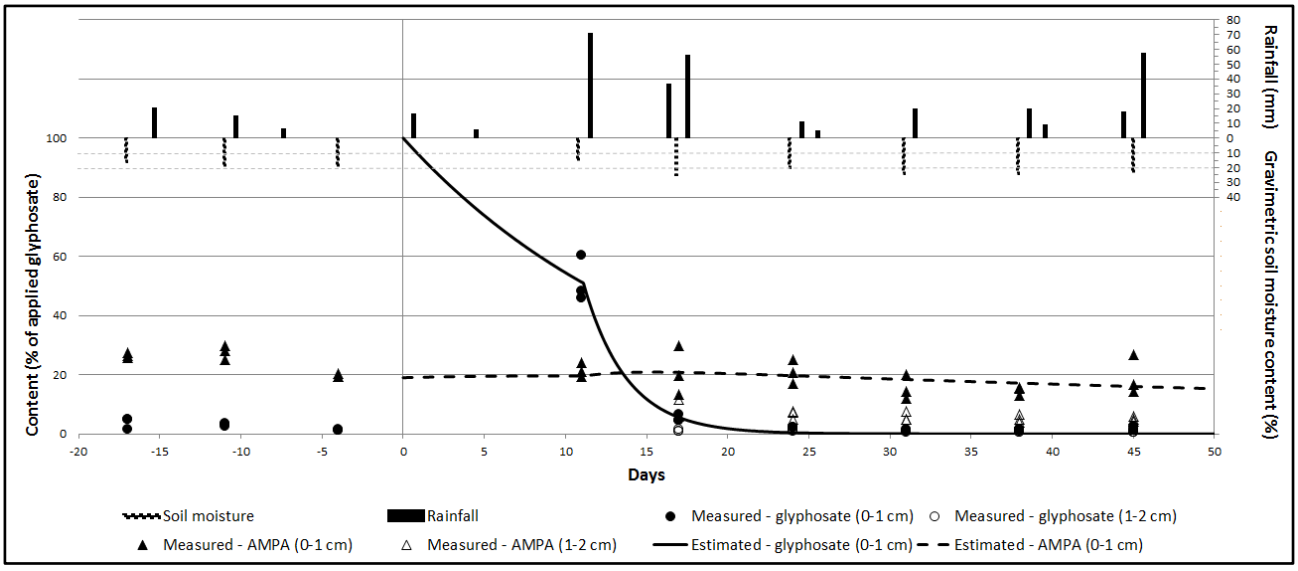

Figure 3: Glyphosate and AMPA residues at 0-1 and 1-2 cm soil depth, their decay behaviour in the top 1 cm soil, and rainfall and soil moisture contents under GR maize. Day of glyphosate application (t = 0) was 26-12-2014. AMPA results were converted to equivalent mass of glyphosate.

Table 1: Soil properties of the soybean and maize cultivation areas.

Parameter	Soybean area	Maize area
Sample depth (cm)	0-10	0-10
Particle size distribution		
<0.002 mm (clay) (%)	26.3	27.4
0.002-0.05 mm (silt) (%)	44.2	40.0
>0.05 mm (sand) (%)	29.5	32.6
pH in $CaCl_2$	5.8	5.9
Organic matter (OM) (%)	5.1	4.6
P available (mg kg^{-1})	1.1	1.2
N total (g kg^{-1})	2.1	2.2
CEC (mmol+ kg^{-1})	243	192
Bulk density (g cm^{-3})[a]	1.0	1.1

[a] Bulk density was measured at 0-5cm depth and it's the average of 3 locations in each cultivation area.

Table 2: Decay parameters of glyphosate using the SFO and HS model for the soybean and maize field, respectively, and the formation and decay parameters of AMPA using the SFO model.

	Glyphosate following SFO or HS				AMPA following SFO[a]		
Field	k ± SE (SFO)	k_1 ± SE (HS) (day^{-1})	k_2 ± SE (HS)	χ^2 error (%)	*ffA* ± SE -	k ± SE (day^{-1})	χ^2 error (%)
Soybean	0.12 ± 0.02*	-	-	47.2[b]	0.24 ± 0.09*	0.013 ± 0.006*	9.0
Maize	-	0.06 ± 0.004*	0.37 ± 0.07*	9.7	0.05 ± 0.04#	0.010 ± 0.006#	12.4

k, k_1 and k_2 - decay rates; *ffA* – formation fraction of AMPA.

[a] AMPA results were converted to equivalent mass of glyphosate.

[b] The χ^2 error is above the acceptable threshold of 15%.

* Estimated parameter is significantly different from zero (*t*-test; p<0.05).

Estimated parameter is significantly different from zero (*t*-test; p<0.1).

Table 3: Glyphosate and AMPA contents (average±SD) in eroded sediment and runoff water collected from the soybean and maize cultivation areas after water-erosive events, corresponding sediment:soil ratios and solid/water distribution coefficients (K_d). Soil values refer to the last sampling date before each water-erosive rainfall event (see Table S1).

Code	OM	Glyphosate					AMPA				
	(sed)	Soil	Sed	Sed/soil ratio	Runoff water	K_d	Soil	Sed	Sed/soil ratio	Runoff water	K_d
	(%)	(mg kg^{-1})		-	(µg L^{-1})	(L Kg^{-1})	(mg kg^{-1})		-	(µg L^{-1})	(L Kg^{-1})
*SP35-41 (n=3)	2.0 ± 0.7	0.36 ± 0.05	1.4 ± 0.7	3.9	< LOD	-	2.5 ± 0.3	2.2 ± 0.1	0.88	< LOD	-
*SW35-41 (n=0)	-		-	-	-	-		-	-	-	-
*MP11-17 (n=2)	2.3 ± 0.2	3.7 ± 0.6	4.2 ± 0.3	1.1	< LOD	-	1.0 ± 0.1	8.3 ± 2.7	8.3	< LOD	-
*MW11-17 (n=3)	2.6 ± 1.8		10.9 ± 6.7	2.9	35.4 ± 27.5	446 ± 445		4.7 ± 1.0	4.7	11.3 ± 4.4	476 ± 202
#SP69 (n=2)	7.2 ± 6.9	0.21 ± 0.11	1.3 ± 1.5	6.1	22.8 ± 22.8	50.1 ± 12.3	1.4 ± 0.4	1.1 ± 0.8	0.77	< LOD	-
#SW69 (n=1)	4.2 ± -		3.7 ± -	17.5	23.4 ± -	157 ± -		2.0 ± -	1.4	< LOD	-
#MP45 (n=1)	3.4 ± -	0.13 ± 0.05	0.54 ± -	4.2	< LOD	-	0.91 ± 0.31	2.0 ± -	2.2	< LOD	-
#MW45 (n=2)	2.5 ± 1.6		2.1 ± 1.0	16.4	< LOD	-		2.6 ± 0.6	2.8	< LOD	-

S (soybean field); M (maize field); P (plot); W (weir – sub-catchment scale); dd (days after application); Sed (eroded sediment); OM (Organic matter content of the eroded sediment); * rainfall events of 06-01 & 12-01-2015; # rainfall event of 09-02-2015

Supplementary material

Dynamics of glyphosate and AMPA in the soil surface layer of glyphosate-resistant crop cultivations in the loess Pampas of Argentina

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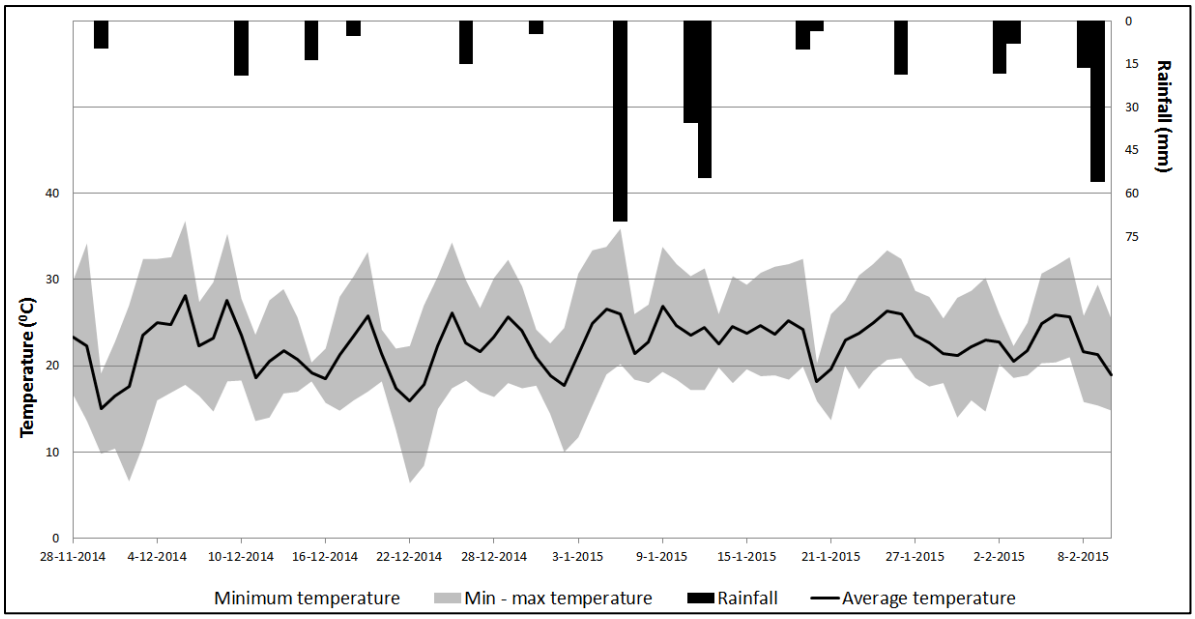

Figure S1: Rainfall and average, minimum and maximum temperatures during the study period. Temperature data were provided by the national meteorological services of Argentina. Rainfall data were collected from on-farm rainfall gauges monitored at 7:00 each morning.

Table S1: Glyphosate and AMPA contents (average±SD) on the top 0-1cm and 1-2 cm soil, and soil moisture (SM) contents (average±SD) on the top 0-5cm soil, in the soybean and maize cultivation areas.

		Soybean[#]			Maize[#]		
Sampling date	Soil depth (cm)	Glyphosate (mg kg^{-1})	AMPA (mg kg^{-1})	SM (%)	Glyphosate (mg kg^{-1})	AMPA (mg kg^{-1})	SM (%)
28-11-2014	0-1	0.42 ± 0.12* bc	1.7 ± 0.03* a	19.6 ± 3.4	-	-	-
9-12-2014	0-1	6.0 ± 3.1 e	2.4 ± 1.3 a	n.d.	0.27 ± 0.13* bc	1.3 ± 0.04* a	15.6 ± 2.4
15-12-2014	0-1	0.88 ± 0.33 cd	2.2 ± 0.7 a	19.5 ± 1.6	0.23 ± 0.03* bc	1.3 ± 0.1* a	18.9 ± 0.1
22-12-2014	0-1	1.2 ± 0.4 d	3.0 ± 0.6 a	16.6 ± 1.9	0.09 ± 0.01* a	0.93 ± 0.03* a	19.5 ± 1.3
6-01-2015	0-1	0.36 ± 0.05 bc	2.5 ± 0.3 a	16.6 ± 2.3	3.7 ± 0.6 d	1.0 ± 0.1 a	14.9 ± 1.2
12-01-2015	0-1	0.28 ± 0.06 ab; A	2.2 ± 0.3 a; A	24.0 ± 2.1	0.38 ± 0.09 c; A	0.99 ± 0.39 a; A	24.6 ± 2.2
	1-2	0.10 ± 0.05 a; B	0.71 ± 0.21 a; B		0.08 ± 0.03 b; B	0.57 ± 0.23 a; A	
19-01-2015	0-1	0.19 ± 0.05 ab; A	2.2 ± 0.7 a; A	18.0 ± 0.5	0.16 ± 0.001 ab; A	0.99 ± 0.19 a; A	19.9 ± 0.7
	1-2	0.07 ± 0.02 a; B	0.69 ± 0.03 a; B		0.07 ± 0.02 ab; B	0.47 ± 0.10 a; B	
26-01-2015	0-1	0.17 ± 0.02 ab; A	1.6 ± 0.1 a; A	22.7 ± 0.9	0.09 ± 0.02 a; A	0.73 ± 0.19 a; A	23.8 ± 1.8
	1-2	0.06 ± 0.02 a; B	0.61 ± 0.10 a; B		0.05 ± 0.004 ab; B	0.41 ± 0.11 a; A	
2-02-2015	0-1	0.13 ± 0.01 a; A	1.6 ± 0.3 a; A	17.7 ± 2.0	0.10 ± 0.01 a; A	0.69 ± 0.07 a; A	23.8 ± 2.4
	1-2	0.07 ± 0.02 a; B	0.69 ± 0.18 a; B		0.05 ± 0.01 ab; B	0.37 ± 0.11 a; B	
9-02-2015	0-1	0.21 ± 0.11 ab; A	1.4 ± 0.4 a; A	23.0 ± 0.9	0.13 ± 0.05 ab; A	0.91 ± 0.31 a; A	23.4 ± 0.9
	1-2	0.10 ± 0.05 a; B	0.62 ± 0.33 a; B		0.03 ± 0.01 a; B	0.36 ± 0.06 a; B	

n.d.: no data

Different lowercase letters within the same column indicate significant differences between sampling dates for the same soil depth ($p<0.05$).

Different capital letters within the same column indicate significant differences between soil depths for the same sampling date ($p<0.05$).

[#] Glyphosate formulation was applied on 2-12-2014 (soybean) and 26-12-2014 (maize)

* Background contents