



## Glyphosate runoff and its occurrence in rainwater and subsurface soil in the nearby area of agricultural fields in Argentina.



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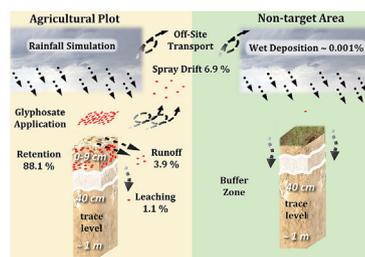
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### HIGHLIGHTS

- Glyphosate and AMPA were largely retained in the surface soil layer.
- Glyphosate loads were similar for spray drift and runoff.
- Trace levels of glyphosate were detected at the subsurface of the riparian zone.
- Glyphosate and AMPA in rainwater exceeded limits for safe human consumption.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Glyphosate-based products are among the most important herbicides applied to enhance the production of food commodities, leading to the worldwide spread of this herbicide. The main goal of this work was to evaluate the off-site transport of glyphosate in a runoff experiment. A micro-plot experiment was conducted to assess the retention, leaching and runoff of glyphosate under rainfall simulation. Glyphosate losses due to spray drift were estimated. Concentrations of glyphosate and AMPA were determined in rainwater and subsurface soil from agricultural and riparian zones. Analyses were performed with UHPLC-MS/MS. Experimental results demonstrated that 88.1% of the applied glyphosate was retained in the surface soil layer (0–9 cm). Glyphosate leaching was negligible compared to its runoff (3.9%) and spray drift (6.9%). Thus, the risk of groundwater pollution would be lower in comparison to that of both surface waters and rainwater. Moreover, under field conditions, glyphosate and AMPA were detected in 52% of the rainwater samples and glyphosate was detected up to 1 m in both soil profiles. Although the experimental application was made with hand-held knapsack under low wind condition to minimize glyphosate aerial dispersion, the spray drift was the main source of glyphosate off-site transport, degrading air quality and rainwater for human consumption. The balance among spray drift, runoff and

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soil absorption of glyphosate when it was sprayed close to the soil surface (hand held equipment), demonstrated the importance of spray drift in mass balance studies during runoff and leaching experiments with glyphosate.

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## 1. Introduction

Glyphosate (N-(phosphonomethyl)glycine) is a non-selective systemic herbicide mainly applied in fallows and genetic modified crops for weed control, but it is also used in urban areas and widely applied to transgenic soybean plants, being Argentina the third soybean producer in the world (Botta et al., 2009; Ybran and Lacelli, 2016). Glyphosate usage worldwide has increased 15-fold since tolerant-glyphosate crops were introduced in 1996 (Benbrook, 2016). Recently this pesticide has been classified as *probably carcinogenic to humans* (group 2A) by the Agency for Research on Cancer, being its fate of great concern worldwide (International Agency for Research, 2015), although studies of AMPA (aminomethylphosphonic acid) toxicity to humans are scarce (Grandçoin et al., 2017). The implications of an increased use of glyphosate, has led to a growing number of glyphosate-tolerant plants, environmental and social impacts and bad consequences for environmental quality (Binimelis et al., 2009).

Organic matter, clays and inorganic particles with polyvalent cations such as iron and aluminum oxides, are important in glyphosate adsorption process, in which the phosphonic moiety is involved (Albers et al., 2009; Borggaard and Gimsing, 2008; Pessagno et al., 2008). In addition, soil phosphorus application as fertilizer might favor desorption, degradation and transport of glyphosate (Sasal et al., 2015). Microbial degradation of glyphosate to AMPA occurs in the range of days to months under environmental conditions with temperature and soil moisture the most important controlling factors (Bento et al., 2016; Guijarro et al., 2018). Glyphosate can be degraded in few hours in saturated surface soils (half-life: 41 h, Bento et al. (2016) and similar dissipation rates were measured in freshwater ecosystems (half-life: 108 h, Vera et al., 2010). In spite of its low persistence, glyphosate and its metabolite AMPA are widely found in the environment (Battaglin et al., 2014; Bonansea et al., 2017; Lupi et al., 2015; Okada et al., 2018; Pérez et al., 2017; Ronco et al., 2016; Van Stempvoort et al., 2016). Therefore, glyphosate should be considered a “pseudo persistent” pollutant, considering that accumulates in agricultural soil after repeated spraying events (Primost et al., 2017).

Preferential flow is an important mechanism for glyphosate leaching in well-structured soils. In addition, the presence of macropores such as fractures and burrows are necessary for bypassing the vadose zone (Kjær et al., 2011; Vereecken, 2005). In a recent study in Argentina, the soil hydraulic properties explained the vertical transport of glyphosate and AMPA in a loam profile (Soracco et al., 2018). The effects of macropore flow on pesticide leaching lead to losses typically less than 1% of the applied dose (Caprié et al., 2017; Okada et al., 2016), though in some studies reach up to 5% (Jarvis, 2007). In addition to rainfall intensity, the delay between pesticide application and rain event is an important factor that influences vertical and horizontal mobility of pesticides in soils (Boithias et al., 2014; Norgaard et al., 2014).

The transport of pesticides in runoff solution might be as important as the transport by particles in suspensions for compounds with high sediment-water partition coefficient, such as glyphosate and AMPA in (Melland et al., 2016). Moreover, runoff might be responsible for a significant contribution to

contamination spread in the environment. Battaglin et al. (2003) found that overland runoff accounted for 90% of herbicide transport to surface waters in some areas of United States. Glyphosate and AMPA were also detected in surface water from different areas in Argentina (Aparicio et al., 2013; Berman et al., 2018; Ronco et al., 2016). In addition, spray drift and unintentional direct application over surface water might contribute to glyphosate off-site transport (Messing et al., 2011). Application techniques and meteorological conditions influence greatly the amount of pesticide reaching the target (e.g. soil, plant; Arvidsson et al., 2011). Thus, a spray fraction might remain in the air, be transported by wind, affecting the air and rain quality from agricultural and urban areas (Chang et al., 2011; Farenhorst et al., 2015). In addition, glyphosate has been detected in rainwater from different regions in Argentina (Alonso et al., 2018).

The aim of this work was to evaluate the off-site transport of glyphosate by overland flow and spray drift in a microplot runoff experiment, from its application area to non-target sites. Moreover, in order to understand these processes in natural systems, the levels of glyphosate and AMPA in deep soil profiles and rainwater during pesticide application periods were determined. We hypothesized that spray drift represents an important fraction of the total pesticide applied under low-drift conditions, being a significant source of pesticide in riparian areas.

## 2. Materials and methods

### 2.1. Study area

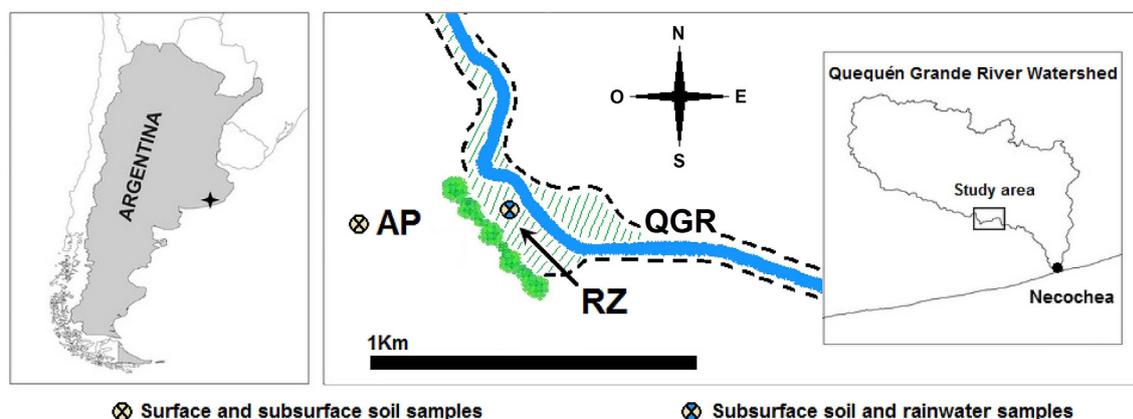
Sampling was performed in an agricultural plot (AP) under no-tillage management, without application of glyphosate since few months before the experiment. This field plot is located in the middle region of the Quequén Grande River watershed having intensive agricultural activities mainly related to soybean production (Fig. 1). This region has a sub-humid climate, with annual mean temperatures ranging from 7 °C to 21 °C. The mean annual rainfall in the area is 931 mm year<sup>-1</sup>. Extensive agriculture (barley followed by soybean) was performed uninterruptedly over the last 7 years. The soil texture is sandy loam, with low silt and clay content (14% and 12%, respectively; Lupi et al., 2015).

### 2.2. Sample collection

Undisturbed soil columns for the runoff experiment (controls and treatments) were taken from AP (Fig. 1) during the uncultivated (June) period, using steel cylinders of 10 cm deep opened at both ends. The cylinder had a slit on the side to allow the runoff collection. The samples were wetted and carefully transported to the rain simulator to avoid cracking.

Subsurface soil was collected between 0.4 and 1.1 m depth from AP and a riparian zone (RZ) by digging pits. The RZ was adjacent to the QGR gully and it was separated from agricultural fields by a row of trees (Fig. 1). The RZ was covered with natural grass without application of pesticides.

Rainwater samples were collected in RZ with a plastic funnel draining into a 5 L plastic bottle during a year period (January 2013–



**Fig. 1.** Study area and sampling points of surface soil, subsurface soil and rainwater samples in Quequén Grande River (QGR) watershed (modified from Lupi et al., 2016). The dashed line delimits the agricultural plots (AP) and the riparian zone (RZ, hatching lines).

februar 2014). The water was collected during the whole rain event, which lasted at most for a few days (weekly rain events).

Subsurface soil and rainwater samples were kept frozen ( $-20^{\circ}\text{C}$ ) until glyphosate and AMPA analysis.

### 2.3. Runoff experiment

#### 2.3.1. Sample treatment and rainfall simulation

Three undisturbed soil columns were employed for controls (C1–C3: no glyphosate product was applied), while other 6 soil columns were used for treatments (T1–T6). Controls and treatments were wetted to field capacity prior to rainfall simulation. Afterwards, treatments were sprayed with Mifos<sup>®</sup> (36% acid equivalent isopropylamine salt). Application of a recommended rate for weed control ( $3\text{ L ha}^{-1}$ ) was made with a hand-held knapsack sprayer at a working pressure of 2.9 bar (carbon dioxide gas source). The sprayer bar had four nozzles (Albuz<sup>®</sup>–ADI–ISO 110 01) separated 0.48 m from each other. The treated samples were placed in line and parallel to the applicator displacement direction to ensure a uniform treatment. The application speed was done at  $1\text{ m s}^{-1}$  with nozzle high of 0.5 m on the T1–T6 samples. The air temperature was  $17^{\circ}\text{C}$ , relative humidity 72% and wind speed lower than  $0.5\text{ m s}^{-1}$ . Columns were placed over a platform with an average landscape slope ( $2^{\circ}$ ) and rainfall simulation began 30 min after wetting the control soil columns (C1–C3) or the glyphosate application treatments (T1–T6). The rainfall simulator had ten nozzles (Naandan-jain<sup>®</sup>–Hadar 7110) distributed in a rectangle of  $2 \times 1.5\text{ m}$  of variable high. It was set at 1.75 m high to enable a uniform intensity and yielding droplets (1.1 mm diameter) with a kinetic energy of  $0.67\text{ kJ m}^{-2}$  (Wirsch, unpublished data). The simulator was feed with a 50 L water reservoir connected to an electric suction pump with adjustable pressure controller (Shurflo, S-8000). The rainfall simulation lasted for 2.5 h at  $20\text{ mm h}^{-1}$  rainfall intensity (2 year recurrence interval, Puricelli, 2014). Soil of controls and treatments at two different depths (0–5 cm and 5–9 cm) were obtained from four pooled subsamples collected with a 20 mL plastic cylinder core. The total runoff was collected with plastic bottles for glyphosate and AMPA analysis, as well as physicochemical properties.

#### 2.3.2. Spray drift estimation

Three different methods were used to determine the amount of glyphosate that reached the soil and to estimate drift during application. Two methods evaluated the quantity of product that reached the soil gravimetrically ( $n = 3$ ) and by glyphosate analysis ( $n = 3$ ). The third method estimated the fraction of the spray

droplet size distribution that contributed to drift (droplet diameter  $<100\text{ }\mu\text{m}$ , Holterman, 2003) using water sensitive cards of  $20\text{ cm}^2$  (Syngenta<sup>®</sup>). The spray droplet distribution was evaluated with CIR 1.5/T&C srl. software for image analysis (Supplementary material for more details).

### 2.4. Analytical procedures

#### 2.4.1. Physicochemical properties

Organic carbon (OC) and total iron (Fe<sub>T</sub>) contents were determined in the soil profile (Holmgren, 1967; Mingorance et al., 2007). Soil bulk density (0–9 cm) was calculated by drying the samples to constant weight ( $105^{\circ}\text{C}$ ). Conductivity in liquid samples was measured with a Hanna<sup>®</sup> probe (model 9829I), while total solids in rainwater samples were quantified by drying samples to constant weight. Nitrate and total phosphorus were determined with standard methods (Keeney and Nelson, 1982; Murphy and Riley, 1962).

#### 2.4.2. Sample extraction procedure

Soil samples were dried at  $30^{\circ}\text{C}$  in forced convection oven until constant weight (24 h). The fine ground soil samples (5 g) were spiked with  $250\text{ }\mu\text{L}$  of  $1\text{ }\mu\text{g mL}^{-1}$  stock solution of isotope-labeled glyphosate ( $1,2\text{-}^{13}\text{C}$ ,  $^{15}\text{N}$ , Sigma-Aldrich International GmbH) to compensate matrix effects. In the case of the rainwater and runoff, 2 mL of thoroughly mixed sample was spiked with  $20\text{ }\mu\text{L}$  glyphosate stock solution. After 30 min rest period, soil and water samples were sonicated for 30 min in 12 mL and 0.5 mL of extracting solution ( $0.1\text{ M}$  of  $\text{KH}_2\text{PO}_4$ ), respectively. After centrifugation, the supernatant was collected and treated with an equal volume of  $0.1\text{ M}$  disodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) solution to adjust pH (9). An aliquot of 2 mL was taken and derivatized with  $2\text{ mL}$  of  $1\text{ mg mL}^{-1}$  of 9-fluorenylmethylchloroformate (FMOC-CL) acetonitrile solution (HPLC-grade, ANEDRA SA, Argentina). After an overnight rest, the samples were vigorously shaken (3 min) with 6 mL dichloromethane (HPLC-grade, ANEDRA SA, Argentina) to extract matrix interferences and derivatizing by-products (Hanke et al., 2008). The aqueous phase was filtrated ( $0.22\text{ }\mu\text{m}$  nylon filter) and transferred to a 1 mL vial for analysis in UPLC–ESI–MS/MS system (Aparicio et al., 2013).

#### 2.4.3. Quality assurance

Blanks and standard curves in the range  $0\text{--}100\text{ }\mu\text{g kg}^{-1}$  of glyphosate and AMPA (99.9%, Sigma-Aldrich International GmbH) and prepared with HPLC-grade water, were carried out with each set of samples. An equivalent amount of isotope-labeled glyphosate

stock solution (20  $\mu\text{L}$ ) was also added to each standard. The limit of detection (LOD) for soil matrix ( $0.3 \mu\text{g kg}^{-1}$ ) and rainwater samples ( $0.25 \mu\text{g L}^{-1}$ ) was defined 3 times the signal-to-noise (S/N) ratio of the compounds, while the limit of quantification (LOQ) was defined as S/N ratio equal to 9. Spiked matrices led to higher recoveries than 75%. Internal standard correction was applied to all samples. In addition to soil samples, runoff samples were thoroughly mixed and determined twice. A single measurement was carried out in rainwater samples; though in order to confirm positive detections 50% of positive samples were randomly selected for a second measurement. All repeated samples were correctly determined. The analytical criteria for reporting positive findings were according to procedures for pesticide residues in food and feed (SANCO/10684, 2009), which involved: retention time, chromatographic area ratio of two precursors ( $Q/Q_1$ ) and a confirmatory transition ( $Q_2$ ).

#### 2.4.4. Instrumental settings

Glyphosate and AMPA analysis were carried out on a Waters Quattro Premier™ XE triple quadrupole mass spectrometer coupled to an ACQUITY UPLC™ system (UHPLC–MS/MS, Waters Milford, MA, USA). The separation was performed on an Acquity UPLC BEH C18 column ( $1.7 \mu\text{m}$ ,  $50 \times 2.1 \text{ mm}$ , Teknokroma Analítica SA, Spain). The mobile phase was water modified with ammonium acetate 5 mM (phase A, flow rate  $0.4 \text{ mL min}^{-1}$ ) with a concentration gradient of methanol (HPLC-grade, ANEDRA SA, Argentina) modified with ammonium acetate 5 mM (phase B). The sample injection volume was  $20 \mu\text{L}$ . Nitrogen was used as drying and nebulizing agent. The cone gas flow was set at  $2 \text{ L h}^{-1}$ , while desolvation gas flow at  $600 \text{ L h}^{-1}$ . Argon (99.99%, PRAXAIR, Bs. As., Argentina) was used as collision gas at a pressure of  $4.04 \times 10^{-3} \text{ mbar}$  in the T-Wave cell. Masslynx NT v 4.1 software was used for data processing.

### 2.5. Data analysis and results expression

#### 2.5.1. Glyphosate loads in runoff

In order to assess the mass balance in the runoff, the load excess in soil for treatments ( $L_{\text{ex-soil}}$ , eq. (1)) was calculated by the mass difference between the mean load of treatments ( $L_{\text{soil-}i}$ ,  $n_i = 6$ ) and controls ( $L_{\text{soil-}j}$ ,  $n_j = 3$ ):

$$L_{\text{ex-soil}} = (\sum_i L_{\text{soil-}i})/n_i - (\sum_j L_{\text{soil-}j})/n_j, \quad (1)$$

$$L_{\text{soil-}i} = M_{\text{gly-}i} + M_{\text{AMPA}^*-i}, \quad (2)$$

$$L_{\text{soil-}j} = M_{\text{gly-}j} + M_{\text{AMPA}^*-j}, \quad (3)$$

$M_{\text{gly}}$  and  $M_{\text{AMPA}^*}$  represent the mass ( $\mu\text{g}$ ) of glyphosate and AMPA expressed on a glyphosate mass equivalent basis (denoted as \*) for the  $i$  treatment and the  $j$  control (subscript  $i$  and  $j$ , respectively), which were calculated by:

$$M_{\text{gly-soil}} = C_{\text{gly-soil}} \times \text{BD} \times V_{\text{soil}}, \quad (4)$$

$$M_{\text{AMPA}^*\text{-soil}} = C_{\text{AMPA}^*\text{-soil}} \times \text{BD} \times V_{\text{soil}} \times \text{MW}_{\text{gly}}/\text{MW}_{\text{AMPA}}, \quad (5)$$

$$C_{\text{AMPA}^*\text{-soil}} = C_{\text{AMPA-soil}} \times \text{MW}_{\text{gly}}/\text{MW}_{\text{AMPA}}, \quad (6)$$

where  $C_{\text{gly-soil}}$  and  $C_{\text{AMPA-soil}}$  are the glyphosate and AMPA concentration in soil ( $\mu\text{g g}^{-1}$ ), BD is the bulk density ( $\text{g cm}^{-3}$ ),  $V_{\text{soil}}$  is the volume of soil sampled ( $\text{cm}^3$ ),  $\text{MW}_{\text{gly}}$  and  $\text{MW}_{\text{AMPA}}$  are the

molecular weight of glyphosate ( $169.07 \text{ g mol}^{-1}$ ) and AMPA ( $111.04 \text{ g mol}^{-1}$ ), respectively (Giesy et al., 2000). Similarly, the load in runoff samples were calculated according with eq. (2) and eq. (3), although the mass of glyphosate and AMPA was calculated by

$$M_{\text{gly-runoff}} = C_{\text{gly-runoff}} \times V_{\text{runoff}}, \quad (7)$$

$$M_{\text{AMPA}^*\text{-runoff}} = C_{\text{AMPA}^*\text{-runoff}} \times V_{\text{runoff}}, \quad (8)$$

Where  $C_{\text{gly-runoff}}$  and  $C_{\text{AMPA}^*\text{-runoff}}$  are glyphosate and AMPA concentration in each runoff sample ( $\mu\text{g L}^{-1}$ ) and  $V_{\text{runoff}}$  is the total runoff volume ( $\text{L}^{-1}$ ). AMPA concentrations were expressed as glyphosate acid equivalent (AMPA\*). The expression TotGly was used to denote the total concentration of glyphosate and AMPA\*.

#### 2.5.2. Statistics

The Student T-test or ANOVA were used for mean comparison when normality and homoscedasticity was achieved. Otherwise, non-parametric test were employed (Mann Whitney U test-MW, Kruskal–Wallis test-KW: independent samples, and Wilcoxon test-Wil: paired samples). Spearman's correlation coefficient-Spr was calculated to evaluate correlation between variables. Type I error ( $\alpha$ ) was set at 0.05 (95% confidence interval) in all cases.

## 3. Results

### 3.1. Runoff experiment

#### 3.1.1. Physicochemical properties

There was no difference in  $\text{Fe}_T$  and OC contents when comparing the soil layers of controls and treatments (Wil:  $P > 0.05$ , Table 1). The mean runoff volume of treatments was lower than the mean volume of controls (MW:  $P < 0.05$ ), although no difference was observed for bulk density between treatments and controls (MW:  $P > 0.05$ ). Runoff volumes of treatments varied from 0 to 550 mL.

#### 3.1.2. Glyphosate and AMPA concentration in soil and runoff samples

The TotGly concentrations in the topsoil layer (0–5 cm) ranged from 89 to  $132 \mu\text{g kg}^{-1}$  in controls, and from 717 to  $2645 \mu\text{g kg}^{-1}$  in treatments, showing higher levels compared to 5–9 cm soil layers (Fig. 2). Concentrations in 5–9 cm soil layers ranged from 17 to  $28 \mu\text{g kg}^{-1}$  in controls and from 211 to  $463 \mu\text{g kg}^{-1}$  in treatments. The TotGly concentrations were statistically different between control and treatments at both depths (MW:  $P < 0.05$ ). In addition, higher amounts of AMPA were detected in the 0–5 and 5–9 cm soil layers of treatments compared to control (AMPA\* excess: 361.8 and 109.9  $\mu\text{g}$ , respectively; MW:  $P < 0.05$ ), resulting in 14.1% degradation of the applied dose during the time of the experiment and sample storage (approximately 5 h).

The TotGly concentration in runoff samples ranged from 49 to  $65 \mu\text{g L}^{-1}$  in controls and from 726 to  $3902 \mu\text{g L}^{-1}$  in treatments (Fig. 2). The glyphosate/AMPA\* mass concentration ratio in control changed from 0.19 in the 0–5 cm soil layer to 2.27 in runoff samples (12-fold increment, MW:  $P < 0.05$ ), while in treatments from 3.6 to 49.6 (14-fold increment, MW:  $P < 0.05$ ). The TotGly concentration in runoff decreased with increasing sample volume, while the load increased at a rate of  $0.71 \mu\text{g mL}^{-1}$  (Fig. 2A–a). The mean load of TotGly in control group was 15  $\mu\text{g}$  higher than some of the treatments with the lowest volume (T5: 5 mL and T6: 8 mL, Fig. 2A and b).

#### 3.1.3. Spray drift and runoff mass balance

The three methods performed to estimate the amount of glyphosate that reached the sample surface of treatments gave similar results (water sensitive card method, UHPLC–MS/MS

**Table 1**  
Surface soil, runoff and subsurface soil physicochemical properties.

Surface soil	n	OC% (SD <sup>a</sup> )	Fe <sub>T</sub> (mg kg <sup>-1</sup> ) (SD)	BD <sup>b</sup> (g cm <sup>-3</sup> ) (SD)
0–5 cm	9	1.9 (0.1)	1034 (121)	1.2 (0.1)
5–9 cm	9	1.8 (0.1)	1089 (70)	
<b>Runoff</b>	n	Mean (SD)		
Total solids (g L <sup>-1</sup> )	5	1.3 (0.2)		
Conductivity (μS cm <sup>-1</sup> )	4	862 (52)		
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	5	3.5 (0.2)		
Total phosphorus (mg L <sup>-1</sup> )	5	1.4 (1.0)		
V <sub>runoff</sub> (ml)	9	342 (344)		
<b>Subsurface soil RZ</b>	n	OC% (RD <sup>c</sup> )	F <sub>T</sub> (mg kg <sup>-1</sup> ) (RD%)	
45–60 cm	2	0.2 (10)	1975 (9)	
70–80 cm	2	0.3 (10)	2255 (14)	
92–104 cm	2	0.7 (10)	2486 (12)	
117–124 cm	2	0.2 (17)	2129 (16)	
132–138 cm	2	0.8 (3)	1757 (16)	
<b>Subsurface soil AP</b>	n	OC% (RD%)	F <sub>T</sub> (mg kg <sup>-1</sup> ) (RD%)	
45–56 cm	2	0.1 (25)	2172 (3)	
70–80 cm	2	0.6 (30)	2293 (1)	
80–90 cm	2	2.0 (4)	1869 (4)	
90–100 cm	2	0.9 (6)	897 (25)	
100–110 cm	2	0.2 (4)	801 (33)	

<sup>a</sup> SD: standard deviation.

<sup>b</sup> BD: bulk density.

<sup>c</sup> RD%: relative percent difference.

method and gravimetric method, ANOVA:  $P > 0.05$ , Table 2). Therefore, the mean amount of active ingredient that contributed to spray drift was 6.9% (test T:  $P < 0.05$ , significantly different from zero) under the experiment conditions.

After the rainfall simulation event, the results indicated that 88.1% was retained in soil samples (0–9 cm). The runoff

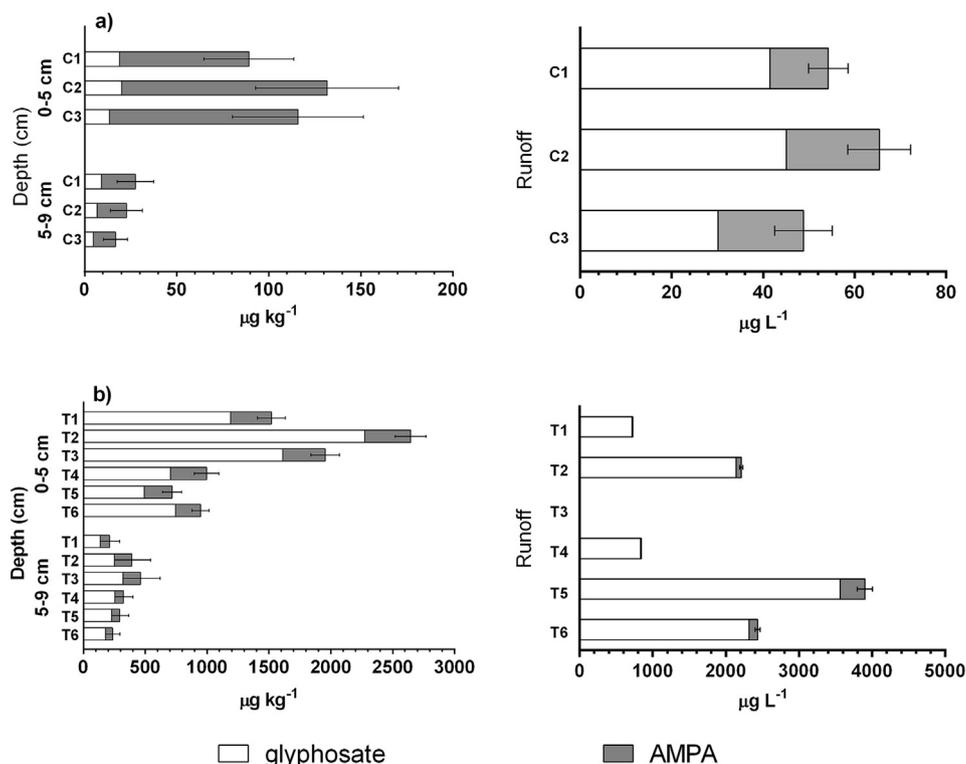
**Table 2**  
Fraction percentage (standard deviation) measured in each matrix.

Fraction	n	Mean % (SD)	TotGly (mg m <sup>-2</sup> )
<b>Contributed to spray drift</b>			
- Water sensible cards	3	8.7 (3.2)	9.4
- UPLC-MS/MS	3	6.6 (3.3)	7.1
- Gravimetric method	3	5.3 (7.6)	5.7
- Mean of the three methods	3	6.9 (0.9)	7.4
<b>Retained in the soil</b>			
- 0–5 cm	6	74.7 (36.0)	80.7
- 5–9 cm	6	13.4 (3.5)	14.5
<b>Transported in runoff</b>			
- Total runoff	6	3.9 (3.4)	4.2
<b>Leachate (estimated percentage)</b>			
- > 9 cm	6	1.1 (1.9)	1.2
Total applied	–	100	108

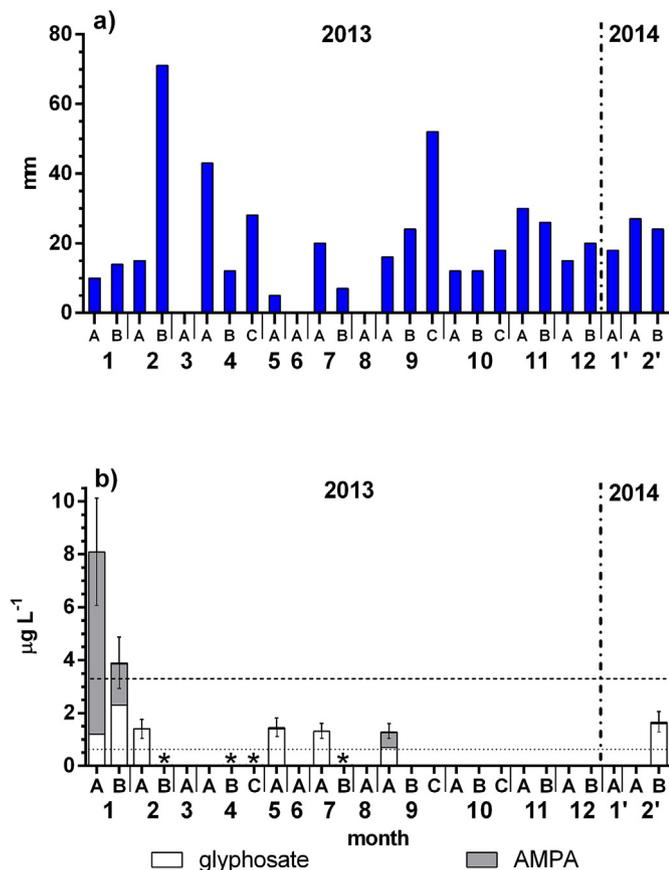
represented 3.9% (test T:  $P < 0.05$ , significantly different from zero), while the estimation for the glyphosate transport to deeper layers than 9 cm in soil profile was not significant (1.1%, test T:  $P > 0.05$ ).

### 3.2. Glyphosate in rainwater samples

The rainwater samples represented approximately 50% of the annual mean rainfall volume (1000 mm, Martinez et al., 2007). The highest glyphosate concentrations were detected in periods with intensive pesticide application (summer and autumn-winter months), corresponding with weed proliferation and chemical fallow (Fig. 3). Mean TotGly concentration of samples above LOQ was 2.7 μg L<sup>-1</sup> (Fig. 3-dashed line), while maximum concentrations reached 8.1 μg L<sup>-1</sup> in a summer rain event. Furthermore, 75% and 66% of positive detections occurred in samples with low precipitation volume (<20 mm) and conductivity (<20 μS cm<sup>-1</sup>), respectively (Fig. 3A y 4A). The TotGly load in precipitation events



**Fig. 2.** Glyphosate and AMPA<sup>\*</sup> concentration (μg Kg<sup>-1</sup>) in the soil layers (0–5 and 5–9 cm) and runoff (μg L<sup>-1</sup>) of controls (a) and treatments (b). Whiskers indicate the relative percent difference for TotGly.



**Fig. 3.** Rainfall (a) and glyphosate and AMPA\* concentration ( $\mu\text{g L}^{-1}$ ) in rainwater samples (b) collected over a 13-month period in RZ. The horizontal axis indicates the month (numbers) and the sampled rainfall event of each month (capital letters). Samples with detectable levels of glyphosate below LOQ were denoted with asterisks. Whiskers indicate the relative percent difference for TotGly.

increased linearly with increasing precipitation volume up to 25 mm ( $R: 0.61, P < 0.05, n = 7$ ). Glyphosate and AMPA were detected in 52% and 13% of analyzed samples, respectively (Fig. 3).

From the comparison of the amount of glyphosate scavenged by rainfall in a single rain event (considering the highest concentration measured) and a single application ( $108 \text{ mg m}^{-2}$  of glyphosate, at a rate of  $3 \text{ L ha}^{-1}$  and 36% acid equivalent), the fraction scavenged by rainfall was low ( $7.5 \times 10^{-4}$  equivalent to  $81 \mu\text{g m}^{-2}$ ). The majority of samples with concentrations higher than LOQ (64%) were above the maximum permitted total pesticide content for drinking water consumption in the European Union (Fig. 3-dotted horizontal line:  $0.5 \mu\text{g L}^{-1}$ , European Union, 2006).

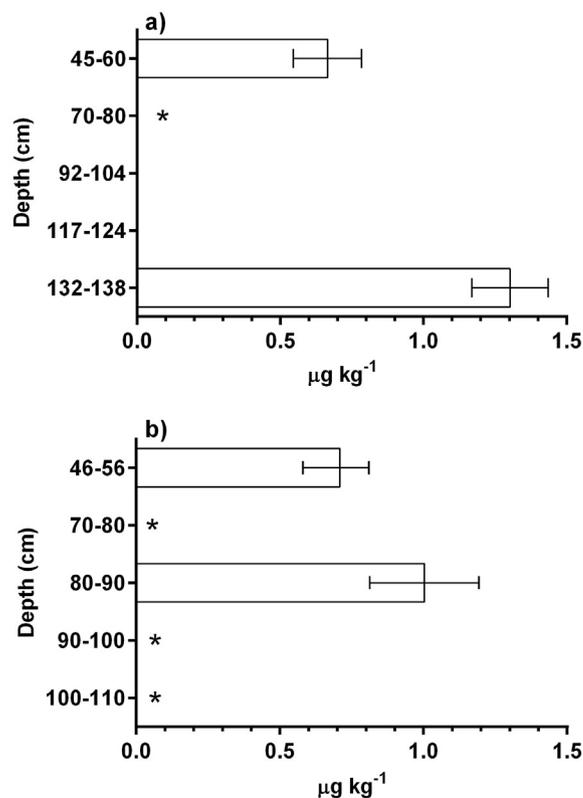
### 3.3. Glyphosate in subsurface soil

Glyphosate was detected in subsurface soil (up to 1 m) in AP and RZ at trace concentration ( $1 \mu\text{g kg}^{-1}$ , Fig. 4). No significant correlation was observed between glyphosate concentration and  $\text{Fe}_T$  or OC (Spr:  $P > 0.05$ , Table 1). Glyphosate concentrations were similar between AP and RZ profiles. AMPA was not detected.

## 4. Discussion

### 4.1. Runoff experiment

It is known that earthworms increment water infiltration in soil due to burrowing activities (Blouin et al., 2013). The presence of



**Fig. 4.** Glyphosate concentration ( $\mu\text{g Kg}^{-1}$ ) in subsurface soil of RZ (a) and AP (b). Samples with detectable levels of glyphosate below LOQ were denoted with asterisks. Whiskers indicate the relative percent difference for glyphosate.

casts in the surface of treatments was observed at the end of the experiment (Fig. 1A). Earthworm casting activity reduces runoff and enhances water infiltration (Jouquet et al., 2008). Moreover, Perreault and Whalen (2006) showed that highly moist samples stimulated earthworm casting at the surface increasing water infiltration. Considering that the bulk density in control and treatments, the difference in runoff volumes could be attributed to the borrowing activity in treatments. This situation would have led to very low runoff volumes in some of the treated samples.

Glyphosate and AMPA\* concentrations in control samples correspond to environmental concentration in agricultural fields under no-till management (Fig. 2-a). Similar concentrations were reported by Aparicio et al. (2013) in surface soils. The higher levels of glyphosate and AMPA\* found in the 5–9 cm soil layer of treatments compared to controls, evidenced transport and degradation of glyphosate during the experiment. Other authors have also found glyphosate transport and degradation after its application and rainfall simulation under similar experimental conditions (Todorovic et al., 2014; Bento et al., 2016). Glyphosate and AMPA should be both well adsorbed to soil particles of controls at the beginning of the experiment, considering that no application was done recently in AP. In spite of that fact, a favored off-site movement of glyphosate by overland flow compared to AMPA was evidenced. In a recent study, Sidoli et al. (2016) reported that the adsorption coefficient of AMPA is more dependent on the composition of the jetter in contact with soil particles than glyphosate. Moreover, Gjettermann et al. (2011) observed important desorption rates (up to 26% in few minutes) of completely sorbed glyphosate to splash-eroded soil particles in the first hour after they were immersed in water. Similarly, Maqueda et al. (2017) observed up to 20% of glyphosate desorption in sediments with loamy sand texture

and low iron and aluminum oxide content. Then, the different proportion observed between soil samples (0–5 cm layer) and runoff of controls, would be attributed to different desorption rate between glyphosate and AMPA in the time of experiment (3 h between sample wetting and the end of the runoff sampling). Unfortunately, comparative sorption studies of glyphosate and AMPA under different experimental conditions are scarce.

The runoff concentration of treatments exceeded national (SRHRA 2003: 240  $\mu\text{g L}^{-1}$ ) and international maximum limits (CCME, 2012: 800  $\mu\text{g L}^{-1}$ ; USEPA, 2017: 700  $\mu\text{g L}^{-1}$ ) for surface water protection and runoff, being similar to the levels reported by Yang et al. (2015) in a short-term transport glyphosate runoff experiment. The findings that some of the control transported higher loads of glyphosate than some of the treatments, highlights the importance of the soil physicochemical properties (e.g. texture, bulk density, roughness) to transport pesticides in runoff, in addition to the pesticide concentration.

#### 4.1.1. Runoff mass balance

Despite the fact that many factors influence the amount of pesticide reaching the target during application, the spray drift is usually underestimated in runoff experiments under low wind speed ( $\sim 0.5 \text{ m s}^{-1}$ ). In addition, spraying variables affecting drift such as boom high and nozzle type, are usually not reported in runoff experiments. In this work, the spray drift contributed significantly to the off-site transport of glyphosate, in spite of the experimental conditions to minimize the pesticide dispersion (low wind speed and low boom high). Consequently, underestimating spray drift could lead to lower recoveries when liquid products are sprayed (Siimes et al., 2006; Yang et al., 2015). The results obtained for glyphosate are in accordance with drift estimations between 3% and 6% summarized by Al Heidary et al. (2014) and Jensen and Olesen (2014) for different applied substances under similar experimental conditions (e.g. terrestrial spraying, nozzles type).

Although glyphosate application was made on a wetted soil and rainfall simulation begun after 30 min, two factors that would enhance glyphosate transport (Baldwin et al., 1975; Boithias et al., 2014), lower amounts of glyphosate were transported in runoff compared to other authors (Warnemuende et al., 2007: 7.1%; Yang et al., 2015: 14%). These differences might be attributed to higher rainfall intensity and higher soil slope in the mentioned works.

#### 4.2. Glyphosate in rainwater samples

Air and rain quality is affected by the presence of a coastline, which influences local winds. Avila and Alarcón (1999) have reported that aerosols from Atlantic Ocean can be transported 50 km inland and be detected in 52% of the rain events. In addition, coastline pollution might be transported tens of kilometers from the shoreline and be dispersed inland by sea-breeze (Abbs and Physick, 1992). Hence, the low detection frequency of glyphosate in rainwater compared to other authors (Battaglin et al., 2014: 71%; Chang et al., 2011: 63–92%) could be related to the influence of sea winds free of pesticides. The same authors reported that a 30 mm rainfall would remove about 90% of glyphosate present in the atmosphere. Our results suggest that a similar rainfall volume (around 25 mm) would be sufficient to wash out most of the glyphosate from the atmosphere. The concentrations of glyphosate in rainwater from the RZ were in accordance with other studies in the region (Alonso et al., 2018) and rain events constitute a source of glyphosate in riparian areas, when this compound is applied in the surrounding agricultural fields.

#### 4.3. Glyphosate in subsurface soil

The trace amounts of glyphosate detected in subsurface soil horizons are reasonable considering the low leaching risk of the active ingredient in massive sandy soils (De Jonge et al., 2000). The RZ was located on a gentle hill and it has never been directly sprayed. Consequently, spray drift and atmospheric wet deposition in RZ would explain TotGly concentrations of 6  $\mu\text{g kg}^{-1}$  in surface soil (Lupi et al., 2015) and as a consequence subsurface glyphosate detection. Similarly, other authors have reported dry and wet deposition of glyphosate in wetlands shallow lakes because of drift events (Messing et al., 2011). Minor or no degradation would be expected in subsurface soil horizons, considering that glyphosate degradation occurs primarily in the uppermost soil layer and decreases with depth (Shushkova et al., 2010; Stenrød et al., 2006). In addition, soil moisture is an important soil property that influence glyphosate occurrence in the soil profile, being likely connected to microbial degradation of the free form (Erban et al., 2018). Despite the unlikely degradation of glyphosate in subsurface soil horizons, recent studies reported that AMPA was detected along the soil profile at a maximum depth of 0.4 m in clay loam soils (Erban et al., 2018; Soracco et al., 2018). The authors suggested that the vertical variation in the transport of glyphosate and AMPA was closely related to higher values of hydraulic conductivity, total macroporosity and effective macroporosity in the soil (Soracco et al., 2018). In conclusion, the massive sandy soil would have hampered AMPA leaching and its formation from in situ glyphosate degradation would be difficult due to the probably low concentration of the free form, in addition to the depleted microbial activity. Consequently, AMPA was not detected in any of the subsurface soil profiles below 0.4 m of depth.

### 5. Conclusions

In spite of the experimental conditions performed to reduce the spray drift during glyphosate application, similar proportions of spray drift and runoff were quantified, while the leaching represented a minor fraction. The results highlight the importance of drift in leaching and runoff experiments when pesticide off-site transport is evaluated and being spraying the application method. Then, assessment of spray drift is strongly suggested in these experiments when a mass balance is attained. Under field conditions, the effect of the spray drift was evidenced by the substantial amounts of glyphosate in rainwater from riparian zones adjacent to rural areas. Moreover, the detection of glyphosate and AMPA in most rainwater samples at concentrations above international regulations for drinking water (0.5  $\mu\text{g L}^{-1}$ , European Union, 2006), it warns us about the risk of rainwater harvesting for human consumption, particularly during application period and after a long time of dry season in areas surrounded by agricultural fields. Although glyphosate and AMPA might be present in harvested water, other processes such as degradation and sorption during the collection, storage and transport in the house water supply system, should be assessed to determine the quality of the drinking water. Spray drift and deposition would be the main processes of glyphosate transport to riparian zones where runoff is unlikely due to topographic features.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.090>.

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