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Glyphosate Loss by Runoff and Its Relationship with Phosphorus Fertilization

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ABSTRACT: The aim of this study was to evaluate the relationship between glyphosate and phosphate fertilizer application and their contribution to surface water runoff contamination. The study was performed in Aquic Argiudoll soil (Tezanos Pinto series). Four treatments were assessed on three dates of rainfall simulation after fertilizer and herbicide application. The soluble phosphorus in runoff water was determined by a colorimetric method. For the determination of glyphosate and aminomethylphosphonic acid (AMPA), a method based on fluorenylmethyloxycarbonyl (FMOC) group derivatization, solid phase extraction (SPE) purification, and ultrahigh-performance liquid chromatography−tandem mass spectrometry (UHPLC-MS/MS) was employed. The application of phosphorus fertilizer resulted in an increased loss of glyphosate by runoff after 1 day of application. These results suggest the need for further study to understand the interactions and to determine appropriate application timing with the goal of reducing the pollution risk by runoff.

KEYWORDS: *glyphosate, phosphorus fertilization, surface runoff, phosphorus−glyphosate interaction*

INTRODUCTION

The most commonly used agrochemicals in Argentina are nitrogen and phosphate fertilizers and the herbicide glyphosate (*N*-(phosphonomethyl)glycine), the latter being used almost exclusively with varieties of transgenic soybeans. Glyphosate is the most globally used herbicide for weed control in urban and rural areas.[1] In Argentina, primary consumption of glyphosate is not only due to weed control pre- and postcrop implementation but also from the practice of chemical fallow for weed control and the preservation of soil water content. Under no-tillage farming systems, crop residues left on the soil surface limit evaporation, conserving water for plant growth, and in addition the enrichment in organic matter helps to increase the soil water-holding capacity.

Glyphosate is an organophosphonate herbicide of systemic postemergence action that, when applied to the canopy, is assimilated by the leaf and quickly translocated.[2,3] The nonselective and wide spectrum action of glyphosate is based on essential amino acid synthesis inhibition. In the soil, glyphosate is absorbed by phosphate links and degraded by microorganisms, underscoring the low mobility of both glyphosate and its main metabolite, aminomethylphosphonic acid (AMPA). Nevertheless, leaching and runoff studies have indicated that glyphosate may be carried to deeper layers of soil due to preferential flow by macropores or to surface waters when applied prior to heavy rainfall.[4−9] The presence of glyphosate in the surface waters in Entre Rios has been detected.[10,11]

The soil sciences frequently analyze the competence of phosphate/glyphosate on exchange sites in the soil matrix. Most of these studies present research results obtained in a laboratory.[2,3,12−15] The relationship between phosphorus and glyphosate in field conditions is unknown. Thus, investigation of this relationship is relevant because the application of glyphosate and phosphorus fertilizers to soybean cultivars is a practice that is usually performed around the advent of spring, which coincides with rainfall that produces runoff in the Pampean region. The aim of the present work was to evaluate the relationship between glyphosate and phosphorus fertilizer application and their contribution to water runoff pollution.

MATERIALS AND METHODS

Trial and Experimental Design. The trial was conducted in the fields of the INTA's Agricultural Experimental Station of Paraná, Entre Ríos, in a no-till plot, with a rotation of wheat, soybean, and corn. The soil is Aquic Argiudoll of the Tezanos Pinto series. The soil is deep, moderately well drained, with a dark mollic epipedon, ranging from silty clay loam to silty loam, which consists of 27.6% clay that is predominantly of the illitic type. The A horizon presents a CEC of 23.8 mequiv/100 g (Ca^{2+} 16.30%, Mg^{2+} 2.7%, K^{+1} 1.9%, Na^{1+} 0.10, and H^{+1} 4.7%) and 2.65% organic matter.[16] An argillic horizon is located below 17 cm.

Four treatments were performed (Table 1) over three rainfall simulation dates after the application of fertilizers and herbicides (Table 2) with a completely random design using 36 plots of 1 m^2. On November 6, 2012, the corn stubble was removed from the soil surface, and glyphosate (Roundup Full; composition: glyphosate (*N*-

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Table 1. Treatments Performed in the Trial

control (C)	without application of agrochemicals
glyphosate (GL)	3 L ha^{-1} of glyphosate, commercial product
phosphorus (P)	100 kg ha^{-1} of calcium triple superphosphate
phosphorus + glyphosate (P+GL)	100 kg ha^{-1} of calcium triple superphosphate + 3 L ha^{-1} of glyphosate, commercial product

Table 2. Rainfall Simulation Dates

1 (Nov 7, 2012)	24 h after application
2 (Nov 11, 2012)	5 days after application
3 (Nov 14, 2012)	8 days after application

(phosphonomethyl)glycine potassium salt), 66.2 g, + inert ingredients and adjuvants, csp 100 cm^3) and phosphate fertilizers (calcium triple superphosphate, dissolved in distilled water; composition: 0−46−0, with 14% of calcium) were applied with manual spraying over the ground and without incorporation. Although glyphosate as foliar systemic herbicide in normal use is not applied on the soil, in this experiment we tried to generate conditions to analyze directly the interaction with P in the soil surface, avoiding crop canopy and residue interception by removing them before starting the treatment. The trial plots were preserved with nylon until the last simulation date to avoid possible variations in soil moisture.

Rainfall simulations at the field were performed using a small portable simulator designed by Irurtia and Mon.[17,18] The microsimulator consists of a metallic angle iron square prism. It is 1.5 m high and 0.25 m per side, holding clear acrylic walls that act as windbreaks (Figure 1). At the top there is a box holder with 49 plastic tubes that produce droplets. This box has a water feed from a reservoir placed in one of the edges of the structure. The reservoir is graduated in millimeters (laminar) of water applied to the microplots. In turn, the reservoir base can be varied in height, providing different pressures to form drops. The droplets formed have average diameters of approximately 4.7 mm. For a 1.5 m drop height the calculated kinetic energy of the microsimulator is 12.7 kJ m^{-2} m^{-1}, representing approximately 32.6% of the energy of natural rainfall.[18] In working position the device is attached to an iron frame, previously driven into the ground. This framework defines the microplot of 0.25 × 0.25 m where the measurements are made. The runoff is received through a funnel into a graduated (mm) container on one side of the bottom framework. With this device constant rainfall intensity is applied between 10 and 130 mm h^{-1} for each test site.

Measurements. Once the simulation process was initiated, sampling started when runoff began, collecting runoff water at the graduated reservoir at 5 min intervals, until constant runoff was verified, when three consecutive constant measurements were obtained (approximately 1 h), meaning that the basic infiltration rate was achieved. The total water volumes collected through the experience ranged from 1.5 to 2.5 L and were used to calculate infiltration and runoff rates. Samples were filtered and chemically analyzed for soluble phosphorus, glyphosate, and AMPA. The soluble phosphorus in the runoff water was determined using a colorimetric method.[19]

Glyphosate and AMPA Analyses.[20,21] Glyphosate (98%), AMPA (98%), glyphosate-FMOC (98.5%), AMPA-FMOC (97%), and isotopically labeled standards (ILS) [1,2-$^{13}C_2{}^{15}N$]glyphosate (98%) and [$^{13}C^{15}N$]AMPA were obtained from Dr. Ehrenstorfer (Augsburg, Germany). All other supplies used were of the best commercially available analytical grade.

Water sample aliquots of 3 mL, previously homogenized and filtered with 0.45 μm regenerated cellulose membrane filters, were placed in 15 mL Teflon centrifuge tubes and acidified with 6 M HCl to pH 1 (to maximize the dissociation of possible analyte−cation complexes). The samples were then spiked with internal standard (40 μL of ILS 1 mg L^{-1}) and neutralized to pH 6−7 with 6 M KOH. The derivatization step was initiated with the addition of 0.5 mL of borate buffer (pH 9), FMOC-Cl (6 g L^{-1}), and acetonitrile. After overnight reaction at room temperature, the derivatization step was quenched by acidification to pH 3 with formic acid (FA).

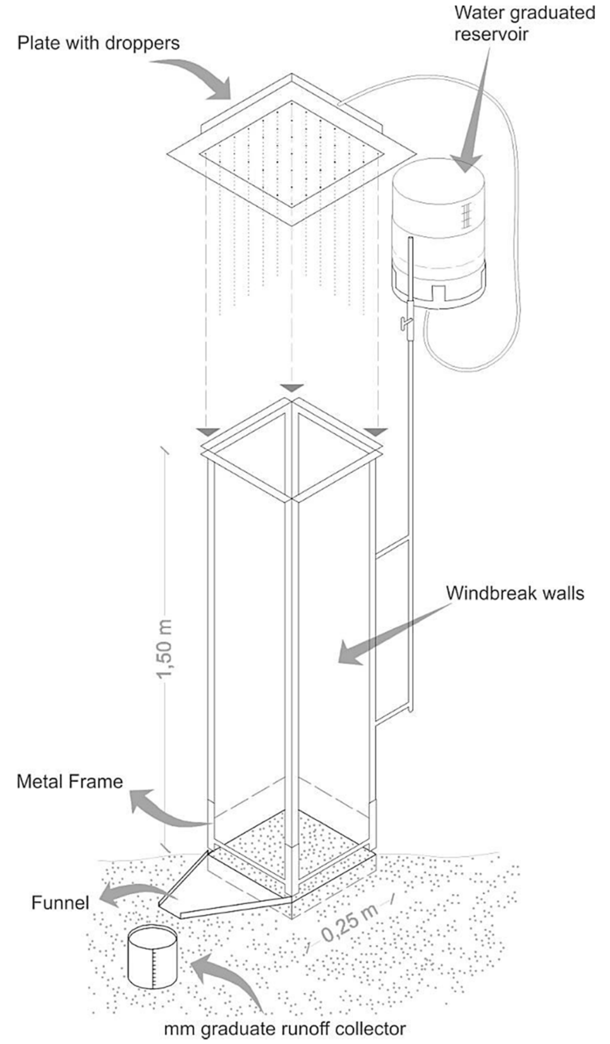

Figure 1. Scheme of portable rainfall simulator.

After filtering with 0.45 μm regenerated cellulose filters, the derivatized extracts were passed through Oasis HLB (200 mg, Waters, Milford, MA, USA) cartridges. Cartridges were conditioned with 5 mL of MeOH, followed by 5 mL of 0.1% FA. Eluates were discarded, and the cartridges were washed with 3.5 mL of dichloromethane. The analytes were eluted with 9 mL of MeOH. The methanol aliquots were evaporated and reconstituted with the mobile phase (H_2O/MeCN 98:2 + 0.1% FA). Following 0.2 μm nylon syringe filtering, the extracts were ready for injection.

Liquid chromatography−tandem mass spectrometry (LC-MS/MS) analyses were performed using an Acquity UPLC liquid chromatograph (Waters) coupled to a triple-quadrupole mass spectrometer equipped with an ESI source (TQD, Waters Micromass, UK). Separations were performed at 40 °C using an Acquity UPLC HSS C18 column (1.8 μm particle size, 2.1 × 100 mm) at a flow rate of 0.35 mL min^{-1}. Standard and/or sample extract aliquots of 10 μL were introduced by means of an autosampler (Waters). The mobile phase consisted of H_2O/MeCN (98:2 + 0.1% FA; A1) and MeCN (+ 0.1% FA, B1), operated with a 10 min gradient run time.

Ionization was performed in positive-ion mode using nitrogen as the desolvation and cone gas at 600 and 15 L h^{-1}, respectively. A 1 kV capillary voltage was applied, and the source temperature was set at 140 °C. The desolvation temperature was 500 °C. Argon (1.32×10^{-5} mbar) was used at the collision cell to produce the respective ion

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fragments, and acquisition was performed in MRM mode. The precursor and fragment *m/z* values for each specific compound, along with their respective cone voltages, collision energies, and dwell values, were optimized (Table 3). Chromatography and mass spectrometry data management was performed using MassLynx software v 4.1 (Waters).

Table 3. Optimized MS/MS Parameters for the FMOC Derivatives of Glyphosate, AMPA, and ILS

compound	precursor ion (*m/z*)	product ion[a] (*m/z*)	cone voltage (V)	collision energy (eV)
glyphosate-FMOC	392.0	Q 88.1	20	30
		q 214.1		10
AMPA-FMOC	334.0	Q 179.1	20	15
		q 112.1		20
GLI-1,2-[$^{13}C_2$,^{15}N]FMOC	395.0	Q 91.1	20	30
		q 217.1		10
AMPA-[^{13}C,^{15}]NFMOC	336.0	Q 114.1	20	15
		q 181.1		20

[a] Q, transition used for quantification; *q*, transition used for confirmation. Dwell time (s): 0.01.

The main parameters from our validation studies are shown in Table 4. Calibration curves from spiked nanopure water standards with concentration levels of 0.1, 0.5, 1, 10, 100, and 500 μg L^{-1} were used for quantification purposes.[22]

Concentrations of glyphosate + AMPA (μg L^{-1}) and phosphorus (mg L^{-1}) were multiplied by the total volume of runoff water in 60 min to obtain the amount of glyphosate + AMPA and phosphorus lost in grams per hectare and kilograms per hectare, respectively.

Statistical Analyses. Data statistical analyses were realized through sampling variance and Tukey's test at a 5% significance level.[23]

■ RESULTS AND DISCUSSION

Runoff Analyses. The treatments applied had no influence on water dynamics. Thus, no significant differences were observed between either the runoff of different treatments or between the dates of simulation.

Phosphorus (P) in Runoff Water. *P Concentration.* The concentration of P in runoff water ranged between 0.3 and 5.9 mg L^{-1}. These values are similar to those obtained in runoff plots in fallow periods of a no-till Aquic Argiudoll.[24] Statistical analysis indicated that no significant interaction between treatment and date ($p < 0.05$) was observed, but significant differences between treatments and simulation dates were observed.

On the first simulation date, the P concentration in water was higher than and different from the third date (Table 5), indicating that nearby rainfall 1 day after the application of fertilizer favors the loss of P by superficial runoff to a representative dose of that used in the region.

With regard to treatment (Figure 2), no significant differences were found between the fertilized treatments, but there were differences with the treatments not fertilized with P. This behavior demonstrates that the higher P concentrations observed in runoff water were influenced by the practice of fertilization and not by the effect of the herbicide.

Table 5. Variance Analysis of Phosphorus Concentrations from Different Simulation Dates

date	concentration of P[a] (mg L^{-1})
1	2.6 a
2	2.1 ab
3	1.6 b

[a] Different letters indicate significant differences (Tukey $\alpha = 0.05$).

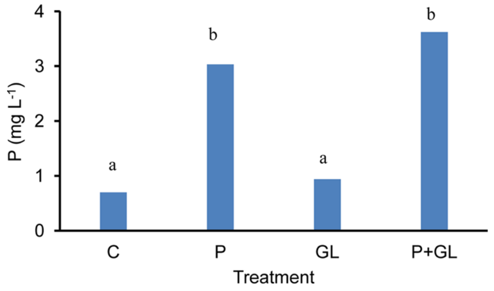

Figure 2. Variance analysis for phosphorus concentration (mg L^{-1}). Different letters indicate significant differences (Tukey $\alpha = 0.05$).

Amount of P in Runoff Water. The amount of P in runoff water ranged between 0.02 and 1.9 kg ha^{-1}. A significant interaction between treatment and date was found. Greater losses of P were observed with phosphate fertilizer treatment.

Treatments with P after a rainfall of approximately 1 h with 60 mm h^{-1} intensity lost 4% of the P applied by fertilization. These losses reduced the efficiency of the fertilization and consequently increased the pollution risk. Austin et al.[25] and Gaynor and Findlay[26] also reported on superficial phosphate transport and the eventual losses of the system under the dissolved or particulate shapes produced by rainfall or irrigation.

Glyphosate and AMPA in Runoff Water. *Glyphosate and AMPA Concentrations.* The glyphosate concentration in runoff water ranged between 18.6 and 1552.9 μg L^{-1}. This finding highlights the presence of glyphosate in all treatments, including the control, most likely because 2 months before the installation of our trial, the plot was sprayed for weed control in fallow with a 3 L ha^{-1} dose of the same commercial product used in the present trial.

A significant interaction was observed between the simulation dates and different treatments (Table 6). Treatment with P+GL on the first simulation date presented a higher concentration of glyphosate in water (19 times that of the control). On the same date, treatment with the same dose of herbicide without P exhibited approximately half the concentration of glyphosate in runoff water. The concentration was

Table 4. Validation Parameters of the Optimized Methodology

compd	LOD[a] (μg L^{-1})	LOQ[b] (μg L^{-1})	recovery (1 μg L^{-1}) (RSD[c] %); $n = 6$	recovery (100 μg L^{-1}) (RSD %); $n = 6$	linearity (0.1−500 μg L^{-1})
GL	0.2	0.6	96−102 (3%)	89−101 (6%)	$y = 82.521x - 761.41$ $R = 0.989$
AMPA	0.2	0.6	105−107 (5%)	121−126 (8%)	$y = 78.581x - 748.57$ $R = 0.987$

[a] Limit of detection. [b] Limit of quantification. [c] Relative standard deviation.

Table 6. Variance Analysis of Glyphosate Concentration

date	treatment[a] (μg L^{-1})			
	P+GL	GL	P	C
1	1417.6 a	767.2 b	40.1 d	74.1 d
2	277.9 c	168.8 cd	26.9 d	39.4 d
3	133.1 cd	65.5 d	29.8 d	32.6 d

[a] Different letters indicate significant differences (Tukey α = 0.05).

diminished during the days after application, and the treatments without glyphosate were not different on any of the dates.

Table 7. Variance Analysis of AMPA Concentration

date	treatments[a] (μg L^{-1})			
	P+GL	GL	P	C
1	453.7 a	561.5 a	144.6 b	199.6 b
2	478.4 a	127.7 b	184.6 b	160.4 b
3	543.3 a	262.2 b	175.1 b	171.8 b

[a] Different letters indicate significant differences (Tukey α = 0.05).

The concentration of AMPA also presented a significant interaction between treatment and date (Table 7). With P+GL treatment, no significant differences between dates were observed, implying that the degradation of the glyphosate molecule was immediate upon application, presenting no differences between the first and eighth days after application. With GL treatment, the first simulation date presented higher concentrations with respect to the others, and no significant difference was observed compared to P+GL.

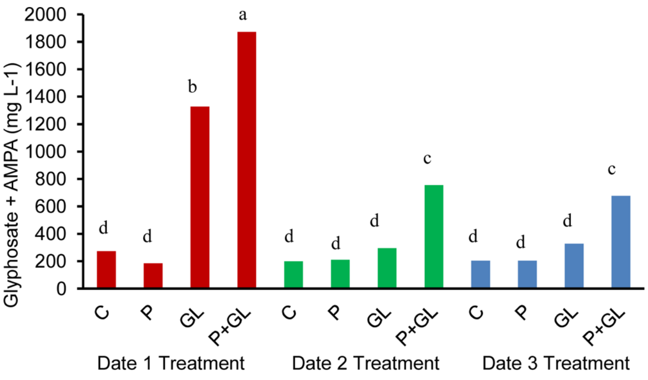

Figure 3. Variance analysis for glyphosate + AMPA concentration (μg L^{-1}). Different letters indicate significant differences (Tukey α = 0.05).

Glyphosate + AMPA Concentration. Analysis of glyphosate + AMPA concentration presented a significant interaction between treatment and date. In Figure 3, P+GL treatment presented a higher concentration on the first date, which was significantly different from GL treatment on the same date. For the other simulation dates, P+GL treatment was different from the other treatments.

Amount of Glyphosate + AMPA. Table 8 represents the analysis of the amount of glyphosate + AMPA lost in 1 h of rainfall simulation, 60 mm h^{-1} above bare soil. There were significant differences for the interaction between date and treatment; treatment with P+GL on the first simulation date was significantly higher than the other treatments.

Table 8. Variance Analysis for the Amount of Glyphosate + AMPA[a]

date	treatments (g ha^{-1})			
	P+GL	GL	P	C
1	607.8 a	236.5 b	60.9 b	56.1 b
2	88.6 b	53.5 b	58.8 b	24.7 b
3	117.9 b	53.3 b	31.1 b	51.2 b

[a] Different letters indicate significant differences (Tukey α = 0.05).

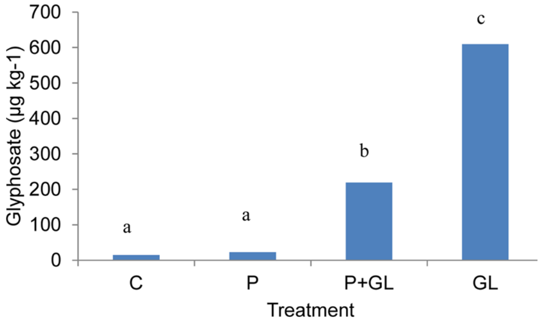

Figure 4. Variance analysis for glyphosate concentration (μg kg^{-1}) in the first 5 cm of the soil prior to each rainfall simulation. Different letters indicate significant differences (Tukey α = 0.05).

The analysis of the first 5 cm of soil prior to the rainfall simulation indicated that no significant differences were observed in the total P concentration between treatments (data not shown). Nevertheless, differences in glyphosate concentration were evident (Figure 4). No difference was observed between the treatments that were not sprayed with glyphosate, and GL treatment had the highest concentration, confirming that 24 h after spraying, P occupied the exchanging sites in P+GL.

After P+GL treatment, 28% of the applied glyphosate was lost in the runoff water. In the case of GL treatment at the same dose, the losses were 2.5-fold less than those of the P+GL treatment, indicating that the practice of phosphate fertilization and the application of glyphosate significantly increase the loss of glyphosate by runoff.

Morillo et al.[27] reported that glyphosate can act in the soil in a similar way to phosphate, possibly through the phosphate group. According to the results obtained by Zhao et al.,[28] the effect of the phosphate application on glyphosate mobility in different soils is due to the combination of reduced pH produced by the addition of acidic phosphate solution and the repulsion between the glyphosate and preabsorbed phosphate.

A significant interaction between P and glyphosate in common sorption sites of no-till Aquic Argiudoll soil was verified in the field conditions. The application of phosphate fertilizer increased the loss of glyphosate with the runoff caused by rain a day after its application.

The rain simulators were useful for analyzing the effect of the time elapsed between application and rainfall, demonstrating competitive adsorption and transport of P and glyphosate on soil exchange sites.

The relationship between the application of glyphosate and phosphate fertilizers and their contribution to pollution by runoff had not been identified using field conditions before this work. Some authors have studied this subject under laboratory conditions and in other parts of the world where the lack of tillage does not have the same importance as in the Argentinean Humid Pampa. As a consequence, the environmental impact of the interaction of those two practices, the most commonly used under no-tillage conditions, was unknown. As such, our results strengthen the necessity to pursue further studies aimed at understanding phosphorus−glyphosate interactions in soils under real conditions to establish an optimized time and conditions in current practice to reduce the risks of pollution by runoff. These results are of great importance for minimizing the environmental impact in the Argentinean setting, where no-tillage practices are extended to >20 Mha.

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Notes

The authors declare no competing financial interest.

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