



Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins



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HIGHLIGHTS

- We measured glyphosate and AMPA concentrations in soil, surface water and sediment.
- Glyphosate and AMPA are present in soils under agricultural activity.
- Glyphosate is more frequent in particulate matter and sediment than in water.
- The surface run-off cause the movement of soil particles with glyphosate adsorbed.
- Glyphosate is accumulated in the bottom sediment and is biodegraded to AMPA.

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ABSTRACT

Argentinian agricultural production is fundamentally based on a technological package that combines no-till and glyphosate in the cultivation of transgenic crops. Transgenic crops (soybean, maize and cotton) occupy 23 million hectares. This means that glyphosate is the most employed herbicide in the country, where 180–200 million liters are applied every year.

The aim of this work is to study the environmental fate of glyphosate and its major degradation product, aminomethylphosphonic acid (AMPA), in surface water and soil of agricultural basins. Sixteen agricultural sites and forty-four streams in the agricultural basins were sampled three times during 2012. The samples were analyzed by UPLC-MS/MS ESI(+/-).

In cultivated soils, glyphosate was detected in concentrations between 35 and 1502 $\mu\text{g kg}^{-1}$, while AMPA concentration ranged from 299 to 2256 $\mu\text{g kg}^{-1}$. In the surface water studied, the presence of glyphosate and AMPA was detected in about 15% and 12% of the samples analyzed, respectively. In suspended particulate matter, glyphosate was found in 67% while AMPA was present in 20% of the samples. In streams sediment glyphosate and AMPA were also detected in 66% and 88.5% of the samples respectively.

This study is, to our knowledge, the first dealing with glyphosate fate in agricultural soils in Argentina. In the present study, it was demonstrated that glyphosate and AMPA are present in soils under agricultural activity. It was also found that in stream samples the presence of glyphosate and AMPA is relatively more frequent in suspended particulate matter and sediment than in water.

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1. Introduction

Argentina is tenth in the world of agricultural nations ranked according to the area under cultivation in a report published by the World Bank, based on figures produced by the Food and Agricultural Organization of the United Nations (FAO). With 31 million hectares given over to agriculture, Argentina ranks

behind the United States, India, Russia, China, Brazil and Australia and accounts for 2.2% of the world's total area under cultivation (Stock Exchange of Rosario, Argentina).

Transgenic crops (soybean, maize and cotton) account for three-quarters of the Argentina's total cultivated land. In addition, 78.5% of agricultural lands in Argentina is no-till (NT) (Aapresid, 2012), where the only way of controlling weeds, during cultivation and during fallow periods, is by using chemicals. This means that glyphosate is the most commonly used herbicide in the country, both in its frequency of use as in the intensity. It is applied extensively;

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around 180–200 million liters of this herbicide are used every year (SAyDS, 2008).

Glyphosate (N-[phosphonomethyl] glycine) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. It works by inhibiting the enzyme 3-enol-pyruvylshikimate-5-phosphate synthase (EPSP Synthase), located in the chloroplast, interfering in the biosynthesis of aromatic amino acids used in the synthesis of proteins (Roberts et al., 1998). The EPSP Synthase is an enzyme that forms part of metabolic pathway of the shikimic acid. This is a process that only occurs in plants, bacteria and fungi and does not exist in animals; due to this fact the acute toxicity in animals is low. Nevertheless, some studies have reported adverse effects on aquatic and terrestrial species (Contardo-Jara et al., 2009; Paganelli et al., 2010) and concern has risen on potential environmental impacts due to the widespread use and large amounts annually applied (Schuette, 1998).

The microbial degradation is considered the most important transformation process to determine the persistence of herbicides in the soil (Souza et al., 1999). This process is carried out both in aerobic and anaerobic conditions by the microflora found in the soil. The primary metabolites are glyoxylate and aminomethylphosphonic acid (AMPA) which eventually degrades to water, carbon dioxide, ammonia and phosphate (Dick and Quinn, 1995). The presence of glyphosate could cause changes in the microbial populations and their activities in the soil. In relation to this, there are different results in the literature suggesting effects that can be minimum or transient with regard to the microbial biomass and its activity (Stratton and Stewart, 1992; Busse et al., 2001; Haney et al., 2002; Gómez et al., 2009) or are constant in time according to the history of application (Araújo et al., 2003).

It is known that glyphosate is adsorbed by mineral clays and by organic matter and is released from these sites by the competence with inorganic phosphates (Schuette, 1998; Prata et al., 2003). With regard to this last aspect, due to the fact that soybean requires high levels of this nutrient, the expansion and intensification of agriculture has highlighted the impoverishment of phosphorous within the Pampa region (Echeverría and García, 1998). On the other hand, published information about the mechanisms of the movement and environmental fate of glyphosate and AMPA in the environment is scarce, with much of it coming from controlled laboratory studies (Mamy et al., 2005; Borggaard and Gimsing, 2008; Tsui and Chu, 2008). Recently, studies about the transport of glyphosate and AMPA in streams located in United States show that glyphosate and AMPA have been frequently detected in surface waters of agricultural basins where it is used and their concentrations are influenced by source, hydrology and water movement pathways (Coupe et al., 2012).

Retention, degradation, and presence of glyphosate in water have scarcely been reported in the literature. The environmental fate of glyphosate and its metabolite degradation has not been studied taking into account the different environmental matrices (sediment, water and particulate matter dissolved in water) of agricultural basins. The environmental fraction of glyphosate transported is very important to develop agronomic management strategies to minimize their impact. Moreover, the analysis of contamination levels and the identification of the compartments where this herbicide accumulates can help to guide ecotoxicological studies.

In view of current production methods, the intensification of farming should not lead us to the accumulation of molecules such as glyphosate and AMPA in the environment. The aim of this study was to examine the environmental fate of glyphosate and AMPA and quantify their concentration in each one of the environmental compartments: soil and surface water (differentiating between water, suspended particulate matter and sediment) of agricultural basins.

2. Materials and methods

2.1. Selection of test sites

Sixteen farms were selected for soil sampling in the southeast of the Province of Buenos Aires (Fig. 1). At each site or farmer, an agricultural plot in which had been used glyphosate was selected. Another plot with the same soil type where there was no history of use of glyphosate in the past 10 years was also selected as control. Plots had a surface area of 60–150 hectares and were located at the same position of the relief. In each case, information about crop rotation over the past two years was recorded as well as the history of glyphosate use over the same period (i.e., time from the first glyphosate application, crop rotation, last spraying dosage) (Table 1).

In order to study glyphosate and AMPA residues in surface water (differentiating water and suspended particulate material) and in sediment, forty-four streams in the southeast of the Province of Buenos Aires were chosen that corresponded to the same catchment area where the soil samples were taken (Fig. 2).

2.2. Testing and conditioning of samples

Soil testing was carried out using two different soil sampling probes, one in the areas that had not been treated with glyphosate and another in the area that had been treated. The soil sample consisted of 50 subsamples to have representation of the plot. The sampling was performed 0–5 cm deep. The probe was cleaned by discarding several extractions in order to avoid any contamination between samples. The samples were conditioned using a hot-air heater set at 30 °C, and then dry milled. Two mills were used, one for treated samples and another for untreated samples. The mills were cleaned between samples. The samples were then passed through a 2 mm sieve.

The water samples were collected in 1 L polypropylene bottles on three dates following the soil samplings (April, August and September 2012) and stored at –20 °C until analysis. Prior to analysis, they were thawed overnight to 4 °C. The samples were filtered through a 0.45 µm nylon membrane to separate the water from the suspended particulate matter, which was filtered out. The sediment samples were collected in a PVC tube using a sediment sampler at the same place that the water samples were collected. Approximately 10 cm of sediment were extracted, which the first 5 cm were separated with a clean knife, air-dried at 30 °C, dry milled and then sieved through 2 mm.

In the EEA INTA laboratory at Balcarce, soil texture of all the samples was determined (Gee and Bauder, 1986), as well as cation-exchange capacity (Chapman, 1965), pH and total organic carbon (Nelson and Sommers, 1982) (Table 2).

2.3. Extraction and qualification of glyphosate and AMPA

A representative sub-sample of water (2 ml), particulates material (0.4 g), sediment (2 g) and soil (5 g) were overload with 10, 15 and 25 µl of isotope-labeled glyphosate (1,2-¹³C, ¹⁵N) stock solution (10 mg L⁻¹) respectively, taking care that its distribution on the particulates, sediment and soil was uniform, followed by a rest of 30 min, in order to stabilize the system. After that, particulates material, sediment and soil were extracting with 1, 3, 5 and 25 ml of extract solution of potassium dihydrogen phosphate in accordance with the method proposed by Peruzzo et al. (2008). Briefly, samples were sonicated (exposed to sonic waves) and then centrifuged to separate the suspended material. Supernatants were adjusted to pH = 9 with 40 mM borate buffer and then derivatized with 9-fluorenylmethylchloroformate (FMOC-CL) in acetonitrile. It was left to rest overnight in darkness at room temperature. At the

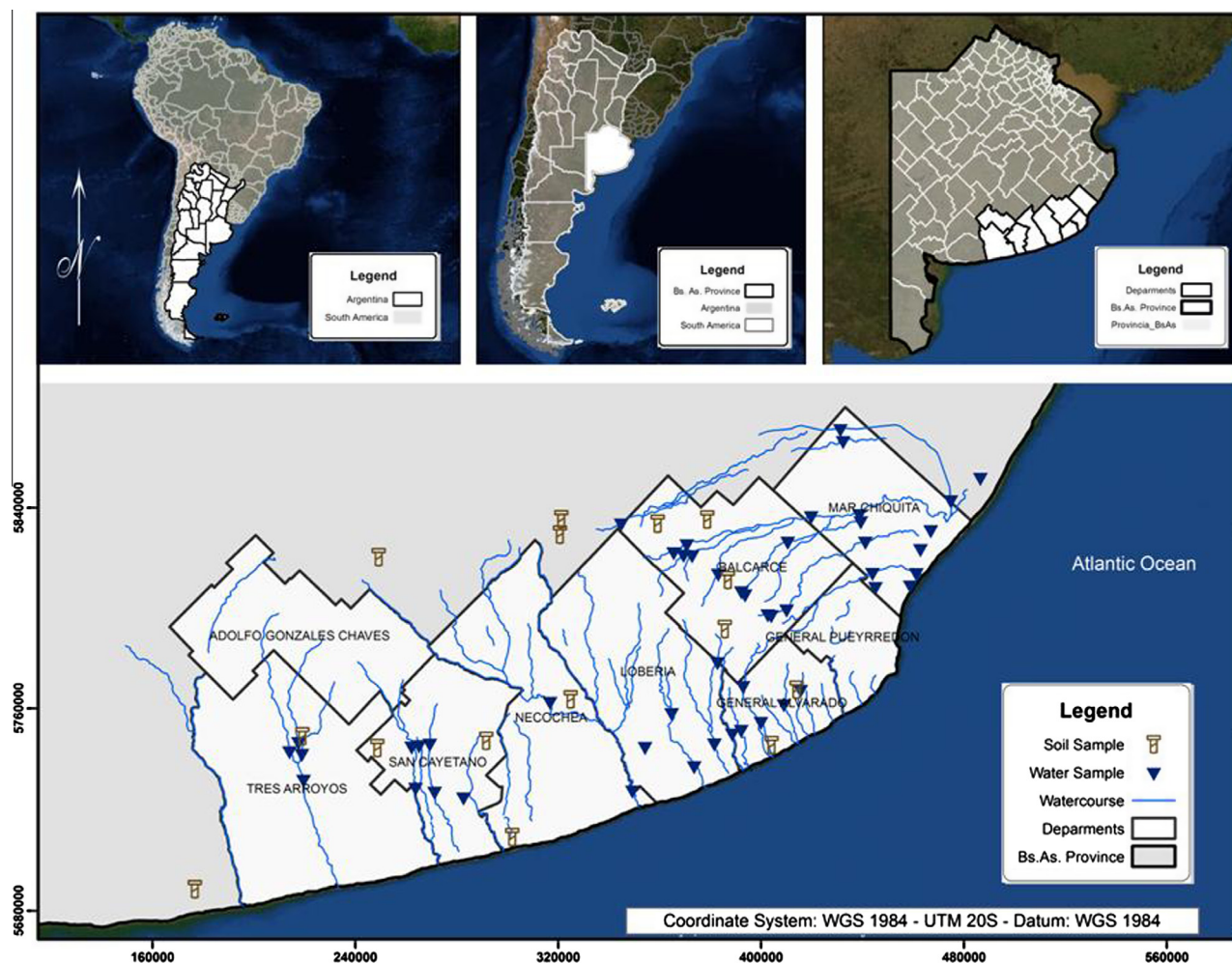


Fig. 1. Geographic location of the study area. It indicates the location of soil sampling after sowing in each farm (■) and sample water, particulate matter and sediments at three moments after soil sampling (▼).

Table 1
Agricultural management practices information of the farms plots.

Farms	TFA (yr)	Crop rotation	Last spraying dosage
		(¹)	g ha ⁻¹ of formula
1	8	P/Su/W/S	2.2
2	10	C/Su/S	2.2
3	10	R(S)/S/W(S)/R(S)	1.4
4	15	C/Su/M	0.5
5	15	Su/W/Su/R(S)	0.5
6	13	W/So/Su	1.4
7	6	S/W/S	3.7
8	19	S/W(So)/S	3.3
9	6	W/S/R-O/S	1.0
10	6	S/R(S)	0.7
11	10	S	1.4
12	5	S	1.4
13	10	S/W(S)/S	1.9
14	10	Su/W/S	2.1
15	4	W(S)/C/S	3.3
16	10	W/S/W/S/W(S)	2.4

TFA: time from the first glyphosate application.

(¹) C: Corn; P: Potato; Su: Sunflower; W: Wheat; S: Soybean; R: Rye; O: Oats; So: Sorghum.

same time, standards of glyphosate and AMPA were prepared in extractant solution in concentrations ranging from 10 µg l⁻¹ to 2000 µg l⁻¹ for each analyte. An amount of isotope-labeled glyphosate was added to this series of solutions, which was equivalent

to that expected in the analyzed samples, in order to evaluate the analytical recovery. The matrix effect was studied spiking isotope-labeled glyphosate solution in control soil extracts and then processing them identically as the samples. The samples and standards were filtered through a 0.22 µm nylon filter and were injected into the Waters Acquity UPLC MS/MS system (Waters) equipment calibrated for positive detection, using a column Acquity UPLC BEH C18 column (1.7 µm, 50 × 2.1 mm) (Waters), with methanol–water 5 mM NH₄Ac gradient. The sensitivity of the instrument for the analytes studied was optimized by injection from the individual derivatives, achieved in afore-mentioned conditions. The analytical criteria applied were the relationship of the chromatographic areas of two mass transitions and the retention times, in both the standards and the samples. Confirmation of positive findings was carried out by calculating the peak area ratios between the quantification (Q) and confirmation transitions (q) and comparing them with ion-ratios obtained from a reference standard (document No. SANCO/10684/2009). A finding was considered positive when the concentration ratio was in the range 0.8–1.2. Retention times for the reference standard and sample were also compared and accepted when a deviation lower than 2.5% was obtained.

The limits of detection (LD) and limits of quantification (LQ) were calculated in the different matrices analyzed. The LD, defined as the lowest concentration that the analytical process can reliably differentiate from background levels, was estimated for a signal-to-noise ratio of three from the chromatograms of standards at

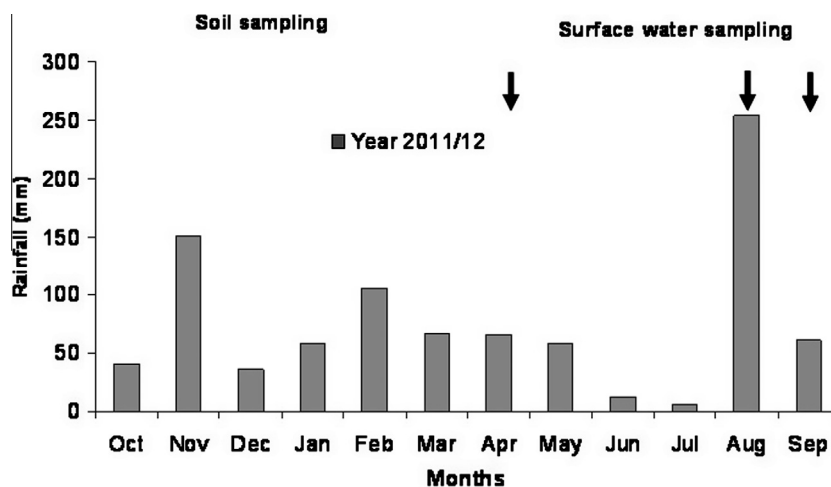


Fig. 2. Monthly rainfall expressed in mm. The soil sampling was conducted between November and January, according to availability of soybean farms. The black arrows indicate months of the water, particulate matter and sediment sampling.

Table 2
Chemical characterization of the studied soils.

Farms	Treatment	Depth (cm)	OM (%)	pH	EC (dS m ⁻¹)	CEC (cmol _e k ⁻¹)	Sand	Silt (%)	Clay
1	Glyphosate	0–5	5.77	6.32	0.12	24.02	42.18	29.75	28.08
	Control	0–5	10.10	6.25	0.13	38.29	33.57	35.86	30.57
2	Glyphosate	0–5	6.45	6.17	0.12	27.95	42.78	33.26	23.96
	Control	0–5	5.15	6.11	0.17	25.49	50.10	21.58	28.32
3	Glyphosate	0–5	6.87	5.16	0.41	29.73	35.05	36.16	28.79
	Control	0–5	7.86	6.10	0.18	29.77	47.44	25.24	27.32
4	Glyphosate	0–5	6.37	5.88	0.27	29.43	45.60	30.02	24.38
	Control	0–5	10.51	6.98	0.36	36.19	57.27	22.15	20.58
5	Glyphosate	0–5	5.02	6.35	0.14	23.87	52.51	28.01	19.48
	Control	0–5	8.67	5.49	0.44	32.51	63.98	27.59	8.43
6	Glyphosate	0–5	3.15	7.64	0.19	20.53	56.88	23.99	19.13
	Control	0–5	3.34	8.14	0.21	19.06	76.35	20.99	2.65
7	Glyphosate	0–5	4.20	5.92	0.98	20.57	57.14	26.32	16.54
	Control	0–5	12.11	6.65	0.43	44.54	42.15	32.47	25.38
8	Glyphosate	0–5	7.57	6.03	0.10	29.11	49.28	32.44	18.27
	Control	0–5	11.08	5.97	0.42	41.35	44.97	39.58	15.44
9	Glyphosate	0–5	5.74	5.37	0.33	27.67	40.37	34.21	25.42
	Control	0–5	12.35	6.57	0.33	49.84	33.66	35.16	31.19
10	Glyphosate	0–5	4.51	5.79	0.17	24.77	36.22	36.38	27.40
	Control	0–5	9.29	6.07	0.28	35.98	43.23	29.85	26.92
11	Glyphosate	0–5	5.40	5.89	0.20	27.68	38.31	33.92	27.76
	Control	0–5	12.97	6.80	0.34	67.44	28.44	39.01	32.55
12	Glyphosate	0–5	5.37	5.86	0.17	26.10	49.15	25.21	25.64
	Control	0–5	7.16	6.75	0.11	27.91	51.00	21.65	27.35
13	Glyphosate	0–5	4.20	5.58	0.25	24.22	41.51	28.91	29.59
	Control	0–5	10.80	6.96	0.37	32.29	48.75	22.88	28.38
14	Glyphosate	0–5	5.92	6.08	0.10	29.19	35.58	29.41	35.01
	Control	0–5	12.93	6.34	0.15	59.78	39.96	27.95	32.09
15	Glyphosate	0–5	5.50	6.34	0.12	33.75	21.48	36.49	42.03
	Control	0–5	12.80	8.05	0.29	53.22	33.13	40.12	26.75
16	Glyphosate	0–5	6.02	6.49	0.19	29.69	35.29	32.48	32.23
	Control	0–5	10.32	6.28	0.17	37.41	43.81	26.85	29.34

low concentration levels (0.05–1 $\mu\text{g l}^{-1}$). The LQ were established as the lowest concentration level for which the method was fully validated using spiked samples with satisfactory recovery (between 70% and 120%) and precision ($\text{RSD} \leq 20\%$).

Simple regressions were carried out between the content of glyphosate and AMPA in soil and its chemical properties as well as with the data from TLA (d).

3. Results and discussion

3.1. Soils

The LD obtained in soil with the present technique was 5 $\mu\text{g kg}^{-1}$, both for AMPA and glyphosate and the LQ was

10 $\mu\text{g kg}^{-1}$. The analytical recovery, referring to the isotope-labeled glyphosate, ranged from 88% to 98% and the ion suppression referring to the same compound was 20%, without finding dependence between the parameters of chemical analysis and the characteristics of the soil (Table 2). All these matrix factors were taken into account for the final expression in the results.

In soils subject to agricultural activity of south-east Buenos Aires Province, glyphosate was detected in concentrations ranging from 35 to 1502 $\mu\text{g kg}^{-1}$ for the 16 farms sampled (Table 3). Previous studies showed the high level of adsorption ($K_f = 412$) of glyphosate in the soil in the south-east of the Buenos Aires Province (Typic Argiudoll), which remained relatively constant across different concentrations (94–99%) (Gómez Ortiz et al., 2012). The content and type of clays in soils, their cation-exchange capacity and

the content of bivalent cations, iron and amorphous aluminum hydroxides are important parameters when it comes to evaluating adsorption (Piccolo et al., 1994; Dion et al., 2001). In other studies in Argentina, greater adsorption was reported in the soil of Pergamino (Typic Argiudoll, $K_f = 344.9 \pm 57$) compared to the soils in Paraná (Aquic Argiudoll, $K_f = 115.4 \pm 8$) and Manfredi (Entic Haplustoll, $K_f = 121.7 \pm 25$) (Okada et al., 2012). Therefore, the soil and its chemical and physical properties determine the level of adsorption of glyphosate and the availability to participate in other processes such as degradation or vertical transport of the analyte, among other things.

The AMPA concentrations found in soils ranged from 299 to 2256 $\mu\text{g kg}^{-1}$ (Table 3). Although the glyphosate adsorbed into the soil is protected from biological degradation, due to a dynamic process of adsorption and desorption the glyphosate can move into the soil solution and, in presence of microorganisms, it can be degraded to the major degradation product, AMPA (de Jonge et al., 2000; Mamy et al., 2005; Vereecken, 2005). The desorption of glyphosate studied in four European soils varied from 15% to 80% of the herbicide adsorbed depending on the soil characteristics (Piccolo et al., 1994), while for a soil of south-east Buenos Aires desorption of 3% was seen 72 h after application with a K_{fd} obtained of 102.7 (Gómez Ortiz et al., 2012). The presence of glyphosate and AMPA has been reported in vertisols soils in the province of Entre Ríos, Argentina (Primost et al., 2012) that agrees with data reported in this study. In addition, these authors indicate that both compounds show affinity with the soil matrix.

In the control samples employed, glyphosate and AMPA were also detected in 4 and 12 soils, respectively (Table 3). These results show that both analytes can be found in environments in which

glyphosate has never been used, probably due to the fact that these substances are transported from zones where it was applied. In this sense, glyphosate was detected in air and rain water samples in concentration ranging from <0.01 to 9.1 ng m^{-3} and from <0.1 to $2.5 \mu\text{g L}^{-1}$, respectively (Chang et al., 2011).

The glyphosate and AMPA concentrations in the soil showed no dependence to the days since application as well as with the soil characteristics. However, in controlled studies of glyphosate retention has been reported the importance of many of the soil properties analyzed in this work (organic matter, clay, pH, cation exchange capacity). Our results show that the processes are complex and multifactorial (agronomic conditions, local agro-meteorological conditions, mineralogy and soil conditions) in the environment and it is difficult to establish the relative weight of each factor.

Moreover, given the reversibility of this retention process, glyphosate can be desorbed and then be degraded to AMPA which accumulates in the soil. Both products may have other environmental fates and heighten the risk of affecting plants, microorganisms, cold- and hot-blooded animals, as has been widely reported (Darwich et al., 2001; Martin and Ronco, 2006; Gómez et al., 2009; Sobrero et al., 2007).

3.2. Surface water, particulate matter and sediment

The limit of detection (LD) reached for both AMPA and glyphosate in water and particulate matter was $0.1 \mu\text{g l}^{-1}$ and the limit of quantification (LQ) was $0.5 \mu\text{g l}^{-1}$. In the sediment samples a LD of $1 \mu\text{g kg}^{-1}$ and a LQ of $5 \mu\text{g kg}^{-1}$ was attained. The analytical recovery for the water samples, particulates and sediment ranged from 75% to 95%. Matrix effects were not much significant for those environmental matrices. All the matrix factors were taken into account for the final expression of the results.

In the surface water studied in April, glyphosate was detected in 35% of the samples whose concentrations ranging from 0.5 to $4 \mu\text{g l}^{-1}$ while AMPA was found in 33% of the samples in concentrations between 0.5 and $2.3 \mu\text{g l}^{-1}$. In August, glyphosate was detected in 10% of the samples, in concentrations of 1.7 to $3.6 \mu\text{g l}^{-1}$ while AMPA was seen in 7% of the samples, in concentrations between detectable but non-quantifiable (trace) and $0.8 \mu\text{g l}^{-1}$. In a later sampling, carried out in September, glyphosate was seen in 4% of the samples, in concentrations ranging from trace to $7.6 \mu\text{g l}^{-1}$ and AMPA was not detected (Table 4). The reduction in positive detection, between May and September, may be due to the effects of dilution caused by rains since the registered rainfall in August was 253.6 mm and in April was 65.7 mm (Fig. 2). In September, precipitation was along the same lines as that seen in April (61.2 mm) but because of the high rainfall in this previous month, it is possible that no glyphosate was applied in the agricultural sites in the area of influence. The precipitations in south-east Buenos Aires measures between October 2011 and September 2012 are shown in Fig. 2.

In the suspended particulate matter, the April samples analyzed contain glyphosate in 53% of them in concentrations between 2.2 and $562.8 \mu\text{g kg}^{-1}$ while AMPA was present in 16% of the samples in concentrations of 4 to $118.7 \mu\text{g kg}^{-1}$. In August increased the amount of positive detection and 87.5% of the samples showed glyphosate concentrations between 1.11 and $298.4 \mu\text{g kg}^{-1}$ while AMPA was founded in 37% of the samples in concentrations ranging from 2.2 to $210.4 \mu\text{g kg}^{-1}$. In September, 66% of the samples had glyphosate in concentrations of 0.5 to $94.8 \mu\text{g kg}^{-1}$ and 11% had AMPA in concentrations between 1.1 and $46.7 \mu\text{g kg}^{-1}$ (Table 4).

In the sediment samples analyzed, glyphosate was detected in 66% of them in concentrations of 5.7 to $221.2 \mu\text{g kg}^{-1}$. AMPA was found in 89% of samples in concentrations between 5.1 and $235 \mu\text{g kg}^{-1}$ (Table 4).

Table 3

Glyphosate and AMPA concentrations in soil studied ($\mu\text{g kg}^{-1}$) and time from the last application.

Farms	Treatment	TLA (d)	Concentration ($\mu\text{g kg}^{-1}$)	
			Glyphosate $\mu\text{g kg}^{-1}$ soil	AMPA
1	Glyphosate	188	190.5	732.8
	Control		<LD	<LD
2	Glyphosate	94	140.9	1052.1
	Control		<LD	<LQ
3	Glyphosate	11	489.6	796.2
	Control		<LQ	20
4	Glyphosate	1	1502.3	299.3
	Control		41.4	22.3
5	Glyphosate	48	429.8	539.8
	Control		<LQ	43.2
6	Glyphosate	73	186.8	895.2
	Control		<LD	18.1
7	Glyphosate	10	257.1	921.3
	Control		<LD	<LD
8	Glyphosate	40	886.5	958.6
	Control		<LD	<LQ
9	Glyphosate	40	34.7	491.2
	Control		<LD	<LQ
10	Glyphosate	4	386.7	789.7
	Control		<LD	<LD
11	Glyphosate	10	79	581.7
	Control		<LD	36.9
12	Glyphosate	8	316.3	458
	Control		<LD	<LQ
13	Glyphosate	8	206.7	518.9
	Control		<LQ	33.5
14	Glyphosate	14	37	727.5
	Control		<LD	<LD
15	Glyphosate	14	1082.8	485.7
	Control		<LD	<LQ
16	Glyphosate	188	190.5	732.8
	Control		<LD	<LD

TLA: time from the last application. LD: limit of detection.

Table 4

Concentration of glyphosate and AMPA in water, suspended particulate matter (SPM) and sediment samples from streams of the southeast Buenos Aires.

Active ingredient: Date of stream sampling Description	Glyphosate							AMPA						
	April 2012		August 2012		September 2012			April 2012		August 2012		September 2012		
	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)
A° Moro route 55	<LD	<LD	<LD	52.0	<LD	5.70	<LD	<LD	<LD	<LD	15	<LD	<LD	<LD
Rio Quequén	<LD	9.1	<LD	92.7	<LD	<LD	Trace	<LD	<LD	Trace	62.1	<LD	<LD	6
A° Seco route 227	0.9	15.6	<LD	32.7	<LD	10.22	6.3	<LD	6.5	<LD	<LD	<LD	<LD	96.2
A° Zabala route 228	0.5	23.5	<LD	1.9	<LD	2.04	Trace	Trace	<LD	<LD	<LD	<LD	<LD	18
Rio Quequén La Dulce	<LD	<LD	<LD	<LD	<LD	<LD	5.7	<LD	<LD	<LD	<LD	<LD	<LD	25.7
A° Cristiano muerto	<LD	<LD	<LD	1.1	<LD	10.41	Trace	<LD	<LD	<LD	<LD	<LD	<LD	117.9
Primer Brazo Tres Arroyos	<LD	<LD	<LD	5.2	<LD	6.57	19.6	<LD	<LD	<LD	<LD	<LD	<LD	38.1
Segundo Brazo Tres Arroyos	<LD	<LD	<LD	<LD	<LD	17.83	34.3	<LD	<LD	<LD	<LD	<LD	<LD	71.2
Tercer Brazo Tres Arroyos	<LD	<LD	<LD	<LD	<LD	15.33	17.6	<LD	<LD	<LD	<LD	<LD	<LD	49.3
A° Unión de los tres arroyos	<LD	<LD	<LD	5.2	<LD	11.61	38.2	<LD	<LD	<LD	<LD	<LD	<LD	41.4
A° Pantanoso route 226	4.0	131.5	–	–	<LD	13.75	14	2.3	118.7	–	–	<LD	<LD	31.5
A° Crespo route 226	<LD	<LD	2.1	183.4	<LD	7.09	Trace	<LD	<LD	<LD	<LD	<LD	<LD	13.3
A° Grande route 29	<LD	<LD	<LD	24.5	<LD	5.37	<LD	<LD	<LD	<LD	<LD	<LD	<LD	Trace
A° El invierno route 226	<LD	<LD	<LD	52	<LD	16.82	Trace	<LD	<LD	<LD	<LD	<LD	<LD	21.2
A° Verano route 226	Trace	6.6	<LD	<LD	<LD	10.70	33.2	<LD	<LD	<LD	<LD	<LD	46.7	72.9
A° Grande route 226	<LD	<LD	<LD	12.4	<LD	<LD	166.4	<LD	<LD	<LD	<LD	<LD	<LD	83.2
A° Napaleofú route 226	0.8	<LD	<LD	<LD	<LD	18.78	<LD	Trace	<LD	<LD	<LD	<LD	<LD	Trace
A° San Felipe route 226	<LD	<LD	–	–	<LD	12.04	98.9	<LD	<LD	–	–	<LD	<LD	235
A° Las chilcas route 226	Trace	12.8	–	–	<LD	<LD	<LD	0.6	<LD	–	–	<LD	<LD	<LD
A° Pantanoso route 55	<LD	4.9	1.7	204.7	<LD	22.43	43.3	0.5	7.2	<LD	10.6	<LD	13.6	53.9
A° Grande route 55	<LD	9.1	<LD	40.6	<LD	9.71	<LD	<LD	<LD	<LD	2.2	<LD	<LD	<LD
A° Chico route 2	<LD	5.9	<LD	27.8	<LD	15.56	<LD	<LD	4.0	<LD	<LD	<LD	<LD	Trace
Canal 5 route 2	<LD	27.9	<LD	30.0	<LD	50.17	<LD	0.4	34.8	<LD	<LD	<LD	3.7	6.5
Canal at 11 km from Mar Azul	<LD	5.0	<LD	298.4	<LD	19.99	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
Canal 5 route 11	Trace	6.8	2.1	36.9	Trace	39.46	7.3	Trace	<LD	<LD	3.3	<LD	1.1	23.4
Canal 7 route 11	Trace	6.4	3.6	118.5	<LD	15.61	28.6	Trace	<LD	<LD	19.3	<LD	<LD	31.1
Canal at 9 km from canal 7	Trace	24.4	<LD	23.6	<LD	0.55	Trace	<LD	<LD	<LD	<LD	<LD	1.9	7.4
A° Vivoratá route 11	<LD	<LD	<LD	30.8	<LD	2.36	17.2	<LD	<LD	<LD	<LD	<LD	<LD	31.8
A° De los cueros route 11	<LD	11.9	<LD	33.7	<LD	4.44	11.2	<LD	<LD	<LD	7.4	<LD	<LD	6.8
A° at 6 km from A° Vivoratá	–	–	<LD	19.9	7.60	17.47	<LD	–	–	<LD	<LD	<LD	<LD	Trace
A° Vivoratá route 2	<LD	2.2	<LD	19.8	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	10.7
A° Dulce route 2	<LD	<LD	<LD	46.9	<LD	94.80	Trace	Trace	<LD	<LD	<LD	<LD	<LD	23.6
A° Grande route 2	Trace	<LD	<LD	87	<LD	25.12	<LD	Trace	<LD	<LD	<LD	<LD	<LD	8.2
A° Dulce route 226	1.3	25.2	<LD	83	<LD	<LD	Trace	0.8	20.5	<LD	25	<LD	<LD	5.1
A° 51 route 226	<LD	26.1	<LD	8.7	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
A° El Volcán route 226	<LD	<LD	<LD	12.9	<LD	<LD	28.8	<LD	<LD	<LD	<LD	<LD	<LD	91.7
A° La Ballenera route 88	<LD	<LD	<LD	136.2	<LD	<LD	7.6	<LD	<LD	<LD	210.4	<LD	<LD	136.8

(continued on next page)

Table 4 (continued)

Active ingredient: Date of stream sampling Description	Glyphosate						AMPA					
	April 2012			August 2012			September 2012			April 2012		
	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)	Water ($\mu\text{g l}^{-1}$)	SPM ($\mu\text{g kg}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)
A° LA Carolina route 88	1.9	562.8	<LD	<LD	<LD	<LD	1.3	71.0	<LD	<LD	<LD	5.6
A° Chocorí route 88	<LD	<LD	221.2	<LD	<LD	20.6	0.6	<LD	Trace	<LD	<LD	133.8
A° El pescado route 88	Trace	35.2	64.1	<LD	<LD	19	Trace	<LD	<LD	<LD	<LD	30.9
A° Nutria Mansa route 88	0.6	64.1	14.4	<LD	<LD	Trace	Trace	<LD	<LD	<LD	<LD	30
A° Malacara route 88	Trace	17.9	125.7	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	16.1
A° El moro route 88	<LD	<LD	63.6	<LD	<LD	<LD	<LD	<LD	0.8	<LD	<LD	10.4
A° Chocorí Mechongue	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	Trace

LD: limit of detection. Trace: value detectable but non-quantifiable.

It has been shown clearly in this study that when the agroclimatic conditions make run-off likely, soil particulates move from production plots towards surface waters.

No-till is a management practice which simplifies agricultural production and is the basic reason why this has had such massive uptake in Argentina where the system is used on 78.5% of the country's agricultural land. At the same time, under NT, the surface cover of crop residue and the increase in the levels of organic matter in the first few centimeters of the soil produce an increase in the hydraulic conductivity of water, the water storage capacity and the reduction in the run-off (ECAF, 1999). However, in different tillage systems, including NT, are not reported differences in the content of soil organic matter (Domínguez et al., 2009), while several authors reported lower values of hydraulic conductivity associated with a greater apparent density in NT corresponding to the cropping systems used in the zone of study (Ferrerías et al., 2000; Aparicio et al., 2002). There was a drop in the hydraulic conductivity in soils under NT as the years go by with the land under continuous agricultural use (Aparicio and Costa, 2007).

These reports lead us to think that in those soils of the Buenos Aires south-east that have gradients between 0% and over 10% in the foothills (the Tandil range) – whose principal characteristic is that the gradients are no more than 600 m long, rain water has more chance of running off the surface towards lower areas of the countryside than it does infiltrating and moving through the soil profile.

The glyphosate adsorbed to the soil is dragged with these particulates which are then deposited to form part of the sediment, where the glyphosate is biodegraded to AMPA (Major et al., 2003). The half-life of this herbicide can be prolonged in the environment due to the formation of metal complexes with highly chelating cations (e.g., Cu^{+2} and Fe^{+2}) which significantly reduce the availability of glyphosate in the microbial decomposition (Tsui et al., 2005). AMPA also suffers degradation in water and soil, but at a rate that is significantly slower than that of glyphosate due to the fact that its adsorption to particulates is possibly stronger and because of the lower penetrability to cell membranes. The concentration of AMPA in the sediment can fluctuate depending on its rate of degradation relative to that of glyphosate.

In a study of surface water carried out in the Rolling Pampa of Buenos Aires (in the northern part of Buenos Aires Province) glyphosate concentrations were found in the order of $100\text{--}700 \mu\text{g l}^{-1}$ (Peruzzo et al., 2008).

Surface runoff can transport pesticides to surface water bodies including rivers, lakes and streams (de Jonge et al., 2000). In this sense, in a study performed in plots of run-off in the Province of Entre Ríos (Argentina), concentrations were reported of glyphosate in the run-off water which ranged between 1 and $12 \mu\text{g l}^{-1}$ (Sasal et al., 2010). In contrast, Screpanti and Accinelli (2005) reported that glyphosate showed low potential to contaminate surface water resources. The authors found a peak of high concentrations of glyphosate ($\sim 16 \mu\text{g l}^{-1}$) in instances of run-off that occurred one day after the herbicide was applied and a total maximum amount of glyphosate loss of 0.031% of the applied active ingredient.

The soil is a natural resource, which we consider to be non-renewable because the time needed for its formation well exceeds the person's life-time. The functions it fulfills are essential to the balanced development of life on earth and managing soil to preserve these functions is the key to maintaining a good quality environment, as it is a natural filter between air and water. The presence of glyphosate and AMPA in the soil constitutes a potential contamination issue. Particles of soil eroded by the wind and/or water are the way in which adsorbed glyphosate moves to zones far away from the agrochemical's point of application. In Argentina there is no reported data on positive detection of glyphosate in particulate matter produced by aeolic erosion, just as

there is none for that in air or rain water. In the international bibliography, in contrast, the detection of glyphosate ranging from 60% to 100% is reported in air and in rain water (Chang et al., 2011).

This study is, to our knowledge, the first dealing with glyphosate fate in agricultural soils in Argentina. Here are reported glyphosate and AMPA concentrations in different environmental matrices over a surface of 1,206,162 hectares and highlights the importance of appropriate soil management to achieve the best development of its functions in the environment.

4. Conclusions

Glyphosate and its principal metabolite AMPA are present in the soil of the agricultural basin studied in a concentrations range from 35 to 1502 and 299 to 2256 $\mu\text{g kg}^{-1}$, respectively

The surface run-off can cause the movement of soil particles which carry glyphosate adsorbed and end up in surface water courses where the glyphosate can also be desorbed, biodegraded and accumulate in the bottom sediment. This information is non-existent so far and is an important contribution to the knowledge of the environmental distribution of these molecules.

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