



Non-point source pollution of glyphosate and AMPA in a rural basin from the southeast Pampas, Argentina

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Abstract

We measured the occurrence and seasonal variations of glyphosate and its metabolite, aminomethylphosphonic acid (AMPA), in different environmental compartments within the limits of an agricultural basin. This topic is of high relevance since glyphosate is the most applied pesticide in agricultural systems worldwide. We were able to quantify the seasonal variations of glyphosate that result mainly from endo-drift inputs, that is, from direct spraying either onto genetically modified (GM) crops (i.e., soybean and maize) or onto weeds in no-till practices. We found that both glyphosate and AMPA accumulate in soil, but the metabolite accumulates to a greater extent due to its higher persistence. Knowing that glyphosate and AMPA were present in soils (> 93% of detection for both compounds), we aimed to study the dispersion to other environmental compartments (surface water, stream sediments, and groundwater), in order to establish the degree of non-point source pollution. Also, we assessed the relationship between the water-table depth and glyphosate and AMPA levels in groundwater. All of the studied compartments had variable levels of glyphosate and AMPA. The highest frequency of detections was found in the stream sediments samples (glyphosate 95%, AMPA 100%), followed by surface water (glyphosate 28%, AMPA 50%) and then groundwater (glyphosate 24%, AMPA 33%). Despite glyphosate being considered a molecule with low vertical mobility in soils, we found that its detection in groundwater was strongly associated with the month where glyphosate concentration in soil was the highest. However, we did not find a direct relation between groundwater table depth and glyphosate or AMPA detections. This is the first simultaneous study of glyphosate and AMPA seasonal variations in soil, groundwater, surface water, and sediments within a rural basin.

Keywords Glyphosate · Rural basin · Soil accumulation · Groundwater · Surface water · Sediments · Water-table depth

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Introduction

Glyphosate (*N*-(phosphonomethyl) glycine) is a broad-spectrum non-selective herbicide, and it is currently the most used pesticide worldwide (Benbrook 2016). Its use has increased exponentially over the past years due to the implementation of genetically modified (GM) glyphosate-resistant crops. In Argentina, more than 200 million liters of glyphosate is applied per year (CASAFE 2012) to control weeds during the fallow period in no-till management practices and in GM soybean, maize, and cotton production (AAPRESID 2012). Over the past years, the overuse of this herbicide has caused the emergence of glyphosate-resistant weeds (e.g., Binimelis et al. 2009), which in turn led to the use of commercial formulations with a higher concentration of active ingredient.

Agricultural production is one of the main causes of non-point source pollution of aquatic ecosystems and a major

contributor to groundwater contamination (Arias et al. 2011). Therefore, the widespread use of glyphosate in agroecosystems has led to major public and scientific concerns regarding glyphosate occurrence and distribution in the environment. Glyphosate has a high water solubility (11.6 g L⁻¹ at 25 °C) (Montgomery 1993), which may increase the risk of being transported in the aqueous phase. However, it is considered to have low mobility in soils because sorption is generally high and nearly an irreversible process (Okada et al. 2016; Gómez Ortiz et al. 2017; Maqueda et al. 2017). This characteristic lowers glyphosate potential to contaminate surface waters or groundwater (Vereecken 2005), but it also decreases its bioavailability to microbial degradation (Okada et al. 2017). Therefore, although the glyphosate half-life in soils is usually short—between 3 and 40 days (e.g., Rueppel et al. 1977; Smith and Aubin 1993)—the less available residues may remain for almost a year after application (Okada et al. 2017) causing its accumulation in soils (Bergström et al. 2011). Glyphosate and its metabolite aminomethylphosphonic acid (AMPA) are usually detected in agricultural areas that have been exposed to herbicide application (Aparicio et al., 2013; Battaglin et al. 2014; Lupi et al. 2015; Primost et al. 2017). The levels of glyphosate and AMPA in agricultural soils range between 34.7–1502.3 and 22.3–921.3 µg kg⁻¹, respectively (Aparicio et al. 2013). Values as high as 2299 and 4204 µg kg⁻¹ (for glyphosate and AMPA, respectively) have also been reported in soils with no-till management and GM glyphosate resistant crops (Primost et al. 2017).

Watercourses that are influenced by agricultural land use may be exposed to detectable levels of glyphosate and AMPA. For example, in the USA, glyphosate concentrations in streams range from 0.08 to 450 µg L⁻¹ (Coupe et al. 2012; Battaglin et al. 2014). In Switzerland, glyphosate concentrations in surface water range from 0.11 to 3.3 µg L⁻¹ (Hanke et al. 2010; Poiger et al. 2017). In Argentina, the levels in surface waters from highly productive agricultural areas range between 0.5 and 7.6 µg L⁻¹ (Aparicio et al. 2013; Pérez et al. 2017a; Primost et al. 2017). Glyphosate may also accumulate in the stream bed bound to the sediment compartment, reaching concentrations as high as 3004 and 5374 µg kg⁻¹ of glyphosate and AMPA, respectively (Ronco et al. 2016). Moreover, once glyphosate reaches the aquatic environment, it can accumulate in aquatic macrophytes (Pérez et al. 2017b).

Despite being a strong sorbing pesticide, glyphosate may leach through the soil profile via macropore-mediated transport (Gjettermann et al. 2009; Kjaer et al. 2011). The occurrence of glyphosate and AMPA residues in groundwater has been reported in studies from Europe (Hanke et al. 2008; Sanchis et al. 2012; Poiger et al. 2017), from North America (Battaglin et al. 2014; Van Stempvoort et al. 2014, 2016), and recently from South America (Olivo et al. 2015; Primost et al. 2017) (Table 1). The maximum reported concentrations in groundwater range from 0.025 to 6.8 µg L⁻¹ for glyphosate

Table 1 Glyphosate and aminomethylphosphonic acid (AMPA) detection frequency and maximum concentrations in groundwater reported in peer-reviewed journals

Country	Number of samples	Water depth (m)	Glyphosate			AMPA			References
			Detection frequency (%)	Maximum concentration (µg L ⁻¹)	LD (µg L ⁻¹)	Detection frequency (%)	Maximum concentration (µg L ⁻¹)	LD (µg L ⁻¹)	
Canada	281	0.2–1.0	13.5	0.042	0.001–0.01 ^a	11.7	2.87	0.05–0.06 ^a	Van Stempvoort et al. (2014)
	401	2.8–38.1	10.5	0.663	0.002–0.01 ^a	5.0	0.698	0.002–0.01 ^a	Van Stempvoort et al. (2016)
United States	1171	n.m.	5.8	2.0	0.02–0.1 ^a	14.3	4.8	0.02–0.1 ^a	Battaglin et al. (2014)
Spain	129	n.m.	47.2	2.5	0.0032	n.m.	n.m.	–	Sanchis et al. (2011)
Switzerland	10	n.m.	n.d.	–	0.0005	n.d.	–	0.0001	Hanke et al. (2008)
	141	n.m.	1.4	0.025	0.005	n.m.	0.65	0.005	Poiger et al. (2016)
Brazil	13	n.m.	38.4	6.8	0.07	n.m.	–	–	Olivo et al. (2015)
Argentina	17	40.0–60.0	n.d.	–	0.07	n.d.	–	0.15	Primost et al. (2017)

LD limit of detection, n.m. not measured, n.d. not detected

^a Authors report different LD for different data sets

and 0.65 to 4.8 $\mu\text{g L}^{-1}$ for AMPA (Table 1). Most of the studies do not report the groundwater depth or its relation with glyphosate detection. However, it has been suggested that groundwater depth may be one of the key factors that determine glyphosate occurrence in this compartment (Van Stempvoort et al. 2014).

The widespread use of glyphosate makes it extremely relevant to study the dispersion to different environmental compartments. In general, previous studies evaluate glyphosate and AMPA occurrence based only in one sampling time. To the authors' best knowledge, there are no studies about the seasonal variations of glyphosate and AMPA in different environmental compartments (soil, groundwater, surface water, and sediments) within the limits of a rural basin. In this work, we center our study in El Crespo upper basin, an agricultural area of the Austral Pampas with extensive crops. The El Crespo watercourse flows through a number of agricultural farms and pastures, without any urban or industrial inputs, which makes it an ideal basin to study agricultural pollution processes. Therefore, the objectives of this study were (a) to study the occurrence and levels of glyphosate and AMPA in soil, groundwater, surface water, and sediments; (b) to evaluate the seasonal variations of glyphosate and AMPA in these environmental matrices; and (c) to assess the relationship between the water-table depth and glyphosate and AMPA levels in groundwater.

Materials and methods

Study site

El Crespo is a third-order effluent stream (Massone 2003) with its headwaters located in the Tandilia Hills system in the southwest, flowing towards the northeast plain area of the southeast Pampas in the Buenos Aires Province (Fig. 1a). This region is characterized by temperate and humid climate. The stream has a total length of 65 km and is a tributary to the Mar Chiquita Lagoon (Natural Reserve MAB-UNESCO) (Fig. 1b). The basin is part of the phreatic Pampeano Aquifer system (Sala 1975), which recharges by infiltration of excess precipitation and discharges towards surface streams, rivers, and water bodies. The Pampeano Aquifer permeability varies between 1 and 5 m day^{-1} , porosity is around 12%, and storativity is 0.0001 (Hernández et al. 1991). The unsaturated zone thickness of the aquifer in the study area ranges from 2 to 24 m.

In this study, we focus in El Crespo upper basin which has a total area of 226 km^2 (Fig. 1c). The area under crop production in the upper basin covers around 95% of the land; therefore, it is an optimal site to study dispersion processes of agrochemicals in the environment, without any urban or industrial inputs. Glyphosate is generally applied several times per year,

since it is used as a pre-plant and post-harvest weed killer for most of the sowed crops under no-till management in application rates that range from 1.08 to 4.08 kg ha^{-1} (Table 2). In the area of study, the fallow period applications of glyphosate are done between April and September depending on the crop rotation. Moreover, glyphosate is also applied as a post-emergence herbicide between December and March during the growth period of glyphosate-resistant crops (i.e., soybean and maize). These crops represent almost half of the total sowed land of the studied area (Table 2). The most common glyphosate commercial formulations reported by the farmers of the area were (active ingredient composition in parenthesis) Roundup FULL II® (glyphosate potassium salt 66.2% w/v), Roundup ControlMax® (glyphosate-monoammonium salt 79% w/w), and ATANOR Power Plus II® (glyphosate potassium salt 64.5% w/v).

Data collected from the INTA Balcarce Weather Station was used to estimate the accumulated rainfalls, evapotranspiration average temperature, and drainage (AquaCrop FAO 2017) for each season during the studied period (Fig. S1).

Soil and groundwater sampling

Groundwater and soil were sampled from 14 farms within the limits of the upper basin (Fig. 1), approximately every 2 months on fall (April, June 2015), winter (August 2015), spring (September, November 2015), and summer (January, March 2016). Composite samples from the first 5 cm of topsoil ($n = 82$) were taken from agricultural plots. Upon arrival to the laboratory, samples were air dried (30 °C) and sieved using a 2-mm mesh and stored until laboratory analysis. Groundwater samples ($n = 81$) were taken on the same day as the soil samples, from windmills or electrical pumps located near the agricultural plots where soil was sampled. The groundwater depth was measured using an electrical probe down the windmill or pump whole. Before taking the sample, water was pumped for 5 min to clean the pipes from any stagnant water. The samples were collected with propylene bottles that had been rinsed three times with the pumped water before taking the sample. The electrical conductivity (EC) was measured with ECTestr pure (Oakton®) and pH with Acorn Series pH meter (Oakton®), in situ. Upon arrival to the laboratory, water samples were stored at -20 °C until further analysis. The Ca_2^+ and Mg_2^+ contents were measured by an atomic absorption spectrophotometer, Na^+ and K^+ with a flame photometer, and CO_2^{3-} and HCO_3^- by titration.

Surface water and sediment sampling

Surface water and sediments were sampled monthly at different sites of the stream (Fig. 1 and Table 3) from April 2015 to March 2016. The sampled months were grouped according to

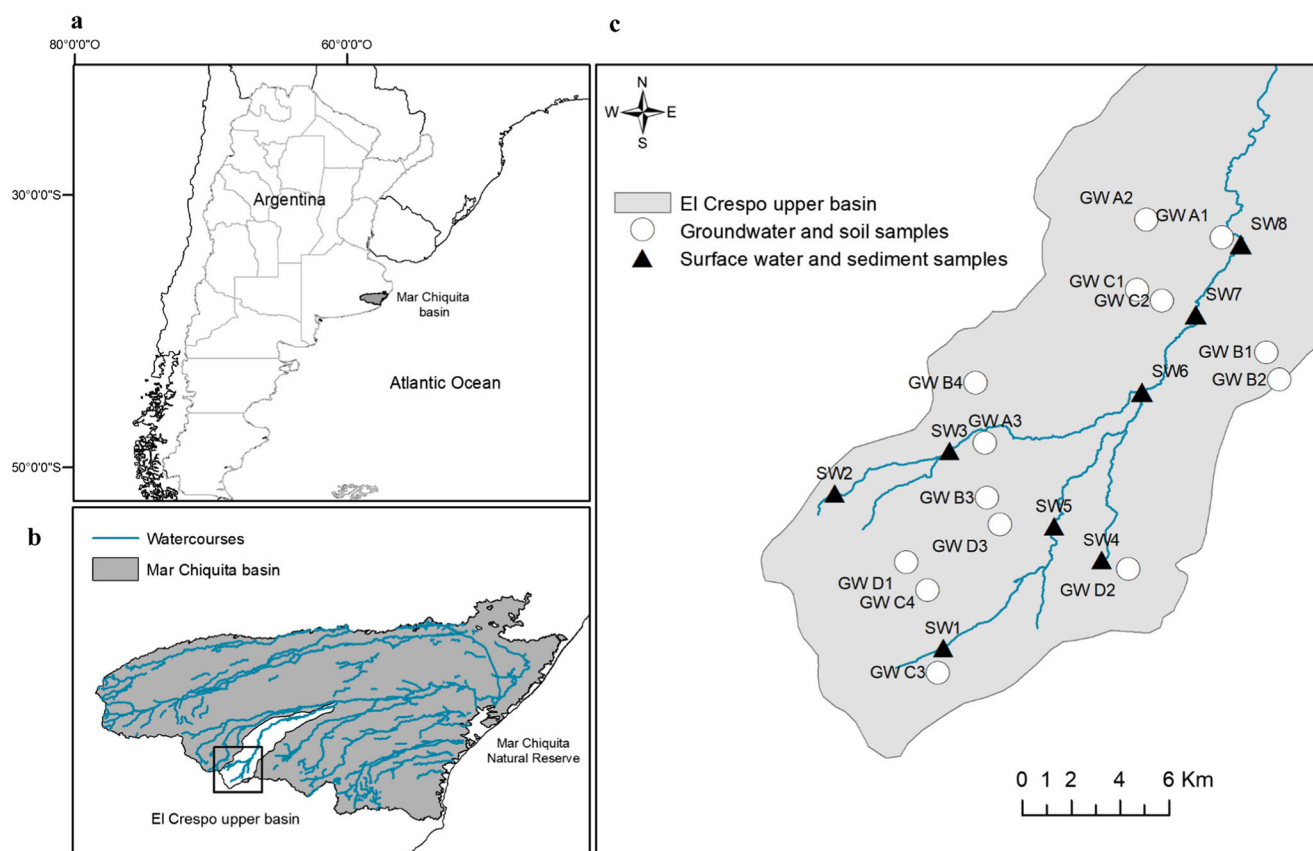


Fig. 1 El Crespo basin is part of the Mar Chiquita basin located southeast of the Buenos Aires Province, Argentina (a). The El Crespo stream flows towards northeast, and it is a tributary to the Mar Chiquita Lagoon Natural

Reserve (MAB-UNESCO) (b). Sampling sites of soil, groundwater, surface water, and sediment samples were located within the upper area of El Crespo basin (c)

seasons: fall (April, May, June), winter (July, August), spring (September, October, November), and summer (December, January, February, March). Sites SW1 and SW2 (headwaters) correspond to the riparian seep area. These sites have an intermittent water flow and were only sampled in spring and summer. Sites SW3, SW4, and SW5 have medium permanent flow and a channel cross section of approximately 1 m. The water from these sites converges into the main branch of the stream, where sites SW6, SW7, and SW8 are located. At these sites, the channel cross section ranges from 3 to 5 m. The estimated mean annual flow at site SW8 is $0.48 \pm 0.2 \text{ m}^3 \text{ s}^{-1}$ (estimated from Pérez et al. 2017a). Grab samples of surface water ($n = 64$) were taken using polypropylene bottles. EC and pH were measured in situ. The Ca_2^+ and Mg_2^+ contents were measured by an atomic absorption spectrophotometer, Na^+ and K^+ with a flame photometer, and CO_2^{3-} and HCO_3^- by titration.

If present, sediment samples from the first 5 cm of the streambed were collected using cylinder samplers. All sediment samples ($n = 44$) were air dried at 30°C and then sieved using a 2-mm mesh. Sediment texture was determined using the pipette method (Gee and Bauder 1986), and organic matter (OM) was measured by the loss ignition method (Schulte and Hopkins 1996) after sieving with a 0.5-mm mesh.

Glyphosate and AMPA analysis

The standard curves were prepared using a stock solution of analytical glyphosate (PESTANAL® 99.9%) and AMPA (PESTANAL® 99%). Isotope-labeled glyphosate ($1,2\text{-}^{13}\text{C}$, ^{15}N , Sigma-Aldrich) was used as an internal standard. HPLC-grade methanol and HPLC-grade acetonitrile (ACN) for analytical procedures were purchased from Seasinglab (Tandil, Argentina). Nanopure water was obtained by purifying demineralized water in ELGA PURELAB Ultra (Illinois, USA).

The extraction and quantification of glyphosate and AMPA in soil was adapted from the method used in Aparicio et al. (2013). Five grams of soil sample was spiked with isotope-labeled glyphosate ($1,2\text{-}^{13}\text{C}$, ^{15}N) and left for 30 min to stabilize. Afterwards, 25 mL of extracting solution (100 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ /100 mM K_3PO_4 , pH = 9) was added to the samples and placed in an ultrasonic bath for 30 min at room temperature. Tubes were then centrifuged for 10 min to separate the phases. An aliquot of 2 mL of the liquid phase was derivatized with 2 mL of 1 mg mL^{-1} 9-fluorenylmethoxycarbonyl chloride (FMOC-Cl) dissolved in ACN. As a cleanup step to remove organic impurities and excess FMOC-Cl, 4.5 mL of CH_2Cl_2 was added to the samples and shaken vigorously. The aqueous

Table 2 Planted crops during 2015–2016 in the El Crespo upper basin, number of glyphosate applications, and commonly applied doses in the study area

Crop	Area sowed 2015/2016 ^a (%)	Glyphosate applications ^b		
		Pre-plant and post-harvest applications in no-till	During crop growth	Application rate (kg ha ⁻¹)
Soybean (<i>Glycine max</i> L.)	40.8	✓✓	✓✓	1.08–4.08
Sunflower (<i>Helianthus annuus</i> L.)	21.2	✓✓	n.a.	1.08–2.60
Barley (<i>Hordeum vulgare</i> L.)	17.0	✓✓	n.a.	1.70
Maize (<i>Zea mays</i> L.)	11.5	✓✓	✓	1.70–2.60
Wheat (<i>Triticum aestivum</i> L.)	6.5	✓✓	n.a.	1.40–1.70
Sorghum (<i>Sorghum</i> spp. L.)	1.3	n.a.	n.a.	–
Oat (<i>Avena sativa</i> L.)	1.2	✓✓	n.a.	1.08–2.60
Rape (<i>Brassica napus</i> L.)	0.4	✓✓	n.a.	1.08–2.60
Other	0.2	–	–	–

n.a. no glyphosate applications, ✓ number of applications per cycle

^a Estimated from the data provided by the Argentinean Agroindustry Ministry (2016)

^b Based on common agricultural practices of the region and from information gathered from the farmers that participated in the study

fraction was separated from the organic solvent after centrifuging for 10 min. The supernatant was collected and filtered through a 0.22-µm nylon filter. The background solution used

Table 3 Sampling sites, groundwater water table-depth, and surface water channel depth

Groundwater and soil		Water-table depth (m)
Group A	GW A1	< 4
	GW A2	< 4
	GW A3	< 4
Group B	GW B1	> 4 < 8
	GW B2	> 4 < 8
	GW B3	> 4 < 8
	GW B4	> 4 < 8
Group C	GW C1	> 8 m
	GW C2	> 8 m
	GW C3	> 8 m
	GW C4	> 8 m
Group D	GW D1	n.m.
	GW D2	n.m.
	GW D3	n.m.
Surface water and sediments		Water depth (m)
Riparian seep area	SW 1	n.m.
Middle channels	SW 2	n.m.
	SW 3	< 0.5
	SW 4	< 0.5
	SW 5	< 0.5
	SW 6	> 0.5
Main channel	SW 7	> 0.5
	SW 8	> 0.5

n.m. not measured

for the standard curve was the extractant solution. An equivalent amount of isotope-labeled glyphosate was added to each point of the standard curve to evaluate the analytical recovery of the method (internal calibration). Calibration curves were adjusted using a weighted least square regression (1/x), considering a satisfactory linearity when $R^2 \geq 0.999$.

The extraction and quantification in water samples was performed by adding 1 mL of extracting solution to a 2-mL water sample that had been spiked with isotope-labeled glyphosate. After shaking, the samples were derivatized by adding 2 mL of 1 mg mL⁻¹ FMOC-Cl solution and incubated overnight at room temperature. After this, the cleanup step was done according to the soil sample procedure. In this case, the background solution for the standard curve was nanopure water.

The chromatographic analysis was performed using a Waters® ACQUITY® UPLC (C18, 1.7 µm 2.1 × 50 mm). The injection volume was 20 µL. The mobile phase flow was set at 0.4 mL min⁻¹ at 60 °C. The solvents used were water 5 mM NH₄Ac (A) and methanol 5 mM NH₄Ac (B), with a gradient set as follows: 100% A (0 to 0.2 min), 30% A/70 %B (0.2 to 2.5 min), 100% B (2.5 to 4.5 min), and 100% A (4.5 to 6 min). The chromatographic retention times were 1.99 and 2.48 min for the derivatized glyphosate and AMPA, respectively. The target molecules were detected with a Waters® Micromass® Quattro Premier XE Mass Spectrometer (MS/MS). The source of ionization was set in positive mode using a capillary voltage of 3 kV. The collision gas was argon 99.99% at a pressure of 44 × 10⁻³ mbar.

Quality control measures included the analysis of procedural blanks that consisted of nanopure water analyzed as samples. No glyphosate or AMPA was detected in these blanks, indicating that the nanopure water and all of the reagents did not contain trace concentrations of the analytes.

Also, spiked blanks with glyphosate and AMPA at concentrations from 0.5 to 10 $\mu\text{g L}^{-1}$ were injected every 8–10 samples. To ensure the lack of carryover between chromatographic analyses, blank injections of pure water and methanol were run every eight samples. The limit of detection of the method for each matrix (LD) was established as the lowest concentration that can be reliably differentiated from the background levels with a signal-to-noise ratio ≥ 3 . The limit of quantification (LQ) was estimated as the lowest concentration level for which the method was fully validated using spiked samples with satisfactory recovery (70–120%), precision (RSD < 20%), and a signal-to-noise ratio ≥ 10 . The LD in the soil and sediment samples was 0.5 $\mu\text{g kg}^{-1}$ and the LQ was 3 $\mu\text{g kg}^{-1}$, both for glyphosate and AMPA. In water samples, the LD was 0.1 $\mu\text{g L}^{-1}$ and the LQ was 0.5 $\mu\text{g L}^{-1}$, for both compounds. The analytical recovery for water samples was > 90% and for soil samples 75–110%.

Data analysis

Samples with concentrations < LD were considered non-detectable and were set to zero, and samples that had concentrations < LQ were set to the LD value in figures and statistical analyses (Struger et al. 2015). The relation between glyphosate and AMPA concentration in each compartment was analyzed by Pearson correlation with a significance level of 0.05. Glyphosate and AMPA concentrations were compared among seasons using the Kruskal-Wallis non-parametric test because assumption of homogeneity of variance was not met. The differences were tested by Dunn's test pairwise multiple comparisons procedure. Also, we analyzed the relation between water-table depth and glyphosate and AMPA occurrence in groundwater by grouping each site according to the measured water-table depth as follows: group A ≤ 4 m; group B > 4 m < 8 m; group C ≥ 8 m (Table 3). We were not able to measure the water-table depth at three farms (group D), so this group was not included in the analysis of water-table depth. Statistical analyses were carried out using InfoStat Software Package (InfoStat 2008).

In order to understand the relationship between the parental compound and its metabolite, we calculated the AMPA ratio. This ratio gives insight into sources, fate, and transport of glyphosate and AMPA in the environment (Coupe et al. 2012; Battaglin et al. 2014).

The AMPA ratio (%) for the soil and sediment samples was calculated as

$$\text{AMPA ratio} = [\text{AMPA}] / ([\text{glyphosate}] + [\text{AMPA}]) \times 100,$$

where [glyphosate] and [AMPA] correspond to the concentration of each molecule in the solid matrix. The AMPA ratio was not estimated if both compounds were not detected.

Results and discussion

General characteristics of the studied environmental compartments and climatic conditions

The summary of the physico-chemical characteristics of soil, sediment, groundwater, and surface water of the studied area are shown in the Supplemental Data Table 1. The main soil type within the upper basin belongs to the Mar del Plata series, which is a fine silty-mixed thermic Typic Argiduoil, well drained and with medium runoff (INTA 2002). The soil texture corresponds to a loamy soil with 4.9% OM (Sainz Rozas et al. 2011, Supplementary Material Table S1). Sediments were characterized as slightly alkaline (pH 7.6–8.4) with 2.9% OM and different textural compositions, including loam, sandy loam, clay loam, and sandy clay loam textures (Supplementary Material Table S1). The groundwater pH ranged from 6.6 to 9.7, and EC varied from 0.5 to 1.43 mS cm^{-1} . In surface water, the pH ranged from 7.7 to 8.6 and EC from 1.0 to 1.2 mS cm^{-1} . The ionic contents (Mg^{2+} , Ca^{2+} , K^+ , Na^+ , HCO_2^- , CO_3^{2-}) in groundwater and surface water samples were similar to those reported in other studies of the Austral Pampas (Romanelli et al. 2011). The accumulated rainfalls during the studied period ranged from 170 mm in fall to 277 mm in summer (Supplementary Material Fig. S1). Due to the seasonal conditions of the air temperature, the lowest evapotranspiration occurred in winter and the highest in summer. Hence, as a combination of the amount of rainfall and the low evapotranspiration, the soil drainage was higher in winter.

Glyphosate and AMPA occurrence in environmental compartments

Glyphosate and its metabolite AMPA occurred in all the studied environmental compartments of El Crespo upper basin (Table 4). The highest detections of both compounds were found in soil and sediments (> 93% of detection). The maximum levels of glyphosate and AMPA were 1224 and 7345 $\mu\text{g kg}^{-1}$ in soils, and 75.5 $\mu\text{g L}^{-1}$ and 226 $\mu\text{g kg}^{-1}$ in sediments, respectively (Table 4). The high detection of glyphosate and AMPA in the soil compartment is a result of the continuous herbicide input due to the farming activities in the studied area. As shown in Table 2, all of the sowed crops in El Crespo basin, except for sorghum, required at least two glyphosate applications during the pre-plant and post-harvest periods under no-till management. Moreover, 40% of the cultivated land was used to grow GM soybean, which adds two more glyphosate applications during the crop growth period, with application rates as high as 4.08 kg ha^{-1} (Table 2). The high detection of glyphosate and AMPA in the soil compartment is the result of a combination of endo-drift processes and glyphosate behavior once it reaches the soil compartment. On the one hand, glyphosate reaches the soil by endo-drift

Table 4 Glyphosate and AMPA occurrence in different environmental matrices of the El Crespo upper basin

Environmental matrix	Total samples	LD/LQ ($\mu\text{g kg}^{-1}$ or $\mu\text{g L}^{-1}$)	Glyphosate			AMPA		
			Detection (%)	Average ($\mu\text{g kg}^{-1}$ or $\mu\text{g L}^{-1}$)	Range	Detection (%)	Average ($\mu\text{g kg}^{-1}$ or $\mu\text{g L}^{-1}$)	Range
Soil	82	0.5/3.0	93	182.5	0.5–1224	99	781.8	0.5–7345
Groundwater	81	0.1/0.5	24	0.4	0.1–8.5	33	0.1	0.1–1.9
Surface water	64	0.1/0.5	28	0.4	0.1–8.2	50	0.2	0.1–3.7
Sediments	45	0.5/3.0	95	7.0	0.5–75.5	100	17.6	0.5–226

LD limit of detection, LQ limit of quantification

processes, i.e., when the foliar spray is deposited in the soil beneath instead of reaching the leaves or when the sprayed herbicide is washed after heavy rains from the foliage on to the ground (Himel 1974). On the other hand, once glyphosate reaches the soil compartment, it is degraded by microorganisms into sarcosine (e.g., Liu et al. 1991) or AMPA (e.g., Araujo et al. 2003). However, glyphosate is also strongly sorbed to the soil matrix (Okada et al. 2016), which in turn reduces its bioavailability and causes a decrease in the dissipation rate (Okada et al. 2017). In this sense, several laboratory degradation studies have noted that glyphosate degradation follows a first order multi-compartment or bi-exponential kinetic degradation model (e.g., Zablotowicz et al. 2009; Simonsen et al. 2008; Bento et al. 2016; Okada et al. 2017). This implies that, while degradation in the first compartment is usually a fast process, the degradation in the second compartment is limited by strong adsorption processes and slow desorption from the soil matrix to the solution (Al-Rajab and Schiavon 2010). The sorbed residues become less available and may remain in soil up to 300 days after application (Okada et al. 2017). Because of this, when the application rate is higher than its dissipation rate, glyphosate behaves as a “pseudo-persistent” pollutant and it accumulates in agricultural soils (Primost et al. 2017). Furthermore, wind (Bento et al. 2017) or water erosion (Yang et al. 2015) may cause the off-site transport of particle-bound residues of glyphosate and AMPA that then accumulate in the sediment compartment.

Glyphosate and AMPA were detected in 24 and 33% of the groundwater samples, respectively (Table 4). The maximum levels of glyphosate were 8.5 and 1.9 $\mu\text{g L}^{-1}$ for AMPA. The occurrence of glyphosate and AMPA in the groundwater compartment is dependent on vertical transport processes combined with other factors such as hydrology, land management, and herbicide application (Van Stempvoort et al. 2016). Experimental field studies have demonstrated that, though glyphosate is strongly sorbed to soil, it can leach through the soil profile via preferential transport pathways (Aronsson et al. 2011; Kjaer et al. 2011). Hence, glyphosate has been detected in drainage water at an average concentration of 3.7 $\mu\text{g L}^{-1}$ (Kjaer et al. 2011). In general, the detection frequencies found in the groundwater from El Crespo basin are within the range

of other studies worldwide (see Table 1). One study from Brazil detected glyphosate concentrations within the same order of magnitude as found in the present study, ranging from 0.4 to 6.8 $\mu\text{g L}^{-1}$ (Olivo et al. 2015). However, a previous study from Argentina conducted in the year 2012 did not find detectable concentrations of either glyphosate or AMPA in groundwater samples (Primost et al. 2017). Therefore, this is the first report of positive detections of glyphosate and AMPA in groundwater reservoirs from Argentina.

The detection frequencies of glyphosate and AMPA in surface water were 28 and 50%, respectively (Table 4). The maximum detected concentration for glyphosate was 8.2 and 3.7 $\mu\text{g L}^{-1}$ for AMPA. The occurrence of glyphosate and AMPA in the surface water compartment results from several exo-drift processes. Glyphosate can reach directly the watercourse by spray drift during application. This could be an important dispersion mechanism in the El Crespo basin, since usually the cultivated fields are sowed right at the edge of the stream channel (e.g., Supplemental Material Fig. S2). Another source of glyphosate is crop residues that have been sprayed with the herbicide. Glyphosate sorption to plant material is a reversible process (Rampoldi et al. 2011). Therefore, glyphosate residues can be easily washed away from the stubbles and then transported by surface runoff after heavy rainfall. Overall, the detection frequencies and concentrations of glyphosate and AMPA in surface water were similar to other studies from agricultural basins under similar land use management. For example, Primost et al. (2017) reported glyphosate and AMPA detection frequencies of 27 and 54%, respectively, from surface water samples located in an agricultural area of the Mesopotamic Pampas under no-till management (the method LD of the study was 0.06 and 0.10 $\mu\text{g L}^{-1}$ for glyphosate and AMPA, respectively). Aparicio et al. (2013) detected glyphosate and AMPA in 15 and 12%, respectively, in samples from several streams of the southeast Pampas (the method LD was 0.1 $\mu\text{g L}^{-1}$ for both compounds).

Glyphosate and AMPA relationship

The average AMPA concentrations in soil and sediments were higher than the concentrations of glyphosate, and therefore,

the values of the AMPA ratio in soil and sediments were higher than 50% with a mean value near 80% (Fig. 2). The interquartile range was 75–95 and 50–90% in soil and sediments, respectively. The fact that AMPA concentrations were higher than glyphosate concentrations in these environmental matrices may be due to AMPA higher persistence in the environment (Mamy et al. 2005), since it is strongly sorbed to the soil matrix through the phosphonate group (Sidoli et al. 2016) and protected against further degradation (Borggaard and Gimsing 2008). Moreover, AMPA dissipation in soils is lower than that of glyphosate under the same environmental conditions (Bento et al. 2016), which also favors its accumulation in this compartment when compared to glyphosate.

In groundwater, the median AMPA ratio was 80% with an interquartile range of 0–100% (Fig. 2). Only nine samples had detectable levels of both glyphosate and AMPA, 19 samples had AMPA but no levels of glyphosate (100% AMPA ratio), while ten samples had glyphosate but no detectable AMPA, which yields an AMPA ratio equal to zero. In the case of surface water, the median AMPA ratio was 70% and the interquartile range was 10–100% (Fig. 2). In this case, 16 samples had detectable levels of both glyphosate and AMPA, 13 samples had AMPA and no detectable glyphosate (100% AMPA ratio), and only two samples had glyphosate but no AMPA (AMPA ratio equal to zero). Previous reports conclude that the detection of glyphosate and AMPA in surface water is usually concomitant (Battaglin et al. 2014; Van Stempvoort et al. 2014). However, our results show that AMPA had a higher detection frequency in water samples compared to glyphosate. It should be noted that AMPA presence in surface water can also be related to non-agricultural sources because it is also a metabolite of phosphonates found in household and industrial detergents (Nowack 2003). However, the occurrence of AMPA in

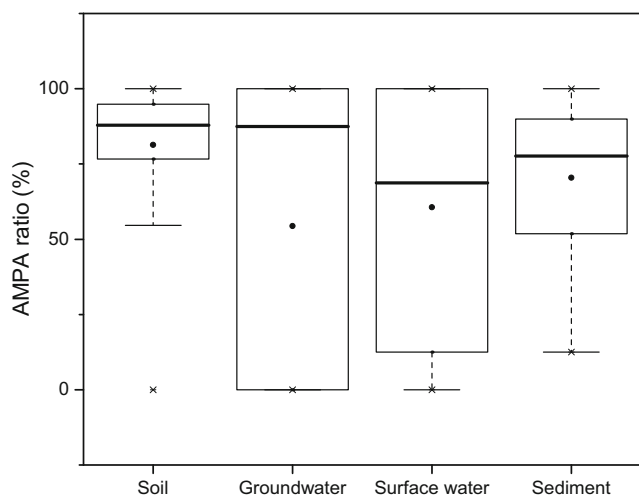


Fig. 2 Boxplot of the AMPA ratio in soil, groundwater, surface water, and sediment samples. The black dot represents the arithmetic mean, the dividing bold line within data boxes represents the data median, the 75th and 25th percentiles of data are the upper and lower boundaries of boxes, dots outside the box are outliers, and error bars represent data range

the El Crespo basin can only be attributed to the agricultural input of glyphosate because there are no industrial or urban inputs into the stream. The fact that AMPA is found even when no glyphosate is present in the water samples suggests that it is a more mobile and persistent compound (Kolpin et al. 2006).

AMPA concentrations were positively correlated to the concentration of its parental compound in soil and sediment samples ($r = 0.737, p < 0.0001$ and $r = 0.590, p < 0.0001$, respectively; Fig. 3). However, this relationship was not observed in the aqueous compartments—there was no correlation between glyphosate and AMPA concentration in groundwater and surface water ($r = -0.04, p = 0.75$ and $r = -0.022, p = 0.86$, respectively). The strong association between AMPA and glyphosate in the solid matrices could relate to the fact that once glyphosate reaches the soil compartment, the soil microflora readily degrades it to AMPA (Bento et al. 2016). The positive relationship between AMPA and glyphosate found in soil and sediments has been observed before in another rural basin (Primost et al. 2017). This suggests that in the solid matrices, biotic degradation is favored over other processes, such as wind erosion, surface runoff, and leaching (Primost et al. 2017). On the other hand, these dissipation processes, along with the spray drift of new applications, contribute to the dispersion of glyphosate towards aquatic environments. Thus, we did not find a significant relation between glyphosate and AMPA concentrations in groundwater and

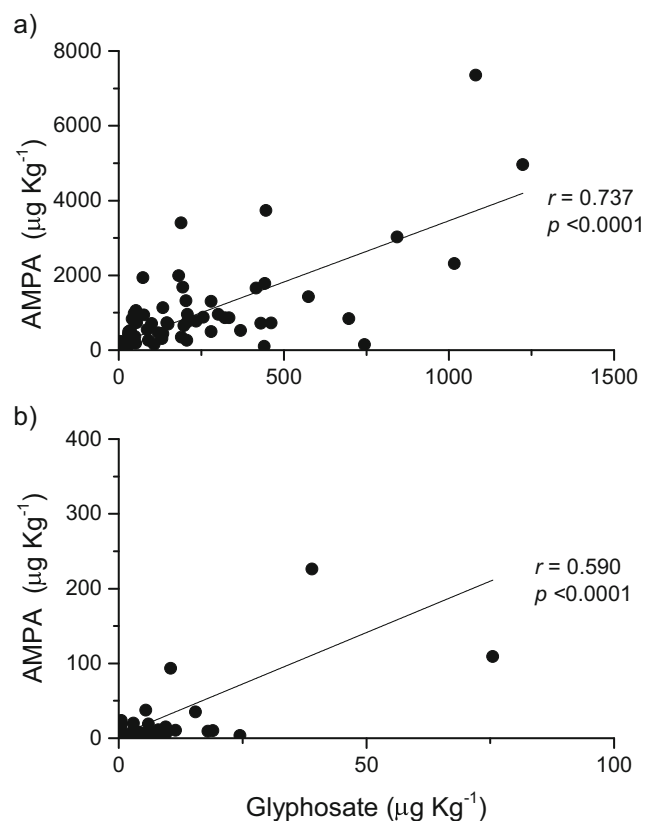


Fig. 3 Glyphosate and AMPA relationship in soil (a) and sediments (b)

surface water because the occurrence of both compounds was not always concomitant (as discussed previously in this section) and the average glyphosate concentrations were higher than the average AMPA concentrations (Table 2).

Seasonal variations in soil

Concentrations in soil varied significantly among seasons (Fig. 4, $p < 0.05$). The highest glyphosate concentrations occurred during fall. In winter and spring, concentrations were significantly lower, and then slightly increased in summer (Fig. 4). When glyphosate is applied in the fallow period, a great part of it is adsorbed on the soil and another part is absorbed to the stubbles and, in both cases, it is protected against microbial degradation (Mamy et al. 2016). When this trapped glyphosate is released from the crop residues during the leaf senescence, it increases the amounts of glyphosate in soil (Mamy et al. 2016). In addition, the soil microbial activity decreases during the colder months (Bento et al. 2016). Therefore, the higher concentrations and detections during fall could be a result of a combination of the weather conditions with previous herbicide applications corresponding to the fallow period, when glyphosate is widely sprayed over weeds and crop residues. During summer, there was an increase in glyphosate concentration (Fig. 4), since glyphosate is re-applied as a post-emergence herbicide in soybean and maize

crops. As mentioned before, AMPA presence in soils is closely related to glyphosate levels, since soil microorganisms readily degrade glyphosate into AMPA. Hence, AMPA seasonal variations in soil were similar to that of glyphosate. The AMPA levels in soil during fall were significantly higher than in the rest of the seasons (Fig. 4, $p < 0.0001$). During winter, glyphosate input to the system decreased and therefore AMPA formation also decreased.

Seasonal variations in groundwater

Glyphosate concentration in groundwater had a significant seasonal variation. The highest glyphosate concentrations were detected in fall and winter ($p < 0.0001$; Fig. 4). Concentrations in spring and summer differed significantly with those of fall but not of winter. The highest detection frequency occurred in fall (80%), whereas in the following seasons detections decreased to less than 9% (Fig. 4). This indicates that the non-point source pollution of groundwater with glyphosate was transient. Van Stempvoort et al. (2016) also noted the short-term duration of glyphosate in shallow groundwater (< 20 m). A number of factors such as hydrology, land management, and herbicide application may influence glyphosate fluctuations in groundwater (Van Stempvoort et al. 2016). Land management in the El Crespo basin does

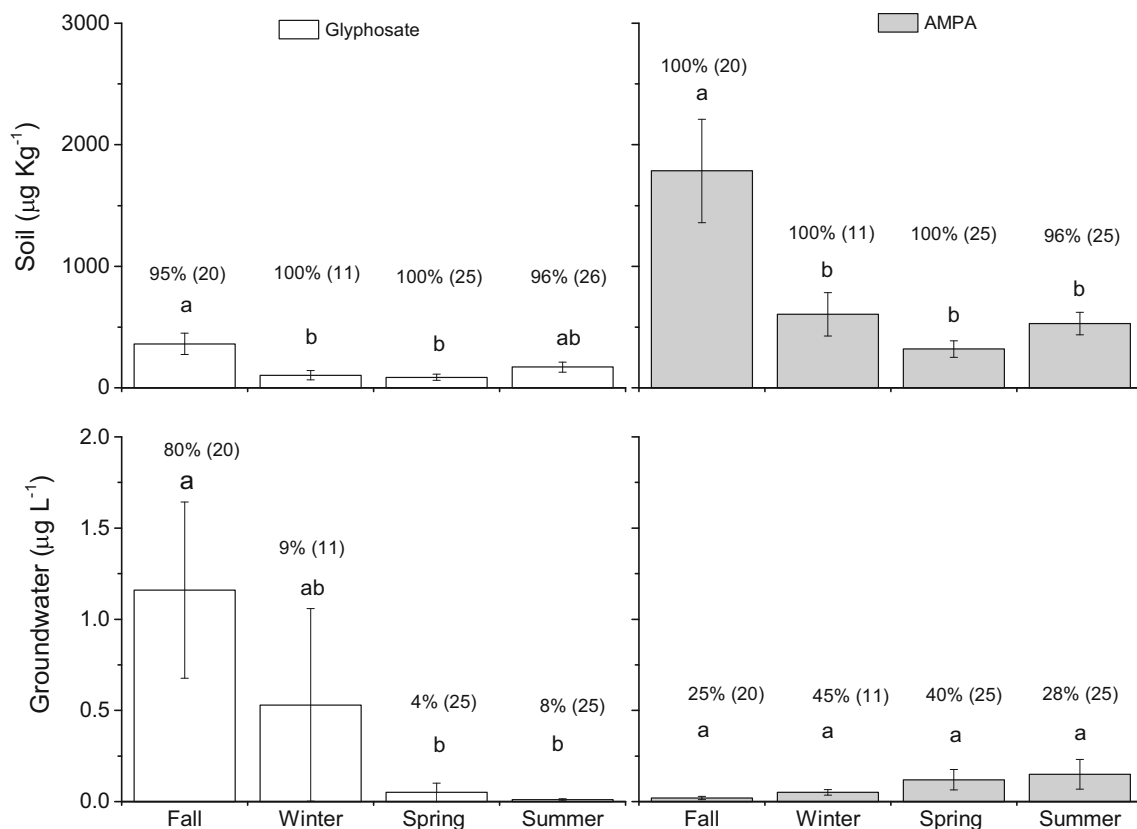


Fig. 4 Seasonal variations of glyphosate and AMPA in soil and groundwater. Different letters indicate significant differences ($p < 0.0001$). Frequencies of detection and number of samples (in parenthesis) are shown on top of each bar. Error bars represent standard error

not vary significantly, since the area is mostly cultivated under no-till. Therefore, the observed temporal variations of glyphosate levels are a result of herbicide application. The high concentrations and detection frequencies of glyphosate in groundwater coincide with the soil results, related to the time of herbicide application during the fall. In addition, the higher recharge of the aquifer that occurred in winter may have diluted the glyphosate concentrations observed in fall.

The detection frequency of AMPA in groundwater was higher than glyphosate (Table 4 and Fig. 4). However, AMPA concentrations did not differ between seasons (Fig. 4). As mentioned before, AMPA detection in groundwater was not strictly related to the presence of the parent compound. In fall, the detection frequency of glyphosate was higher than that of AMPA. However, in winter, spring, and summer, AMPA detection frequencies surpassed those of glyphosate. Contrary to glyphosate, we did not find a direct association between the fluctuations of AMPA levels in groundwater with the variations of concentrations in the soil compartment. There is a lack of studies regarding glyphosate degradation and AMPA in groundwater. However, it has been suggested that AMPA presence in groundwater may be linked to in situ degradation of previous lixiviated glyphosate (Van Stempvoort et al. 2016). On the other hand, AMPA lixiviation from the top soil is less significant, because AMPA has a higher sorption to soil than glyphosate (Sidoli et al. 2016).

Groundwater reservoirs are an important source of potable drinking water in several regions of Argentina. In the studied area, groundwater is used for crop irrigation, in cattle, and as potable water. However, at present there is no regulation regarding the maximum allowed levels of glyphosate in drinking water. If we compare our results with other international standards, the maximum glyphosate and AMPA concentrations found in this study exceed the EU limit for drinking water of $0.1 \mu\text{g L}^{-1}$ (Council Directive 91/414/EEC, European Union, Brussels 1991). However, they do not exceed the limit established by the Canadian Drinking Water Quality Guidelines of $280 \mu\text{g L}^{-1}$ (Guidelines for Canadian Drinking Water Quality 2014) and the US EPA maximum allowed concentration of $700 \mu\text{g L}^{-1}$ (US EPA 2002).

Relation between water-table depth and glyphosate and AMPA occurrence

To analyze if glyphosate or AMPA concentrations in groundwater varied according to the water-table depth, we grouped the groundwater sampling sites according to the measured water-table depth. We found no differences in glyphosate and AMPA concentrations among groups of different water-table depth ($p > 0.05$; Fig. 5). Van Stempvoort et al. (2014) proposed that the sporadic occurrence in shallow groundwater is attenuated by biodegradation and sorption in the subsurface, and therefore, glyphosate is less likely to be found at greater depths.

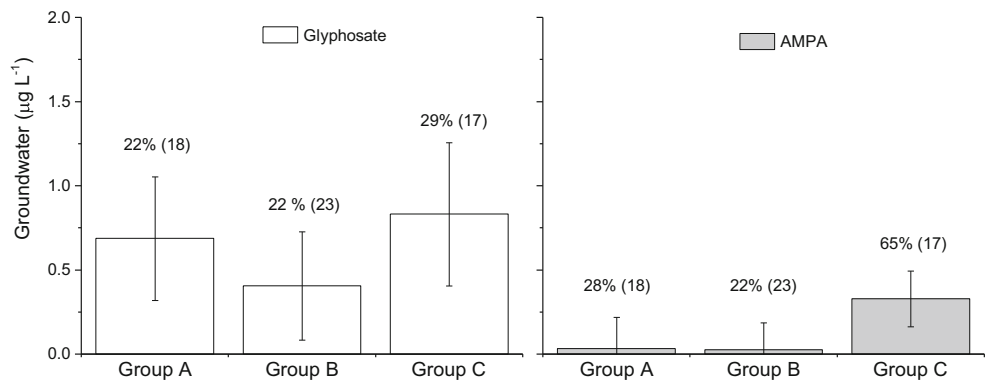
Hence, we expected to find higher concentrations in the shallow groundwater group (group A). However, we did not find a direct association between the groundwater depth and glyphosate or AMPA detections. In another study, Primost et al. (2017) sampled groundwater in an agricultural basin that had glyphosate and AMPA levels in soil 10-fold higher than those reported in this study, and did not find detectable levels of glyphosate or AMPA at groundwater depths > 40 m. Also, Van Stempvoort et al. (2016) reported glyphosate levels in groundwater from several water-table depths (from 0.8 to 38.1 m) without a clear association between the water depth and glyphosate levels and frequencies of detection in groundwater. Therefore, water depth may not be the main risk factor involved in glyphosate occurrence in groundwater. Further studies are needed to elucidate the main factors that contribute to glyphosate and AMPA occurrence in groundwater reservoirs.

Seasonal variations in surface water and sediments

The sites located at the headwaters area (SW1 and SW2) were only sampled during spring and summer, and therefore, the surface water and sediment data were not included in the statistical analysis. However, it is important to note that in this group, two out of nine samples had detectable levels of glyphosate (8.2 and $7.8 \mu\text{g L}^{-1}$) and of AMPA (3.3 and $3.7 \mu\text{g L}^{-1}$). These values were the maximum registered concentrations found in the El Crespo stream. The high concentrations detected in sites SW1 and SW2 can be a result of new sprayings combined with the fact that these sites were extremely shallow and had a very narrow watercourse. This low-water flow can result in an increase in the concentration of the pesticide residues present in surface water (Ccanccapa et al. 2016).

The data collected from the Middle and Main channels of the stream indicate that glyphosate concentration in surface water did not differ significantly among seasons (Fig. 6). However, there was a tendency of high levels of glyphosate during fall and summer. As mentioned before, there are several processes that are responsible for the fate and transport of glyphosate to surface water. On the one hand, glyphosate may be easily washed away from stubbles during the fallow period, since glyphosate sorption to crop residues is a reversible process and sorption is less strong than to the soil compartment (Rampoldi et al. 2011). This could explain why the concentrations observed during the fall season were higher than in the rest of the seasons. Also during the application periods, glyphosate may be transported by atmospheric deposition towards non-intended targets of application (Messing et al. 2011). In addition, glyphosate has been detected in rainfall water (Battaglin et al. 2014; Van Stempvoort et al. 2016), which contributes to the non-point source pollution of surface water. In the case of AMPA, the highest levels in surface water occurred during winter and the lowest concentrations were detected in spring (Fig. 6). Overall, the detection frequencies of

Fig. 5 Glyphosate and AMPA concentrations in groundwater according to the water-table depth (group A < 4 m, group B > 4 < 8 m, group C > 8 m). Frequency of detection and number of samples (in parenthesis) are shown on top of each bar. Error bars represent standard error

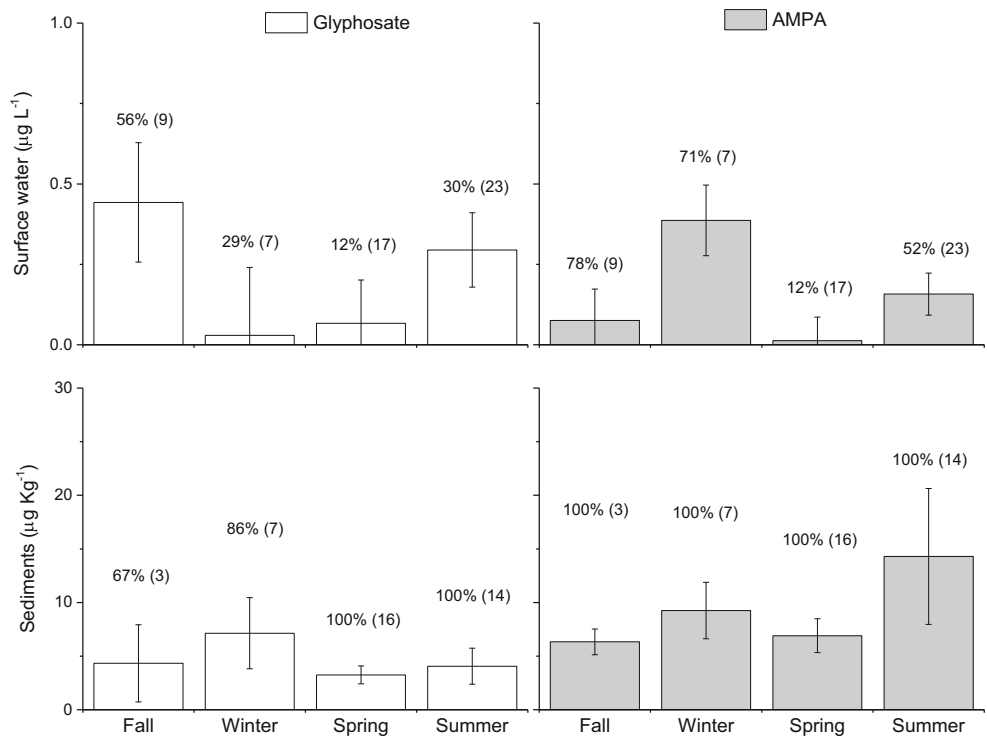


AMPA in surface water were higher than 50%, except during spring. This continuous AMPA input into the stream can be a result of glyphosate degradation in the sediment compartment and the fact that it is more persistent than glyphosate in sediment-water systems (Wang et al. 2016).

The seasonal variations of glyphosate and AMPA levels in sediments are shown in Fig. 6. In many occasions, there were no bottom sediments in the sampling sites, reducing the number of samples of this compartment. Glyphosate deposition over time in the bottom sediments of the stream are a result of different processes. For example, glyphosate can be transported by wind gusts from the fields bound to dry sediment particles (Bento et al. 2017) or by surface runoff, bound to colloids that have been washed after heavy rainfall. The fact that glyphosate is present in the El Crespo basin soils all year round increases the risk of being transported off-site bound to fine soil particles, especially since soybean is a low-residue

crop that leaves soil unprotected from erosion processes. Also, glyphosate that enters the water column is rapidly adsorbed to sediment particles (Wang et al. 2016). Glyphosate adsorption to sediment particles can be related to the amorphous iron and aluminum oxides and the clay content of the sediments (Maqueda et al. 2017). Glyphosate adsorption may also be favored by the organic matter content (Yu and Zhou 2005), since glyphosate possibly binds through hydrogen bonds to the phenolic groups of the humic substances (Albers et al. 2009). In this case, the nature of the sediments found in the El Crespo stream may enhance the retention of glyphosate due to the presence of clay particles and the high organic matter content (Supplementary Table 1). Glyphosate affinity to the sediment particles along with the different dispersion mechanisms from the soil matrix to the stream sediments results in the high frequency of detection of glyphosate and AMPA in this compartment during the entire sampling period.

Fig. 6 Seasonal variations of glyphosate and AMPA in surface water and sediments. Frequencies of detection and number of samples (in parenthesis) are shown on top of each bar



Conclusions

The simultaneous study of various environmental compartments shows that the application of glyphosate in agricultural soils causes the non-point source pollution of groundwater, surface water, and sediments. Both glyphosate and AMPA were present in agricultural soils all year round. In spite of being considered a molecule with low vertical mobility, glyphosate was detected in groundwater samples. The maximum levels of glyphosate in soil and groundwater were detected in fall. We found no association between the water-table depth and glyphosate or AMPA occurrence in groundwater. Although glyphosate concentrations in surface water did not differ significantly among seasons, there was a tendency of higher levels of glyphosate during the fall and summer seasons.

This is the first report of positive detections of glyphosate and AMPA in groundwater reservoirs from Argentina. Therefore, the information obtained in this study is an important head start for future risk assessments and conservation policies, especially since groundwater is the main source of drinking water supply in many regions and countries of the world.

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