



# Pesticides detected in surface and groundwater from agroecosystems in the Pampas region of Argentina: occurrence and ecological risk assessment

Josefina Vera-Candioti · Patricia Inés Araujo · Ignacio Roberto Huerga · Dante Emanuel Rojas · Diego Sebastián Cristos · Alberto David Malmantile

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**Abstract** The objective of this study was to evaluate the occurrence of pesticides in surface and groundwater of agricultural areas of the Pampas region of Argentina and to develop an ecological risk assessment (ERA) of pesticides in freshwater ecosystems. Eight agricultural sites from south Santa Fe province, in the north of the Pampas region, were sampled seven times between 2016 and 2018. Pesticides were analysed by gas chromatography-mass spectrometry (GC/MS) and liquid chromatography-mass spectrometry (UPLC-LC/MS). Twenty compounds

among herbicides, insecticides and fungicides in 84% and 79% of groundwater and surface water samples, respectively, were detected. Atrazine was the most ubiquitous pesticide, following by metolachlor, acetochlor and glyphosate, with maximum concentrations of 28, 24, 77 and 111 µg/L, respectively. An ERA was performed by employing the risk quotient (*RQ*) method. Atrazine, azoxystrobin, pirimiphos-methyl, acetochlor and epoxiconazole posed a high and very high risk for aquatic organisms (*RQ* > 1) and glyphosate, metolachlor and 2,4-D exhibited negligible to medium risk. The herbicides were the major contributors to risk. This study is the first contribution on the presence and concentration of pesticides in surface and groundwater from agricultural areas of south Santa Fe province, north Pampas region, Argentina, and a starting point for pesticide ecological risk assessment.

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J. Vera-Candioti (✉) · I. R. Huerga · A. D. Malmantile  
Instituto Nacional de Tecnología Agropecuaria (INTA), Agencia de Extensión Rural Venado Tuerto, Venado Tuerto, Santa Fe, Argentina  
e-mail: josefinavc@hotmail.com

J. Vera-Candioti · P. I. Araujo  
Consejo Nacional de Investigaciones Científicas Y Técnicas (CONICET), Buenos Aires, Argentina

P. I. Araujo  
Instituto Nacional de Tecnología Agropecuaria (INTA), Estación Experimental Agropecuaria Pergamino, Buenos Aires, Argentina

D. E. Rojas · D. S. Cristos  
Instituto Nacional de Tecnología Agropecuaria (INTA), Instituto Tecnología de los Alimentos, Hurlingham (1686), Buenos Aires, Argentina

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## Introduction

Among the sustainable development goals approved by the UN for 2030 worldwide, there is a need to improve water quality by reducing pollution, protect and restore water-related ecosystems, including wetlands and aquifers, as well as to reduce the release of chemicals to air, water and soil in order

to minimize their adverse impacts on human health and the environment (United Nations, 2020). The presence of pesticides in surface and groundwater is well documented worldwide (Palma et al., 2004; Thodal et al., 2009; Fava et al., 2010; Ansara-Ross et al., 2012; Gonzalez et al., 2012; Palma et al., 2004; Papadakis et al., 2015; Teklu et al., 2015; Albuquerque et al., 2016; Ccancapa et al., 2016; Mekonen et al., 2016; Ronco et al., 2016; Khanna & Gupta, 2018; Daam et al., 2019). A number of authors have reported the presence of pesticides in surface water and groundwater of Argentina, primarily associated with agriculture activities in the nearby areas (Aparicio et al., 2013; Caprile et al., 2017; Castro Berman et al., 2018; De Gerónimo et al., 2014; Montoya et al., 2011; Pérez et al., 2017; Porfiri et al., 2018; Portocarrero et al., 2016; Sasal et al., 2017; Vazquez-Amabile et al., 2014). However, few researchers have investigated the impact of pesticides in water bodies from north of the Pampas region, southern Santa Fe province (Iturburu et al., 2019).

Ensuring the conservation, restoration and sustainable use of terrestrial and inland freshwater ecosystems and their services, in particular wetlands, constitutes a goal within the objectives of the Agenda for Sustainable Development by 2020 (United Nations, 2020). Legislation in the EU countries includes regulations and guidelines for the risk assessment on the three inland environmental compartments, i.e. aquatic environment, terrestrial environment and air (EC, 2003). The use of a site-specific ecological risk assessment (ERA) has been promoted and applied by the authorities in Australia and New Zealand (Daam and van den Brink, 2010). The USA has developed guidelines, handbooks, framework and general standard operating procedures in order to conduct ecological risk assessments (EPA, 2020). While in some parts of the world such as Europe, North America, Australia or New Zealand, a legal framework for pesticide environmental risk assessments exists, in Argentina, a national monitoring program of pesticides is lacking and studies about ecological risk assessment due to the presence of pesticides in aquatic environments are scarce (Bonansea et al., 2018; Iturburu et al., 2019; Peluso et al., 2014).

Pesticide ERA is expressed as a function of environmental exposure and ecotoxicological effects and is usually expressed as the ratio of the predicted environmental concentration (PEC) to predicted

no-effect concentration (PNEC) (Vryzas et al., 2009). PEC values are calculated using several models taking into consideration application rates, persistence, leaching, sorption and compound bioaccumulation or directly from monitoring data while PNEC consists of short-term toxicity data for algae, crustaceans and fish and applying an appropriate assessment factor (AF) when data set is limited (Backhaus & Faust, 2012). The Risk Quotient ( $RQ$ ) as  $PEC/PNEC$  has been used for ecotoxicological risk assessment of pesticides in various water bodies (Palma et al., 2004; Vryzas et al., 2009; Palma et al., 2014; Papadakis et al., 2015; Ccancapa et al., 2016; Bonansea et al., 2018; Iturburu et al., 2019).

Argentina is one of the world's largest exporters of corn, soybeans, wheat, barley and sorghum and the leading exporter of soybean oil and soybean meal worldwide (FAO, 2019). A major portion of this production is carried out in the Pampas region (BCR, 2019), one of the world's largest croplands and central agricultural area of Argentina (Pinto et al., 2017). Nowadays, agricultural activity has increased with the widespread use of no-till farming, agrochemicals and transgenic crops (Pinto et al., 2017).

The Pampas wetlands, particularly the lagoons, provide a diverse number of environmental services, among which the provision of water for productive, urban and industrial uses, fish for local consumption, vegetable raw materials for pastures and handicrafts and the availability of habitats for a wide number of mammals and birds (Benzaquén et al., 2017). The south of Santa Fe province, i.e. north of the Pampas region, is characterized by the presence of innumerable water bodies, and some of them are important concentration centres for migratory birds from the northern hemisphere and from Patagonia (Benzaquén et al., 2017; Biasatti et al., 2016; Burkart et al., 1999).

The first ecological risk assessment of pesticides in aquatic ecosystems relevant to the Pampas region that employed the  $RQ$  approach was recently presented (Iturburu et al., 2019). The authors highlight the contribution of different current use pesticides in risk for aquatic biota and present a risk map according to the  $RQ$  values from different sites. The results not only indicate that the north of the Pampas region presents the highest risk, but there is a notable lack of information in a large part of the pampas territory (Iturburu et al., 2019).

According to the above considerations, the aim of this study was to determine the levels of pesticides in surface and groundwater of agroecosystems from the south of Santa Fe province and to assess the ecological risk impact of the present pesticides to quantify their potential environmental effects.

## Materials and methods

### Study area

The study was conducted within a radius of 40 km around Venado Tuerto city, located in General López Department, south Santa Fe Province, Argentina (33° 45' 00" S 61° 58' 00" W). The area belongs to the Humid Pampas, a sub region of the "Argentine Pampas" ecoregion, characterized by an extensive system of fresh or brackish water lagoons, flat relief and reduced drainage (Burkart et al., 1999). Since runoff of surface water is carried out through a poorly developed hydrographic network with little slope, in wet periods, lagoons and baths are formed, and floods usually occur (Bilenca & Miñarro, 2004; Giraut et al., 2007). The deep, well-drained and fertile soils of the study area belong to the order of the Mollisols: in the north-east, Argiudols predominate with the development of silty loam textures and towards the south-west, and Hapludols predominate with the development of sandy loam textures (INTA, 2021). Something very common is the rapid infiltration of rainwater on relatively high surfaces, followed by subsurface flow to neighbouring depressions, where it occurs slowly the upwelling. Water moves slowly, and stagnation and drainage predominate over runoff (Iriondo, 2012).

The area is dominated by a humid temperate climate with a dry season. The annual mean temperature is 16.6 °C (10.2 °C min–23.1 °C max), and the annual rainfall is 1000 mm, with a large volume difference between the winter and summer rains (Martin, 2014). The dominant vegetation is the steppe or pseudosteppe, combined with prairie and scrubland. In the pseudosteppe of mesophytes, abound species such as *Poa ligularis*, *Nassella tenuissima* and *Hypochaeris pampasica*, among others. The halophyte steppe in flat and low areas near lentic environments includes

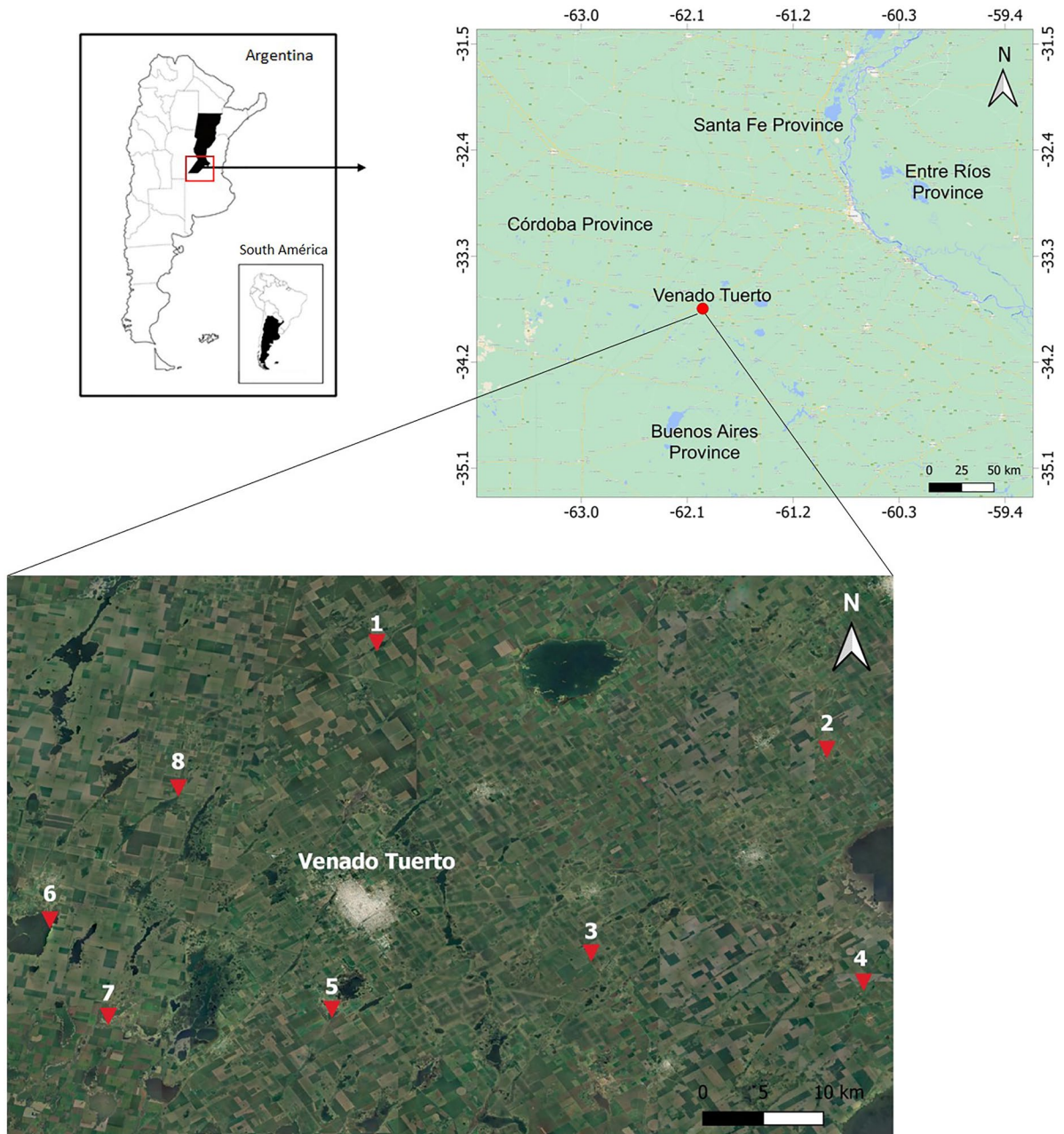
species such as *Leptochloa fusca*, *Juncus acutus* and *Lepidium spicatum*, among others (Oyarzabal et al., 2018). Pampas agriculture is characterized by simplified production schemes with a predominance of spring–summer crops, mainly soybeans and secondarily corn, under no-tillage (NT) with high dependence on broad-spectrum herbicides (Viglizzo et al., 2010). Soybean, corn and wheat are the main crops grown in the region, accounting for about 60, 20 and 10% of the estimated gross production, respectively (BCR, 2019).

### Sampling sites

Eight agriculture sites were studied (Fig. 1). Each one included grain production as the chief activity, being maize, soybean and wheat the main crops; a drilling for groundwater extraction on the edge of the agricultural plot and a water body close to. At the groundwater extraction point, there is a PVC tube 5 cm wide and 4 m deep flush with the floor. Underground water seeps into the tube through many 1-mm slots along the entire wall. The distance between the two furthest and nearest sites was 67 km and 10 km, respectively.

### Water sampling

Pesticides were evaluated during seven sampling campaigns, performed from November 2016 to May 2018, according to seasons: spring (November 21–23th 2016, November 28–29, 2017), summer (February 20–21, 2017, February 15–16, 2018), fall (June 6–7, 2017, May 16–17, 2018) and winter (September 14–15, 2017). During the study period, 103 water samples were collected. Surface water samples were collected in 250-mL plastic bottles at a depth of about 60 cm within the lagoon. Before that, each bottle was washed three times. The transport to the laboratory was carried out taking care that the samples remain below 5 °C and, once there, they were stored at –20 °C until analysis. Groundwater samples were collected manually from the groundwater extraction point through a container adapted for this purpose and stored in 250-mL plastic bottles, after the triple wash, transported and stored in the same way as the surface water samples.



**Fig. 1** Map of the study area showing the agriculture sites (red triangles)

Environmental variables were registered in situ at each sampling date: water temperature with a digital thermometer (°C), pH with a portable pH meter (ALTRONIX TPA-V) and dissolved oxygen concentration (DO), with a portable oximeter (LUTRON). Groundwater table depth was measured with a metric rope.

#### Pesticide residues analysis in water

All pesticides determinations were conducted in the Center of Agroindustrial Investigation (CIA), National Institute of Agricultural Technology (INTA), Hurlingham, Buenos Aires, Argentina.

Water samples were maintained under 5 °C until pesticide analysis. In the laboratory, pesticide residue determination was conducted by solid phase extraction (SPE) using Oasis HLB cartridges (3 cc, 60 mg) following outlines described in EPA method 3535A (EPA, 2007). A direct method was applied to study glyphosate and AMPA (aminomethylphosphonic acid) in water samples (QuPPE-Method 1.3 “Glyphosate and Co. Hypercarb” from EU). The methods applied in this study were previously validated following guidelines established in EU-SANTE Guide 2017 (EC, 2017).

A 200-mL sample portion is centrifuged to remove suspended solids. It is passed through an Oasis HLB cartridge, previously conditioned with 3 mL methanol and 3 mL deionized water. It is then eluted with 2 mL of acetonitrile/methanol. Next, the elution was evaporated (45 °C) and reconstituted with 0.5 mL acetonitrile.

Direct residue determination of glyphosate and AMPA was performed on 0.3 mL sample previously homogenized and centrifuged, with the addition of 0.1 mL methanol containing 1% formic acid.

The extracts obtained were analysed for pesticide residues (Table 1 SI) with gas chromatography-mass spectrometry (GC-MS) (Perkin Elmer Clarus 600) and liquid chromatography-mass spectrometry (LC-MS) (Waters Acquity UPLC-SQD) as described below:

Liquid chromatography analyses were performed using a Waters Acquity ultra performance liquid chromatography (UPLC) apparatus equipped with a single quadrupole mass detector. The ODS column XBridge BEH 2.5  $\mu\text{m}$  2.1  $\times$  150 mm was used. The mobile phase used was 0.1% acetic acid in water and 0.1% acetic acid in methanol at the following gradient: initial condition during 2 min was (95:5), (95:5)–(80:20) 2–8 min, (80:20)–(20:80) 8–10 min, (20:80)–(0:100) 10–15 min, (0:100)–(0:100) 15–17 min, (0:100)–(95:5) 17–18 min and (95:5) 18–23 min. The selected ion monitoring mode was used in quantification analysis. The mass-spectrometer acquisition settings were ESI negative or positive (see Table 1 SI), and retention time and abundance of the confirmation ion (Ion C) relative to that of quantification ion (Ion Q) were used as identification criteria.

Gas chromatography analyses were performed using a Perkin Elmer Clarus 600 gas chromatograph

equipped with a single quadrupole mass detector. Sample volumes of 2.0  $\mu\text{l}$  were injected into the programmable split/splitless injector, in splitless mode with the split outlet opened after 1.5 min with injector port temperature at 290 °C. The capillary column used was DB-5MS (30 m 0.25  $\mu\text{m}$  I.D.; 0.25 mm film thickness) (Agilent Technologies). The helium carrier gas was programmed with a constant flow of 1 ml/min. The oven temperature program was initially set at 80 °C with 5 min hold and ramped (80–178) °C at 25 °C/min, (178–205) °C at 2 °C/min, (205–300) °C at 30 °C/min with a hold of 5 min. The selected ion monitoring mode was used for quantification analysis. The mass-spectrometer acquisition settings were electron impact ionization 70 eV; retention time and abundance of the confirmation ion (Ion C) relative to that of quantification ion (Ion Q) were used as identification criteria. In all cases, the limit of detection (LOD) was 1  $\mu\text{g/L}$ , and the limit of quantification (LOQ) was 4  $\mu\text{g/L}$ .

A method without derivatization was used for glyphosate and AMPA based on the QuPPE-Method 1.3 “Glyphosate & Co. Hypercarb” from EU. Determination was done by LC-MS with a Hypercarb column 100  $\times$  2.1 mm, 3  $\mu\text{m}$  (Thermo-Fisher), and the injection volume was 10  $\mu\text{L}$ . The mobile phase used was 0.1% acetic acid in water and 0.1% acetic acid in methanol at the following gradient: initial condition during the first minute was (90:10), (90:10)–(50:50) 1–4 min, (50:50)–(0:100) 4–5 min, (0:100)–(0:100) 5–6 min, (0:100)–(90:10) 6–7 min, (90:10)–(90:10) 7–11 min. The LOD for this technique was 0.2  $\mu\text{g/L}$  while the LOQ was < 0.6  $\mu\text{g/L}$ .

The selectivity of each method applied was evaluated obtaining no interferences during the analysis of an un-spiked water sample from the laboratory. The linearity was evaluated for each compound analysed as the correlation coefficients (*R*) obtained from the constructed calibration curves during this study. Recovery study was conducted to evaluate accuracy as recovery (*R* %) and precision as relative standard deviation (RSD%). Six recovery studies were carried out with blank water samples from the laboratory (spiked at 10  $\mu\text{g/L}$ ). The LOQ was established as the lowest concentration level of the matrix-matched calibration curve, because it meets the reproducibility criterion (EC, 2017) and has a signal-noise ratio greater than 10.

**Table 1** Statistical summary of different parameters of (a) groundwater and (b) surface water from November 2016 to May 2018 in the Pampas Region

	(a)					(b)				
	Sampling dates					Sampling dates				
	Nov	Feb	Jun	Sep	May	Nov	Feb	Jun	Sep	May
Temperature (°C) ( <i>n</i> =49)	Mean	17.28	23.32	16.57	15.71	18.65	21.54	19.18	16.03	24.28
	Min	16.70	21.40	15.50	14.30	15.20	19.30	18.10	11.20	20.00
	Max	18.00	25.00	18.10	16.60	20.50	24.30	20.00	21.00	28.70
	Std	0.67	1.48	0.80	0.77	1.67	1.82	0.59	3.72	5.45
pH ( <i>n</i> =49)	Mean	7.74	7.61	7.69	7.44	7.55	7.49	7.53	8.75	9.52
	Min	7.37	7.04	6.91	6.12	6.85	7.12	7.12	7.99	9.05
	Max	8.26	8.66	8.82	9.05	8.50	8.08	8.00	9.77	10.32
Table depth (cm) ( <i>n</i> =50)	Mean	214	188	156	149	188	275	229	9.79	8.79
	Min	150	140	130	70	80	170	120	4.06	3.26
	Max	250	230	200	210	245	330	290	17.18	11.84
	Std	41.59	31.89	24.40	49.12	61.05	47.28	53.86	4.29	3.79

(*n*=*x*): total samples during the monitoring study.  
 DO dissolved oxygen.

As mention above, selectivity, linearity, accuracy, precision, uncertainty and sensibility were studied in the laboratory for the validation of the methods, applying satisfactorily the criteria established in EU-SANTE Guide 2017 (EC, 2017). Table 1 SI summarizes the results of the methods performance for each compound analysed.

To determine the concentrations of pesticide residues, matrix-matched calibration curves were constructed for all analyses in the range of 4 to 200 µg/L (for glyphosate and AMPA 0.6 to 100 µg/mL). The calibration curves were processed together with the samples to ensure the correct performance of the analysts and the chromatographs. Concentrations were calculated by interpolation.

### Risk assessment

Risk assessment was performed based on the use of the risk quotient ( $RQ$ ) index. Instead of the PEC values derived from the application of exposure models, concentrations obtained from the monitoring data were used as the measured environmental concentration (MEC) (Bonansea et al., 2018; Thomatou et al., 2013; Vryzas et al., 2009).  $RQ$  was calculated as MEC divided by PNEC ( $RQ = MEC/PNEC$ ) (Iturburu et al., 2019; Thomatou et al., 2013). MEC was the measured environmental concentration of a pesticide in surface water above the LOQ. PNEC was calculated according to the critical concentration (CC) and an assessment factor (AF) ( $PNEC = CC/AF$ ). CCs for water were set as the lowest concentration among no observed effect concentrations (NOECs) for chronic endpoints for fish, aquatic invertebrate and algal species (growth for fish and algae, reproduction for invertebrates). In case of absence of NOEC for all these taxa, the lowest value of L(E)C50 was employed. In case of absence of data for previously mentioned species, data of the same group of organisms reported in the Pesticide Properties Database (PPDB, Lewis et al., 2016) were employed. AF was 10 when three NOECs were available, 50 when there were two NOECs available, 100 when there was only one NOEC value (for fish or invertebrate) and 1000 when there was no NOEC values, and an L(E)C50 was employed (Iturburu et al., 2019; Papadakis et al., 2015).  $RQ$  values less than 1 indicates that the compound involved is less likely to pose a considerable risk to the environment (Iturburu et al., 2019;

Papadakis et al., 2015; Vryzas et al., 2009). The risk assessment of the water samples (mixture of  $n$  pesticides) was calculated as the sum of the risk quotient of each individual pesticide found to be present in the sample (Backhaus & Faust, 2012):

$$RQ_s = \sum_{i=1}^n RQ_i$$

The ecotoxicological data were obtained from the Pesticide Properties Database (PPDB) (Lewis et al., 2016).

## Results and discussion

### Water physicochemical variables

The descriptive statistics of sampling data for groundwater (GW) and surface water (SW) are summarized in Table 1. Water table level showed significant variations among seasons with maximum values on summer period (February 2018). Average water level varied from 149 cm in winter (September) to 275 cm in summer with a maximum value of 330 cm (February 2018). High table depth values observed in February and May 2018 coincided with a drought period all around the study area even throughout a large part of the province. In the centre-south of Santa Fe Province, rainfall deficits were highlighted with large negative anomalies below 50%, that is, January 2018 precipitation for south of Santa Fe was less than half the expected for that period (SMN, 2018).

### Detected compounds in groundwater and surface waters

During the study period (November 2016–May 2018), seven sampling campaigns were conducted at eight agricultural sites, and 103 water samples were collected, a lower number than expected, due to the drought occurred during part of the campaign, which prevented water sampling in some cases. Of the 83 analites evaluated (Table 1 SM), 20 pesticides and degradation products were detected (Table 2). Herbicides were the most frequently detected pesticides (75%), followed by the fungicides (15%) and the insecticides (10%).

Considering the 103 water samples analysed, 82% were contaminated with at least one pesticide. Only

**Table 2** Number of analysed samples (N); frequency of detection (FD; %), number of samples with concentration below the LOQ (<LOQ), number of samples above the LOQ (>LOQ), and maximum concentration above LOQ of pesticides in groundwater (a) and surface water (b) samples from 8 sampling stations during the study period (November 2016–May 2018)

		(a)				(b)						
Compounds	Total (N)	FD (%)	Samples		Compounds	Total (N)	FD (%)	Samples		Max (µg/L)	Max (µg/L)	
			<LOQ	>LOQ				<LOQ	>LOQ			
<i>Site 1</i>												
Atrazine	7	57	3	1	Acetochlor	7	14	0	1	5.2	6.8	
Azoxystrobin	7	14	1	–	Atrazine	7	43	2	1	8.1	6.5	
Epoxiconazole	7	14	–	1	Carbaryl	7	14	1	0	–	–	
Glyphosate	7	14	1	–	Epoxiconazole	7	14	0	1	7.8	144	
Metholachlor	7	57	2	2	Metholachlor	7	29	1	1	–	6.6	
Picoxystrobin	7	14	1	–	Pirimiphos-methyl	7	14	0	1	–	166.20	
<i>Site 2</i>												
2,4-D	7	14	–	1	Glyphosate	7	14	1	–	18.64	–	
Acetochlor	7	29	1	1	Atrazine	7	29	1	1	15.61	13.1	
Atrazine	7	71	4	1	Azoxystrobin	7	14	1	1	6.82	–	
Azoxystrobin	7	14	–	1	Metholachlor	7	43	3	–	5.28	–	
Glyphosate	7	14	–	1	<i>Site 3</i>						96.20	–
Metholachlor	7	29	2	–	2,4-D	7	14	1	–	–	–	
Pyraclostrobin	7	14	1	–	Glyphosate	7	14	–	1	–	7.40	
Trifloxystrobin	7	14	1	–	AMPA	7	29	2	–	–	–	
<i>Site 3</i>												
Acetochlor	7	29	1	1	Acetochlor	7	29	1	1	5.50	64.6	
AMPA	7	14	1	–	Atrazine	7	29	–	2	–	6.6	
Atrazine	7	43	3	–	Metholachlor	7	14	–	1	–	4.6	
Chlorpyrifos methyl	7	14	–	1	Picoxystrobin	7	14	1	–	–	–	
Glyphosate	7	14	–	1	Pyraclostrobin	7	14	1	–	105.23	–	
Metholachlor	7	14	–	1	Pirimiphos-methyl	7	29	1	1	7.27	194.65	
Pirimiphos-methyl	7	14	–	1	Trifloxystrobin	7	14	1	–	11.2	–	
<i>Site 4</i>												
Acetochlor	6	17	0	1	AMPA	7	14	1	–	–	–	
AMPA	6	33	1	1	Acetochlor	7	29	1	1	7.7	39.9	
					Atrazine	7	14	1	–	233	–	



Table 2 (continued)

		(a)				(b)					
Compounds	Total (N)	FD (%)	Samples		Compounds	Total (N)	FD (%)	Samples		Max (µg/L)	Max (µg/L)
			<LOQ	>LOQ				<LOQ	>LOQ		
Atrazine	6	67	1	3	Azoxystrobin	7	29	2	-	15.98	
Azoxystrobin	6	33	0	2	Metholachlor	7	29	1	1	10.9	6.7
Glyphosate	6	50	2	1	Picoxystrobin	7	29	2	-	111	
Metholachlor	6	33	2	0	<i>Site 5</i>						
					2,4-D	7	29	1	1		4.3
Acetochlor	7	29	1	1	Glyphosate	7	29	-	2	56.5	35.17
AMPA	7	43	2	1	AMPA	7	29	2	-	15.93	
Atrazine	7	43	1	2	Acetochlor	7	14	-	1	17.12	5.9
Azoxystrobin	7	14	1	-	Atrazine	7	57	2	2		28.0
Dicamba	7	14	1	-	Bifenthrine	7	14	1	-		
Glyphosate	7	43	2	1	Metaxyl	7	14	1	-		
Imidacloprid	7	14	1	-	Metholachlor	7	43	3	-		
Lambda-cyhalothrin	7	14	-	1	Pirimiphos-methyl	7	14	1	-		
Metholachlor	7	14	-	1	<i>Site 6</i>						
Pirimiphos-methyl	7	14	1	-	Glyphosate	7	14	1	-		
					Acetochlor	7	29	-	2		77.0
					Atrazine	7	29	2	-		
2,4-D	7	14	1	-	Epoxiconazole	7	14	-	1		5.7
AMPA	7	14	1	-	Metholachlor	7	29	2	-		
Atrazine	7	29	-	2	Pirimiphos-methyl	7	14	-	1		6.2
Glyphosate	7	29	1	1	Trifloxystrobin	7	14	1	-		
Metaxyl	7	14	1	-	<i>Site 7</i>						
Metholachlor	7	14	1	-	Glyphosate	7	29	1	1		14.6
Pirimiphos-methyl	7	14	1	-	AMPA	7	43	2	1		2.3
					Acetochlor	7	14	1	-		
					Atrazine	7	29	1	1		6.0
Acetochlor	5	20	-	1	Azoxystrobin	7	14	-	1		
AMPA	5	20	-	1							
Atrazine	5	40	2	-							

Table 2 (continued)

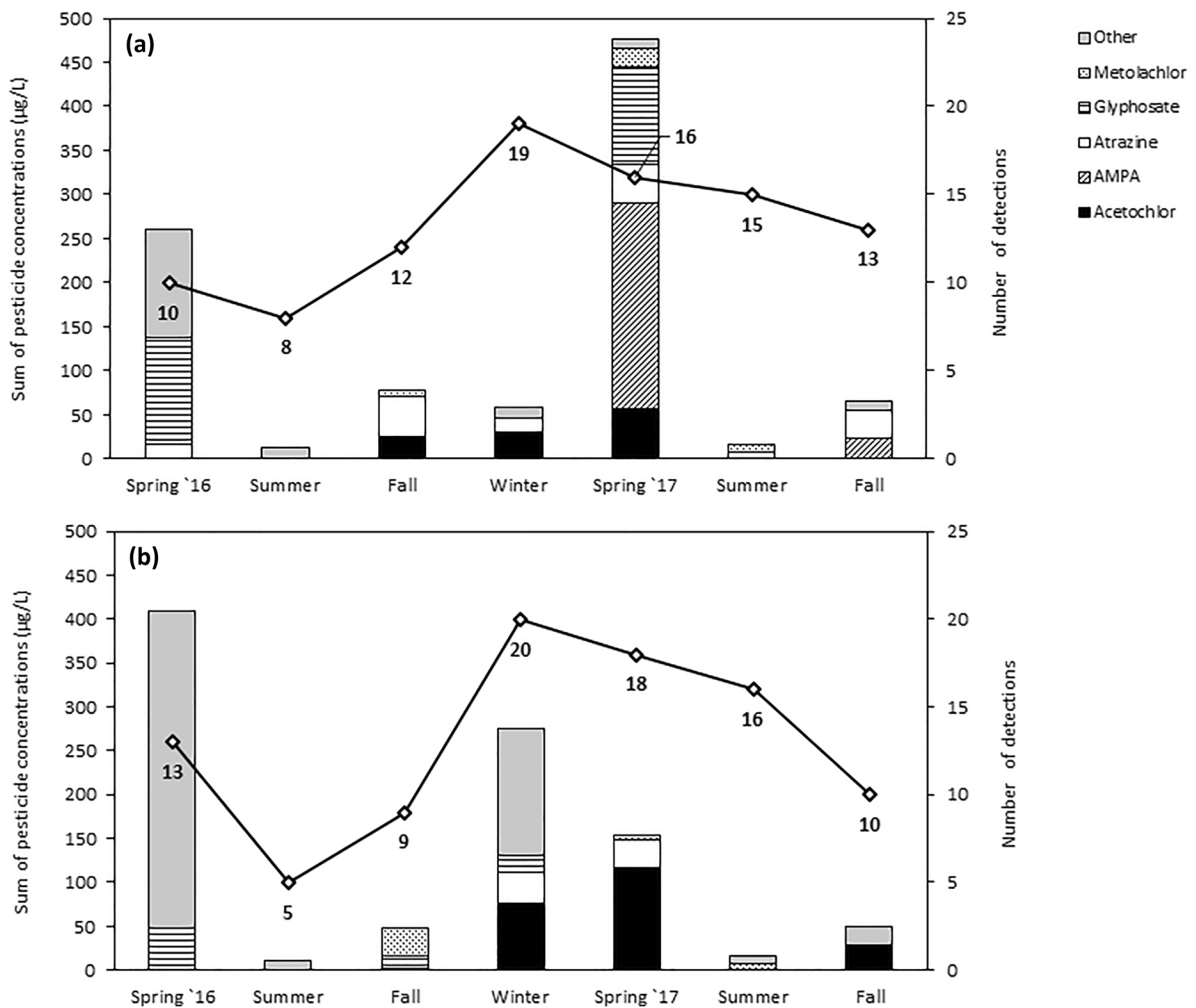
Compounds	Total (N)	FD (%)	Samples		Max ( $\mu\text{g/L}$ )	Compounds	Total (N)	FD (%)	Samples		Max ( $\mu\text{g/L}$ )
			<LOQ	>LOQ					<LOQ	>LOQ	
Glyphosate	5	40	2	-		Chlorpyrifos ethyl	7	29	1	1	4.1
Metholachlor Site 8	5	40	1	1	4.1	Imidacloprid	7	14	1	-	
Acetochlor	4	50	1	1	15.4	Metholachlor	7	71	4	1	24.0
Atrazine	4	75	-	3	18.2	Site 8					
Azoxystrobin	4	25	1	-		Acetochlor	4	50	1	1	15.9
Dicamba	4	25	1	-		Atrazine	4	50	2	-	
Metalaxyl	4	25	1	-		Metalaxyl	4	25	1	-	
Metholachlor	4	25	1	-		Metholachlor	4	50	2	-	

eight pesticides (40%) were detected in concentrations that did not exceed the respective LOQ: bifenthrin, carbaryl, dicamba, imidacloprid, metalaxyl, picoxystrobin, pyraclostrobin and trifloxystrobin. On the other hand, the insecticides chlorpyrifos-methyl and lambda-cyhalotrin were recorded in concentrations above the LOQ, but only once during the entire study. Compounds with a low detection frequency were 2,4-D, azoxystrobin, chlorpyrifos-ethyl, epoxiconazole and pirimiphos-methyl, with five, ten, two, three and eight positive detections, respectively. Finally, the five most detected compounds were acetochlor, atrazine, glyphosate and its metabolite AMPA and metholachlor.

Seasonal variation of the sum of pesticide concentrations in all sampling sites is shown in Fig. 2. The highest sum concentration levels of total pesticides were detected on November 2016, spring season. Taking into account the total positive detections for groundwater and surface water by sampling date, that is, concentrations either above or below its LOQ, September 2017, winter time, was the most relevant period with 39 positive detections (Fig. 2).

Atrazine was the most ubiquitous contaminant, and it was present in all sampling sites (Table 2). This herbicide is widely used for pre- and post-emergence control of annual broad-leaved weeds, mainly in corn crops. It has selective, systemic action with residual and foliar activity. It was detected in 43% of the analysed samples (103) and in over 50% of the positive samples (84). Detection frequency was higher in groundwater than in surface water, with 26 positive samples registered. The highest occurrence of this herbicide in groundwater was detected at site 8 (75% of the samples), and the maximum value was 22.8  $\mu\text{g/L}$  at site 6. The highest occurrence of atrazine in surface water was detected on September at site 5 (71% of the samples), with the maximum residue level registered (28.0  $\mu\text{g/L}$ ) of the entire study (Table 3).

In the period between September and November, corn production predominates in the region, a crop closely associated with the use of atrazine. Atrazine can remain in the surface layer of the soil or transported to deeper layers, among other factors, due to soil moisture, crop phenology, time of application and rain events since its application (Candela, 2016; Caprile et al., 2017). It has a low aqueous solubility, it is volatile and, based on its physicochemical



**Fig. 2** Seasonal variation of the sum of pesticide concentrations and total positive detections in all sampling sites in **a** groundwater and **b** surface water from the Pampas Region

properties such as its high leaching potential (GUS index: 3.2), there is some concern that it could leach to groundwater. During August and September 2017, precipitation values exceeded the monthly average recorded during the same months for 8 years (from 2006 to 2014) (Martin, 2014), and considering the cumulative rainfall in August, September and October, values above 150 mm were recorded. Atrazine was frequently detected on November 2017 (spring time), with 12 positive samples, probably due to, among other factors, rain events and runoff effects, as well as the number of applications in that period.

Concentrations of atrazine found in this study are within the highest values reported so far in

Argentina. Our values are greater than those reported in surface water for agricultural basins in other regions of the country (Bonansea et al., 2013; De Gerónimo et al., 2014; Portocarrero et al., 2016; Regaldo et al., 2018), and greater than those reported for groundwater in different rural areas (Avila-Vazquez et al., 2017; Etchegoyen et al., 2015; Porfiri et al., 2018; Portocarrero et al., 2016; Vazquez-Amabile et al., 2014). On the other hand, our values did not exceed the maximum value registered in La Pampa Province (Montoya et al., 2011).

Metolachlor was the second most detected compound (Table 3). From the total analysed samples, 33% contained metolachlor, and only among the

**Table 3** Concentrations of the most frequently detected compounds in groundwater (GW) and surface water (SW), for each sampling date and each sampling site from the Pampas Region

Sampling date	Compound	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6		Site 7		Site 8		
		GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	
November 2016	Acetochlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Atrazine	-	-	-	-	-	-	-	-	17.12	5.71	-	-	-	-	-	-	
	Metolachlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Glyphosate	-	-	<LOQ	7.40	7.27	7.40	-	-	-	11.86	35.17	4.54	-	-	<LOQ	-	-
	AMPA	-	-	-	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	-	-	<LOQ	-	-
February 2017	Acetochlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Atrazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Metolachlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Glyphosate	-	-	-	-	-	-	<LOQ	-	-	<LOQ	-	-	<LOQ	-	-	-	
	AMPA	-	-	-	-	-	-	<LOQ	-	-	<LOQ	-	-	-	-	-	-	
June 2017	Acetochlor	-	-	-	-	5.5	7.7	7.7	-	-	-	-	-	12.78	-	-	-	
	Atrazine	<LOQ	-	6.82	-	<LOQ	15.09	15.09	-	<LOQ	-	22.81	-	-	<LOQ	-	-	
	Metolachlor	7.8	-	-	-	-	-	6.7	-	-	-	-	-	-	24.0	-	-	
	Glyphosate	-	-	-	-	-	-	-	-	-	-	-	-	-	14.6	-	-	
	AMPA	-	-	-	-	-	<LOQ	-	-	-	-	-	-	-	2.3	-	-	
September 2017	Acetochlor	-	-	15.61	-	-	<LOQ	<LOQ	-	-	-	-	77.0	-	15.4	-	-	
	Atrazine	5.21	<LOQ	<LOQ	<LOQ	<LOQ	6.0	-	-	-	28.0	-	<LOQ	-	9.74	-	-	
	Metolachlor	<LOQ	-	-	<LOQ	-	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
	Glyphosate	-	-	-	-	-	-	-	-	<LOQ	20.5	-	-	-	-	-	-	
	AMPA	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	<LOQ	-	-	
November 2017	Acetochlor	-	-	-	-	-	64.6	-	39.9	56.50	-	-	11.9	-	-	-	-	
	Atrazine	<LOQ	6.5	<LOQ	13.1	-	6.6	13.66	<LOQ	13.12	-	-	<LOQ	6.0	18.17	<LOQ	<LOQ	
	Metolachlor	5.0	<LOQ	<LOQ	<LOQ	11.2	4.6	<LOQ	-	<LOQ	-	<LOQ	4.1	<LOQ	-	-	-	
	Glyphosate	-	-	-	-	-	111	-	-	-	-	-	-	-	-	-	-	
	AMPA	-	-	-	-	-	233	-	-	-	-	-	-	-	-	-	-	
February 2018	Acetochlor	-	-	<LOQ	-	-	-	-	-	<LOQ	-	-	-	<LOQ	-	<LOQ	<LOQ	

Table 3 (continued)

Sampling date	Compound	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6		Site 7		Site 8		
		GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW	
May 2018	Atrazine	<LOQ	<LOQ	<LOQ	-	-	-	<LOQ	-	<LOQ	-	<LOQ	7.87	<LOQ	<LOQ	-	-	<LOQ
	Metolachlor	<LOQ	6.6	<LOQ	-	-	-	-	-	9.4	<LOQ	-	-	<LOQ	<LOQ	<LOQ	-	<LOQ
	Glyphosate	-	-	-	-	-	-	-	-	-	-	<LOQ	-	<LOQ	-	-	-	-
	AMPA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Acetochlor	-	6.8	-	-	<LOQ	-	-	<LOQ	-	5.9	-	-	-	-	-	<LOQ	15.9
	Atrazine	-	-	<LOQ	-	<LOQ	-	15.98	-	-	<LOQ	-	-	-	-	-	15.24	-
	Metolachlor	-	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-
	Glyphosate	<LOQ	-	-	-	-	-	<LOQ	-	-	-	-	-	-	<LOQ	-	-	-
	AMPA	-	-	-	-	-	-	-	-	15.92	-	-	-	-	-	7.67	-	-

positive samples, 40% contained the herbicide. It was present at the eight sampling sites with the highest occurrence at site 7 (71% of the samples), with the maximum residue level registered (24 µg/L) of all the study. Metolachlor was more frequently detected in surface water and at levels below the LOQ. The herbicide was detected with similar frequency on both, September and November 2017 (29 and 32% of the samples, respectively). All samples registered on September were below the LOQ, while on November, only 36% of samples were above the LOQ, with a maximum concentration of 11.2 µg/L. Concentrations for groundwater were considerably lower than values reported before in our country (Costa et al., 2011), and values registered for surface water were higher than concentrations reported before for Pampas region (Pérez et al., 2017).

Acetochlor was registered in 25% of the positive samples (Table 3). Acetochlor concentrations in groundwater reached levels from 5.5 to 56.5 µg/L, while concentrations in surface water reached levels from 5.9 to 77.0 µg/L. Levels of acetochlor detected in surface water in this study are within the highest values reported so far in Argentina (Bonansea et al., 2013; De Gerónimo et al., 2014; Pérez et al., 2017; Vazquez-Amabile et al., 2014). On the contrary, values reported for groundwater are within the range concentrations registered for other agricultural areas (Costa et al., 2011; Vazquez-Amabile et al., 2014). Finally, acetochlor found could correspond to past and not recent applications, as only one application of the herbicide has been made in a single site, throughout the study. Actually, according to previous studies, acetochlor was detected in water drainage up to 9 years after the last application (Caprile et al., 2017).

The presence of these herbicides in groundwater reinforces the idea that they can leach through the soil profile, in this case, at a depth of 330 cm, representing a real risk of groundwater contamination in agreement with previous studies (Costa et al., 2011; Bedmar et al., 2013; 2017). In recent years, the appearance of glyphosate-resistant weeds in the Pampas region caused an increase in the use of products with active ingredients other than glyphosate (CASAFE, 2016). At a national level, acetochlor, atrazine and metolachlor were the most widely used pesticides among herbicides (CASAFE, 2016), so this could explain the high frequency of detection of these products in this study. In fact, the sum of all positive

samples of all three herbicides represented 54% of the total of positive samples.

Levels of glyphosate and its metabolite AMPA were measured in groundwater and surface water from eight agricultural sites (Table 3). From all the analysed samples, 24% contained glyphosate, AMPA, or both compounds. Glyphosate was detected in all sampled periods with a greater frequency on November 2016 (spring season), and it was present in seven studied sites, with a higher detection frequency at site 5. The herbicide was registered with a greater detection frequency and higher concentration levels in groundwater than in surface water. AMPA was observed in 16% of the analysed samples. It was detected on six sampling dates, with a greater frequency in November 2016. It was observed in five sampling sites and with similar frequency in surface and groundwater samples. AMPA was more frequently detected in concentrations below the LOQ than in concentrations over the LOQ.

Glyphosate (96.2 µg/L) and AMPA concentrations (15.9 µg/L) recorded in groundwater from site 2 and site 5, respectively, were higher than those recorded in Argentina and other countries worldwide (Avila-Vazquez et al., 2017; Etchegoyen et al., 2015; Montoya et al., 2011; Okada et al., 2018; Primost et al., 2017; Vazquez-Amabile et al., 2014). It is worth mentioning that glyphosate and AMPA were detected at maximum levels of 111 and 233 µg/L, respectively, in the same groundwater sample on November 2017 at site 4. The occurrence of these compounds in 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). The morphological, geological and edaphological characteristics of the Pampean Region, with its incipient water drainage networks, and the humid climate favour infiltration and deep drainage, mainly in autumn and spring when the water balance is positive (Caprile et al., 2017). The levels of glyphosate and AMPA found in the groundwater at site 4 are well above the range of other studies worldwide (Okada et al., 2018), and on the other hand, it is the only record of these two compounds, in the entire study area on that sampling date (November 2017). Considering that groundwater extraction point was located at the edge of the crop field, next to the inlet and outlet area of the spraying machine, and that no extreme precipitation event was recorded

before the sampling date (62 mm in 2 months), the high levels detected could be attributed to point source contamination. Glyphosate may reach the environment by direct human action, such as accidental spillage due to equipment calibration prior to application, discarding of empty containers with herbicide residues or disposal of herbicide residues from the spray machine after application (Bonansea et al., 2018; Palma et al., 2014; Vryzas et al., 2009).

The results showed that maximum value observed for glyphosate in surface water (35.17 µg/L) is within the range concentrations registered for other aquatic environments associated to agricultural fields in Argentina (Aparicio et al., 2013; Bonansea et al., 2018; Castro Berman et al., 2018; Etchegoyen et al., 2015; Lupi et al., 2015; Okada et al., 2018; Peruzzo et al., 2008; Ronco et al., 2016; Vazquez-Amabile et al., 2014). None of the registered concentrations of glyphosate exceeded the maximum acceptable value (240 µg/L), corresponding to protection of aquatic biota according to the Argentine legislation (SRHN, 2003). AMPA was detected in surface water ranging from <LOQ to 2.3 µg/L. Similar concentrations were found in other agricultural areas of Argentina (Aparicio et al., 2013; Lupi et al., 2015; Ronco et al., 2016; Bonansea et al., 2018; Castro Berman et al., 2018). Glyphosate can directly reach water bodies by spray drift during application or it can be easily washed from stubble and then transported by surface runoff after heavy rainfall (Aparicio et al., 2013; Vazquez-Amabile et al., 2014; Castro Berman et al., 2018; Okada et al., 2018). Considering that AMPA is the main degradation product of glyphosate, the percentage of AMPA to the total herbicide concentration has been proposed to provide clues on the fate and transport of the herbicide (Coupe et al., 2012). Regarding groundwater samples, seven samples had detectable levels of both, glyphosate and AMPA; one sample had AMPA but no levels of glyphosate, while six samples had glyphosate but no detectable AMPA. Regarding surface water samples, five of them had detectable levels of both compounds; three samples had AMPA but no levels of glyphosate, while two samples had glyphosate but no detectable AMPA. Although the detection of glyphosate and AMPA in surface waters is often concomitant, we did not find a significant relationship between both compounds, in agreement with a previous report (Okada et al., 2018), as they were found together in the same sample, as well as each one

separately. 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). The likelihood of detecting the herbicide and its metabolite can vary widely from site to site and over time, depending on the application rates and the rain events, among other factors (Castro Berman et al., 2018; Peruzzo et al., 2008; Sasal et al., 2010). The major amount of positive glyphosate detections was observed in November 2016, with 40% of the samples of the whole study, in coincidence with the period of greatest amount of applications in the field. The reduction in positive detections, from the second sampling period onwards could be explained mainly by a reduction in the use of the herbicide and the application instead of the products mentioned above such as atrazine and metolachlor.

Pirimiphos-methyl appeared in 8% of the samples analysed and in four of the eight sites. Although it was recorded only twice in November 2016, those levels were very high and occurred in surface water. Pirimiphos-methyl is a broad-spectrum insecticide for the treatment of stored grains of wheat and corn. It can be applied directly to the grain, in facilities such as grain bins and ship holds, and in means of transporting grain as ships, trucks and trains. Although a maximum residue limit (MRL, the maximum concentration of residue of a legally permitted pesticide in agricultural products and sub-products) for pirimiphos-methyl in Argentina has been established, no reference values have been established for the protection of freshwater biota. On the second sampling date (February 2017), insecticide residues at three sites and in both compartments were found, i.e., at the

site where it was detected in groundwater, it was also detected in surface water. In this case, concentrations were below the LOQ (except one: 6.2 µg/L).

In respect of fungicides, metalaxyl, picoxystrobin, pyraclostrobin and tryfloxystrobin were registered in two to four samples and all of them below the LOQ. Meanwhile, azoxystrobin and epoxiconazole were detected at levels that exceed the LOQ but in a very low detection frequency. Data for azoxystrobin and epoxiconazole in surface and groundwater in Argentina is scarce. They were detected in network water samples on trace levels as well as in surface water in agricultural areas at levels below 1 µg/L De Gerónimo et al., 2014; Etchegoyen et al., 2015; Avila-Vazquez et al., 2017; Pérez et al., 2017; Corcoran et al., 2020.

**Risk assessment**

To assess the real impact of pesticides in freshwater ecosystems, both concentrations and harmful effects on aquatic organisms must to be jointly considered. This is very important because some pesticides may be present in surface water at low concentrations but are still sufficient to cause deleterious effects in certain species because of their high toxicity (Palma et al., 2014).

The PNEC values and the *RQs* corresponding to the maximum concentrations for every pesticide detected above the respective LOQ in the surface waters are presented in Table 4. From the 18 compounds registered in surface water, 5 showed *RQs* higher than 1. According to the literature’s reported levels of concern (i.e.  $RQ \geq 10$ , very high risk (Iturburu et al.,

**Table 4** Ecotoxicity endpoints for fish, aquatic invertebrates and algae and related PNEC values (µg/L) for pesticides detected above their respective LOQ in agroecosystems from Pampas Region

Pesticides	Fish	Aquatic invertebrates	Algae	Critical concentration	Assessment factor	PNEC	<i>RQ</i> <sub>max</sub>
2,4-D	27,200	46,200	100,000	NOEC: 27,200	10	2720	0.002
Acetochlor	130	22	0.59	NOEC: 0.59	10	0.059	1305.75
Atrazine	2000	250	100	NOEC: 100	10	10	2.80
Azoxystrobin	147	44	800	NOEC: 44	10	4.4	4.86
Epoxiconazole	10	630	7.8	NOEC: 7.8	10	0.78	184.65
Glyphosate	1000	12,500	2000	NOEC: 1000	10	100	0.35
Metolachlor	1000	707	3000	EC50: 707	10	70.7	0.34
Pirimiphos-methyl	23	0.08	1000 (EC <sub>50</sub> )	NOEC: 0.08	50	0.0016	121,656.25

2019);  $RQ \geq 1$ , high risk;  $0.1 \leq RQ < 1$ , medium risk;  $0.01 \leq RQ < 0.1$ , low risk (Sánchez-Bayo et al., 2002)), pirimiphos-methyl, acetochlor and epoxiconazole were found at levels that represented a very high risk for aquatic organisms ( $RQ$  values  $> 10$ ). In the case of pirimiphos-methyl, the three times it was detected in surface water above the LOQ, the three times it exhibited a very high risk, being the highest values from the entire study (November 2016 and February 2017). Acetochlor revealed non-acceptable risk in 7 cases between September 2017 and May 2018 within the range values for  $RQ$  from 100 to 1306, being the major contributor to the environmental risk in terms of the amount of samples in which it was present showing a very high aquatic risk. In Argentina, there is no guideline level of water quality for the herbicide acetochlor. However, all concentrations found in surface water above the LOQ represented an ecological risk. These results support previous studies that showed that acetochlor represents a high environmental risk due to its great potential for groundwater contamination and a high risk for the aquatic biota (Arregui et al., 2010; Gaona et al., 2019; Iturburu et al., 2019). In respect of epoxiconazole, it appeared twice in surface waters, and both times had  $RQ > 1$ . The other fungicide detected, azoxystrobin, was found once in surface water over the LOQ at levels that pose a high risk to aquatic life ( $RQ > 1$ ). The occurrence of fungicides in Argentinian streams has seldom been studied (Pérez et al., 2017), but the environmental concentrations measured in this study demonstrate that they effectively represent a risk to aquatic life.

Atrazine exhibited medium to high risk in five and two samples, respectively. Argentina establishes the environmental water quality guide level for protection of aquatic biota corresponding to atrazine in  $\leq 3 \mu\text{g/L}$ . Although atrazine showed only two  $RQ$  values above 1, all concentrations quantified (LOQ =  $4 \mu\text{g/L}$ ) in surface water exceeded this water quality guide level. Consequently, our results indicate, in one way or another, that there is a risk to aquatic organisms associated with the presence of atrazine in water.

The other pesticides exhibited low to medium risk (glyphosate and metolachlor) and negligible risk (2,4-D). The levels of glyphosate found in this study did not surpass the Argentinean environmental water quality guidelines for the protection of the aquatic biota in freshwaters established in  $240 \mu\text{g/L}$  (SRHN, 2016). Nevertheless, given the  $RQ$  values obtained

( $0.01 < RQ < 1$ ), the presence of glyphosate in water meant a risk for the aquatic organisms in few cases, mainly for fish, hence the importance of integrated approaches, combining the chemical and the ecotoxicological analysis of pesticides. Although metolachlor was the second most detected compound in the entire study, the herbicide contributed to ecological risk with levels from low to moderate risks, primarily attributed to its toxicity to aquatic invertebrates.

The process of herbicide transport and degradation is highly dynamic and complex (Castro Berman et al., 2018). Regional-scale processes are likely to dictate the timing of herbicide pulses, due to increased rates of application and water runoff due associated with rain events. However, local process (i.e. individual farmers' choices on crops and herbicide application timing, washing of fumigating machinery) would probably play important roles. Due to the results obtained in this study and because of data for acetanilide herbicides (metolachlor and acetochlor) in Argentinean streams are scarce (Pérez et al., 2017), it is of utmost importance to continue monitoring acetochlor and metolachlor in aquatic ecosystems.

Another problem caused by pesticide contamination is the simultaneous occurrence of several of them and the need to establish the real impact of these mixtures on biota (Cancappa et al., 2016). In this study, mixtures of pesticides were commonly found in water samples. Throughout the study, 33% of the positive samples contained 1 pesticide and 67% contained 2 to 5 pesticides. Considering only samples from surface water, 15 out of 42 positive samples (36%) contained 1 pesticide and 27 samples (64%) contained 2 to 5 pesticides. The risk assessment of these mixtures was calculated as the sum of the risk quotient of each individual pesticide found in the sample (Palma et al., 2014). November 2017 was the period with the highest number of samples that involved a risk, namely 6. This means that all but two sites presented samples with any risk in that sampling period. Besides, it was the period with the major amount of pesticides found at risk levels. Only one sample with 5 pesticides was registered in surface waters. Pesticides from that sample were picoxystrobin, piraclostrobin ( $< \text{LOQ}$ ), acetochlor, atrazine and metholachlor ( $> \text{LOQ}$ ). Out of the 3 pesticides registered with values above the LOQ, only acetochlor reached values of  $RQ > 10$ , while the other two compounds reached  $RQ$  values smaller than 1. The sample exhibited a very high



risk associated with acetochlor toxicity almost exclusively, because the medium risk associated with atrazine and metolachlor did not significantly increase the risk level of it.

All sites presented ecological risk at least once. A cumulative risk level was calculated for each site, according to the risk quotients for all the pesticides reported in each site. Since several calculated  $RQ$  values were markedly greater than unit, a category of  $\Sigma RQ_{\text{site}} > 10$  was included which corresponds to high probabilities of harmful effects expected (very high risk, Iturburu et al., 2019). The 75% of the monitored sites in this study indicated a very high risk ( $\Sigma RQ_{\text{site}} \geq 10$ ) and the other 25% indicated a high risk ( $1 < \Sigma RQ_{\text{site}} < 10$ ). Our results are in agreement with those of Iturburu and coworkers (2019) which also pointed out that the north of the Pampas region (Córdoba, Santa Fe and Entre Rios provinces) showed high and very high risk.

## Conclusions

This work provides the first data on the presence and concentration of a wide range of pesticides in surface and groundwater from agriculture areas of south Santa Fe province, one of the most productive zones of Argentina, within Pampas Region. Results are strong new evidences that herbicides, insecticides and fungicides are arriving effectively to surface and groundwater, and in some cases, at concentrations that exceed quality guide levels for water for human consumption or for protection of aquatic biota. Atrazine was the most ubiquitous pesticide. Glyphosate and AMPA were detected together most of the times. Pirimiphos-methyl, an insecticide for the treatment of stored grains, was also found in water samples, even at toxic levels for freshwater organisms.

The risk quotients calculated demonstrated, on the one hand, that atrazine, azoxystrobin, epoxiconazole, acetochlor and pirimiphos-methyl posed high and/or very high ecotoxicological risk for aquatic organisms in surface water and, on the other hand, that the compliance with water quality standards does not necessarily indicate absence of risk.

The herbicides were the most frequently detected pesticides and were also the most responsible for the ecotoxicological risk occurred during the study, in opposite to other authors that found that the

insecticides were more often responsible for the ecotoxicological risk in water bodies (Albuquerque et al., 2016; Palma et al., 2014; Papadakis et al., 2015).

This work contributes to the knowledge about the presence of multiple pesticides in groundwater and surface water associated to agricultural lands and emphasizes that ecotoxicological risk needs to be considered when dealing with pesticides risk assessment. Further studies are necessary not only to identify areas susceptible to contamination from pesticides but also plan and design buffer zones, with vegetation strips, for example, among some other options.

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**Availability of data and material** The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

**Code availability** Not applicable.

## Declarations

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Conflict of interest** The author declare no competing interests.

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