Research Article

Pesticides in water sources used for human consumption in the semiarid region of Argentina

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Abstract

Presence of pesticides in drinking water is an issue of great concern in agricultural areas. In Argentina's semiarid regions, where surface water sources are scarce and groundwater may be of poor quality, rainwater becomes important for safe water supply. The expansion of agriculture in these regions due to no till management has led to a high use of pesticides which jeopardize the safety of all water sources used for human consumption. The objective was to monitor the presence of pesticides in different water sources from two agricultural areas of Santiago del Estero. Samples belonged to cisterns in which rainwater is collected, wells and dams. The most contaminated sources were dams, followed by cisterns and wells. Applied doses and frequency of use played an important role in the presence of pesticides. Thus, the most frequent molecules were mainly herbicides; atrazine and metolachlor were the most abundant. Glyphosate and aminomethylphosphonic acid presented the highest concentrations. Almost all measured values were below the US Environmental Protection Agency limits, but 73% of the samples exceeded the limit of 0.5 µg L^{-1} established by the European Union for the sum of molecules although only 7.4% of individual molecules exceeded the limit of 0.1 µg L^{-1}. However, risk assessment showed that pesticides from all sources presented a low potential risk to human health through drinking water exposure route.

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1 Introduction

Presence of pesticides in drinking water is an issue of global concern. For this reason, environmental legislation in the world sets increasingly lower maximum residue limits (MRLs).[1] The European Union (EU) establishes a maximum concentration for the sum of pesticides of 0.5 µg L^{-1}, where the concentration per individual molecule cannot exceed 0.1 µg L^{-1} [1]. In the USA, MRLs are established according to the toxicity of the active ingredient: MRL for atrazine is 3 µg L^{-1} while it is 700 µg L^{-1} for glyphosate [2]. In Argentina, the Argentine Food Code [3] determines MRLs for 26 organic products, but 90% of them are in disuse.

According to the World Health Organization (WHO), 2.1 billion people worldwide lack access to drinking water. In Argentina, two-thirds of the territory does not have access to safe water which means that 7 million people, particularly from rural areas, rely on alternative methods to provide themselves with drinking water. Rural populations in semiarid regions of Argentina have historically been supplied by dams fed by runoff water supplemented with groundwater [4]. In these environments, groundwater quality is usually regular to poor and rainwater becomes important for water supply since there are no nearby watercourses [5]. Nowadays, rainwater is collected from roofs of houses and public buildings and stored in tanks or cisterns built for this purpose. This system is increasingly promoted through state policies as a simple way for rural residents to access safe water.

Agricultural production is the main source of water pollution with nitrates, phosphates and pesticides. In Argentina, the pesticide market consists mainly of herbicides [6]; among them glyphosate, atrazine and 2,4-D are the most used. No till management (NT) is the predominant soil management system, taking up 91% of agricultural land [7] and requiring the use of herbicides as almost the only form of weed control. Thus, in the east of the province of Santiago del Estero during the 2016–2017 agricultural year 10 L ha^{-1} of glyphosate were used in soybean crops and 6–9 L ha^{-1} in corn, complemented with other herbicides such as atrazine, acetochlor and 2,4-D, at rates of 3.8, 2 and 1.2 L ha^{-1}, respectively [8].

Precipitation is a major pathway for returning air pollutants to water bodies [9]. Volatilization linked to aerosol dispersion probably causes transport of pesticides into the atmosphere, resulting in quantifiable amounts in rainwater away from application sites [10]. Some studies indicated that herbicides were more prevalent in rainwater and had higher concentrations than insecticides and fungicides [11, 12]. Pesticides have also been detected in surface waters all over the world. In seven states of the USA, more than 90% of samples from different watersheds were contaminated with pesticides and the most frequently detected were aminomethylphosphonic acid (AMPA, glyphosate's primary metabolite), glyphosate and atrazine [13]. Loos et al. [14] conducted an EU-wide study on the occurrence of organic pollutants in European rivers: Herbicides were found in low concentration ranges probably because the survey was conducted in autumn, which is an atypical application period for these compounds. Nevertheless, atrazine was detected in 68% of the samples with a maximum value of 0.08 µg L^{-1}. In Argentina, De Gerónimo et al. [15] analyzed 29 pesticides in watercourses of basins from south of Buenos Aires, Tucumán and Misiones and determined that atrazine was present in all basins but the occurrence of other pesticides was related to the production systems of each region. In groundwater, Battaglin et al. [16] detected glyphosate in 5.8% and AMPA in 14.3% of samples from 807 sites throughout the USA. The pan-European study carried out by Loos et al. [17] determined that pesticides and their secondary metabolites were among the most relevant chemicals found in groundwater samples: atrazine and deethylatrazine (DEA) were among the most frequent compounds (56 and 55% of frequency, respectively).

The aim of this study is to analyze the presence of 30 pesticides and four secondary metabolites in water sources used mainly as drinking water in two agricultural areas of Santiago del Estero, Argentina.

2 Materials and methods

2.1 Sampling area

The East of Santiago del Estero is located within the Western Chaco District, and its climate is warm continental with rainfall concentrated in summer [18]. The average annual temperature is 19.6 °C; predominant winds are from the South and North quadrants [19]. The strongest winds blow in July, August and September, with hot and dry winds blowing from the North quadrants [20]. The sampled zones belong to the area of influence of the cities of Bandera and Sachayoj (Fig. 1); both correspond to semiarid agricultural-livestock areas with predominance of soybean and corn fields. Practically all the regions are managed under NT system. The average annual rainfall

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[1] MRLs are the maximum levels of pesticide residues that are legally permissible in or on food or animal feed, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers.
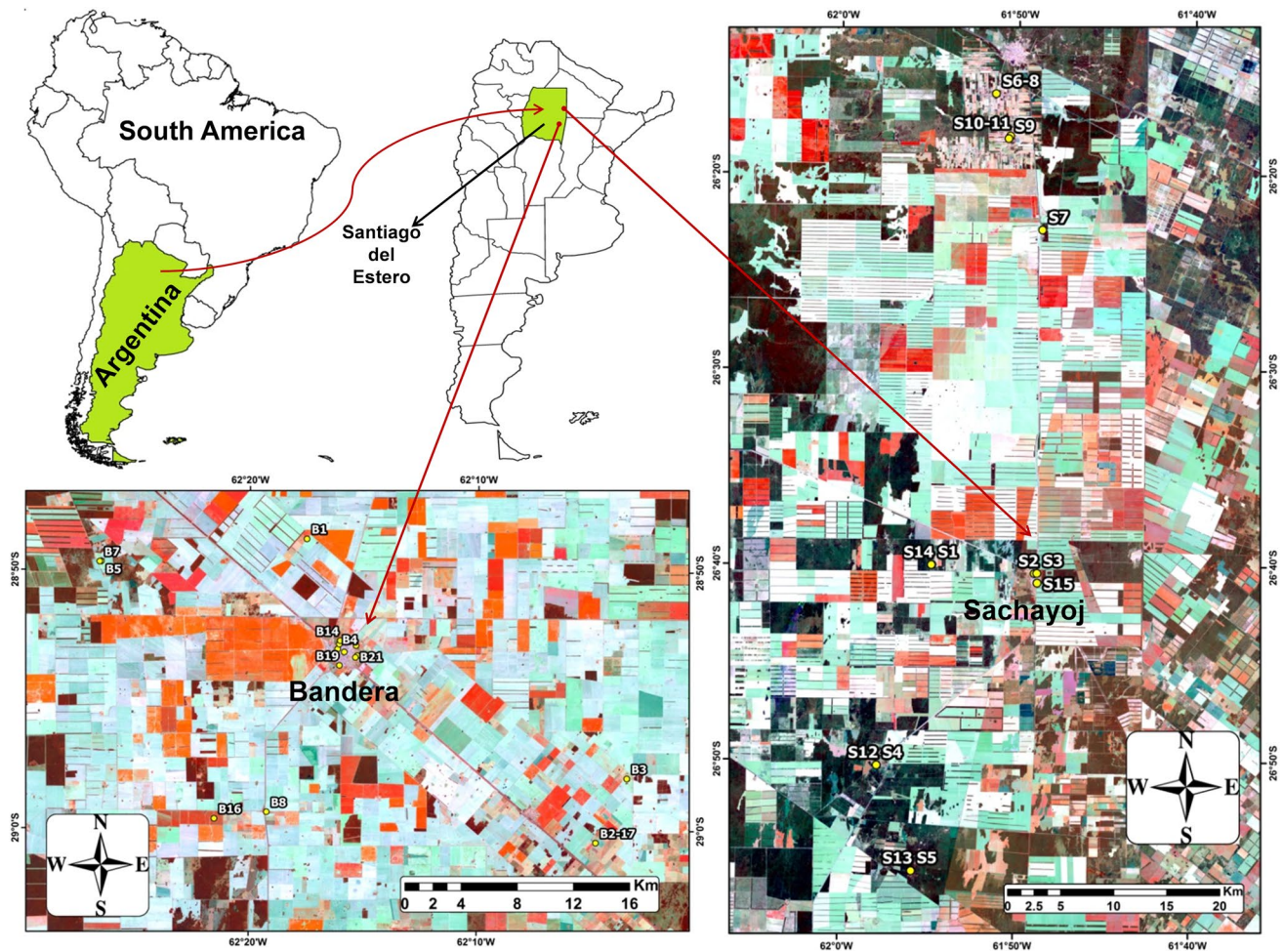
Fig. 1 Location of sampling sites

for the period 1949–2014 was 688 mm in Sachayoj and 822 mm in Bandera [21].

2.2 Sampling

Different water sources were selected: 26 cisterns collecting rainwater from roofs, 5 hand-dug wells (shallow water tables in Bandera), 2 boreholes (water table > 50 m, in Sachayoj) and 3 dams collecting runoff water (Table 1). Sampling points were selected based on their use: sites specifically used for human consumption (almost all the cisterns, wells B4 and B5 and dam B6) or consumed under certain conditions, such as periods of drought. Dams and wells were also included in the study because of their local relevance and the need to know whether they can really provide safe drinking water. Dams are used for urban supply and occasional consumption by the inhabitants or for animal consumption, while the water from wells is generally used for livestock consumption or household chores, except in times of water scarcity. Since

the objective of this study is to evaluate contamination of drinking water, it was preferred to sample the tanks in which rainwater is collected and not rainwater itself, since their characteristics may differ due to the concentration or dilution of pesticides inside the cisterns. Four samples were taken per agricultural year coinciding with periods of pesticide application. Thus, sampling periods were spring fallow (September–October), pre-seeding and pre-emergence applications (December), application of insecticides (February) and post-harvest fallow (April–June). Sampling began in April 2014 and continued until June 2017. Figure 1 shows the location of sampling points, while Fig. 2 shows rainfall for the analyzed period. A total of 353 water samples, 159 from Sachayoj and 194 from Bandera, were analyzed to evaluate the presence of 34 molecules, including herbicides and secondary metabolites, insecticides and fungicides (see Table 2 and Online Resource 1).

Table 1 Sampling sites, location, type of water source and use

ID	Location	Latitude (S)	Longitude (W)	Source	Type	Use[a]
B1	Bandera	28° 48′ 45.07″	62° 17′ 35.63″	Dug well	Rural	AD
B2	Bandera	29° 00′ 28.51″	62° 04′ 47.35″	Dug well	Rural	AD
B3	Bandera	28° 57′ 58.97″	62° 03′ 26.44″	Dug well	Rural	AD
B4	Bandera	28° 53′ 01.90″	62° 16′ 08.82″	Dug well	Urban	HC
B5	Bandera	28° 49′ 40.17″	62° 26′ 30.78″	Dug well	Rural	HC
B6	Bandera	28° 52′ 22.98″	62° 16′ 31.98″	Dam	Urban	HC
B7	Bandera	28° 49′ 40.44″	62° 26′ 34.80″	Cistern	Rural	HC
B8	Bandera	28° 59′ 20.54″	62° 19′ 13.98″	Cistern	Rural	HC
B9	Bandera	28° 53′ 08.58″	62° 15′ 51.36″	Cistern	Urban	HC
B10	Bandera	28° 53′ 08.58″	62° 15′ 51.36″	Cistern	Urban	HC
B11	Bandera	28° 52′ 34.14″	62° 15′ 44.88″	Cistern	Urban	HC
B12	Bandera	28° 52′ 44.70″	62° 15′ 37.80″	Cistern	Urban	CI
B13	Bandera	28° 52′ 50.27″	62° 16′ 04.58″	Cistern	Urban	HC
B14	Bandera	28° 52′ 42.42″	62° 16′ 01.74″	Cistern	Urban	HC
B15	Bandera	28° 53′ 17.04″	62° 15′ 16.98″	Cistern	Urban	HC
B16	Bandera	28° 59′ 36.50″	62° 21′ 31.60″	Cistern	Rural	HC
B17	Bandera	29° 00′ 28.87″	62° 04′ 54.16″	Cistern	Rural	HC
B18	Bandera	28° 53′ 20.50″	62° 16′ 48.10″	Cistern	Urban	HC
B19	Bandera	28° 53′ 39.80″	62° 16′ 04.00″	Cistern	Urban	HC
B20	Bandera	28° 52′ 53.51″	62° 15′ 20.32″	Cistern	Urban	HC
B21	Bandera	28° 53′ 21.00″	62° 15′ 22.00″	Cistern	Urban	HC
S1	Sachayoj	26° 39′ 59.69″	61° 54′ 44.46″	Cistern	Rural	HC
S2	Sachayoj	26° 40′ 24.96″	61° 48′ 55.04″	Cistern	Urban	HC
S3	Sachayoj	26° 40′ 24.20″	61° 48′ 46.44″	Cistern	Urban	HC
S4	Sachayoj	26° 50′ 16.04″	61° 57′ 48.96″	Cistern	Rural	HC
S5	Sachayoj	26° 55′ 38.50″	61° 55′ 48.07″	Cistern	Rural	HC
S6	Sachayoj	26° 15′ 54.22″	61° 51′ 18.72″	Cistern	Rural	HC
S7	Sachayoj	26° 22′ 51.49″	61° 48′ 37.44″	Cistern	Urban	HC
S8	Sachayoj	26° 15′ 54.22″	61° 51′ 18.72″	Cistern	Rural	CI
S9	Sachayoj	26° 18′ 11.77″	61° 50′ 34.94″	Cistern	Rural	HC
S10	Sachayoj	26° 18′ 3.46″	61° 50′ 29.04″	Cistern	Rural	HC
S11	Sachayoj	26° 18′ 3.46″	61° 50′ 29.04″	Cistern	Rural	CI
S12	Sachayoj	26° 50′ 15.94″	61° 57′ 49.25″	Borehole	Rural	CI
S13	Sachayoj	26° 55′ 39.47″	61° 55′ 49.04″	Borehole	Rural	CI
S14	Sachayoj	26° 40′ 00.04″	61° 54′ 46.85″	Dam	Rural	AD
S15	Sachayoj	26° 40′ 54.06″	61° 48′ 45.47″	Dam	Urban	R

[a]*HC* human consumption, *AD* animal drink, *CI* cleaning and orchard irrigation, *R* runoff water collection

2.3 Analytical procedure and instrumental analysis

Analytical procedures were carried out following the methodology described by De Gerónimo et al. [15] and Aparicio et al. [22]. Water samples were collected in polyethylene terephthalate bottles and stored in the dark at −20 °C until analysis. Prior to analysis, they were thawed overnight at 4 °C and filtered through a 0.45 μm nylon membrane to separate water from suspended particulate matter.

Ultrahigh-performance liquid chromatography (UPLC) MS/MS analysis was performed using an Acquity UPLC system coupled to a Quattro Premier XE tandem quadrupole mass spectrometer (Waters, Mildford, MA). For chromatographic separation, an Acquity UPLC BEH C18 column (1.7 μm, 100 × 2.1 mm, Waters) fitted with an Acquity VanGuard BEH C18 pre-column (1.7 μm, 5 × 2.1 mm, Waters) were used. The mobile phase consisted in water/methanol (95:5) modified with ammonium acetate 0.1 mM and formic acid 0.01% (phase A) and methanol modified with ammonium acetate 0.1 mM and formic acid 0.01% (phase B) in gradients from 10 to 100% of phase B. Drying and nebulizing gas was nitrogen from a nitrogen generator from pressurized air in

Fig. 2 Rainfall events in the cities of Bandera (**a**) and Sachayoj (**b**) during the 2014–2017 period. Triangles correspond to the sampling dates
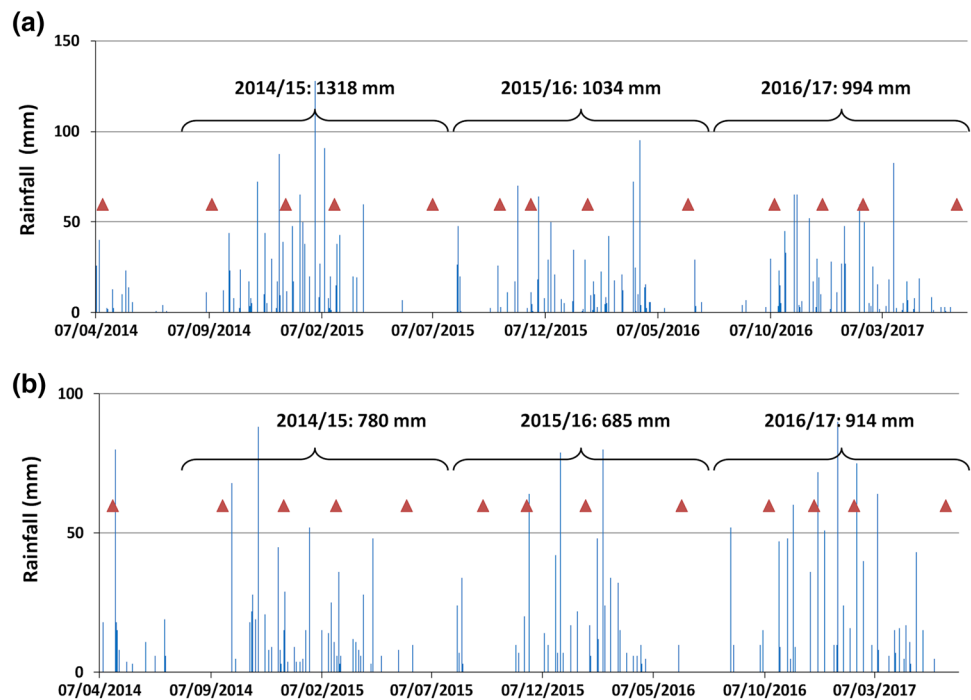
a N_2 LC–MS. The collision gas was argon 99.99% with a pressure of 6.3×10^{-3} mbar in the T-Wave cell. Mass-lynx™ 4.1 (Waters) was used to process all data. MS/MS conditions for analyzed compounds are shown in Online Resource 2.

2.4 Human health risk assessment

To evaluate the risk of water consumption from all sources, the hazard quotient (HQ) was calculated using the following formula [23]:

$$HQ = \frac{CDI}{RfD}$$

where the chronic daily intake (CDI) represents the estimated amount of ingested pesticide per kilogram of body weight and RfD is the reference dose of the contaminant ($\mu g \ kg^{-1} \ day^{-1}$) via the oral exposure route. The CDI was calculated by the equation [24]:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

where C is the measured concentration of each pesticide in water ($\mu g \ L^{-1}$); IR is the water ingestion rate (1 L day^{-1} for children; 2 L day^{-1} for adults); EF is the exposure frequency (365 days $year^{-1}$); ED is the exposure duration (6 years for children and 70 for adults); BW is the body weight of the exposed person (15 kg for children; 60 kg for adults); AT is the average lifespan (2190 days for children; 25,550 days

for adults). Cumulative risk assessment (HQs) was calculated using an additive approach by summing the individual HQ posed by each pesticide [25]. The sum of hazard quotients HQ for individual pesticide was:

$$HQs = \sum_{i=1}^{n} HQi$$

2.5 Statistical analysis

Analysis of variance (ANOVA) was performed using a mixed linear model with the PROC MIXED procedure [26]. The "sampling date" variable was considered as a repeated measure, the ID as "subject" and source and location were "groups."

3 Results and discussion

3.1 General observations

All compounds were detected in at least two samples and twenty of them showed a frequency higher than 10%: the most frequent compounds were mainly herbicides and their secondary metabolites (Table 2), which is consistent with other reports [12, 25, 27]. One groundwater sample

Table 2 Summary table of pesticides and secondary metabolites analyzed in water samples

Chemical	Use[b]	Detection frequency (%)[c]	Concentration of samples > LQ[d] ($\mu g\ L^{-1}$)			Cases > LQ	Cases < LQ	LQ ($\mu g\ L^{-1}$)
			Mean (± SD)	Min	Max			
2,4-D	H	49	0.084 (± 0.119)	0.015	0.925	115	59	0.015
Acetochlor	H	69	0.070 (± 0.203)	0.008	1.807	172	71	0.008
Alachlor	H	5	0.197 (± 0.128)	0.063	0.326	4	12	0.053
Ametryn	H	28	0.006 (± 0.007)	0.001	0.035	45	55	0.0003
AMPA[a]	H	67	0.602 (± 0.577)	0.2	5.1	214	21	0.13
Atrazine	H	99	0.261 (± 0.522)	0.001	7.921	344	5	0.0004
Carbaryl	I	8	0.008 (± 0.010)	0.001	0.033	21	9	0.00009
Carbofuran	I	1	0.001 (± 0.000)	0.001	0.001	3	2	0.0006
Chlorimuron-ethyl	H	18	0.013 (± 0.018)	0.001	0.094	51	13	0.0007
Chlorpyrifos	I	10	0.032 (± 0.031)	0.012	0.094	6	30	0.011
DEA[a]	M	93	0.041 (± 0.077)	0.002	1.227	292	37	0.0012
DIA[a]	M	85	0.049 (± 0.070)	0.006	1.075	285	16	0.006
Dichlorvos	I	7	0.007 (± 0.001)	0.006	0.007	2	24	0.006
Epoxiconazole	F	40	0.019 (± 0.062)	0.001	0.448	71	69	0.0002
Fipronil	I	17	0.025 (± 0.028)	0.004	0.09	17	42	0.003
Flurochloridone	H	8	0.004 (± 0.006)	0.001	0.02	9	20	0.0006
Glyphosate	H	53	1.251 (± 3.549)	0.1	35	163	25	0.10
HOA[a]	M	99	0.434 (± 1.101)	0.0081	13.812	334	15	0.009
Imazapic	H	4	0.013 (± 0.008)	0.005	0.023	6	7	0.0035
Imazapyr	H	30	0.023 (± 0.020)	0.004	0.095	38	69	0.004
Imazaquin	H	6	0.007 (± 0.006)	0.004	0.019	7	15	0.001
Imazethapyr	H	52	0.015 (± 0.022)	0.001	0.161	57	128	0.0004
Imidacloprid	I	54	0.043 (± 0.097)	0.008	0.798	124	65	0.008
Malathion	I	1	–	–	–	0	2	0.0004
Metconazole	F	3	0.005 (± 0.003)	0.002	0.009	5	7	0.0006
Methomyl	I	7	0.042 (± 0.057)	0.008	0.161	7	18	0.006
Metolachlor	H	90	0.059 (± 0.076)	0.001	0.495	254	65	0.0004
Metribuzin	H	1	0.004 (± 0.003)	0.002	0.007	3	0	0.0007
Metsulfuron-methyl	H	34	0.018 (± 0.063)	0.001	0.501	63	57	0.0006
Piperonyl-butoxide	I	14	0.006 (± 0.005)	0.003	0.015	6	44	0.00025
Pirimicarb	I	4	0.003 (± 0.003)	0.001	0.005	2	11	0.0003
Tebuconazole	F	65	0.012 (± 0.017)	0.001	0.116	148	81	0.0005
Tetramethrin	I	2	0.018 (± 0.007)	0.014	0.027	5	2	0.0032
Triticonazole	F	1	–	–	–	0	4	0.0004

[a]*HOA* hydroxyatrazine, *DEA* deethylatrazine, *DIA* deisopropylatrazine, *AMPA* aminomethylphosphonic acid

[b]H: herbicide; I: insecticide; F: fungicide; M: secondary metabolite

[c]Both > and < LQ cases were considered to determine the frequency

[d]*LQ* limit of quantification

[e]*ND* not detected

was free of contaminants. Next, we will analyze the most important compounds found in this study.

3.2 Glyphosate and its metabolite AMPA

Glyphosate is the most widely used compound in number of applications per year and doses and this is reflected in the high concentrations we found, as previously stated by other authors [27–29]. Its intensive use extends throughout the agricultural year and this caused a diffuse occurrence (Fig. 3a), as reported by Quaghebeur et al. [30]. However, detection frequency fell from 77% in the 2014/15 season to 32% in 2015/16 and 54% in 2016/17. This variation occurred more noticeably in cisterns and wells and could be due to several factors: The year 2014 was very rainy in Sachayoj (1381 mm)
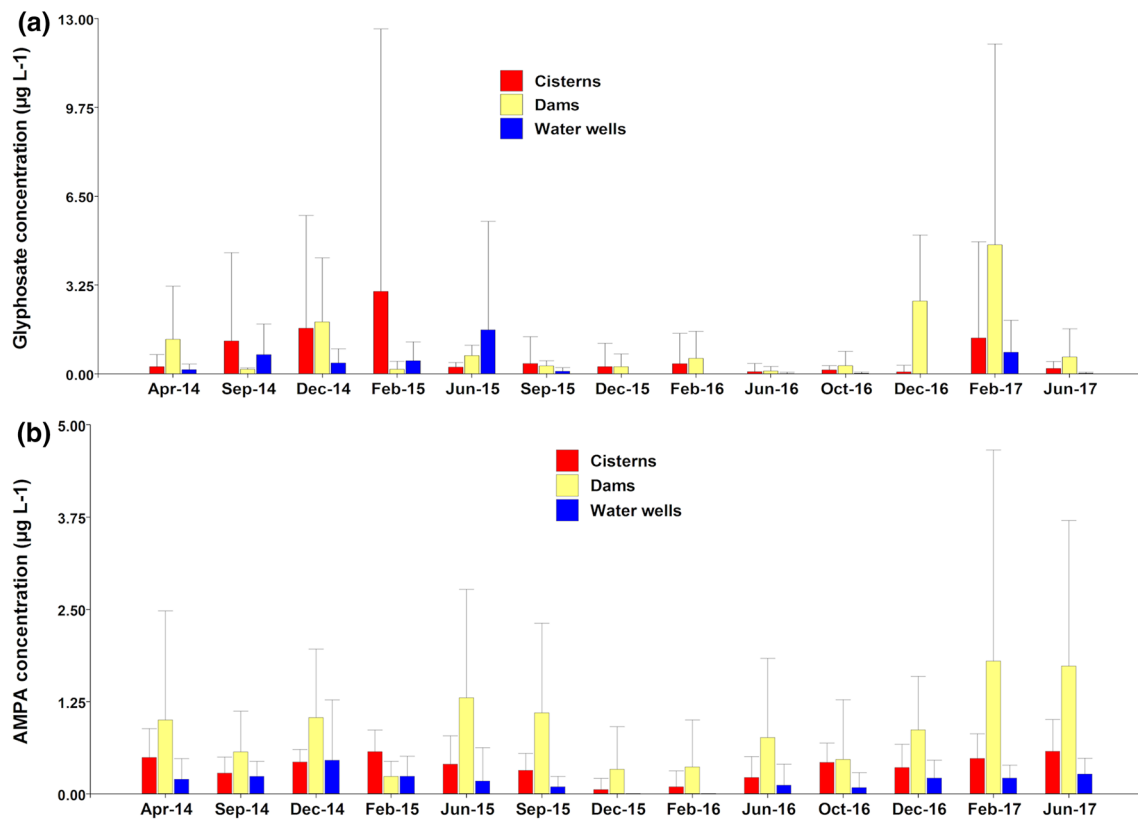
Fig. 3 Glyphosate (**a**) and AMPA (**b**) concentrations in the different water sources and sampling dates. Error bars represent standard deviation

and the 2014/15 season was rainier than the second and third ones in Bandera (Fig. 2), which could have generated a greater movement of glyphosate toward the different water sources during the first sampling season [28, 31]. Additionally, during the second and third sampling year a larger area of wheat was sown: the increase was greater than 100% between the first season and the next two. This crop implies a lower use of herbicides than winter fallow and reduces the environmental movement of pesticides by reducing erosion since it generates coverage in the season of stronger winds and decreases wind erosion, which is responsible for displacing soil particles enriched with glyphosate and AMPA [32]. Finally, due to the emergence of resistant weeds and spot spray systems, there is a downward trend of applied doses although the number of applications per year remains constant. Half-life values of glyphosate in soils range 1 to 68 days while those of AMPA range 39–331 days [33], showing that AMPA is more persistent. Sorption is considered to decrease glyphosate and AMPA degradation since they are both small molecules with polar functional groups, and they are strongly sorbed by soil minerals [34, 35]. Freundlich adsorption coefficient (K_f) ranged 9.4–700 L kg^{-1} and Freundlich constant

normalized to organic carbon (K_{foc}) ranged 1.600–60.000 for glyphosate while K_f ranged 10.0–1570 L kg^{-1} and K_{foc} ranged 1.119–11.100 L kg^{-1} for AMPA [33], proving that adsorption is the dominant process in the behavior of these compounds. According to several authors [36, 37], organic carbon content is not a major factor in glyphosate adsorption due to the high polarity of the molecule, which minimizes the contribution of the K_{foc} index as a descriptor of this herbicide retention. The persistence of both compounds would enable their movement in the environment through soil erosion [38, 39].

Since the limit of quantification (LQ) is 0.10 µg L^{-1} for glyphosate and 0.13 µg L^{-1} for AMPA quantifiable values of both compounds were above the EU limit of 0.1 µg L^{-1}. Concentrations of glyphosate were highly variable; therefore, no significant differences were found between sources, locations or sampling dates ($p > 0.05$). On the contrary, significant differences were found for AMPA between sources (dams > cisterns and wells, $p < 0.0001$), locations (Sachayoj > Bandera, $p = 0.006$) and dates ($p < 0.0001$), since for both locations the concentrations of AMPA in dams were higher during the last agricultural year. The results of both compounds were grouped by water source to analyze their possible origin.

In cisterns, maximum concentrations were 35 µg L^{-1} for glyphosate (mean 1.20 ± 3.93 µg L^{-1}) and 1.90 µg L^{-1} for AMPA (mean 0.52 ± 0.28 µg L^{-1}). Presence of AMPA (Fig. 3b) suggests that drift is not the only transport mechanism: glyphosate is degraded by soil microorganisms [40] and AMPA is the main product of its partial degradation [41]. Occurrence of AMPA implies contact of glyphosate with soil, its partial decomposition and transport of AMPA to the atmosphere through soil erosion.

Due to its very low vapor pressure, glyphosate has two ways of reaching water sources: spray drift from fields and wind erosion of soil particles enriched with it [28]. In semiarid areas, wind erosion plays an important role since the risk of transporting glyphosate and AMPA with suspended dust is very high and they hardly decompose under dry soil conditions [38]. Aparicio et al. [32] analyzed sediments collected in the province of Chaco, Argentina, and found 0.66–313 µg kg^{-1} of glyphosate and 1.3–83 µg kg^{-1} of AMPA, confirming that wind-eroded material can contribute to water pollution. Furthermore, glyphosate reaching the atmosphere through drift or wind erosion can be washed away by rain. US studies found glyphosate and AMPA frequencies greater than 50% in rainwater samples from agricultural areas and determined that intense rainfall is more efficient in removing glyphosate from the atmosphere [16, 28], which may explain our higher frequency during the first season. In Argentina, Alonso et al. [29] found a high frequency of detection of glyphosate (> 80%) in rainwater and pointed out that its atmospheric deposition through rain in surface water bodies, soils and urban sites constitutes a relevant source of population exposure to this pollutant. Lamprea and Ruban [42] consider atmospheric deposition to be possibly the main contributor to glyphosate and AMPA runoff on rooftops.

Presence of bacterial communities in cisterns and persistence of glyphosate in dark conditions should be considered for future studies since Mercurio et al. [43] determined that microorganisms present in seawater were able to degrade glyphosate and the herbicide persistence in darkness was much greater than in dim light (267 vs. 47 days). According to Mallat and Barcelló [44], the complexity of the water matrix can change the rate of glyphosate degradation and the main factors affecting this process are a combination of microbial activity, temperature and photolysis.

Concentrations in dams were up to 13.2 µg L^{-1} of glyphosate and 5.1 µg L^{-1} of AMPA (mean 1.70 ± 2.82 and 1.19 ± 1.24 µg L^{-1}, respectively). Frequencies reported by other authors in watercourses of agricultural regions were generally lower but concentrations were several times higher [31, 45, 46]. Okada et al. [47] monitored a stream southeast of the province of Buenos Aires (Argentina) and found glyphosate and AMPA in 28% and 50% of the samples, with a maximum concentration of 8.2 µg L^{-1} and 3.7 µg L^{-1}, respectively. On the other hand, Mac Loughlin et al. [48] detected glyphosate and AMPA in a water body passing through a horticultural region in the Carnaval basin at concentrations up to 17.0 µg L^{-1} for glyphosate and 4.5 µg L^{-1} for AMPA, with a non-distinguishable behavior between seasons like our case. Likewise, Battaglin et al. [16] detected glyphosate in 33.7% and AMPA in 29.8% of samples belonging to lakes, ponds or wetlands, with maximum concentrations of 301 µg L^{-1} and 41 µg L^{-1}, respectively. All the dams in our study receive runoff water from surrounding fields, so that would be the most important source of pollution [49], not ruling out atmospheric deposition and groundwater discharge in the case of the Bandera as other possible pollution pathways [50].

Groundwater concentrations reached 10.6 µg L^{-1} for glyphosate in Bandera (mean 1.1 ± 2.29 µg L^{-1}) and 0.9 µg L^{-1} in Sachayoj (mean 0.6 ± 0.36 µg L^{-1}) while AMPA concentrations were up to 1.9 µg L^{-1} (mean 0.49 ± 0.36 µg L^{-1}) and 0.5 µg L^{-1} (mean 0.35 ± 0.21 µg L^{-1}), respectively. The greater presence of both molecules in shallow groundwater of Bandera (although difference was not significant for glyphosate) could be attributed mainly to leaching through soil profile. In fine-textured well-structured soils, such as the ones from Bandera, preferential flow would constitute an important pathway [51]. In groundwater from southeast of Buenos Aires, Okada et al. [47] detected glyphosate and AMPA in 24% and 33% of the samples, with maximum levels of 8.5 µg L^{-1} and 1.9 µg L^{-1}, respectively. The lower frequencies and concentrations found in boreholes coincide with other studies [16, 31], although Primost et al. [46] did not detect these compounds in aquifers of the province of Entre Ríos with depths similar to Sachayoj, and Okada et al. [47] did not find an association between depth and presence of glyphosate or AMPA. Lutri et al. [52] detected glyphosate (1.2–2.0 µg L^{-1}) and AMPA (1.5–3.1 µg L^{-1}) in 15.8% of groundwater samples, pointing out that their detection was related to areas with shallow water table (< 4 m), low hydraulic conductivity (1.5 m d^{-1}), low hydraulic gradient (0.16%) and very low flow rate (0.024 m d^{-1}). Their presence in an unconfined aquifer shows that their use under the predominant agricultural model exceeds the degradation potential of the soil system, causing groundwater contamination.

Higher concentrations and frequency of AMPA would be explained by its greater persistence in the environment, as mentioned above [33, 40]. To understand the fate and transport of pesticides, the relation between pesticide metabolites and the parent compound is often used to indicate the closeness of sampling to application source,
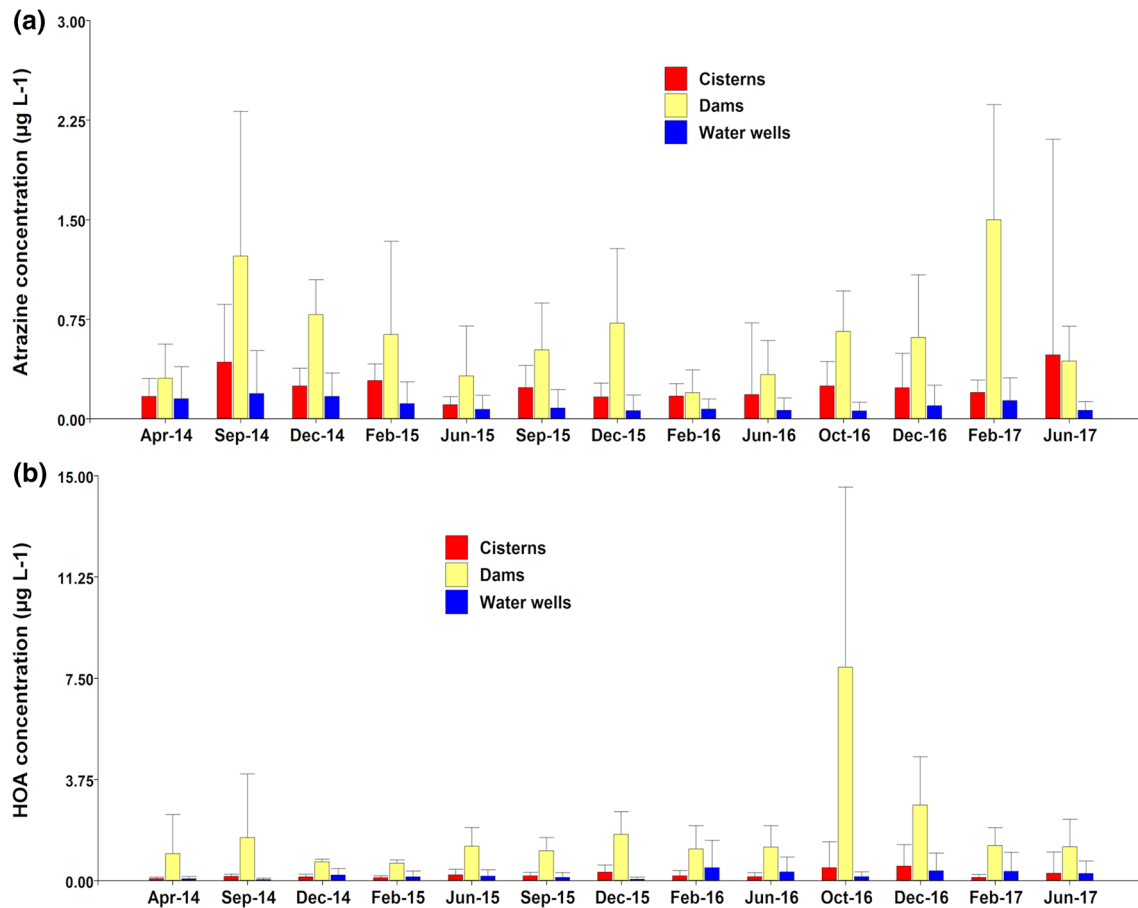
Fig. 4 Atrazine (**a**) and HOA (**b**) concentrations in water sources. Error bars represent standard deviation

either in time or space [16]. The %AMPA would be calculated as follows:

$$\% \; AMPA = \frac{[AMPA]}{([AMPA] + [glyphosate])} \times 100$$

where [AMPA] and [glyphosate] are their concentrations in water. Battaglin et al. [16] found the highest values for this ratio in groundwater samples (median 100%) and the lowest values in rainwater (median 20%). In our case, the %AMPA was very variable in all sources but it tended to be a higher in cisterns (mean 66% ± 32%) and dams (61% ± 31%) than in wells (52% ± 43%) due to accumulation of AMPA and/or glyphosate degradation to AMPA in these sources. This would indicate that these compounds came from ancient sprays or distant sites, possibly mobilized by surface runoff or wind erosion, confirming that spray drift would not always be the main source of water pollution.

3.3 Atrazine and its metabolites hydroxyatrazine (HOA), deethylatrazine (DEA) and deisopropylatrazine (DIA)

The widespread use of atrazine throughout the season determines a diffuse occurrence, as described for glyphosate and by Quaghebeur et al. [30], although the lower doses used in comparison with those of glyphosate are reflected in the concentrations we found. Other factors affecting its presence in water samples are its low adsorption to soil [53] and its persistence and ease of movement in the environment by drift, leaching or runoff [54], behavior similar to its secondary metabolites [55]. Thus, Solomon et al. [56] collected half-life values of atrazine in water of 41–237 days and some authors reported residues of atrazine and its metabolites in surface and groundwater several years after use [51, 57]. This causes a higher frequency compared to glyphosate and AMPA (see Table 2). Other studies also showed high frequencies, even similar to ours [12, 14, 17]. The environmental behavior of this molecule is one of the reasons for its prohibition in the European Union [58].
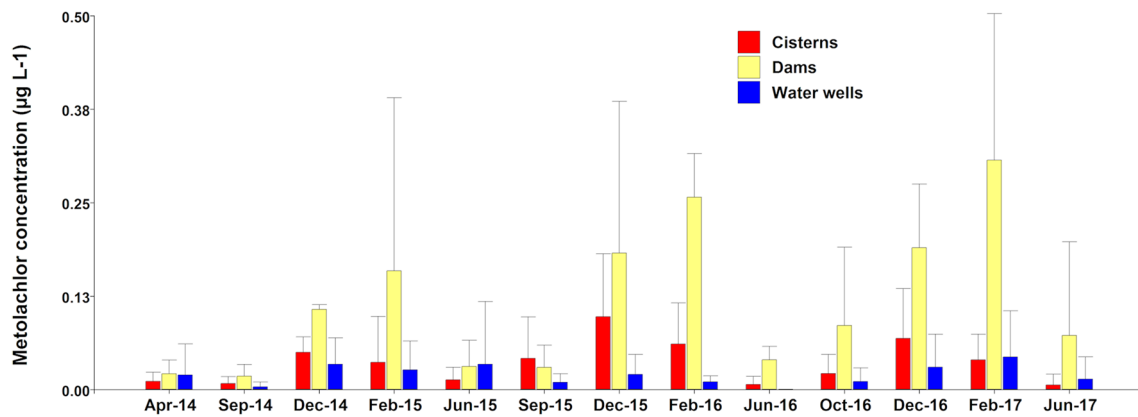
Fig. 5 Mean concentrations of metolachlor in water sources. Error bars represent standard deviation

33% of quantified values of atrazine were below the EU limit of 0.1 μg L^{-1}. HOA exhibited a similar percentage, while more than 90% of the quantifiable DIA and DEA values were below that limit. The concentration of HOA was on average 13 times higher than DEA and DIA and 2.4 times higher than atrazine. The %HOA ratio was calculated in a similar way to the %AMPA ratio and presented a wide variability in all sources but it was higher for dams (68% ± 21%) than groundwater (49% ± 32%) and cisterns (47% ± 20%). This may be due to degradation of atrazine during transport or in the water source [59] and because HOA has the longest half-life of the triazines in this study [33]. The higher concentration of HOA than DIA and DEA in all sources indicates that degradation would be a chemical process since the latter two are products of atrazine biodegradation [60].

Atrazine concentrations differed between water sources (dams > cisterns > wells, $p = 0.012$) and sampling dates (the last agricultural year showed higher concentrations, $p = 0.019$) but not between locations ($p = 0.898$). HOA had a similar behavior, with differences between water sources (dams > cisterns and wells, $p < 0.0001$) and sampling dates, since dams exhibited higher values during the last agricultural year, especially in Sachayoj ($p < 0.0001$). Figure 4 shows the concentrations of atrazine and HOA in the different water sources throughout the sampling period.

Maximum concentrations of atrazine in cisterns were 7.92 μg L^{-1} (mean 0.24 ± 0.56 μg L^{-1}) and 3.83 μg L^{-1} for HOA (mean 0.24 ± 0.48 μg L^{-1}). Mechanisms for reaching these water sources would include spray drift, transport associated with soil particles and volatilization from the surface of treated soils [61]. Although atrazine presents a vapor pressure and a Henry's constant barely greater than glyphosate and therefore a low volatility [33], Goolsby et al. [62] considered that its greater persistence in soil would allow volatilization to be an important process and explain its long detection period. These authors found values of 0.11–0.40 μg L^{-1} in rainwater from some states of the USA. In our country, Alonso et al. [29] detected atrazine in 80% of rain samples from several sites in the Pampean Region with concentrations of 0.10–26.9 μg L^{-1}. Transport of atrazine by wind erosion of soil particles to which it is adsorbed can also move it several kilometres from where it was applied [11, 61, 63].

The highest values of atrazine and HOA corresponded to dams, showing the importance of runoff as the main transport route [56]. Quantifiable atrazine concentrations were up to 2.45 μg L^{-1} (mean 0.65 ± 0.57 μg L^{-1}) and HOA maximum concentrations were 13.81 μg L^{-1} (mean 1.82 ± 2.56 μg L^{-1}). Decrease in surface runoff caused by NT is not always accompanied by a lower loss of pesticides: Mickelson et al. [64] determined that a lower volume of runoff generated by a maize crop under NT was compensated by higher concentrations of atrazine in runoff water, resulting in a greater herbicide loss. Besides, the lack of flow in dams determines that, although the amount of active ingredient entering is similar to a watercourse, dilutions will be lower and water evaporation may even increase concentrations [56].

In groundwater, atrazine concentrations reached up to 0.8 μg L^{-1} (mean 0.11 ± 0.16 μg L^{-1}) and those of HOA up to 2.53 μg L^{-1} (mean 0.28 ± 0.49 μg L^{-1}). Preferential flow would play an important role in vertical movement of atrazine in soil, as demonstrated by Hang et al. [65]: when comparing two soils, the one with the higher retention capacity due to its more clayey texture presented, however, the highest herbicide losses through leaching. Vryzas et al. [66] concluded that adsorption and dissipation were not sufficient to decrease concentrations of atrazine in soil water when rain events occurred shortly after its application and most of the leaching would take place within the first month after application. Finally, atrazine is more persistent in groundwater than in soil due to the lack of degrading microorganisms, low organic carbon content

which is determinant for their growth and low oxygen content in groundwater [60].

3.4 Metolachlor and acetochlor

Metolachlor concentrations showed significant differences between water sources (dams > cisterns and wells, $p = 0.0008$) and sampling dates ($p = 0.016$): It exhibited concentration peaks (in December in the case of cisterns and in February for dams) since it is applied exclusively in pre-emergence of summer crops coinciding with December samplings (Fig. 5). Other authors reported similar behaviors in surface and rainwater [12, 67, 68]. Concentrations of metolachlor were well below those of glyphosate and atrazine due to its lower use (treated area and field doses): 84% of concentrations were underneath the EU limit of 0.1 μg L^{-1}.

In cisterns, maximum quantifiable concentrations were 0.291 μg L^{-1} (mean 0.05 ± 0.06 μg L^{-1}) with 91% of detection. A similar frequency was found by Majewski et al. [11] in rainwater from sites in the central-eastern USA and it was detected at a control site away from agricultural areas, indicating that atmospheric transport would play an important role. Years later, detections in rainwater from the same area decreased due to a reduction in the use of the product [27]. Potter and Coffin [68] concluded that the high volatility of metolachlor would produce wet deposition and estimated it would represent approximately 1% of the applied product, five-fold greater than that mobilized by surface runoff. Vogel et al. [12] detected a mean frequency of 83% in rainwater from four basins of the USA. They concluded that as metolachlor vapor pressure is two orders of magnitude higher than that of atrazine, a greater amount of metolachlor would volatilize into the atmosphere; however, it would be susceptible to rapid degradation and therefore more ephemeral, which would explain the peak of concentration in cisterns.

Dams had the highest occurrence of metolachlor: it was absent in only one sample and quantifiable samples had mean and maximum values (0.13 ± 0.14 μg L^{-1} and 0.495 μg L^{-1}, respectively) that doubled the other sources. This highlights the importance of surface runoff. Like atrazine, it was found that lower runoff volumes in plots under NT were compensated by higher concentrations resulting in greater herbicide losses [64]. Other surface water studies found similar frequencies but different concentrations. Fairbairn et al. [69] found metolachlor in 88% of samples from the Zumbro river basin (US), with a mean concentration of 10 ng L^{-1}. Zablotowicz et al. [67] found very disparate frequencies of metolachlor in oxbow lakes of the Mississippi river delta and concentrations up to 14.9 μg L^{-1}.

Wells had the lowest frequency (86%) and concentrations: mean and maximum values were 0.04 ± 0.05 μg L^{-1} and 0.224 μg L^{-1}, respectively. European studies [17] showed frequencies of 20% in groundwater. However, in north-eastern Greece frequency of metolachlor was 63% with a mean of 0.33 μg L^{-1} [70] and in France metolachlor was detected in all samples with a mean concentration of 0.25 ± 0.32 μg L^{-1} [71]. Similarly, in a field leaching test conducted in Greece [66] it was detected in 99% of soil water samples, showing a high persistence (values of 10 μg L^{-1} were found 18 months after application). Macroporosity and adsorption are the predominant factors governing leaching of metolachlor [72].

Acetochlor behaved in a similar way to metolachlor (higher concentrations in December) since it is also used as a pre-emergent herbicide in maize and soybean crops, although it had a lower frequency due to the preference of metolachlor for its better herbicidal effect. In this case, apart from differing between water sources (dams > cisterns and wells, $p = 0.0009$) and sampling dates ($p = 0.0068$), there were also significant differences between locations (Sachayoj > Bandera, $p = 0.037$).

Frequency of detection in cisterns was 75%, with maximum concentrations of 1.70 μg L^{-1} (mean 0.05 ± 0.15 μg L^{-1}). Majewski et al. [11] also found a high frequency of acetochlor in rainwater from agricultural sites. However, it was not detected at the control site; therefore, its atmospheric life would be short and it would be transported over limited distances. Besides, it was detected in gas and particle phase of air samples from those sites [63], demonstrating that volatilization and wind erosion would contribute to contamination of cisterns.

Dams showed a similar frequency to cisterns, but higher mean and maximum concentrations: 0.18 ± 0.42 μg L^{-1} and 1.81 μg L^{-1}, respectively. Lerch and Blanchard [73] also detected high frequency of acetochlor in surface waters of Missouri and Iowa (US). Ferenczi et al. [74] determined that acetochlor was transported mainly in its dissolved form by surface runoff and loss represented 1% of the applied product, with a mean concentration of 48 μg L^{-1} (range 7–81 μg L^{-1}).

Groundwater exhibited the lowest values and frequency: 0.04 ± 0.03 μg L^{-1} and 0.10 μg L^{-1} of mean and maximum concentration, respectively, and 47% of detection, which is similar to other studies [75, 76]. In gravity lysimeters, Caprile et al. [51] detected acetochlor 7 years after its last application; the formation of non-extractable residues would constitute a significant reservoir that could result in a long time of permanence in the soil and a source of acetochlor to water tables as a result of its desorption.

3.5 Other pesticides: tebuconazole and imidacloprid

Top ten pesticides included tebuconazole and imidacloprid, the only ones that are not herbicides. Tebuconazole is a fungicide used to control diseases in different extensive crops. All sources showed concentrations < 0.1 µg L^{-1}, except for two samples from dams. The number of cases < LQ was also important (35% for cisterns, 17% in dams and 58% in wells). Quantifiable concentrations presented significant differences between sources (dams > cisterns and wells, $p = 0.0004$) and sampling dates (some sampling dates exhibited higher concentrations but varying among sources, $p < 0.0001$).

Detection frequency in cisterns was 68%, with mean and maximum concentrations of 0.01 ± 0.01 µg L^{-1} and 0.06 µg L^{-1}, respectively. Hüskes and Levsen [10] detected tebuconazole mainly in rain samples in Germany that coincided with the application of the product, in concentrations ranging 0.003–0.32 µg L^{-1}. Potter and Coffin [68] detected a low frequency (11%) in rainwater from southeastern USA but concentrations were up to 2 µg L^{-1}.

Dams had the highest concentrations (mean 0.02 ± 0.03 µg L^{-1}, maximum 0.12 µg L^{-1}) and detection frequency (92%), highlighting the importance of runoff as a source of pollution. According to Potter et al. [77], runoff caused losses of 3.6–9.8% of the product, depending on the tillage system. De Gerónimo et al. [15] detected tebuconazole in surface waters of a basin from southeast of Buenos Aires, with 91% of detection frequency and mean concentration of 0.033 µg L^{-1}. Glinski et al. [78] found it was the second most frequent pesticide in ponds and streams from an agricultural area in the USA, with a frequency of 62% and a maximum concentration of 0.48 µg L^{-1}.

Wells exhibited the lowest detection frequency (43%) and concentrations (mean 0.007 ± 0.008 µg L^{-1}, maximum 0.03 µg L^{-1}). In contrast, Herrero-Hernández et al. [75] detected tebuconazole in 75% of groundwater samples from La Rioja, Spain (maximum concentration: 3.24 µg L^{-1}). Differences between studies are due to a higher use of fungicides in vineyards than in crops such as soybean and corn.

Imidacloprid is an insecticide used for pest control mainly in soybean cultivation and as a seed therapist. It was generally found in concentrations < 0.1 µg L^{-1} and frequency was similar in all sources. Like glyphosate, it showed no significant differences between locations, sources or sampling dates.

Cisterns presented the lowest mean (0.03 ± 0.05 µg L^{-1}) and maximum concentration (0.41 µg L^{-1}). Its high persistence in soil [33] would turn wind erosion into a source of pollution of cisterns, but no records were found about rain to establish the importance of this mechanism.

Dams exhibited slightly higher mean (0.05 ± 0.10 µg L^{-1}) and maximum concentrations (0.46 µg L^{-1}) than cisterns. Battaglin et al. [50] detected imidacloprid almost in all vernal pools and streams, although concentrations were mostly below the laboratory reporting limit. Hladik et al. [79] also found this insecticide in US rivers, with a frequency of 53% and concentrations up to 0.15 µg L^{-1}.

Wells had a slightly lower frequency than the other sources (42%), but mean and maximum concentrations were higher: 0.08 ± 0.18 µg L^{-1} and 0.80 µg L^{-1}, respectively. Herrero-Hernández et al. [76] detected imidacloprid in less than 20% of groundwater samples but sometimes exceeding the EU limit. The Groundwater Ubiquity Score (GUS) of imidacloprid is 3.74 [33]; therefore, it has a high possibility of leaching and this would explain its presence in groundwater.

3.6 Sum of pesticides and health risk assessment

Up to this point, the main molecules were considered; in this section, we will analyze the set of pesticides and the risks to human health. Only 7.4% of all values exceeded the limit of 0.1 µg L^{-1} per individual molecule set by the EU. However, 73% of the samples exceeded the tolerance of 0.5 µg L^{-1} established for the sum of organic contaminants. Percentages varied depending on the source and sum of molecules differed mainly due to changes in concentration and frequency of the main pesticides. Thus, cisterns presented a 7% frequency of concentrations greater than 0.1 µg L^{-1}, but the sum exceeded 0.5 µg L^{-1} in 76% of the samples. All samples from dams presented sums higher than 0.5 µg L^{-1}, confirming they were the most polluted source, with 12% of values above 0.1 µg L^{-1}. Conversely, wells had the lowest contamination since concentrations greater than 0.1 µg L^{-1} and sums greater than 0.5 µg L^{-1} were 4% and 51%, respectively. Besides, significant differences were found in the mean sum of molecules between sources (dams > cisterns > wells, $p = 0.0004$) and dates ($p = 0.0003$), but not between locations. Similarly, more than 50% of surface and groundwater from La Rioja, Spain, exceeded the sum of 0.5 µg L^{-1} [76]. In a pan-European study on the presence of organic pollutants in groundwater [17], 29% of the samples had at least one pesticide exceeding the limit of 0.1 µg L^{-1} and 10% exceeded the tolerance of 0.5 µg L^{-1}. Compared to samples from rivers in Europe [14], groundwater was less contaminated.

Another remarkable issue was the contribution of the most used pesticides and their metabolites: glyphosate, atrazine, AMPA and HOA. Their high concentration and/or frequency reflected in their participation in water pollution (Fig. 6). They contributed to 80% of the total sum

Fig. 6 Sum of molecules and proportions of main pesticides in (**a**) cisterns, (**b**) dams and (**c**) wells for the different water sources and sampling dates
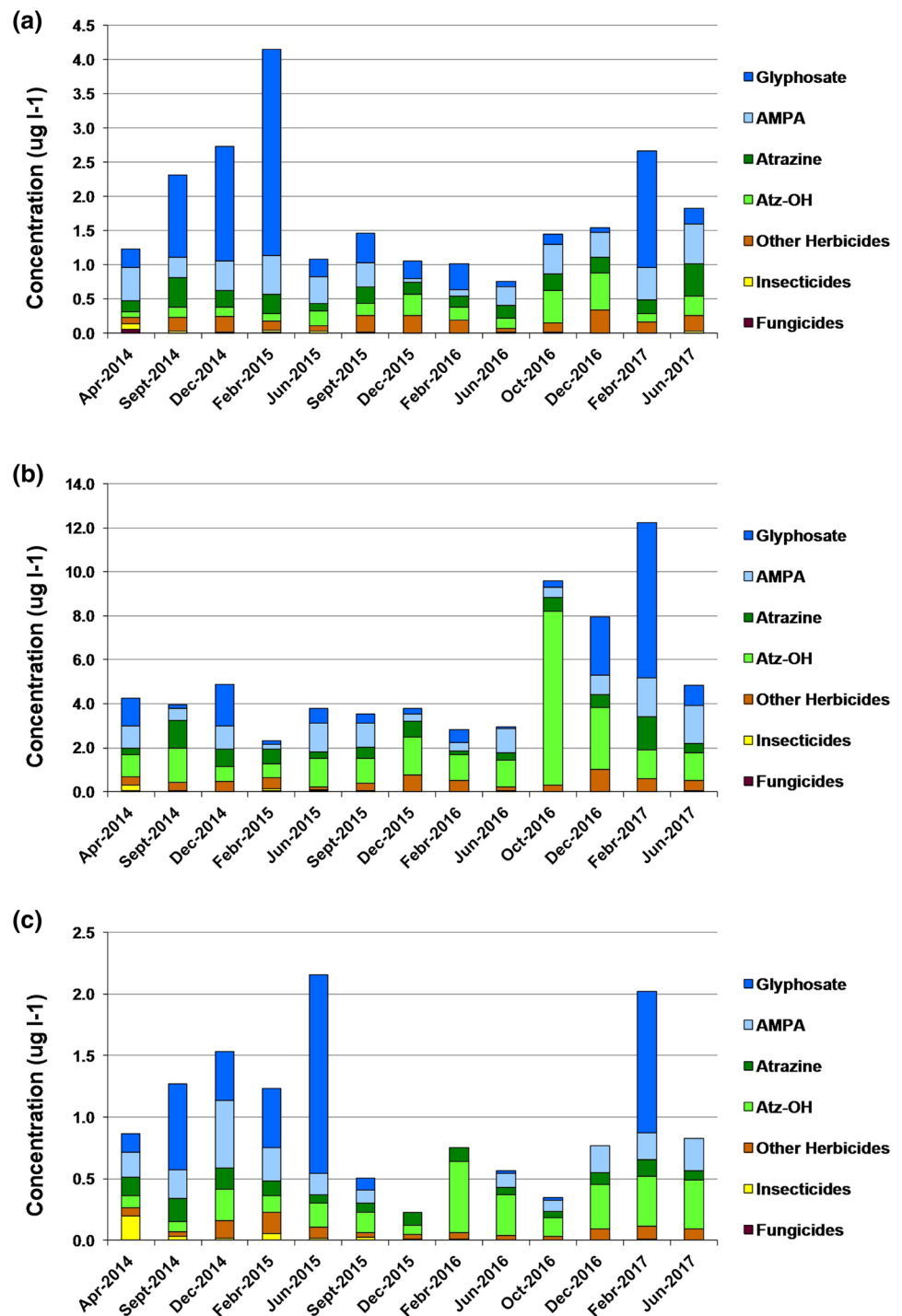
of pesticides; 14% of that percentage corresponded to glyphosate, 22% to AMPA, 20% to atrazine and 24% to HOA. They represented at least 50% of the sum of molecules in 328 out of 353 samples. However, percentages were very variable and their contribution varied from 0% (samples in which they were not detected) to 100% (some well samples that had atrazine/HOA as the only quantifiable molecule).

Table 3 shows the RfD for all compounds. The RfD defines the maximum dose which, according to all known facts at the time, will result in no harm to human health when consuming it for a lifetime. When the CDI exceeds the value of the RfD (HQ > 1), it means that water consumption can have an adverse effect on human health. In our study, HQ values for adults and children were less than 1 (Table 3), suggesting that these levels

Table 3 Risk assessment of detected pesticides for children and adults

Chemical	RfD (µg/kg bw/day)	HQ-Child Mean (± SD)	Max	HQ-Adult Mean (± SD)	Max
2,4-D	20[a]	1.97E−04 (±3.42E−04)	3.08E−03	9.87E−05 (±1.71E−04)	1.54E−03
Acetochlor	3.6[a]	9.43E−04 (±3.21E−03)	3.35E−02	4.71E−04 (±1.60E−03)	1.67E−02
Alachlor	10[c]	5.03E−04 (±6.14E−04)	2.17E−03	2.51E−04 (±3.07E−04)	1.09E−03
Ametryn	15[c]	1.26E−05 (±2.39E−05)	1.56E−04	6.32E−06 (±1.19E−05)	7.78E−05
AMPA	300[c]	1.24E−04 (±1.27E−04)	1.13E−03	6.18E−05 (±6.33E−05)	5.67E−04
Atrazine	20[a]	8.58E−04 (±1.73E−03)	2.64E−02	4.29E−04 (±8.66E−04)	1.32E−02
Carbaryl	7.5[a]	4.70E−05 (±7.98E−05)	2.93E−04	2.35E−05 (±3.99E−05)	1.47E−04
Carbofuran	0.15[a]	3.38E−04 (±1.46E−04)	4.44E−04	1.69E−04 (±7.30E−05)	2.22E−04
Chlorimuron-ethyl	62.5[d]	1.11E−05 (±1.75E−05)	1.00E−04	5.56E−06 (±8.74E−06)	5.01E−05
Chlorpyrifos	1[a]	7.59E−04 (±1.01E−03)	6.27E−03	3.80E−04 (±5.07E−04)	3.13E−03
DEA	20[b]	1.20E−04 (±2.44E−04)	4.09E−03	6.01E−05 (±1.22E−04)	2.05E−03
DIA	20[b]	1.54E−04 (±2.31E−04)	3.58E−03	7.71E−05 (±1.15E−04)	1.79E−03
Dichlorvos	0.08[a]	3.49E−03 (±5.78E−04)	5.83E−03	1.75E−03 (±2.89E−04)	2.92E−03
Epoxiconazole	8[a]	8.08E−05 (±3.74E−04)	3.73E−03	4.04E−05 (±1.87E−04)	1.87E−03
Fipronil	0.2[a]	2.81E−03 (±5.94E−03)	3.00E−02	1.41E−03 (±2.97E−03)	1.50E−02
Flurochloridone	40[a]	2.47E−06 (±6.09E−06)	3.33E−05	1.24E−06 (±3.05E−06)	1.67E−05
Glyphosate	300[c]	2.43E−04 (±7.40E−04)	7.78E−03	1.21E−04 (±3.70E−04)	3.89E−03
HOA	40[b]	6.93E−04 (±1.80E−03)	2.30E−02	3.47E−04 (±9.01E−04)	1.15E−02
Imazapic	460[a]	1.04E−06 (±1.06E−06)	3.33E−06	5.19E−07 (±5.31E−07)	1.67E−06
Imazapyr	2500[a]	2.60E−07 (±4.15E−07)	2.53E−06	1.30E−07 (±2.07E−07)	1.27E−06
Imazaquin	250[a]	7.12E−07 (±1.16E−06)	5.07E−06	3.56E−07 (±5.79E−07)	2.53E−06
Imazethapyr	440[c]	7.04E−07 (±2.06E−06)	2.44E−05	3.52E−07 (±1.03E−06)	1.22E−05
Imidacloprid	60[a]	3.33E−05 (±8.92E−05)	8.87E−04	1.67E−05 (±4.46E−05)	4.43E−04
Malathion	30[a]	6.67E−07 (±0.00E+00)	6.67E−07	3.33E−07 (±0.00E+00)	3.33E−07
Metconazole	10[a]	1.43E−05 (±1.81E−05)	6.00E−05	7.17E−06 (±9.03E−06)	3.00E−05
Methomyl	2.5[a]	3.93E−04 (±8.88E−04)	4.29E−03	1.96E−04 (±4.44E−04)	2.15E−03
Metolachlor	100[a]	3.12E−05 (±4.78E−05)	3.30E−04	1.56E−05 (±2.39E−05)	1.65E−04
Metribuzin	13[a]	2.22E−05 (±1.29E−05)	3.59E−05	1.11E−05 (±6.45E−06)	1.79E−05
Metsulfuron-methyl	220[a]	2.89E−06 (±1.41E−05)	1.52E−04	1.45E−06 (±7.04E−06)	7.59E−05
Piperonyl-butoxide	20[e]	2.94E−06 (±8.24E−06)	5.00E−05	1.47E−06 (±4.12E−06)	2.50E−05
Pirimicarb	35[a]	1.19E−06 (±2.54E−06)	9.52E−06	5.93E−07 (±1.27E−06)	4.76E−06
Tebuconazole	30[a]	1.72E−05 (±3.28E−05)	2.58E−04	8.61E−06 (±1.64E−05)	1.29E−04
Tetramethrin	20[f]	4.49E−05 (±3.14E−05)	9.00E−05	2.24E−05 (±1.57E−05)	4.50E−05
Triticonazole	25[a]	6.67E−07 (±0.00E+00)	6.67E−07	3.33E−07 (±0.00E+00)	3.33E−07
HQs		3.71E−03 (±5.54E−03)	4.43E−02	1.85E−03 (±2.77E−03)	2.21E−02

[a] https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN

[b] https://www.who.int/water_sanitation_health/dwq/chemicals/antrazine.pdf

[c] https://sitem.herts.ac.uk/aeru/footprint/index2.htm

[d] http://pmep.cce.cornell.edu/profiles/herb-growthreg/cacodylic-cymoxanil/chlorimuron-ethyl/herb-prof-chlorim-ethyl.html

[e] https://www.who.int/whopes/quality/PBO_specs_eval_WHO_Sep_2011.pdf

[f] https://apvma.gov.au/node/26596

of pesticides are unlikely to pose any adverse health effects. Similar results have been reported in previous studies [23–25]. The maximum estimated value of HQ was 3.35 E-2 for children and 1.67 E-2 for adults. Since HQ was well below 1 for all pesticides, sampling dates and sites, accumulated risk (HQs) was also minimal and far from 1 both in children and adults.

According to Hernández et al. [80], human exposure to mixtures of pesticides in low doses can occur from environmental or nutritional sources and can have a long-term negative impact on health, related to the

increase in chronic and degenerative diseases, developmental neurotoxicity and cancer. In addition, for some pesticide mixtures, health effects may be higher or lower than expected from the simple addition of the effects of the individual components, which raises concern about their possible impact on health. These authors conclude that, from a regulatory view, it is important to advance in understanding the hazard assessment of pesticide mixtures at realistic doses and to model their cumulative effects in humans and the environment. More research is needed to identify the lower thresholds for real pesticide mixtures to prevent their impact on human and environmental health.

3.7 Water treatment and pollution prevention

Several methods can be used to remove pesticides from water but their efficiency depends on the characteristics of the pesticides and they are not always applicable at household level. Compounds like atrazine and its metabolites (molecules with low solubility in water) are easily adsorbed by the powdered activated carbon (PAC), while glyphosate and AMPA show low adsorption onto PAC due to their high polarity [81, 82]. On the other hand, ozone oxidation produces complete degradation of glyphosate and AMPA, but not for atrazine, HOA, DIA or DEA [81, 83]. Therefore, total elimination would be achieved with a combination of both methods [81]. Sand filtration is moderately effective in glyphosate and AMPA elimination, but removal is highly dependent on conditions and therefore variable [82]. According to Brosillon et al. [84], chlorination can provide full degradation of glyphosate. Low-pressure direct photolysis using high UV fluences degrades substances such as atrazine [85], but is not effective for glyphosate and AMPA. Membrane filtration (nanofiltration and reverse osmosis) proved to be highly effective for the removal of several pesticides, including glyphosate, atrazine and AMPA [82, 86].

To prevent environmental pollution with pesticides, usual practices include control of weather conditions during and after spraying activities and spot spray systems. However, some of the studies cited above show it is necessary to implement soil conservation practices in order to reduce erosion and the movement of pesticides along with soil particles and/or water runoff. Although NT is currently the main cultivation system, researches demonstrate that soil continues to be eroded under this management system [87]. Contour tillage is the simplest soil erosion control measure, which reduces runoff and increases water infiltration compared to that which occurs with cultivation parallel to the slope [88]. Winter cover crops also reduce wind and water erosion, since they increase soil cover and water infiltration, and protect aggregates from the impacts of raindrops; besides, they can compete with weeds and reduce herbicide use [89]. Terraces are more complex land management practices and consist in earth embankments constructed across the slope to intercept surface runoff. They convey runoff to a stable outlet at a non-erosive velocity and shortened slope length [90]. The use of living windbreaks, which are rows of trees and shrubs, reduces wind erosion: in dry areas, suitably distributed windbreaks on 5% of the area can reduce wind speed by 30–50% and soil losses even by 80% [91]. Therefore, reforestation should be a land management practice promoted by governments. Finally, riparian vegetation strips (RVS) reduce surface runoff volume and retain sediments, pesticides and nutrients that are transported across them from adjacent crop fields and a significant factor affecting this process is the floristic composition of the RVS [92]. In this way, Yang et al. [39] propose setting protection areas located between farming lands and public rivers.

4 Conclusions

Three types of water sources were analyzed to determine the environmental fate of pesticides. They were found mainly in dams and cisterns, confirming the importance of runoff and atmospheric deposition in the movement of pesticides in the environment. Although environmental behavior was governed by the characteristics of the compounds, doses and frequency of use also played an important role in defining presence and concentration of a compound. Hence, the most frequent molecules were herbicides and the most important compounds were glyphosate, atrazine, AMPA and HOA. Nevertheless, occurrence of active ingredients with little or no use in the area, such as ametryn, suggests the need to carry out research on a larger scale to determine movement of pesticides at a macro-regional level.

Consumption of rainwater is a common practice in rural areas of semiarid region of Argentina and it is encouraged by different state policies tending to improve the quality of life of rural populations with no access to tap water. Although rainwater is safe according to the health risk assessment, population is exposed to regular pesticide consumption at levels that exceed the standards of the EU.

In different agricultural areas of Argentina, pesticides are distributed in all the environmental matrices thus contaminating sources of water used for human consumption. Current focus on agricultural practices in order to reduce water contamination usually refers to spraying systems and conditions, but it is necessary to include other practices that will have an impact on the reduction in water pollution.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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