



Multiple pesticides occurrence, fate, and environmental risk assessment in a small horticultural stream of Argentina



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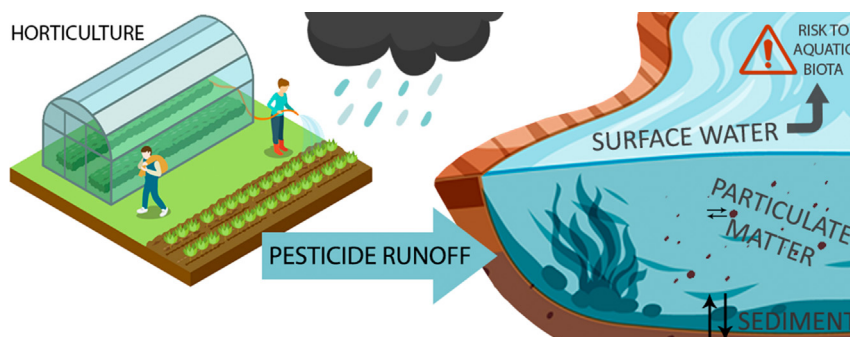
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HIGHLIGHTS

- Glyphosate and AMPA were the most frequently pesticides in horticulture.
- In three years of study, chlorpyrifos was detected in >50% of the water samples.
- Pyrethroids concentrations in bottom sediments exceeded those previously reported.
- Rains prior to samplings were a relevant factor to water concentrations.
- The ecological assessment showed a high risk for pesticides used in horticulture.

GRAPHICAL ABSTRACT



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ABSTRACT

Peri-urban horticulture is crucial to local populations, but a global paucity of information exists regarding the contamination of the associated waterways because of this activity. The aim of this study was to assess pesticide pollution of surface water, suspended particulate matter and bottom sediments from the Carnaval Creek Basin (La Plata, Buenos Aires, Argentina) – a representative system of waterways surrounded by horticultural production – by over 40 selected herbicides, insecticides, and fungicides by gas-chromatography–time-of-flight mass spectrometry and ultraperformance liquid chromatography tandem mass spectrometry. Six sampling campaigns were conducted biannually from 2015 to 2017. Glyphosate and (aminomethyl)phosphonic acid (AMPA), surprisingly, were the most frequently detected pesticides, in concentrations comparable to those reported in areas with genetically modified extensive crops (maximum in water, 20.04 and 4.86 $\mu\text{g}\cdot\text{L}^{-1}$; in sediment, 1146.5 and 4032.7 $\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, respectively). The insecticides chlorpyrifos, cypermethrin and λ -cyhalothrin were detected in more than 30% of the samples. The concentrations tended to greatly exceed those previously reported – by up to more than 800 times for chlorpyrifos in water (maximum 2.645 $\mu\text{g}\cdot\text{L}^{-1}$) and more than 400 times for lambda-cyhalothrin in sediments (maximum 2607.7 $\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$). The total pesticide concentration in surface water was found to be influenced by precipitation regimes but was independent of the season of the year, with precipitations of more than 140 mm diluting the pesticide concentrations to levels below detection limits. An environmental risk assessment performed with the pesticide concentrations of pesticides in surface water revealed that the surrounding horticultural activity posed a high risk for aquatic biota, with 30% of the samples exceeding the threshold value by more than a thousand times. We conclude that pesticides from horticultural use are a major threat to small streams and their biodiversity. This work provides valuable information that is scarce regarding the impact on watercourses exclusively as a consequence of horticulture.

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1. Introduction

Pesticides are widely used in agricultural-production systems to control unwanted pests. In particular, the current horticultural-production system is highly reliant on those agents (Kreuger et al., 2010; Oliver et al., 2012; Sarandón, 2015). The pesticide-use regime employed is primarily influenced by the different threats faced by the vegetables being produced, with each production unit having multiple crops being cultivated simultaneously. Consequently, a substantial variety and load of pesticides is constantly being applied in horticulture. In the horticultural greenbelt of La Plata (Buenos Aires, Argentina) in particular, up to 168 active ingredients have been declared as in use (Sarandón, 2015). This greenbelt is one of the most productive in the country, where more than 6000 ha are devoted to the production of fresh vegetables. Since this activity continues throughout the year, the use of pesticides is ongoing, but with more applications occurring during warmer seasons (Mac Loughlin et al., 2017; Marino and Ronco, 2005; Wightwick et al., 2012).

Pesticides can mobilize from cultivated land to nontarget compartments by several processes – such as surface waters, where drainage from greenhouses can rapidly mobilize pesticides (Kreuger et al., 2010), and surface-runoff containing eroded soil particles from the topsoil with adsorbed pesticide residues (Cruzeiro et al., 2016; Topaz et al., 2018).

The presence of pesticides in water bodies has been studied widely in Argentina (Bonansea et al., 2013; Etchegoyen et al., 2017; Hunt et al., 2016; Marino and Ronco, 2005; Primost et al., 2017; Ronco et al., 2016), and the rest of the world (Ccanccapa et al., 2016; Chen et al., 2018; Cruzeiro et al., 2016; Feo et al., 2010; Herrero-Hernández et al., 2013; Postigo et al., 2021; Reilly et al., 2012; Smalling et al., 2013; Weston and Lydy, 2010). Most investigations, however, have focused on nonpoint sources from large monoculture crops in major rivers. In comparison, little information is available on pesticide pollution resulting exclusively from horticultural activity (Allinson et al., 2014; Kreuger et al., 2010; Mac Loughlin et al., 2017; Solis et al., 2021; Wightwick et al., 2012), and in addition a small fraction of those studies have been conducted in small water bodies, systems that are characterized by high risk of contamination by pesticides (Szöcs et al., 2017).

The occurrence of mixtures is a greater concern because of their potential additive or synergistic effects. Environmental Risk Assessment (ERA), expressed as a function of environmental exposure (pesticide concentrations) and ecotoxicological effects, facilitates the modeling of the expected toxicity of pesticide mixtures with different modes of action. This approach has previously been used in Argentina (Iturburu et al., 2019; Pérez et al., 2021), but not to estimate the risk that horticulture represents to aquatic environments.

Despite the relevance of this world-wide activity, only a paucity of information is available on the negative impact of horticulture on aquatic environments. Furthermore, little information exists altogether about the pesticide pollution of small bodies of water. Within this context, the objective of the present work was to evaluate the risk on aquatic organisms derived from the use of pesticides in horticulture, based on real information on the concentrations of herbicides, insecticides, and fungicides in the different matrices of the aquatic environment, as well as to evaluate the behavior of these agents with respect to rainfall dynamics.

2. Materials and methods

2.1. Chemicals and reagents

Acetonitrile and methanol, HPLC grade, were purchased from Carlo Erba and pesticide-residual-grade acetone, dichloromethane, and n-hexane were purchased from J.T. Baker. Nanopure water was obtained in the laboratory with a Sartorius Arium (Phillipsburg, NJ, USA) water purification system. The analytical-grade salts were obtained from J.T. Baker: anhydrous magnesium sulfate, sodium chloride, potassium phosphate dibasic, and ammonium acetate. For liquid-chromatography derivatization,

9-fluorenylmethoxycarbonyl chloride ($\geq 99.0\%$, Fmoc-Cl) was acquired from Sigma Aldrich; pesticide reference standards (purity $\geq 95.0\%$) were purchased from AccuStandard and Sigma Aldrich; and isotopically labeled glyphosate- $2\text{-}^{13}\text{C}$, ^{15}N (98 atom % ^{15}N , 99 atom % ^{13}C ; GLY*), atrazine- d_5 , PESTANAL® (ATZ*), and cypermethrin-phenoxy- d_5 (CYP*) were obtained from Merck.

2.2. Study area and sampling

La Plata has a humid subtropical climate. The average annual temperature is $16.3\text{ }^\circ\text{C}$, with average temperatures in the coldest month of $5\text{ }^\circ\text{C}$ (July, winter) and $29\text{ }^\circ\text{C}$ in the warmest month (January, summer). Due to the city's proximity to the Río de la Plata, humidity tends to be abundant, with an average annual humidity of 80%. La Plata receives 1067.6 mm of precipitation annually, with winters being the drier months and summer the wetter ones (SMN, 2021).

Originating in the outskirts of La Plata, the Carnaval Creek and its tributaries constitute a suburban basin (Fig. 1). The catchment size of 54.5 km^2 is responsible for the creek's classification as a small stream according to the European Union's Water Framework Directive (Szöcs et al., 2017). The main channel has an average depth of 0.8 m, a high turbidity, and a low current velocity. Samples were taken from the upper and middle parts of the basin, where the principal mainland use activity is intensive horticulture (Mac Loughlin et al., 2017). The sampling was performed in summer and winter over a three-year period: 12 August 2015 (winter, WIN15), 24 January 2016 (summer, SUM16), 9 July 2016 (winter, WIN16), 25 February 2017 (summer, SUM17), 31 August 2017 (winter, WIN17), and 16 December 2017 (summer, SUM18). The time between samplings was based on seasonal-production practices and the consequent pesticide use (Sarandón, 2015). The surface water, suspended particulate matter (SPM), and bottom sediments were collected from 5 sites, S1 through S5; with those being increasingly numbered starting from the closest to the headwater in the García Lagoon. Rainfall records were obtained from the meteorological station located at La Plata's aerodrome. The dissolved oxygen, temperature, conductivity, and pH were measured *in situ* with a Lutron WA-2017SD multiparameter instrument.

Surface water was collected in a 500-mL amber glass bottle, spiked with 50 ng of ATZ* and CYP*. To prevent analyte loss, 5 mL of n-hexane were added. To obtain the suspended particulate matter, another sample of 100 mL was filtered *in situ* through nylon membrane (47 mm-diameter, 0.45- μm pore size) previously weighed dry. Ten milliliters of the filtered water (soluble phase) were saved in a propylene tube and spiked with 10 ng of GLY* for glyphosate analysis. Filtering details and equipment are indicated in Mac Loughlin et al. (2020). Sediment samples from the first 5 cm were collected in and handled as described in Mac Loughlin et al. (2017). All samples were transported in an ice-cold container to the laboratory within fewer than 2 h after sampling was conducted.

In the laboratory, the nylon membranes were spiked with 50 ng of ATZ* and CYP*, and 30 ng of GLY*, then placed in a desiccator to remove excess moisture, weighed to determine the dry SPM mass, and finally stored at $-20\text{ }^\circ\text{C}$ until pesticide analysis. The water samples were stored at $4\text{ }^\circ\text{C}$ in the dark until extraction within 24 h thereafter. The sediment samples were homogenized and divided into subsamples: the first subsample was dried to constant weight at $105\text{ }^\circ\text{C}$ to determine the dry weight and later calcined in a muffle furnace at $550\text{ }^\circ\text{C}$ to determine the percent organic carbon percentage by loss on ignition (Heiri et al., 2001); the second subsample was stored at $-20\text{ }^\circ\text{C}$ until pesticide analysis.

2.3. Chemical analysis

2.3.1. Pesticide extraction

Surface water (500 mL) was extracted three times with 30 mL of dichloromethane (USEPA, 1996). For glyphosate and (aminomethyl)

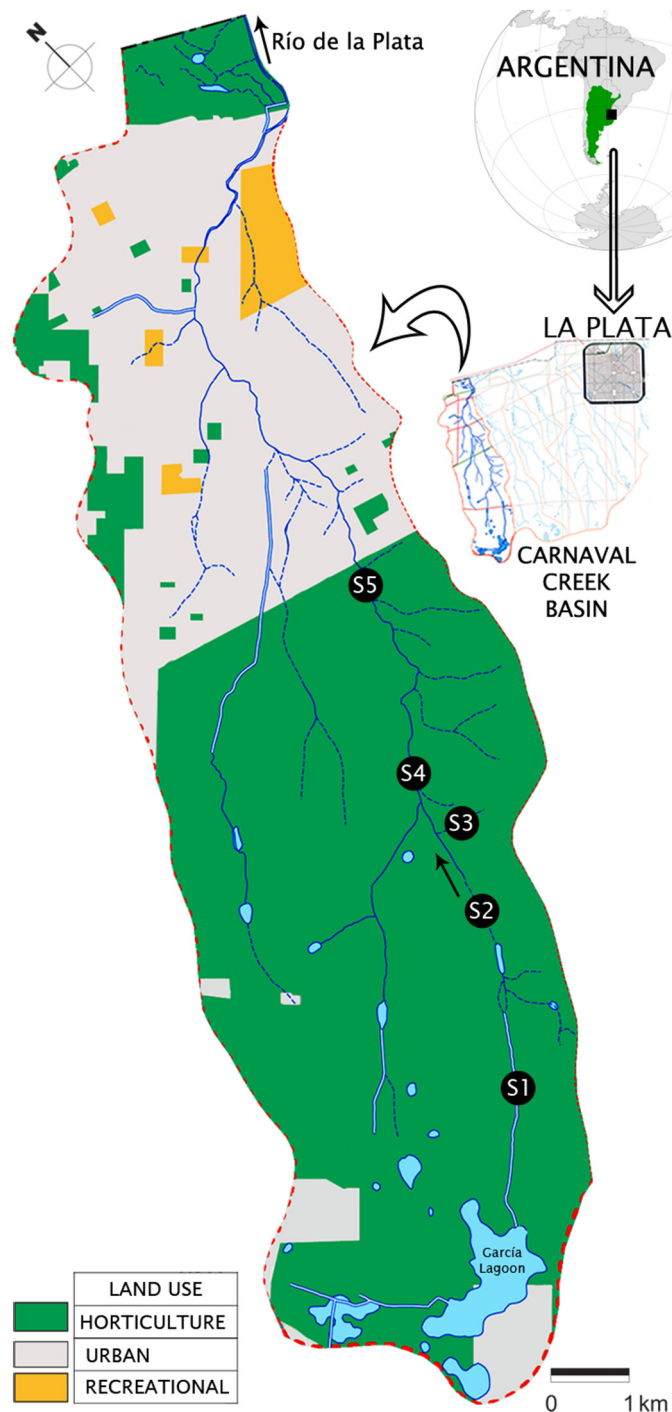


Fig. 1. Carnaval Creek Basin in La Plata, Buenos Aires, Argentina. The insert to the upper right depicts the location of La Plata along the eastern coast of Argentina. The circled numbers indicate the sampling sites along the main course and tributaries. The arrows describe the flow direction of the streams. Key to the colors representing the land use: green, agriculture; gray, urban development; orange, recreational. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

phosphonic acid (AMPA), 1 mL was adjusted to pH = 9 and derivatized with FMOC-Cl (Mac Loughlin et al., 2020). For SPM analysis, the nylon filters were extracted by sonication in a methanol-acetone mixture (Darwano et al., 2014), followed by glyphosate and AMPA extraction with 3 mL of 100 mM phosphate dibasic buffer and sonication. One mL was then derivatized with FMOC-Cl (Mac Loughlin et al., 2020). The sediments were extracted with a modified multiresidue QuEChERS

procedure for pesticides (Mac Loughlin et al., 2017), and with sonication with 100 mM phosphate dibasic buffer, centrifuged, extract adjusted at pH = 9 and derivatized with FMOC-Cl for glyphosate and AMPA (Ronco et al., 2016). The organic-solvent extracts for all the matrices monitored were concentrated under a gentle nitrogen stream and reconstituted in 500 μ L of n-hexane for instrumental analysis.

2.3.2. Analytical determination, quality control and quality assurance

The pesticides were analyzed by a gas chromatograph model Master GC coupled to a time-of-flight mass spectrometer model Master TOF-MS Plus, at 1 μ m resolution (DANI Instruments, Milan, Italy). For glyphosate and AMPA, a Waters Acquity ultraperformance liquid chromatograph coupled to a Quattro Premier XE Tandem Quadrupole Mass Spectrometer was used. The chromatographic conditions and operational parameters are described in Mac Loughlin et al. (2017) and Primost et al. (2017), respectively.

The extraction methodologies used in this present work: recovery, linearity, precision, accuracy, and limit of detection (LOD), and limit of quantification (LOQ) have all been previously validated in the laboratory (Etchegoyen et al., 2017; Mac Loughlin et al., 2017, 2020; Primost et al., 2017; Ronco et al., 2016). During sample analysis, reagent blanks and duplicates were used as quality controls. Isotopically labeled atrazine, cypermethrin, and glyphosate were used as internal standards to evaluate extract holding time and recovery throughout all the analytical procedures. The quantification in both chromatographic systems was carried out by an external calibration curve in the 0 to 100 μ g \cdot L⁻¹ range (Mac Loughlin et al., 2017; Primost et al., 2017). The ratio between the quantification and confirmation ions or transitions in the pesticide standards and analyzed samples was used as a criterion for the identification and confirmation of analytes (SANTE, 2019).

2.4. Environmental risk assessment (ERA)

The toxicity endpoints were obtained from the Pesticide Properties Database (Lewis et al., 2016). The acute (96-h median lethal concentration, LC₅₀) and chronic (21-day no-observed-effect concentration, NOEC) toxicities in fish (e. g., rainbow trout *Oncorhynchus mykiss*), the acute (48-h median effective concentration, EC₅₀) and chronic (21-day NOEC) toxicities in aquatic invertebrates (e. g., the water flea *Daphnia magna*), and the acute (72-h EC₅₀) and chronic (96-h NOEC) toxicities in algae (e. g., *Scenedesmus subspicatus*) were selected as toxicity endpoints. When no data were available for the previously mentioned species, data were used from same group of organisms reported in the Pesticide Properties Database.

Chronic risks in surface water were assessed on the basis of risk-quotient (RQ) analysis, as described by Vryzas et al. (2009). RQ was calculated according to Eq. 1:

$$RQ = \frac{MEC}{PNEC} \quad (1)$$

where MEC is the measured environmental concentration of a pesticide, and PNEC is the predicted no effect concentration. PNEC was calculated according to Eq. 2:

$$PNEC = \frac{CC}{AF} \quad (2)$$

where CC is the critical concentration and AF is an assessment factor.

CCs were set as the lowest concentration among the NOECs for chronic endpoints for fish, aquatic invertebrate, and algal species. Where NOECs for all three taxa were absent, the lowest value of (acute) median lethal or effective concentration (LC₅₀ or EC₅₀, respectively) was employed. The AF was 10 if three NOECs were available, 50 if two, 100 with only one value, and 1000 for no values, where a median concentration was used (Papadakis et al., 2015).

As the RQ approach assumes an additive concentration effect, where mixture toxicity is based on the addition of effects of each pesticide, the sum of RQ for each sample ($\sum RQ$) was calculated for each sampling site in the different campaigns, according to Eq. 3:

$$\sum RQ = \sum_{i=1}^n RQ_i \quad (3)$$

where RQ_i is the risk quotient for the i pesticide. $\sum RQ < 0.01$ indicates a negligible environmental risk, $0.01 \leq \sum RQ < 0.1$ indicates a low risk, $0.1 \leq \sum RQ < 1$ indicates a medium risk, and $\sum RQ \geq 1$ indicates a high risk (Vryzas et al., 2009).

2.5. Data analysis

For the data analysis, the concentrations of the different pesticides were used, both as total and individually, or as their sum by type – *i. e.*, herbicides, insecticides, or fungicides; with the glyphosate and AMPA data analyzed separately from the other herbicides in order to avoid masking any pattern in the herbicide analysis, since these analytes were found in more than 80% of the samples. The pesticide concentrations below LOD were replaced by half of the corresponding LOD, and concentrations below LOQ (detectable, but nonquantifiable) were replaced by the mean between the LOD and the LOQ (Etchegoyen et al.,

2017; Mac Loughlin et al., 2017). Since the data presented a nonnormal distribution, nonparametric tests were used for the analysis. The Mann-Whitney U test was used to assess significant differences between the seasons, while the Kruskal-Wallis H test was used to examine the spatiotemporal differences in pesticide concentrations. For all tests, the level of significance was set at $\alpha = 0.05$. Statistical analysis was performed by means of the XL-STAT (Addinsoft 2005, version 7.5.3) and STATISTICA (Stat Soft, Inc. 2001; version 7) software.

3. Results and discussion

A total of 41 compounds were analyzed: 7 herbicides (including 1 degradation metabolite), 5 pyrethroids, 5 organophosphates (including 1 metabolite), 1 phenylpyrazole, 17 organochlorines (including metabolites and isomers), 5 fungicides, and 1 pesticide synergist. All analytical methods were performed in accordance with international regulation (SANTE, 2019) and the previously reported literature (Darwano et al., 2014; Etchegoyen et al., 2017; Mac Loughlin et al., 2017, 2020; Ronco et al., 2016). Table 1 summarizes the compounds analyzed, the abbreviations used, and the instrumental performance for each matrix.

Table 2 lists the physicochemical parameters measured *in situ*, SPM concentration, the sediment humidity and the percent organic carbon, and the precipitations 14-days before sampling. The pH values were

Table 1
Pesticides analyzed, abbreviations used, type of pesticide, limits of detection and quantification in each environmental matrix, and instrumental coefficients of determination.

Pesticide	Abbreviation	Type ^b	Limit of detection ^a			Limit of quantification ^a			r ²
			SW	SPM	SED	SW	SPM	SED	
Glyphosate	GLY	H	0.03	0.2	0.3	0.1	0.5	1	0.990
(Aminomethyl)phosphonic acid	AMPA	H	0.04	0.3	0.6	0.1	0.9	2	0.992
Atrazine	ATZ	H	0.002	0.01	0.4	0.006	0.03	1	0.989
Acetochlor	ATC	H	0.001	0.005	0.2	0.003	0.02	0.6	0.968
Metolachlor	MTC	H	0.001	0.005	0.2	0.002	0.01	0.4	0.992
Pendimethalin	PEN	H	0.004	0.02	0.8	0.01	0.06	2	0.970
Trifluralin	TRF	H	0.0001	0.0005	0.02	0.0005	0.003	0.1	0.972
Bifenthrin	BIF	I PYR	0.0005	0.003	0.1	0.002	0.01	0.4	0.991
Cypermethrin	CYP	I PYR	0.002	0.01	0.4	0.008	0.04	2	0.921
Deltamethrin	DEL	I PYR	0.001	0.005	0.2	0.004	0.02	0.8	0.902
Permethrin	PER	I PYR	0.0004	0.002	0.08	0.001	0.005	0.2	0.987
Lambda-cyhalothrin	λ-CYHAL	I PYR	0.0005	0.003	0.1	0.002	0.01	0.4	0.958
Chlorpyrifos	CLP	I OP	0.002	0.01	0.4	0.006	0.03	1	0.959
Diazinon	DZN	I OP	0.002	0.01	0.4	0.006	0.03	1	0.973
Malathion	MAL	I OP	0.0008	0.004	0.2	0.003	0.02	0.6	0.965
Parathion	PAR	I OP	0.002	0.01	0.4	0.005	0.03	1	0.986
Methyl parathion	Me-PAR	I OP	0.006	0.03	1	0.02	0.1	4	0.988
Fipronil	FIP	I	0.0006	0.003	0.1	0.002	0.01	0.4	0.917
Endosulfan	END	I OC	0.001	0.005	0.2	0.005	0.03	1	0.996
Endosulfan sulfate	END-SO4	I OC	0.0005	0.003	0.1	0.002	0.01	0.4	NA ^c
α-Lindane	α-HCH	I OC	0.007	0.04	1	0.02	0.1	4	0.976
β-Lindane	β-HCH	I OC	0.01	0.05	2	0.03	0.2	7	0.959
γ-Lindane	γ-HCH	I OC	0.01	0.06	2	0.04	0.2	7	0.945
Heptachlor	HPC	I OC	0.01	0.05	2	0.03	0.2	7	0.983
Heptachlor epoxide (isomer A)	HCE(A)	I OC	0.002	0.01	0.4	0.006	0.03	1	0.985
Heptachlor epoxide (isomer B)	HCE(B)	I OC	0.003	0.02	0.6	0.007	0.04	1	0.983
Aldrin	ADN	I OC	0.01	0.07	3	0.04	0.2	9	0.991
Dieldrin	DND	I OC	0.006	0.03	1	0.02	0.1	4	0.988
Endrin	EDN	I OC	0.01	0.07	3	0.04	0.2	9	0.993
Methoxychlor	MXC	I OC	0.0004	0.002	0.08	0.001	0.005	0.2	NA ^c
p,p'-DDT	p,p'-DDT	I OC	0.004	0.02	0.8	0.01	0.07	3	0.966
o,p'-DDT	o,p'-DDT	I OC	0.001	0.005	0.2	0.004	0.02	0.8	0.953
o,p'-DDE	o,p'-DDE	I OC	0.0005	0.003	0.1	0.002	0.01	0.4	0.981
p,p'-DDE	p,p'-DDE	I OC	0.0009	0.005	0.2	0.003	0.02	0.6	0.978
p,p'-DDD	p,p'-DDD	I OC	0.005	0.03	1	0.02	0.09	3	0.977
Azoxystrobin	AZX	F	0.002	0.01	0.4	0.007	0.04	1	0.999
Pyraclastrobin	PYR	F	0.003	0.02	0.6	0.009	0.05	2	0.992
Epoxiconazole	EPX	F	0.004	0.02	0.8	0.01	0.07	3	0.966
Cyproconazole	CPZ	F	0.007	0.04	1	0.02	0.1	4	0.967
Tebuconazole	TEB	F	0.006	0.03	1	0.02	0.1	4	0.969
Piperonyl butoxide	BXP	S	0.0001	0.0005	0.02	0.0003	0.002	0.06	0.973

^a SW, surface water ($\mu\text{g}\cdot\text{L}^{-1}$); SPM, suspended particulate matter ($\mu\text{g}\cdot\text{L}^{-1}$); SED, sediment ($\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$).

^b H, herbicide; I, insecticide; F, fungicide; PYR, pyrethroid; OP, organophosphate; OC, organochlorine; S, synergist.

^c NA: not analyzed.

Table 2

Minimum-maximum values for physicochemical parameters, suspended particulate matter concentration, and sediment moisture and organic-carbon content, and the accumulated precipitation of 14 days before the sampling campaign is presented.

Parameter ^a	WIN15 ^b	SUM16	WIN16	SUM17	WIN17	SUM18
pH	7.21–8.09	6.24–7.01	6.72–7.40	7.56–8.16	6.98–7.76	7.13–7.60
T (°C)	11.7–18.3	24.3–30.0	10.8–14.0	21.1–26.6	17.4–20.4	23.3–26.1
DO (mg·L ⁻¹)	5.40–9.90	4.00–7.30	6.00–10.50	1.90–6.60	4.80–6.00	0.60–4.10
σ (μS·cm ⁻¹)	304–374	90–860	124–174	662–867	185–667	828–957
SPM (mg·L ⁻¹)	25.0–236.0	24.0–273.0	34.0–57.0	8.0–188.5	24.3–218.5	18.0–292.0
Moisture (%)	31.0–62.9	42.4–65.0	38.8–58.0	40.2–57.9	38.1–69.1	42.9–62.4
OC (%)	2.0–8.9	4.5–7.2	2.3–7.8	3.8–9.1	2.3–9.2	2.4–7.8
14-d rains (mm)	89.9	8.4	151.9	57.9	44.2	83.1

^a T, temperature; DO, dissolved-oxygen concentration; σ, conductivity, SPM, suspended particulate matter; OC, organic carbon; 14-d rains, accumulated precipitations 14 days before sampling.

^b WIN15, winter 2015; SUM16, summer 2016; WIN16, winter 2016; SUM17, summer 2017; WIN17, winter 2017; SUM18, summer 2018.

within the environmental range for surface water bodies in the region (Ronco et al., 2016). When the temperature increased during the summer, the DO became lower since temperature inversely affects oxygen solubility. At the same time, the conductivity was significantly higher due to the electrolytes in the underground water being used for irrigation. Throughout the 6 campaigns, S1 constantly exhibited the maximum concentration of suspended matter. The sediment moisture ranged between 31.0% and 69.1% and the organic carbon was between 2.0% and 9.2%, while S2 manifested the maximum for both parameters in all the sampling campaigns. Nevertheless, no statistical differences were found between the winter and summer sampling campaigns for the percentage of organic carbon in the bottom sediments.

3.1. Detection frequency

In 5 out of 6 sampling campaigns, pesticides were detected in all the matrices analyzed at every site sampled. In the weeks before the third campaign, WIN16, the total precipitations amounted to 151.9 mm (Table 2), 3 times the historical average for that month. That sampling was conducted purposely in order to determine if, after heavy rains, mobilization or dilution of pesticides in the environment occurred. As no pesticides were detected, dilution was logically the main effect after such rains totaling greater than 150 mm (Aparicio et al., 2013; Mac Loughlin et al., 2020). Since the study system was “washed down”, WIN16 was no longer considered for the following discussion. Despite this finding, we hasten to add that, in sampling campaigns following that precipitation peak, pesticides were detected once again, both in the winter and summer campaigns. That pesticides became detectable after that time simply reflects the continuous use of those products in horticultural activity (Mac Loughlin et al., 2017; Sarandón, 2015); where in just 6 months later, 6 pesticides were found in those sediments.

Fig. 2 displays the overall detection frequency of all those pesticides in each environmental matrix. The detection frequency of each compound by matrix and campaign is detailed in the Supplementary Material (Table S1). In total, of the 41 pesticides analyzed, 12 were detected in surface water, 7 in the SPM, and 11 in the sediment samples. The number of pesticides and the detection frequencies were significantly different statistically, with higher percentages resulting during the summer campaigns ($p = 0.0015$). At the same time, differences were also found between the matrices analyzed, with pesticides resulting more frequently in sediments, which finding is to be expected since that this compartment acts as a natural sink for such contaminants (Burton and Landrum, 2003; Mac Loughlin et al., 2017; Ronco et al., 2016).

A relevant observation was the ubiquitous presence of glyphosate (GLY) and AMPA, with those compounds being the most frequently detected overall – i. e., in more than 80% of the samples from all the matrices analyzed. An in-depth analysis of GLY and AMPA in the water and SPM of these same samples had been carried out in a previous publication (Mac Loughlin et al., 2020). In the sediments, AMPA was detected in

100% of the samples. As this compound is the environmental metabolite of GLY, the parental compound was, at some specific time, present in the system (Aparicio et al., 2013; Ronco et al., 2016). In horticulture, GLY is used to kill weeds around greenhouses and to prepare the soil (in a chemical fallow) before planting. Primost et al. (2017) and Soracco et al. (2018) has previously proposed GLY to be classified as a so-called *pseudo-persistent* pollutant in agrarian soils, as the pesticide, under continuous application outpaces the degradation capability of the environment. Since the half-life of GLY in water varies from a 2 to 91 days and up to 215 days in sediments (Ronco et al., 2016), it was expected that between sampling campaigns GLY would have degraded to its metabolite AMPA; however, GLY quantification between samplings did not show significant differences (further discussed in Section 3.2 and Section 3.3.3.1). The continuous occurrence of GLY and/or AMPA after 3 years of sampling in all the environmental matrices analyzed and at quantifiable concentrations further supports GLY's classification as a *pseudo-persistent* pollutant, now in aquatic productive environments as well.

The herbicides trifluralin and atrazine (ATZ), were detected at frequencies greater than 10%. Allinson et al. (2014) analyzed the herbicides in surface water in a horticultural-production catchment in southeastern Australia and found ATZ in only 6% of the 106 samples analyzed. Nevertheless, in Sweden, the ATZ-detection frequency was considerably higher at 22% in areas with horticultural crops (Kreuger et al., 2010),

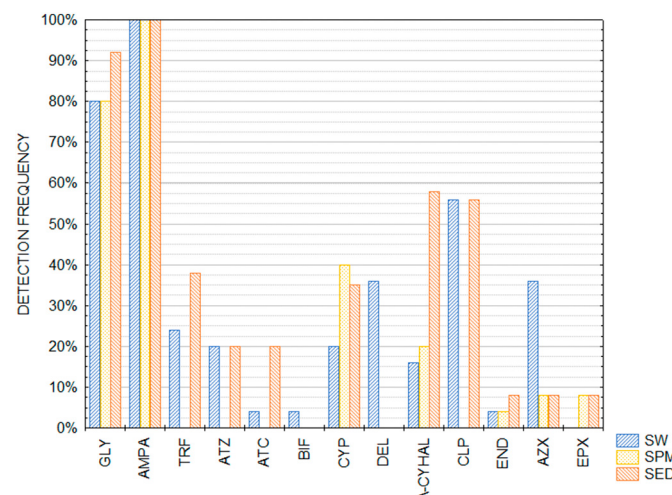


Fig. 2. Detection frequency of the 6 sampling campaigns in each matrix. In the bar graph, the percent detection frequency is plotted on the ordinate for each of the matrices investigated itemized on the abscissa. Key to abbreviations: surface water (SW), blue; suspended particulate matter (SPM), yellow; bottom sediments (SED), orange. Table 1 contains a list of all the pesticide abbreviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

similarly to our findings of 20%. Reilly et al. (2012) reported detecting trifluralin at 13% in 60 water samples, while we found that compound in more than 20% of the water samples and, even more frequently, at 38% in the associated sediments.

The most frequently detected insecticide was chlorpyrifos (CLP), present in 37% of all the samples from the three matrices analyzed. At a close second in frequency, the pyrethroids cypermethrin (CYP) and λ -cyhalothrin (λ -CYHAL) were detected in 30% of the samples, mainly associated with solid matrices. Other insecticides, such as deltamethrin, endosulfan and bifenthrin likewise were present, but at frequencies at or below 10%. Because pyrethroids such as bifenthrin and permethrin are usually found exclusively in urban streams (Weston and Lydy, 2010), the detection of only bifenthrin among the compounds analyzed – and there in only a single water sample – confirms that the pesticides found in this watercourse are a consequence of the surrounding horticultural activity. The presence of CLP in more than 50% of the water and sediment samples, as shown in Fig. 2, is related to the frequent use of this insecticide in fruit and vegetable production (Mac Loughlin et al., 2018). Chlorpyrifos had been detected in all the water samples and in bottom sediments (56%) in the Argentine stretch of the Paraná Basin (Etchegoyen et al., 2017). Those authors also found CYP in 100% of the water and sediment samples analyzed. In Sweden, CLP and CYP were among the pesticides analyzed that were being used in the field cultivation of horticultural crops and in greenhouses, but those two agents were nevertheless not detected in any sample (Kreuger et al., 2010). From observations such as those, the two insecticides have been preferentially used in agricultural production in Argentina and for more than 15 years, as they have been detected in surface water in different agricultural productive regions of the country (Marino and Ronco, 2005).

Finally, the fungicides epoxiconazole and azoxystrobin were detected. The presence of the former, though at low frequencies, is relevant since that this active ingredient is not approved in horticultural production (Mac Loughlin et al., 2018; Sarandón, 2015). Therefore, the presence of that compound in the environment is testimonial to an illegitimate use. More than 30% of the water samples had quantifiable concentrations of azoxystrobin, whereas that agent had been quantified in 50% of the samples from Swedish streams (Kreuger et al., 2010) and in the United States (Reilly et al., 2012), in this instance being a fungicide authorized to be used in horticultural crops (Sarandón, 2015). The detection of a pesticide whose use is not authorized for horticultural production is a reflection of the misinformation and lack of regulation existing in the Argentine food-production systems (Mac Loughlin et al., 2018).

3.2. Spatial and temporal variation

No significant differences could be found with respect to the sampling sites within each campaign, most likely due to the large number of pesticide sources in this catchment (Szöcs et al., 2017). Therefore, the sites were considered as replicates within the basin. A temporal evaluation of the sampling campaigns with respect to the total pesticide concentration, both when considering GLY + AMPA ($p = 0.0012$) and when not ($p = 0.0053$) manifested differences for at least one, and thus a variation in the system over time. Consequently, we explored differences in each matrix according to the type of pesticides used.

The total pesticide concentration in surface water, with and without GLY + AMPA, exhibited differences between the sampling campaigns for at least one ($p = 0.0036$, $p = 0.0071$). On a deeper analysis, as illustrated in Fig. 3, Panel A, we were able to observe, once again, significant differences in the total concentration of herbicides, with and without GLY + AMPA ($p = 0.0053$, $p = 0.0159$). Likewise, statistically significant differences were found in the insecticide ($p = 0.0005$) and fungicide ($p = 0.0366$) concentrations. These differences indicated that surface water, it being the compartment that receives the pesticide input – either due to application drift or runoff – reveals current

information on the pesticides that are being used. Furthermore, a seasonal pattern could not be discerned, and this variation may be related to meteorological factors, which will be addressed in Section 3.3.4.

As in the surface water, in the SPM samples statistically significant differences were found for at least one of the samplings campaigns either with or without considering the contribution of GLY + AMPA ($p = 0.0006$ and $p = 0.0017$, respectively). The types of pesticides evidenced significant differences separately in this matrix (Fig. 3, Panel B): GLY + AMPA ($p = 0.0017$), insecticides ($p = 0.0017$), and fungicides were detected only in SUM16. Topaz et al. (2018) had reported a correlation between the magnitude of flood events and pesticide concentrations in the particulate phase of the water column. Because of the somewhat transient nature of the SPM, the difference found here could very well be a result of rather recent inputs into the system and/or the resuspension and mobilization of deposited material from the bottom sediments (Burton and Landrum, 2003). Regardless of the reason, these differences pointed to a need for further investigation of this environmental matrix in future work.

Unlike the previous matrices, no differences in the total concentration of pesticides were found for the sediment, either with or without GLY + AMPA included in the total concentration ($p = 0.1136$, $p = 0.0880$). Nevertheless, when the same analysis was carried out according to pesticide type (Fig. 3, Panel C), significant differences were detected for the herbicides, with ($p = 0.0383$) and without ($p = 0.0072$) GLY + AMPA. Moreover, differences in the concentration of GLY + AMPA in the bottom sediments ($p = 0.0035$) were observed between campaigns. This variation between campaigns was not reflected in the concentrations of insecticides ($p = 0.1417$) or fungicides ($p = 0.0898$), where no significant differences occurred between the sediments analyzed at different times of the year. The concentrations of these latter two groups of pesticides managed to dampen the time-varying concentration of herbicides in the sediments. The presence of insecticides and fungicides is a result of their continuous use in the different horticultural productions carried out in the area (Sarandón, 2015). In addition, the continuous loading of these types of pesticides in sediments over time further supports the notion of this matrix as constituting a *de facto* sink.

In the analysis of this same system for 3 years, the concentrations of pesticides in the surface water and SPM matrices were found to fluctuate throughout the seasons of the year, while in the sediments no statistically significant differences were found for insecticides and fungicides between sampling campaigns, evidencing the demand for these types of compounds in the horticultural production (Kreuger et al., 2010; Wightwick et al., 2012), and corroborated by surveys made to producers in the region (Sarandón, 2015). Similarly, Fairbairn et al. (2015) had observed seasonality in water concentrations, but not in sediments. We therefore could propose that, very likely, the surface water and the SPM better reflected the pesticides currently being applied in the different stages of horticultural production, whereas the bottom sediment provided historical information on the inputs that the system had received, thus maintaining a record of the compounds used long ago.

3.3. Most relevant pesticides associated with horticulture

3.3.1. Surface water

Table 3 summarizes of the most relevant concentrations found in surface water, with those compounds all being insecticides. The maximum CLP concentrations reported by Bonansea et al. (2013) and Ccanccapa et al. (2016) were below the LOQ in the present work ($0.006 \mu\text{g}\cdot\text{L}^{-1}$, cf. Table 1). Therefore, the lowest concentration quantified here turned out to be greater than these maxima. Similarly, the maximum CYP concentration reported here was more than 30 times the maximum reported in other countries. When, however, these values are compared with those of other publications from Argentina where extensive agriculture was carried out, the maximum in the Carnaval basin was seen to be similar to or lower than the other. In areas with

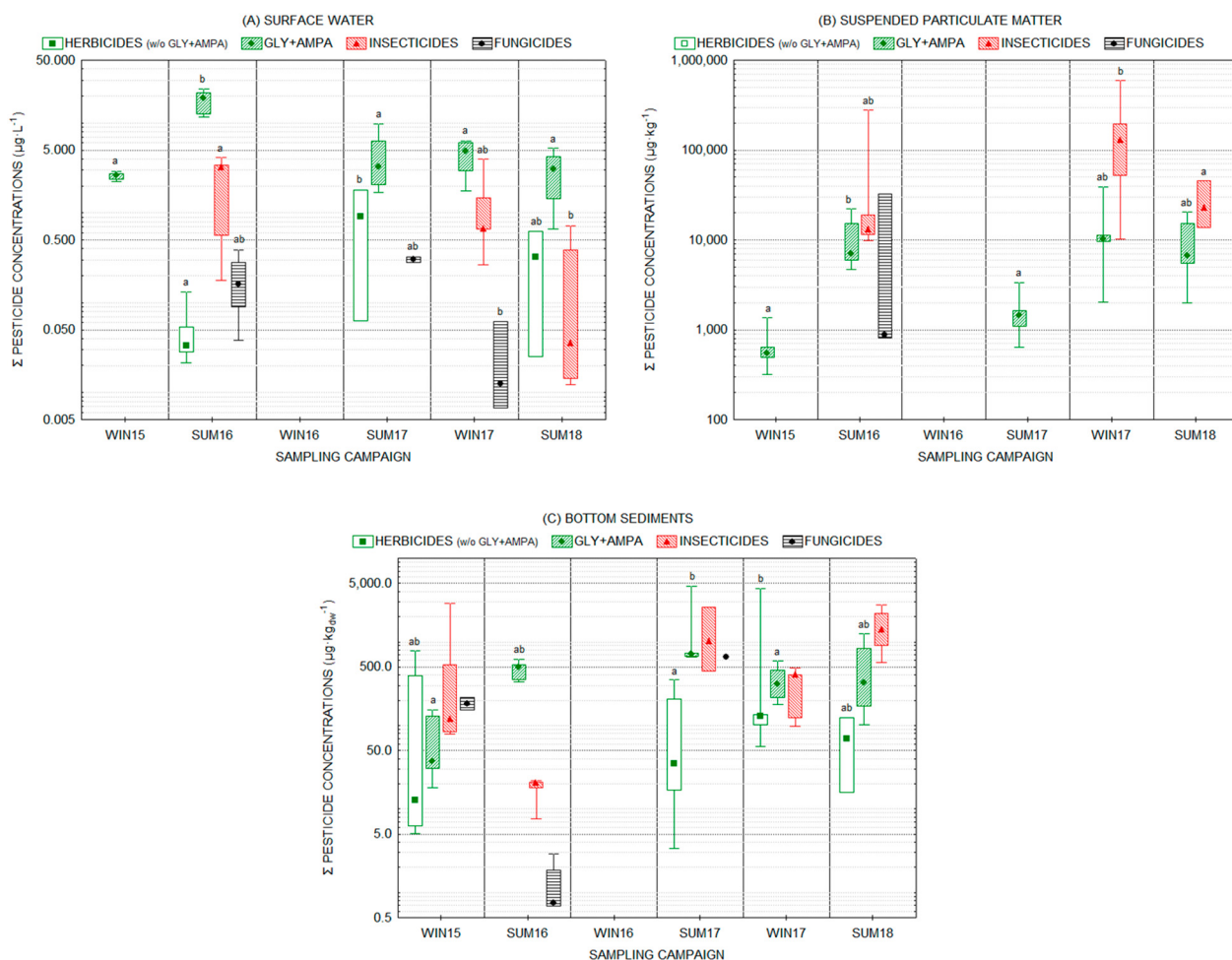


Fig. 3. Concentration of pesticides grouped by target organism – *i. e.*, herbicides (white and green-hatched boxes), insecticides (red-hatched boxes), fungicides (black-hatched boxes) – in (Panel A) surface water, (Panel B) suspended particulate matter, and (Panel C) bottom sediments. In each of the figures, the concentrations of the pesticides are plotted on the *ordinate* on a logarithmic scale for each sampling campaign indicated on the *abscissa*. In the boxplots, the box represents the 25th and 75th percentiles, the whiskers the minimum–maximum values, and the solid marker denotes the median concentration. The letters indicate significant differences between the sampling campaigns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Pesticide concentrations in surface water in comparison with the literature.

Pesticide	Sampling campaign ^a	Average (min–max) concentration ($\mu\text{g L}^{-1}$) ^b		Comparison with the maximum concentration	Site, reference
		Carnaval Creek	Reported		
CLP	SUM16	0.722 (0.044–2.645)	0.0018 (max 0.0056)	$\times 472$	Suquía River, Argentina ¹
	WIN17	0.023 (0.007–0.054)	0.001–0.003	$\times 882$	Ebro River, Spain ²
	SUM18	0.201 (0.012–0.720)	0.11 (max 0.47)	$\times 6$	Paraná Basin, Argentina ⁵
CYP	SUM16	1.354 (0.085–3.888)	0.0315 (max 0.1217)	$\times 32$	Suquía River, Argentina ¹
			max 0.04958	$\times 78$	Dongjiang River, China ³
			0.74 (0.01–6.62)	$\times \frac{1}{2}$	Paraná Basin, Argentina ⁵
			max 0.0572	$\times 68$	Ebro River, Spain ⁶
			max 3.58	\approx	Arrecifes River, Argentina ⁷
DEL	SUM16	0.179 (0.115–0.259)	max 0.044	$\times 90$	Dongjiang River, China ³
	WIN17	1.383 (0.257–3.944)	0.00803 (0.00017–0.03556)	$\times 110$	Tagus River, Portugal ⁴
λ -CYHAL	SUM16	0.004–0.010	0.01810	$\times \frac{1}{2}$	Dongjiang River, China ³
			0.04209 (0.01468–0.10107)	$\times \sqrt{10}$	Tagus River, Portugal ⁴
			max 0.031	$\times \sqrt{3}$	Lake Vistonis, Greece ⁸
			max 0.0175	$\times \frac{1}{2}$	California Delta, United States ⁹

^a WIN15, winter 2015; SUM16, summer 2016; WIN16, winter 2016; SUM17, summer 2017; WIN17, winter 2017; SUM18, summer 2018.

^b The maximum quantified concentration is underlined.

¹ Bonansea et al. (2013).

² Ccancapa et al. (2016).

³ Chen et al. (2018).

⁴ Cruzeiro et al. (2016).

⁵ Etchegoyen et al. (2017).

⁶ Feo et al. (2010).

⁷ Marino and Ronco (2005).

⁸ Papadakis et al. (2015).

⁹ Weston and Lydy (2010).

horticultural crops in Sweden, CLP and CYP were detected at only trace concentrations (Kreuger et al., 2010).

The lowest concentration of deltamethrin found here was still higher than the maximum concentration found in China (Chen et al., 2018) and Portugal (Cruzeiro et al., 2016). The low occurrence and concentrations of λ -CYHAL in surface water may be a result of its physicochemical properties: He et al. (2008) found a fast rate of dissipation of said compound from the aquatic environment, with only 30% of the applied dose remaining after 1 day in the water phase. This behavior is reflected in the occurrence and concentrations of λ -CYHAL in sediments, which matrix will be discussed below.

Two other pesticides of significance, found in more than 20% of the water samples, are the herbicide trifluralin (26%), and the fungicide azoxystrobin (36%). Both compounds are used in the production of tomatoes (Sarandón, 2015), a characteristic product of the area during the summer. The former was detected only during the summer sampling campaigns, in concentrations ranging from below the LOQ ($<0.0005 \mu\text{g}\cdot\text{L}^{-1}$) to $1.8305 \mu\text{g}\cdot\text{L}^{-1}$, while azoxystrobin was found in the range of 0.007 – $0.385 \mu\text{g}\cdot\text{L}^{-1}$ range. Similarly, Reilly et al. (2012) had found up to $2.1 \mu\text{g}\cdot\text{L}^{-1}$ of trifluralin in areas where the potatoes are grown. The strobilurin fungicide azoxystrobin was found at a median concentration of $0.142 \mu\text{g}\cdot\text{L}^{-1}$, doubling the maximum concentration found ($0.065 \mu\text{g}\cdot\text{L}^{-1}$) in a multi-stressed catchment in Spain, where crops are highly diverse and cultivated land is spread over multiple small-extension properties, similar to the scenario studied here (Postigo et al., 2021). The maximum concentration of $3.9 \mu\text{g}\cdot\text{L}^{-1}$ in Sweden (Kreuger et al., 2010), however, exceeded by 10 times the maximum in the present investigation.

Overall, the pesticide water concentrations reported here, in a small water body impacted exclusively by horticultural production, exceed previously reported concentrations in other systems where pesticide input is the result of various productive activities, but mainly the extensive agriculture of grains and oilseeds. In addition, the data offers further evidence supporting the postulate stating a risk of pesticides to small streams and asserts the need for further studies on this type of water body, which turns out to be a primary receptor for diffuse contamination by pesticides.

3.3.2. Suspended particulate matter

A paucity of information exists regarding pesticide concentrations in the SPM, as most research papers analyze surface water, in its entirety or the soluble fraction, and do not examine the contribution of pesticides associated with the particulate fraction of the water column.

Therefore, insecticide data are presented in this section and compared with the available literature. This differentiation is more frequent for GLY and AMPA; and, as already mentioned, the discussion of these results has been carried out in depth in a previous publication (Mac Loughlin et al., 2020).

Pyrethroids CYP and λ -CYHAL were the most frequently detected insecticides in the SPM, there at concentrations ranging from 5296 to $194,137 \mu\text{g}\cdot\text{kg}^{-1}$ for CYP and 4970 – $538,970 \mu\text{g}\cdot\text{kg}^{-1}$ for λ -CYHAL. In the Tagus River, Cruzeiro et al. (2016) reported CYP concentrations from $109,770$ to $198,910 \mu\text{g}\cdot\text{kg}^{-1}$ and a maximum concentration of $1600 \mu\text{g}\cdot\text{kg}^{-1}$ for λ -CYHAL. Most CYP concentrations in the present study were below the minimum reported for the Tagus River, but the maximum here fell between those Tagus values. In contrast, λ -CYHAL concentrations were higher than the $1600 \mu\text{g}\cdot\text{kg}^{-1}$ maximum, with the lowest concentration being more than 3 times of that value. Similarly, in both examples a higher SPM pesticide concentration was observed during the warmer seasons, probably because of fewer precipitations, resulting in a decreased river flow and a greater amount of suspended particulate matter in the water column (cf. SPM and precipitations in Table 2).

3.3.3. Bottom sediments

Table 4 summarizes of the most relevant pesticide concentrations found in the sediments. In general, the concentrations of pesticides detected in this study far exceeded the concentrations previously reported in the reference literature. Chlorpyrifos and λ -cyhalothrin were the most frequently detected insecticides in the bottom sediments, both in more than 50% of the samples. The highest CLP concentration was $2258 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, detected at S3 in WIN15. At that same site, $649.0 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ of λ -CYHAL were found. According to previous studies, this sediment sample had induced lethal effects on the benthic amphipod *Hyalella curvispina* (Mac Loughlin et al., 2017). The minimum CLP concentration was between 2 and 10 times above many of the reported maxima. These results are in accordance with the location of the sampling sites, since S3 is in the core production area.

Trifluralin was detected at concentrations between 2.99 and $740.34 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, with the maximum occurring at S3, with concentrations of $740.34 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, $205.34 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, $55.88 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, and $124.06 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ for the WIN15, SUM17, WIN17, and SUM18 campaigns, respectively. In WIN17, acetochlor was detected at concentrations between 98.6 and $4315.3 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, with the maximum recorded in S1 also being the highest pesticide concentration found in this study. Furthermore, in the previous

Table 4
Pesticide concentrations in sediments in comparison with the literature.

Pesticide	Sampling campaign ^a	Average (min-max) concentration ($\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$) ^b		Comparison with the maximum concentration	Site, reference
		Carnaval Creek	Reported		
CLP	WIN15	613 (78–2258)	7.66 (max 36.17)	×62	Ebro River, Spain ¹
	WIN17	132 (70–202)	max 13.5	×167	Paraná Basin, Argentina ²
	SUM18	295 (163–562)	max 7.41	×305	Buenos Aires, Argentina ⁴
CYP	SUM16	8 (4–15)	2.5–1605	×1.4	La Plata, Argentina ⁵
	SUM18	839 (651–1076)	max 211	×5	Paraná Basin, Argentina ²
	SUM16	4.4 (1.8–9.3)	max 71.9	×15	Ebro River, Spain ³
λ -CYHAL	SUM17	1349.9 (443.4–2607.7)	max 8.32	×129	Buenos Aires, Argentina ⁴
	WIN17	247.1 (53.1–403.7)	6.8–202	×5	La Plata, Argentina ⁵
	SUM18	1222.8 (654.7–1790.8)	max 6.09	×428	Buenos Aires, Argentina ⁴
	SUM18	1222.8 (654.7–1790.8)	6.8–20.2	×129	La Plata, Argentina ⁵

^a WIN15, winter 2015; SUM16, summer 2016; WIN16, winter 2016; SUM17, summer 2017; WIN17; winter 2017; SUM18, summer 2018.

^b The maximum quantified concentration is underlined.

¹ Ccanccapa et al. (2016).

² Etchegoyen et al. (2017).

³ Feo et al. (2010).

⁴ Hunt et al. (2016).

⁵ Solis et al. (2021).

campaign (SUM17), acetochlor had been detected at only S1 at a concentration of $171.0 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$; and, in that same sample, $183.0 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ of ATZ were also detected. Finally, and despite being rarely detected, fungicide concentrations exceeded those previously reported. For example, Smalling et al. (2013) had reported a maximum azoxystrobin concentration of $2.5 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, while we measured a maximum azoxystrobin concentration of $153 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ in S3 of WIN15. In addition, epoxiconazole was detected in concentrations up to $652 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ at S1 in SUM17. Those sites and campaigns have been previously mentioned for presenting notable concentrations of other pesticides such as CLP, λ -CYHAL, and trifluralin in the example of azoxystrobin, and the herbicides acetochlor and ATZ in the example of epoxiconazole. A determination of any temporal pattern in the detection of these pesticides was impossible because of the randomness with which those compounds were detected. At the same time, these data represent the first report for some of these pesticides in sediments in the country. That the quantified concentrations are of the order of other compounds that were more frequently detected is also highly relevant.

3.3.3.1. Glyphosate and AMPA in horticulture: sediment-water distribution.

As in the surface water and SPM, GLY and AMPA were the most frequently detected compounds in the bottom sediments. Statistically significant differences were found between the concentrations of GLY + AMPA among all the sampling campaigns ($p = 0.0025$), though no respective differences were found between the various summer or between those in the winter *per se*. The median concentrations of the summer campaigns (GLY = $350.1 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, AMPA = $131.9 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$) were higher than the winter values (GLY = $114.6 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, AMPA = $50.3 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$), which difference reflects the horticultural cycle involving greater applications during the warmer months (Sarandón, 2015). Likewise, the maxima were quantified during the summer: GLY = $1146.5 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ and AMPA = $4032.7 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, and the minima during the winter: GLY = $11.0 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ and AMPA = $4.6 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$.

Publications reporting the concentrations of GLY and AMPA in Argentina have focus on areas with extensive agriculture. Aparicio et al. (2013) found maximum concentrations of GLY and AMPA of $221 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ and $235 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, respectively; whereas Primost et al. (2017) found maximum concentrations of GLY = $1549 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ and AMPA = $4028 \mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$. These concentrations for the sediments of water bodies impacted by extensive GLY-dependent agriculture are within the concentration ranges reported here for a small basin with horticultural activity. We might possibly conclude that GLY has gone from being used only in the cultivation of resistant organisms to a practice where the herbicide's use has spread to the production of nonresistant crops in order to prepare the soil for horticultural cultivation and to keep the greenhouse margins free of weeds.

The observed sediment-water-distribution coefficients ($K_{\text{d-obs}}$) were calculated for GLY and AMPA and analyzed between the soluble fraction and the sediment. We need to note that these are *pseudo* coefficients since a flowing system, no matter how slow that flow might be, cannot be assumed to be at equilibrium (Fairbairn et al., 2015). The median (minimum-maximum) $K_{\text{d-obs}}$ for GLY and AMPA were 54 (18–488) $\text{L}\cdot\text{kg}^{-1}$ and 53 (4–1861) $\text{L}\cdot\text{kg}^{-1}$, respectively. These values are within the reported K_{d} values for GLY: 5.3–900 $\text{L}\cdot\text{kg}^{-1}$ and AMPA: 15–1554 $\text{L}\cdot\text{kg}^{-1}$ (EC, 2002). No significant differences were observed with respect to the sampling campaigns, as well as for possible correlations with temperature or rainfall.

The sorption of polar and thus hydrophilic compounds, such as GLY and AMPA – as evidenced by their solubility (GLY at $10,500$ and AMPA at $1,466,561 \text{ mg}\cdot\text{L}^{-1}$ at 20°C), and negative $\log K_{\text{OW}}$ – is strongly influenced by non-hydrophobic interactions when relevant mineral or soil organic matter components are present. Since sediment samples were obtained from the same basin, no major differences in the mineral composition were expected. Likewise, temporal and spatial variation in

organic matter content presented no statistically significant differences. This range of coefficients thus appears to be more related to the variations in concentrations in the environment and to the speed of the different physicochemical processes of sorption, rather than to the characteristics of the solid matrix.

As presented above, significant differences were detected in the concentrations of GLY and AMPA in water. Recent inputs of GLY and/or AMPA would result in water concentrations that change more rapidly than sorption-desorption processes. Fairbairn et al. (2015) proposed that water concentrations are partially responsible for the variations in observed distribution coefficients, which notion corroborates, as observed in this particular study, that the system is in fact not at equilibrium. Alternatively, in sediments these compounds may not biodegrade as quickly as in water, owing to anoxic conditions. Both scenarios would result in an increased $K_{\text{d-obs}}$.

3.3.4. Relationship between rainfalls and pesticide concentration in surface water

To evaluate the influence of the rainfall dynamics on the mobilization of pesticides towards the water body, the accumulated precipitations 3, 5, 7, 10 and 14-days before to sampling and the total pesticide concentrations in surface water (as the sum of pesticide concentrations in each given sample) were taken into consideration. The sampling sites in each campaign were considered as replicates of the system for the regression models since no differences were previously found in the spatial distribution of the pesticide concentrations.

The resulting model groups the concentrations of pesticides in the sampling campaigns based on the rainfall recorded in four statistically different groups (Fig. 4). The best fit was obtained with an exponential curve upon taking into consideration the accumulated precipitations for 14-days before the sampling date ($p < 0.0001$). First, significant differences were found in the total concentrations of pesticides in the surface water between the different sampling campaigns ($p = 0.0036$). For the pairs of campaigns WIN15-SUM18 and SUM17-WIN17, with similar rainfall volumes, however, no differences were observed ($p = 0.6905$ and $p = 0.8413$, respectively). For the environments that receive continuous applications, such as horticulture, the rainfall regime was more influential than the season of the year (Andrade et al., 2021). Therefore, the complete data set was used along with the average rainfall.

The pesticide movement throughout the aquatic environment depends on the area of the basin, the flow of the water body, and especially

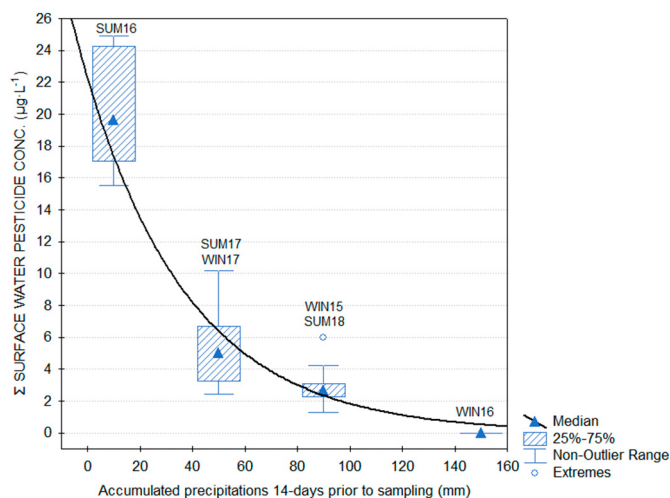


Fig. 4. Effect of combined rainfall on the surface-water pesticide levels. In the figure, the total pesticide concentration in surface water in $\mu\text{g}\cdot\text{L}^{-1}$ is plotted on the ordinate as a function of the accumulated precipitation in mm for 14 days before sampling on the abscissa. The solid black line traces the regression function. The boxes represent the same statistical parameters as those in Fig. 3.

the circumstance that the pollution is from a non-point source in both space and time (Szöcs et al., 2017). Rainfalls, however, should certainly be considered one of the most influential mechanisms, which, because of surface runoff, mobilizes pesticides from cultivated fields to nearby streams (Andrade et al., 2021; Topaz et al., 2018). In general, the pesticide mobility in water bodies is associated with seasonality as a determining element, either through crop cycles, or through chemical and/or biological stability as a function of temperature (Chow et al., 2020; Didoné et al., 2021). In the present study, after 3 years of monitoring the horticultural stream, the pesticide concentrations in the surface water, even in different years and seasons, were mainly the result of meteorological conditions such as rainfall.

The relationship between runoff versus dilution processes could be determined on the studied system studied here, where precipitations above 140 mm led to a non-detection of pesticides. Furthermore, concentrations of these compounds after precipitations between 40 and 90 mm tend to remain stable, regardless of the season of the year; so, if surface water sampling is planned, such a monitoring is recommended to be carried out after a rainfall within that range. This correlation between rainfall and pesticide concentrations was found to influence the environmental risk, as discussed in the next section. We conclude that pesticide sampling for only few periods of time can lead to spurious results, rather than properly characterizing a region.

3.4. Environmental risk assessment (ERA)

Fig. 5 illustrates the $\sum RQ$ (sum of the RQ) for each site and sampling campaign. More than half of the sites exhibited a $\sum RQ \geq 1$. Furthermore, 30% of the samples represented sites with a $\sum RQ$ greater than 1000, with two values exceeding 10,000 and one surpassing 300,000. In Table S2, available in the Supplementary Material, all the RQs calculated for each pesticide are presented.

To date, few ERAs have been carried out in Argentina for pesticides. Irtururu et al. (2019), conducting a review of all the publications where

concentrations of pesticides are reported in the pampas region and calculating the consequent ERA from the data collected, concluded that persistent pesticides are major contributors to the RQs, underscoring that this group of pesticides are often overlooked which respect to risk assessments, despite the persistence of those agents in the environment. Although pesticides belonging to this group, such as organochlorines, were analyzed in the present work, the only one that was detected, and in only one sample, was endosulfan. This single detection of $0.33 \mu\text{g}\cdot\text{L}^{-1}$ (SUM16-S5), however, was sufficient to signify the maximum RQ calculated in our survey ($>300,000$). In particular, pyrethroid insecticides contributed considerably to the higher values of $\sum RQ$, with the lowest concentration representing $RQ = 20$ (λ -CYHAL, SUM16-S3) and the highest $RQ = 48,094$ (deltamethrin, WIN17-S5).

More recently, Pérez et al. (2021) conducted an investigation on the Tapalqué Stream (in the center of the Province of Buenos Aires), influenced by various land uses – such as mining, industry, rurality, and urbanization. Of the 3 sampling events, in no instance was a $\sum RQ \geq 1$ recorded. The herbicides ATZ, GLY, and acetochlor were identified as the main contributors to potential chronic toxicity to aquatic organisms. In the present study, herbicides did not play a major role, as GLY and AMPA were always detected, but the herbicides did contribute, on average, an RQ of 0.06. We need to note that the only detection of acetochlor ($0.618 \mu\text{g}\cdot\text{L}^{-1}$, SUM18-S1) resulted in an RQ of more than 10 and, despite also having CLP detected in the same sample, contributed to the $\sum RQ$ by more than 90%. Another herbicide that reached concentrations leading to a $RQ \geq 1$ was trifluralin (SUM17-S3 and SUM17-S4). Our results are in agreement with those of (Papadakis et al., 2015), where the insecticides detected presented the highest RQ exceedances.

Coincidentally, the $\sum RQ$ values that represented a high risk (≥ 10) resulted in the campaigns where less rainfall occurred before the sampling (cf. Fig. 4): SUM16, WIN17, and SUM17; with 4 out of 5 and 5 out of 5 sites, respectively, for the first two campaigns exceeding 2200 RQ units. Compared to systems with multiple influences – especially extensive agriculture – horticulture, in particular, because of currently

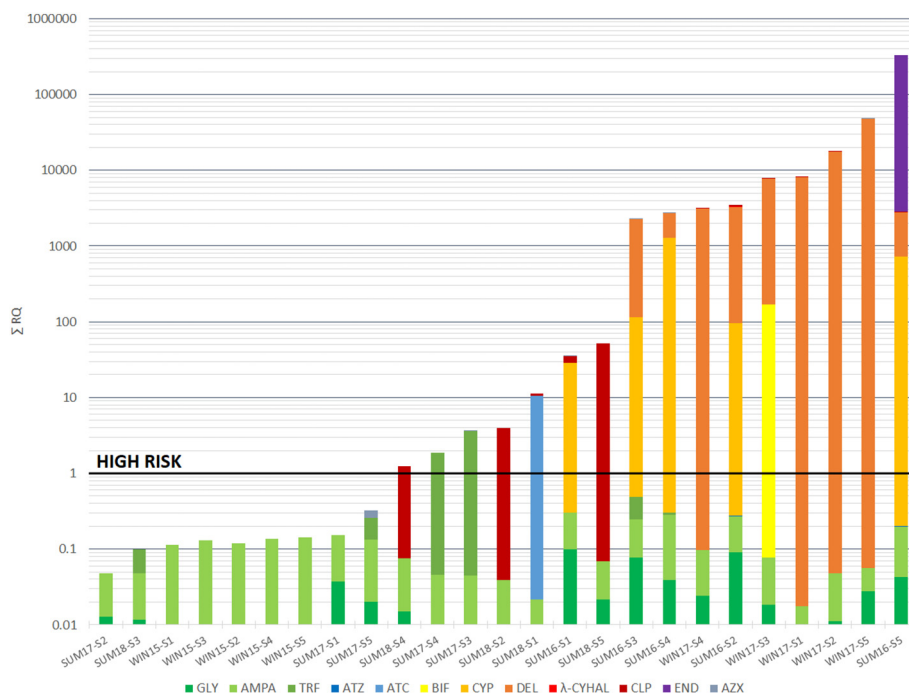


Fig. 5. Profile of pesticide risk quotient at the sites over time. In the figure, the sum of the risk quotients ($\sum RQ$) is plotted on the ordinate on a logarithmic scale over time as monitored at each site during each sampling campaign indicated on the abscissa. Risk is categorized as: $\sum RQ < 0.01$ = negligible risk, $0.01-0.1$ = low risk, $0.1-1$ = medium risk, ≥ 1 = high risk (solid horizontal black line). The colors within the segments of the cumulative bars represent the contribution of different pesticides at a given site. Table 1 lists the abbreviations used for the compounds in the key to the bar coloring below the figure.

used insecticides, poses a greater risk to aquatic biota, as evidenced by the high \sum RQ values calculated in this ERA, where the maximum value due to the currently used pesticides of the present work exceeded 60 times the maximum total risk previously reported for Argentina (Iturburu et al., 2019) and more than 100 times the those reported in other parts of the world (Ccanccapa et al., 2016; Papadakis et al., 2015).

4. Conclusions

- Overall, the pesticide concentrations in the matrices studied exceeded those previously reported, both for Argentina and for other parts of the world, a reflection of the dependence on pesticides for horticultural production. Those previous studies had focused mainly on the impact of extensive agriculture, whereas research on horticultural scenarios *per se* was still lacking.
- The prevalence of glyphosate and AMPA in a basin encircled by horticulture reveals that this herbicide is no longer exclusively used on resistant crops, rather, use of glyphosate has spread to other agricultural practices. Moreover, we are now able to state that glyphosate behaves as a *pseudo-persistent* pollutant in the aquatic system investigated. The observed sediment-water-distribution coefficients for glyphosate ($18\text{--}488\text{ L}\cdot\text{kg}^{-1}$) and AMPA ($4\text{--}1861\text{ L}\cdot\text{kg}^{-1}$) confirm the affinity of these compounds for the solid matrix.
- Sediment insecticide and fungicide concentrations did not show statistically significant differences over time and presented the highest detection frequencies, reinforcing the role of that matrix as a sink for pollutants. Chlorpyrifos and λ -cyhalothrin were the most frequently detected insecticides in bottom sediments, with maximum concentrations of $2258\text{ }\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$ and $2607.7\text{ }\mu\text{g}\cdot\text{kg}_{\text{dw}}^{-1}$, respectively. Historical information on the pesticides previously used can be obtained from this environmental compartment.
- While it is common in the study of environmental dynamics of pesticides to investigate their seasonality – as it is usually related to the application cycles – after 3 years of monitoring the horticultural system, rainfall had a more relevant role in the mobilization of pesticides than seasonality. The volume of the precipitation conditioned the resulting environmental risk.
- Pesticide concentrations in surface water samples represented a medium-to-high risks to aquatic biota. Insecticides contributed mostly to the calculated risk, though certain herbicides were present at concentrations sufficient to represent a risk to aquatic biota.
- Because of the horticultural activity and the pesticides used in this form of land use, nearby surface watercourses are negatively impacted. Strategies must be implemented to protect these ecosystems, e. g., wider riverbanks, and policies that tend to reduce the use, and eventually eliminate, the use of pesticides in horticultural production.

CRedit authorship contribution statement

Tomás M. Mac Loughlin: Conceptualization, Investigation, Formal analysis, Writing – original draft. **María Leticia Peluso:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Damián J.G. Marino:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Haggerty, a retired academic career investigator and native English speaker, edited the final version of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149893>.

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