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Evaluation of pesticide pollution in the Gualeguay Basin: an extensive agriculture area in Argentina.

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Abstract   The current agricultural production model was established in the 1990s based on the use of genetically modified organisms and agrochemicals, mainly pesticides. Despite pesticide spread and prevalence, data on the associated concentrations in surface watercourses are comparatively scarce. The aim of this work was to evaluate to what extent the more than 20 years of agricultural activity with the use of pesticides has impacted on the Gualeguay-River basin, with respect to the different stream orders: the tributary streams and main channel. Thirteen sites within the lower Gualeguay basin were sampled once every season (autumn, winter, spring and summer) in 2017-2018. The samples were analyzed by gas chromatography time-of-flight mass-spectrometry (GC-TOF-MS) and ultraperformance liquid chromatography tandem mass-spectrometry (UPLC-MS/MS). The most frequently detected pesticide was glyphosate along with its metabolite (aminomethyl)phosphonic acid (AMPA), at 82% and 71% of surface water samples and 97% and 92% of bottom sediments, respectively; followed by atrazine in 73% of the water samples. The concentrations of these compounds, each in their respective matrices, did not present sufficient statistically significant differences for differentiating a tributary stream from the main channel. Regardless of glyphosate's affinity for the suspended particulate and bottom sediments, over the entire basin the soluble fraction contributed on average to more than 80% of the total concentration in surface water. Despite not being so frequently detected, certain

insecticides, mostly deltamethrin, were likewise detected at concentrations above their water-quality guidelines for the protection of aquatic life, even in samples from the main channel. Upon comparison of the pesticide profiles of extensive- and horticultural-production systems in the country, atrazine emerged as a prime candidate to be used as a tracer of extensive agriculture contamination in the environment. Further research is required to establish to what degree pesticides used in agriculture and mobilized by watercourses have an impact on their associated wetland ecosystems.

Key words: glyphosate; pseudopersistence; atrazine; mass spectrometry; soybean

1. Introduction

Argentina has an economy that has historically operated the basis of on the export of commodities, particularly those originating from agriculture and livestock. The extensive agricultural-production model promoted in the 1960s, and adopted in the country in the 1990s, is based on three main pillars: labor-saving technologies (*e. g.*, direct seeding); genetically modified organisms (GMOs); and chemical inputs, such as fertilizers and pesticides (Bernasconi et al., 2021). Since the model's implementation, a notable increase has occurred in the volume of agrochemical use, involving both fertilizers and pesticides: from 1990 to 2019 (FAO, 2022), the former increased from 165,500 to 2,075,900 tons (a greater than 12.5-fold increase), while in the same period the use of pesticides increased from 26,160 to 204,600 tons (a greater than 7.8-fold increase). Extensive agriculture is characterized by large areas, generally from 50 to 100 ha, of a single crop for the production of commodities for export and industrialization. Consequently, the spectrum of pesticides is narrower than in more complex systems, such as in horticulture: in this latter model, where food is produced for fresh consumption, much smaller areas, which can range from 1 to 3

ha, are cultivated with a broad range of plant species, therefore, requiring a wider selection of pesticides (Demetrio et al., 2022).

The pampean region of Argentina—comprising the provinces of Buenos Aires, La Pampa, Entre Ríos, Santa Fe, and Córdoba—is a wide plain of more than 50 million ha with a temperate climate and lands suitable for the cultivation and cattle raising. For these reasons, the pampa constitutes the area of greatest production in the country due to natural conditions and the historical development that facilitated its exploitation Of those provinces, the Province of Entre Ríos in particular ranks first in the country in the area cultivated with citrus and in the production and export of poultry meat, second in rice production, and finally fourth in the area planted with soybeans—presenting on a smaller scale maize, wheat and sunflower plantations—and in the number cattle farms (Engler et al., 2008).

The Gualeguay-River basin occupies approximately a third of the Province of Entre Ríos, constituting that part of the Paraguay-Paraná Plata river system, South America's second largest catchment after the Amazon Basin. The Gualeguay River discharges into the Paraná Delta, a wetland system covering 17 500 km^2. Natural wetlands are systems that provide essential ecologic services: such wetlands enhance water quality, control erosion, buffer against flooding, are highly productive (*e. g.*, in carbon fixation), and are biologically diverse; providing a home to a prodigious number of species (Kandus & Quintana, 2016). Pollution by nutrients (Primost et al., 2022) and veterinary ionophore antibiotics (Alonso et al., 2019) has already been studied in this region. Both these publications noted how the streams that flow into the Paraná delta introduce contaminants to it, which are thereafter retained in the wetland. As to ionophores, Alonso et al. (2019) noted that the removal capacity is challenged by the ever-increasing contribution of these pollutants, prompting for urgent steps in order to protect these ecosystems. The expansion of agriculture upstream has been identified as one of the threats and future challenges for the conservation of the Paraná-delta biodiversity (Kandus & Quintana, 2016; Sica et al., 2016).

The objective of this work was therefore to evaluate how the current production model based on genetically modified organisms impacts this major subbasin within the larger Río-de-la-Plata basin, in both the former's main channel and its tributaries. For that purpose, we evaluated the distribution of 40 pesticides in different environmental matrices (surface water, suspended particulate matter, and bottom sediments) in 13 sites along the main channel and in the tributaries of the Gualeguay River after each of the different stages of crop cycles and then compared those data to ecologic thresholds. Consequently, the pesticide concentrations reported here constitute a new, substantial contribution to the inventory of contaminants present in the Gualeguay basin that have already been analyzed (*e. g.*, nutrients, veterinary drugs).

2. Materials and Methods

2.1. Chemicals and reagents

Acetonitrile, methanol (liquid-chromatography-grade), acetone, dichloromethane, and n-hexane (pesticide-residual-grade) were purchased from J. T. Baker (Phillipsburg, NJ, USA). Ultrapure water was generated in the laboratory with a Sartorius arium® purification system (Göttingen, The Netherlands). All salts were analytical grade and obtained from Merck Millipore (Darmstadt, Germany). Pesticide standards (≥95%), isotopically-labelled glyphosate-2-^{13}C, ^{15}N (98 atom % ^{15}N, 99 atom % ^{13}C), atrazine-d$_5$, cypermethrin-(phenoxy-d$_5$), 1-octanol (anhydrous, ≥99%), and 9-fluorenylmethyloxycarbonyl chloride (≥99.0%, FMOC-Cl) came from Sigma Aldrich (St. Louis, MO, USA). Isotopically-labelled internal-standard solutions of glyphosate-2-^{13}C, ^{15}N (GLY*), and a mixture of atrazine-d$_5$ and cypermethrin-(phenoxy-d$_5$) (IS*) were prepared in ultrapure water and methanol, respectively, both at a nominal concentration of 1 ng·µL^{-1}, for *in situ* sample spiking.

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2.2. Study area and sample collection

The Gualeguay basin drains an area of 22,350 km^2, occupying 28% of the territory of the Province of Entre Ríos (Martínez, 2004). The main channel, in the basin's north-south extension, runs for 857 km and has an average flow of 210 m$^3 \cdot$s^{-1} at its mouth towards the Paraná delta; constituting the second-largest wetland system in South America and sixth in the world, with a total area of 17,500 km^2. The main water source for the watercourses in the basin comes from rainfall: that rainwater is collected by the many streams in the basin and circulates slowly through the meandering ones. The average annual rainfall is around 1,000 mm, with the rainiest months occurring from October to March (>100 mm, spring-summer) and the least during June through August (around 60 mm, winter). The main land use is extensive agriculture: soy, maize and wheat (64% of the basin area), followed by native forest (22%) at the north of the basin (Quignard et al., 2013). Four sampling campaigns, once every season (autumn, winter, spring, summer), were carried out between the years of 2017 and 2018 in the lower region of the basin (**Figure 1**), between the cities of Rosario del Tala and Gualeguay, with sites selected on the main channel (M) and the tributaries (T). **Table 1** summarizes the names of the waterways sampled and all the geographic coordinates. Because of climatologic and road conditions, during certain campaigns we could not access all the sampling points; for example, 121 mm of rain fell 72 h before the autumn campaign of 2017 making access to some of the sites impossible owing to the poor conditions of the rural dirt roads. In the sampling period, the surrounding area was planted (MAGyP, 2021) mainly with soybeans (479,500 ha), followed by maize (155,500 ha) and wheat (132,300 ha). For these crops, glyphosate is applied during chemical fallow (autumn through winter) as well as during crop growth (spring though summer), with at least two additional applications during the growing period of soybean, with application rates ranging from 1 to 4 kg·ha^{-1} (Bernasconi et al., 2021; Okada et al., 2018). Atrazine is most commonly used in the cultivation of maize at application rates of 2 to 3 kg·ha^{-1}. Insecticides and fungicides are also applied for postplanting maintenance (late spring though summer), but

generally at lower doses: chlorpyrifos at 0.4-0.7 kg·ha^{-1}, deltamethrin at 0.6 kg·ha^{-1}, and azoxystrobin at 1 kg·ha^{-1} (Pérez et al., 2021).

Whole surface water samples (500 mL) were collected into prerinsed amber-glass bottles, spiked with 25 µL of IS* solution, and 5 mL of n-hexane was added to prevent analyte loss. For the specific analysis of glyphosate and (aminomethyl)phosphonic acid (AMPA), 100 mL were filtered *in situ* through a preweighed 0.45-µm-pore-size nylon filter (∅=47 mm), of which 10 mL of the soluble fraction were transferred to a propylene plastic tube and spiked with 10 µL of GLY*. A second 50-mL aliquot was transferred to another amber-glass bottle without additives to determine the chemical oxygen demand. Filters containing the particulate fraction were spiked with 30 µL of GLY*, folded, and sealed in aluminum-foil packets. Upon arrival at the laboratory, the filters were placed in a desiccator for 24 h, weighed to determine the particulate-matter weight (±0.1 mg), and then stored at −20 °C. Sediment samples were collected from the first 5 cm with an Ekman grab. All the samples were kept in an ice-cold container until arrival to the laboratory and then stored in the refrigerator (4 °C) until analysis within the next 48 h. Conductivity, pH, temperature, and dissolved-oxygen concentration were measured *in situ* using a multiparameter instrument Lutron WA-2017SD. Sediment moisture was determined by weighing approximately 5 g of wet sediment, drying the sample at 105 °C to constant weight, and then further heating to 550 °C to determine total organic carbon.

2.3. Chemical analysis

2.3.1. Sample preparation and pesticide extraction

The multiresidue pesticides in whole surface water were extracted with dichloromethane according to method 3510C of the United States Environmental Protection Agency, concentrated under a nitrogen stream with 1-octanol as a *keeper*, reconstituted with 500 µL of n-hexane, and transferred to chromatographic vials (Mac Loughlin et al., 2022). Of the wet sediment, 7 g were spiked with 75 µL of IS* solution and extracted by a nonbuffered

multiresidue *QuEChERS* procedure (*Quick, Easy, Cheap, Effective, Rugged, and Safe*) as described in Mac Loughlin et al. (2017). The extracts of these two matrices were analyzed by gas chromatography.

In view of the chemical nature of glyphosate and AMPA—such as low molecular weight and high solubility in water—a different and specific method was necessary for the analysis of these compounds via precolumn derivatization. The procedure stated in brief: a 1-mL aliquot of the soluble fraction was adjusted to pH=9 and then 1 mL of FMOC-Cl (1 mg·mL^{-1} in acetonitrile) was added. The particulate matter was extracted with 3 mL of a phosphate dibasic buffer (pH=9) and sonication, after which step 1 mL was derivatized with FMOC-Cl (Mac Loughlin et al., 2020). For the sediments, 7 g of wet sample were spiked with 50 µL of a 10 ng·µL^{-1} GLY* solution, extracted through sonication at pH=9, and derivatized with FMOC-Cl (Ronco et al., 2016). Blanks and calibration curves from standard solutions were performed under the same operational conditions. During derivatization, the samples were kept in the dark overnight at room temperature. The following day, the derivatized samples were extracted with 3 mL of dichloromethane and centrifuged and the aqueous phase filtered through 0.22-µm nylon filters into vials. The extracts of these three matrices were analyzed by liquid chromatography.

2.3.2. Instrumental methods and quality assurance

The multiresidue extracts were analyzed for multiple pesticide residues with a DANI Master™ gas chromatograph coupled to a coupled to a Master TOF Plus MS™ time-of-flight mass spectrometer, equipped with a Phenomenex® Zebron ZB-SemiVolatiles™ column (30 m × 0.25 mm × 0.25 µm). A total of 38 out of 40 compounds were analyzed with this equipment—namely, 5 herbicides: atrazine, acetochlor, metolachlor, trifluralin, pendimethalin; 5 pyrethroid insecticides: bifenthrin, cypermethrin, deltamethrin, permethrin, λ-cyhalothrin; 5 organophosphate insecticides: chlorpyrifos, diazinon, malathion, parathion, methyl parathion; 1 phenylpyrazole insecticide: fipronil, 18 legacy organochlorine

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insecticides: endosulfan (I and II), endosulfan sulfate, α-, β-, and γ-HCH, heptachlor, heptachlor epoxide (A and B isomers), aldrin, dieldrin, endrin, methoxychlor, p'p- and o,p'-DDT, o,p'- and p,p'-DDE, p'p-DDD; 5 fungicides: azoxystrobin, pyraclostrobin, epoxiconazole, cyproconazole, tebuconazole; and a pesticide synergist: piperonyl butoxide. Glyphosate and AMPA were analyzed in a Waters Acquity ultraperformance liquid chromatograph coupled to a Quattro Premier XE™ tandem quadrupole mass spectrometer. The limits of detection (LOD) and quantification (LOQ), the methods performance, and the operational parameters for both chromatographic systems were set according to previously published methods (Mac Loughlin et al., 2017, 2020).

2.4.   Data analysis

The normality and homoscedasticity of the data set were determined by the Shapiro-Wilk test and Levene's test, respectively. Since the pesticide concentration data did not follow a normal distribution, nonparametric tests were used. For graphical representation, the data were organized according to the order of the sampling sites—main channel (M) or tributary (T)—and seasons—autumn (AUT), winter (WIN), spring (SPR), summer (SUM). The glyphosate-to-AMPA ratio was calculated for each sample in which both concentrations were above the LOQ, thus providing insights into the sources and transport of these compounds, with higher ratios indicating a faster transport from the source to the waterways, and *vice versa* for lower ratios. Since the concentrations of glyphosate and AMPA were determined in both the soluble and the particulate fractions and in the bottom sediments, the partition coefficients (K_d) —the ratio of solid-phase–to–solute concentrations—could be calculated. For all the tests, the level of significance was set at α = 0.05. Statistical analyses were performed by means of STATISTICA (Stat Soft, Inc. 2001; version 7) software.

3. Results and discussion

3.1.   Detection frequencies

Out of a total of 40 pesticides analyzed, 11 of them were detected: The herbicide glyphosate, and its environmental metabolite AMPA, long with the insecticides chlorpyrifos and λ-cyhalothrin—with those all being detected in both surface water and bottom sediments. The herbicides atrazine, acetochlor, and trifluralin; the pyrethroid insecticides bifenthrin, cypermethrin, and deltamethrin; and the fungicide azoxystrobin were detected exclusively in the water samples. **Figure 2** displays the detection frequencies in surface water, while **Figure 3** illustrates those found in bottom sediments. In both figures, the sampling sites in the main channel and the tributaries are differentiated between according to the colors of the bars.

Glyphosate was present in 82% and AMPA in 71% of both the filtered water and the suspended particulate-matter samples; with the exception of the autumn campaign, where neither compound was detected—i.e., in every sample where glyphosate or AMPA was detected in the soluble fraction, that respective compound was also found in the particulate fraction. Therefore, by adding both concentrations, the concentration of these two compounds in the whole water can be obtained—concentrations that will be used below to be compared with previous reports. The detection frequencies of the herbicide and its metabolite were higher in the sediments, with glyphosate being present in 97% of all the sediment samples, and AMPA in 92%; where, unlike in the surface water, both were indeed detected during the autumn sampling campaign. The herbicide atrazine was the third most often detected pesticide in surface water at 73%, with a 100% detection frequency during the spring campaign and the lowest value occurring during the summer (38%). The detection frequencies of these herbicides are a reflection of the production cycles, with most applications occurring during soil preparation in the winter and sowing in the spring and the least in autumn (Bernasconi et al., 2021). The persistence of glyphosate and AMPA in bottom sediments in the autumn sampling campaign underscores the capacity of the

sediments to preserve information from previous applications (Mac Loughlin et al., 2022; Ronco et al., 2016).

Insecticides and fungicides were sparsely detected in surface water, with the pyrethroid insecticide deltamethrin being the most frequently found in 20% of the samples (or in 75% of those from the winter campaign), followed by the organophosphate insecticide chlorpyrifos in 17% if all the samples. Azoxystrobin was the only fungicide detected, being present in just a single water sample. The insecticides λ-cyhalothrin and chlorpyrifos were detected in only the autumn sampling campaign and then in 3% and 8% of all sediment samples, respectively; with those two pesticides being present in the sediments other than glyphosate and AMPA. The concentrations of insecticides in winter are particularly notable because winter is not the season when this type of pesticide is usually applied. Of high probability is that occurrence of those compounds in surface water is due to a mobilization from the bare soils and the less abundant riparian vegetation during winter (Andrade et al., 2021; Topaz et al., 2018).

Table 2 summarizes the most relevant detection frequencies and concentrations of glyphosate and AMPA in the environmental matrices analyzed in different countries. The detection frequencies for glyphosate and AMPA in the surface-water samples reported here for the Gualeguay basin of Argentina were higher than in most of the publications cited, whereas for the sediments those values were only slightly greater than previously reported data. The detection frequencies of these compounds in sediment tend to be lower in larger watercourses, such as those studied by Ronco et al. (2016) along the main channel of the Paraná River. In the present work, however, glyphosate and AMPA were detected in 92% and 67% of the sediments sampled from the main channel of the Gualeguay River, respectively. The greater detection frequency is an indicator of the impact of the agricultural production in the study region, where the quantities of these compounds that reach the main channel—whether due to the contribution of the tributaries, the surface runoff, or both—are sufficient for detection in the sediments.

In the water and sediment data collected during the 2001-2010 period in the United States, Battaglin et al. (2014) found glyphosate in the absence of AMPA in 2.3% of the samples, while AMPA without glyphosate was detected in 17.9% of the samples. More recently, in Brazil, Mendonça et al. (2020) reported a cooccurrence of these two compounds in 12.1% of the samples analyzed, with detection frequencies for glyphosate and AMPA of 37.1% and 21.8%, respectively. Moreover, glyphosate was detected without AMPA in 25.0% of the samples and AMPA without glyphosate in 9.7% of the samples. In the present study, in 13% of the samples where glyphosate was found, AMPA was not detected. The results from the last two examples, both in Latin-American countries, unlike those from the United States, can be a consequence of more recent inputs of glyphosate into the environment. Furthermore, the opposite scenario, the detection of AMPA but not glyphosate, unlike in those previous studies, did not occur in this investigation, thus further supporting the hypothesis that inputs into the Gualeguay basin are recent.

Moreover, in the present work, in all of the water samples where glyphosate and AMPA were detected in the soluble fraction, the two pesticides were also present in the particulate fraction. Previous publications did not find corresponding results that were consistent with ours: In the Province of Buenos Aires, Aparicio et al. (2013) detected glyphosate in 16% of the soluble fraction and in 69% of the particulate fraction of those same surface-water samples, amounting to a difference greater than 50% in the detection frequencies between the two fractions. In surface water from around the city of Urdinarrain, located within the Gualeguay basin (*cf.* **Figure 1**), Primost et al., (2017) also detected higher frequencies of both glyphosate and AMPA in the particulate fraction.

During the autumn, winter, and spring sampling campaigns, the detection frequency of atrazine in surface water was greater than 70%, reaching 100% during the spring campaign. In the summer campaign, however, the detection of this herbicide decreased to less than 50%. Battaglin et al., (2005) had observed a similar increase in the detection frequency and concentrations of herbicides, among them atrazine, during the preemergence of crops and

weeds, coinciding with the spring sampling campaign; followed by a decrease in both detection and concentrations measured for samples obtained during the postemergence. In accordance with the previous observation, the results of this study point to the relevance of monitoring water bodies over time, since a number of studies that have been published involved only a single sampling, where those reported did not detect the occurrence of a pollution in the environment. At the same time, the increase in the detection frequencies of compounds such as glyphosate and atrazine are a consequence of the intensification of the pesticide-dependent production model.

3.2. Comparison of tributary versus main channel

The whole surface-water concentrations of the most frequently detected pesticides (glyphosate, AMPA, and atrazine) were compared between the orders of the Gualeguay basin from where the samples were taken—*i.e.,* the tributary or the main channel (**Figure 4**). For all three compounds, no statistically significant differences were found between the stream orders from which the samples were obtained (glyphosate: *p = 0.6566*, AMPA: *p = 0.2352*, atrazine: *p = 0.6298*). Consequently, the greater flow of the main channel and the greater dilution power were of no consequence: the quantity of glyphosate, AMPA, and atrazine input into the basin did not differ in distribution with respect to the concentrations in the main channel and in considerably smaller water bodies of lesser flow. Despite this similarity, the maximum concentrations in the whole surface water were detected at the tributary sites—*e. g.*, glyphosate = 10.90 µg·L^{-1} (WIN-T7), AMPA = 9.60 µg·L^{-1} (SUM-T7), atrazine = 2.133 µg·L^{-1} (SUM-T5)—evidenced a more pulsatile pattern, as represented by a greater concentration range than that of the main channel; with the latter evidencing a more limited variation that indicated a certain degree of dampening due to dilution.

This consistency in the distribution of concentrations underscores the high mobility of the herbicides, regardless of the input surfaces and the flow of the water bodies. An evaluation of the mass of these compounds mobilized warrants consideration: the Gualeguay River has

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an average flow of 210 $m^3 \cdot s^{-1}$ at the mouth. Upon assuming a homogeneous concentration of the compounds in the water column, during the summer a total 0.29 $g \cdot s^{-1}$ of glyphosate, 0.15 $g \cdot s^{-1}$ of AMPA, and 0.07 $g \cdot s^{-1}$ of atrazine are introduced into the Paraná delta. As mentioned above, the Paraná delta has the capacity to capture and remove contaminants of agricultural and livestock origin from surface water (Alonso et al., 2019; Primost et al., 2022). In view of previous observations ns (Ronco et al., 2016), the same would happen for these pesticides. Nevertheless, the direct and indirect effects on wetland fauna and flora as a consequence of these chemical mixtures and their interaction with the environmental matrix are still not fully understood; as wetland loss and degradation can be caused by a myriad of reasons—such as changes in land use and management resulting in alterations to wetland hydrology, or drainage to gain arable land or for urban and/or infrastructure development (Sica et al., 2016).

The same analysis was performed for the glyphosate and AMPA concentrations in the bottom sediments. Once again, the maximum glyphosate concentration occurred in a tributary sediment: 208.6 $\mu g \cdot kg^{-1}$ (SUM-T7), but the maximum concentration of AMPA was detected in the main channel at 104.4 $\mu g \cdot kg^{-1}$ (SUM-M3). This last result could be reflecting the biotransformation of the herbicide to its metabolite during transport and the eventual deposition in the bottom sediments. Because of these findings in the following sections, the dataset for concentrations was used without distinguishing the order of the watercourse since no statistically significant differences were found between them.

3.3. Pesticide concentrations in relation to seasons and the crop cycle

The concentrations of glyphosate and AMPA in the soluble and particulate fractions and those of atrazine in the whole water were analyzed with respect to the seasons, and, in turn, to the cultivation cycles of extensive crops in the region (Bernasconi et al., 2021). **Figure 5** summarizes the temporal variation of these three herbicides in whole surface water. In at

least one campaign, the results revealed statistically significant differences in the concentrations of glyphosate in the soluble (*p = 0.0002*) and particulate (*p < 0.0001*) fractions, as well as for AMPA in both fractions (*p = 0.0089, p = 0.0038*). Upon consideration of the whole water concentration for these two compounds—expressed as the sum of the concentration in the soluble and particulate fraction—statistically significant differences were also detected for glyphosate (*p = 0.0001*) and AMPA (*p = 0.0064*) between seasons. As mentioned above, during the autumn campaign neither the parental compound nor the metabolite was detected in either fraction. This sampling campaign was carried out in April after the period of greatest rainfall (February and March, both at >120 mm), thus indicating a marked dilution rather than a contaminant mobilization (Aparicio et al., 2013; Mac Loughlin et al., 2022). With respect to the concentrations of glyphosate and AMPA in the soluble fraction, the particulate fraction, and the whole water among the seasons; the spring campaign evidenced significant differences from the other seasons for both compounds, characterized by lower concentrations than those of winter and summer and coinciding with the first periods of application and lower rainfall. Atrazine, detected in all of the campaigns, also exhibited seasonal variations, with statistically significant differences occurring in the summer campaign (p = *0.0486*) when the maximum concentration of 2.113 µg·L^{-1} at T5.

The maximum concentrations in the soluble fraction were glyphosate = 7.74 µg·L^{-1} (WIN-T7) and AMPA = 9.25 µg·L^{-1} (SUM-T7); values comparable to the maxima reported by Medalie et al. (2020), who had analyzed the soluble fraction in a survey carried out on different streams throughout the United States. In Canada, Montiel-León et al. (2019) assayed the soluble fraction of the St. Lawrence River, where the maxima were 2.6 and 14 times lower than the maxima for glyphosate and AMPA, respectively, in the Gualeguay basin. Scenarios of greater differences occurred in Germany (Tauchnitz et al., 2020) and Italy (Masiol et al., 2018), where the maximum concentrations in whole surface water listed in the previous section exceeded the maxima of those countries by 5 to 54 times for glyphosate and 7 to 46 times for AMPA; with the use of glyphosate in these countries, coincidentally, being an

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estimated 40 to 50 times less than in Argentina: 4,690 and 3,700 tons, respectively (Antier et al., 2020), versus 187,000 tonnes (CASAFE, 2014).

Primost et al. (2017) carried out a study around the city of Urdinarrain, from where samples for the present work were also obtained (at site T2). With the passage of time, the average concentrations of glyphosate and AMPA, in both the soluble and the particulate fractions, in that area increased; which pattern could indicate an elevation in the doses of this herbicide because of the appearance of resistant weeds, as reported by the Argentine Association of Direct Sowing Producers (AAPRESID, 2022). In the Province of Buenos Aires (*cf.* insert in **Figure 1**), Aparicio et al. (2013) had reported a maximum concentration of 7.6 µg·L^{-1} for glyphosate in the soluble fraction, while more recently Pérez et al. (2021) reported a maximum of 4.36 µg·L^{-1}. The maximum of glyphosate (soluble fraction) in the present work was 7.74 µg·L^{-1} (WIN-T7), which value is slightly higher than the previously reported maxima. Moreover, the maximum AMPA concentrations in those studies were lower than the one from this study: 9.25 µg·L^{-1} (SUM-T7). The median concentrations in the particulate fraction (glyphosate = 1,751.4 µg·kg^{-1}, AMPA = 317.1 µg·kg^{-1}) furthermore exceeded the maxima reported by Aparicio et al. (2013). Contrary to expectations, the median and maximum for both compounds reported in a suburban stream surrounded by horticultural activity (Mac Loughlin et al., 2020) were even higher than in the present work, where extensive agriculture is the main herbicide source. In contrast, the maximum concentrations in the particulate matter were higher than those in the horticultural environment; which difference can be explained by the partition coefficients observed in this system—a topic that will be addressed in later sections—and also by the concentrations in soil for the region, which are among the highest reported worldwide (Primost et al., 2017).

The maximum atrazine concentration (2,113 µg·L^{-1}, SUM-T5) exceeded the maximum reported by Pérez et al. (2021) of 0.134 µg·L^{-1}. At the same time, the maximum concentration in this study exceeded 3 times the maximum reported by Montiel-León et al. (2019) for Canada (0.666 µg·L^{-1}) and was slightly below the maximum for the United States

(2.66 µg·L^{-1}) reported by Mahler et al. (2017). **Figure 6** is a graphical summarization of the comparison between the concentrations of glyphosate, AMPA, and atrazine found in the Gualeguay basin and those previously reported for Argentina and other countries.

Figure 7 reveals a significant seasonality among the sediment glyphosate concentrations (*p = 0.0105*), unlike the AMPA concentrations (*p = 0.7195*), most likely owing to the longer half-life of the latter compound (Bonansea et al., 2017). For sediments from the same area, the average concentrations quantified by Primost et al. (2017) were higher than the maximum concentrations of the present work. In high-order tributaries of the Paraná River, Ronco et al. (2016) had detected even higher concentrations, with the maximum for both compounds occurring in the Luján River, in the Province of Buenos Aires. In that province, the concentrations of glyphosate in sediments reported by Aparicio et al. (2013) were on a par with the maximum concentration of the compound in sediments of the Gualeguay basin, while the maximum AMPA concentration there proved to be double the value found in this work. More recently, Pérez et al. (2021) reported maximum concentrations below the present median concentrations (glyphosate = 51.6 µg·kg^{-1}, AMPA = 35.1 µg·kg^{-1}). The basin studied here evidenced concentrations more comparable to those last two publications, where the areas analyzed had multiple crops, while the study by Primost et al. (2017) had focused specifically on an area with soybean production.

3.4. Implications of glyphosate detection

3.4.1. Glyphosate-to-AMPA ratio

The concentration ratio of glyphosate to AMPA provides information on the source, fate, and transport of glyphosate in the environment; where the larger proportions indicate a faster transport from the source to the watercourse, and smaller values suggest longer residence times or distances between the application site and the watercourse (Battaglin et al., 2014; Medalie et al., 2020). When glyphosate and AMPA were not both detected, the ratio was not calculated and was directly considered >1, since in those samples glyphosate was detected

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but not AMPA. In 84% of the instances, the glyphosate-to-AMPA ratios were >1, that is, glyphosate concentrations were higher than those of AMPA. In the remaining 16% cases, where glyphosate-to-AMPA ratios were <1, the ratio values were all above 0.7. While Medalie et al. (2020) found lower ratios for large watersheds and high ratios for small watersheds, no significant differences were found in the ratios calculated between samples from the main channel and tributaries in the present work (*p = 0.1320*). These results suggest fast transport times and short mobilization distances from the application areas to the water bodies analyzed. Therefore, the origin of the AMPA found in these samples was in the fields where glyphosate was applied. With a half-life 8 times longer in soil than glyphosate's (Bonansea et al., 2017), soils become AMPA reservoirs, which through runoffs are able to reach the watercourses that are part of the Gualeguay basin.

The glyphosate-to-AMPA ratio in sediment samples was >1 in 62% of the instances. For the calculated ratios with values <1, lower values with a higher variability were observed, averaging 0.4 ± 0.2. Sediments are complex environmental matrices with unique compositions (*e. g.*, organic matter, sulfides, inorganic ions, texture) exhibiting anaerobic conditions that can influence the microbial degradation and the half-life of these pollutants (Ronco et al., 2016). In view of these influences, the results indicated that in sediments, in contrast to water, AMPA acquires a greater relevance because of the passage of time, which favors the biodegradation of glyphosate and highlights the longer half-life of the degradation product in the sediments.

3.4.2. Partition coefficients in the environment

The partition coefficient K_d—the relationship between the pesticide concentrations associated with the solid matrices and the soluble phase—was calculated in every sample, for glyphosate and AMPA, with the solid matrices being the suspended particulate matter (K_{d-SPM}) and sediment (K_{d-SED}), both expressed in $L \cdot kg^{-1}$.

3.4.2.1. Partition coefficient for the suspended particulate matter

The $K_{d\text{-SPM}}$ median (minimum-maximum) values were 1,240 (151-8,292) $L \cdot kg^{-1}$ and 757 (45-25,206) $L \cdot kg^{-1}$ for glyphosate and AMPA, respectively. Possible relationships between $K_{d\text{-SPM}}$ and the measured physicochemical parameters (conductivity, pH, temperature, dissolved-oxygen concentration, chemical oxygen demand) we were explored by means of the Spearman correlation matrix, but no significant relationships were found. Despite the high solubility in water of glyphosate and AMPA, these results again confirmed the high affinity of these compounds for the particulate fraction, with concentrations there, expressed as $\mu g \cdot kg^{-1}$, being more than three orders of magnitude higher than those found in water: For example, in the winter campaign at site T7, where the highest concentration of glyphosate was detected, 10.90 $\mu g \cdot L^{-1}$ were quantified in the soluble fraction, whereas 41,013 $\mu g \cdot kg^{-1}$ were quantified in the particulate fraction, equivalent to 3.16 $\mu g \cdot L^{-1}$, when expressed with respect to the volume of water. Bonansea et al. (2017) made a similar observation for water samples from the Suquía River, where the concentrations of the glyphosate and AMPA in the suspended particulate matter (again, expressed as $\mu g \cdot kg^{-1}$) were 12 and 20 times higher than the respective values in the soluble fraction.

The percent contribution of the soluble and particulate fraction to the total concentration of glyphosate and AMPA in surface water was calculated in each sample. In all the samples, the contribution of the soluble fraction was always greater than that of the particulate fraction: for glyphosate, the average contribution was 82.0%, with a minimum contribution of 58.3% and a maximum of 97.0%; while for AMPA, the average was 86.6% and the minimum and maximum values 56.1% and 99.4%. These results are in agreement with those previously observed by Mac Loughlin et al. (2020), where the $K_{d\text{-SPM}}$ partition coefficients of 833 (81-7,564) $L \cdot kg^{-1}$ and 325 (25-3,584) $L \cdot kg^{-1}$ for glyphosate and AMPA, respectively, proved to be lower than those calculated here of 1,240 (151-8,292) $L \cdot kg^{-1}$ and 757 (45-25,206) $L \cdot kg^{-1}$. Consequently, the soluble fraction contributed more than 90% of the total concentration of glyphosate and AMPA in the surface water.

Few publications have reported the concentration of glyphosate and AMPA associated with the suspended particulate matter. Most of the analyses have been carried out on the whole water or on only the soluble fraction, frequently without explicitly stating the matrix investigated (Battaglin et al., 2014; Medalie et al., 2020). An analysis of the concentrations of these compounds in solid matrices is of great relevance, since their sorption capacities can influence the transport and fate of pollutants (Primost et al., 2017; Ronco et al., 2016). In the publications cited (*cf.* **Table 2**), the detection frequencies in water were lower than those in the particulate-matter. Ronco et al. (2016) had postulated that the greater sensitivity of the extraction method enabled the detection and quantification of those analytes in a higher number of particulate samples. This difference occurs because during the filtration of the surface water the particulate material is concentrated. A difference between the water- and particulate-extraction methods is that the former lacks a concentration step; whereas the latter effects a concentration of around 30-fold, assuming 100 mL of surface water is filtered. The concentration coefficient, however, can vary depending on the volume of water being filtered. On the basis of these results, since the soluble fraction contributes much more of the mass than the particulate fraction, to discard that fraction from the analysis is definitely not recommended.

3.4.2.1. Partition coefficient for the bottom sediments

The $K_{d\text{-}SED}$ median values (minimum-maximum) for glyphosate was 30 (1-188) $L \cdot kg^{-1}$ and for AMPA 59 (7-307) $L \cdot kg^{-1}$. Although no significant differences were observed among the sampling campaigns, a decreasing pattern in $K_{d\text{-}SED}$ could be distinguished as the seasons became warmer (**Figure 8**)—that is, from winter to summer, and, accordingly, along with an increase in temperature. To explore the relationship of the sediment partition coefficients and temperature, a Spearman correlation matrix was carried out, with the variables $K_{d\text{-}SED}$, the physicochemical parameters (conductivity, pH, temperature, dissolved-oxygen concentration, chemical oxygen demand), and the properties of the sediments determined in

the laboratory (moisture and total organic carbon). In the resulting matrix, a statistically significant and negative correlation was observed between the K_{d-SED} of glyphosate and AMPA and the temperature. This finding signifies that, at higher temperatures, the K_{d-SED} values were lower, which pattern corresponds to the aforementioned seasonal trend and the associated effect of temperature-dependent sorption-desorption equilibria. The negative correlation between the conductivity and K_{d-SED} was also of interest to us, where an increase in the temperature led to a decrease in the values of the partition coefficients. This pattern can be explained by the increase in ions competing for mineral active sites (Dollinger et al., 2015; Padilla & Selim, 2019), thus decreasing the amount of glyphosate and AMPA on the solid matrix. At the same time, the chemical complexing of glyphosate and AMPA with divalent ions is favored (Subramaniam & Hoggard, 1988), thus decreasing the sorption to the bottom sediments due to a drop in the concentration of the free glyphosate in the equilibrium of the chemical speciation within the aquatic environment. Another significant negative correlation occurred between pH and K_{d-SED} for glyphosate. As glyphosate exists in the environment as a zwitterion (pK_{a1} = 0.8, 1st phosphonic; pK_{a2} = 2.3, carboxylate; pK_{a3} = 6.0, 2nd phosphonic; and pK_{a4} = 11.0, amine), the molecule's chemical speciation is modulated by pH, and therefore its interaction capability with the environment will be affected by the pH (McConnell & Hossner, 1985). These dynamics are not true for AMPA because of the absence of the carboxylic group.

3.4.3. *Pseudopersistence* in the Gualeguay Basin

In soils from the same region where the present investigation was carried out, Primost et al. (2017) proposed the classification of glyphosate as a *pseudopersistent* pollutant, justifying this classification by the rate of the compound's application being higher than the rate of dissipation: consequently, the continuous introduction of new molecules replaces those that were removed from the system. A similar scenario occurs in the water bodies that make up the Gualeguay basin, with those soils being a reservoir that continually replenishes the

herbicide in the water column, as evidenced not only by the high frequency of glyphosate detection in the samples of the matrices analyzed, but also by the compound's reappearance from one campaign to another. If no new inputs of this herbicide into the system existed, the concentrations would have decreased; or at least the glyphosate to AMPA ratios would have increased over time, given the herbicide's half-lifes in the water of 9.9 days and in the water sediment of 74.5 days (Lewis et al., 2016). Notwithstanding, an increase in the water and sediment concentrations was observed from spring to summer (*cf.* **Figure 5** and **Figure 7**), which pattern coincides with that of the crop cycles and the correspondingly greater applications of the compound (Bernasconi et al., 2021). Thus, on the basis of the detection frequencies and the concentrations measured of glyphosate and its metabolite in surface water and bottom sediment, we can affirm that this compound behaves, in the basin studied, as a *pseudopersister* pollutant in water.

3.5. Insecticides in the basin from an ecotoxicological perspective

Quality guidelines for the protection of aquatic life (GPAL) are derived from local and international ecotoxicological sensitivity data (*e. g.*, No Observed Effect Concentration-NOEC, LC_{50}, and EC_{50}) obtained from acute and chronic experiments with fish, invertebrates, and algae, among other species. These guidelines are intended to safeguard all forms of aquatic life, including the most sensitive life stage of a species from anthropic stressors—*i. e.*, chemical inputs or changes in physical components. Depending on the country, different methods are used to calculate these guideline values, such as the assessment-factor method and the species-sensitivity-distribution method, the latter being the methodology used in Argentina, based on chronic endpoints or extrapolating the latter from acute assays.

Although glyphosate and AMPA were the most frequently detected compounds in the water samples, the maximum concentration was more than 20 times below its GPAL of 240 $\mu g \cdot L^{-1}$

established in Argentina (SRHN, 2003c). Likewise, atrazine concentrations were all below the 3 $\mu g \cdot L^{-1}$ guideline for Argentina (SRHN, 2003a), but the maximum detected did, however, exceed the 1.8 $\mu g \cdot L^{-1}$ guideline applied in Canada (CCME, 1994).

Most of the insecticide detections (bifenthrin, cypermethrin, deltamethrin, λ-cyhalothrin, and chlorpyrifos; *cf.* WIN in **Figure 2**) occurred particularly during the winter campaign, with those concentrations exceeding their respective GPAL values. Furthermore, in that same campaign, the herbicide trifluralin was also detected in only two samples, with one of those exceeding its GPAL (CCME, 1999b). **Figure 9** illustrates the concentrations of the pesticides detected in the winter campaign with the existing associated GPALs, except for glyphosate and atrazine, which pesticides were discussed at the beginning of this section.

All the deltamethrin detections exceeded the GPAL, with the maximum occurring at the T3 site (0.044 $\mu g \cdot L^{-1}$) and exceeding the guideline by a factor of 110-fold (CCME, 1999a). At the same site, other pyrethroid insecticides evidenced concentrations above their respective guidelines: cypermethrin and λ-cyhalothrin, for example, were 13 and 4 times higher than their respective GPALs (Silva et al., 2008, SRHN, 2003b).

Of relevance here is that—for pesticides such as deltamethrin, bifenthrin, and chlorpyrifos—the concentrations quantified in the main channel exceeded their guidelines for the protection of the aquatic life (*cf.* black rectangular markers in **Figure 9**); and, as previously described for glyphosate and AMPA, the river flow at these sampling sites suggested that these results should be taken into consideration to generate management policies for the land use of the basin in order to recover the water quality. In addition to this consideration, we need to note that the sampling sites M1 to M3 correspond to beaches and campsites with recreational use, where human-exposure scenarios very likely occur. Unfortunately, no pesticide guidelines for the quality of water for recreational use exist. This finding emphasizes the need for new analysis tools and benchmarks to protect the population from adverse-exposure scenarios.

In the other sampling campaigns, and even though insecticide detections were more sporadic, the latters' concentrations also exceeded their respective GPALs. During the autumn, chlorpyrifos was detected at M1 and T3 at 14, and 25 times the 0.006 µg·L^{-1} guideline, respectively (SRHN, 2005). In that same campaign, at the T5 site, a sole bifenthrin concentration was quantified at 0.147 µg·L^{-1}, 245 times above its GPAL (Palumbo et al., 2010), was quantified. In the spring campaign, only the herbicides glyphosate, AMPA, and atrazine were detected, as previously discussed. Finally, in the summer chlorpyrifos was detected at only T3, but at 40-fold above its guideline. In general, the sampling sites on tributary streams exhibited higher examples of excesses, since at those sites the occurrence of insecticides was mostly higher.

The finding of pesticide concentrations that exceed their GPAL is both a reflection of the level of pesticide use and the pulsation of the system (Mac Loughlin et al., 2022; Pérez et al., 2017). Even though the sampling methodology used here, with seasonal grab samples, harbors distinct probabilities of missing peak concentrations that may exceed reference values (Norman et al., 2020; Stackpole et al., 2021), the concentrations found still exceeded the guidelines. Therefore, future studies ought to implement sampling strategies capable of documenting those peak concentrations. We must stress the need to carry out laboratory tests with autochthonous species to reflect the real situation of the study system more accurately since most standardized test species from which GPALs are derived are not native, and therefore their biologic responses can differ widely, with the native species manifesting either greater or lesser sensitivity to the same pesticide. Furthermore, the implementation of guidelines should be required for certain pesticides that are not covered by government entities, both nationally and internationally, as well as an updating of the guidelines for those compounds for which more recent research is available.

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3.6. Pesticide profiles: extensive agriculture *versus* horticulture

Several publications have reported the presence of pesticides in surface watercourses in Argentina as a result of the agroproductive activities carried out in the area surrounding them (Andrade et al., 2021; De Gerónimo et al., 2014; Pérez et al., 2021), but none was carried out in a watershed comparable to the size of the Gualeguay basin, or with the same number of sampling campaigns following seasons and crop cycles. From the analysis of these publications, herbicides emerge as the type of pesticides with the highest detection frequency, glyphosate being the herbicide that stands out above the others. I The relevance of glyphosate varies in accordance with the sales volume: according to the latest statistics available, herbicides accounted for 87% of total pesticide sales, with glyphosate representing 62% of that subtotal and other herbicides the remaining 25% (CASAFE, 2014). The investigations mentioned were carried out in regions where extensive agriculture prevailed.

Pesticides, however, are exclusively used not only in extensive agriculture but also in horticulture. These two contrasting production models cause negative impacts on associated surface water bodies, with horticulture being the one that has seemed to produce the greater frequency of ecotoxicologic effects on a battery of test species, in both the water and the sediment (Demetrio et al., 2022). Recently, in an article that analyzed the impact of pesticide residues exclusively in the horticultural greenbelt of La Plata in the Province of Buenos Aires, Argentina (*cf.* insert in **Figure 1)** for over three years (Mac Loughlin et al., 2022), insecticides emerged—in addition to glyphosate— as the type of pesticides with not only higher detection frequencies, but also with a higher concentration than in the present study, which was carried out in a strictly agricultural basin. In the horticultural area, chlorpyrifos was detected in 37% of all the samples from the three matrices analyzed (surface water and suspended particulate matter: n = 30; bottom sediments: n = 29) at a maximum concentration of 2.645 µg·L^{-1} in the surface water and 2,258 µg·kg^{-1} in the bottom sediments, followed by the pyrethroids cypermethrin and λ-cyhalothrin in 30% of all samples,

at maximum concentrations of 3.888 µg·L^{-1} and 0.010 µg·L^{-1} in the surface water, and 1,076 µg·kg^{-1} and 2,607.7 µg·kg^{-1} in the bottom sediments, respectively. Both the frequencies and the concentrations of the insecticides in the horticultural system were higher: in surface water, the maximum deltamethrin concentration (3.944 µg·L^{-1}) surpassed the recommended guideline by 648-fold, while the aforementioned maximum cypermethrin concentration was equal to 6,480 times its GPAL. In the Gualeguay River, however, the maximum cypermethrin concentration was just 13 times the GPAL. For the sediments, the maximum concentration of chlorpyrifos in the present study (7 µg·kg^{-1}) was but one-tenth the minimum recorded in the horticultural areas (70 µg·kg^{-1}). For λ-cyhalothrin, the other insecticide detected in sediments of the Gualeguay basin, the concentration of 3.9 µg·kg^{-1} proved to be only twice the minimum reported in the other production system (1.8 µg·kg^{-1}). What was surprising was that, since glyphosate is a broad-spectrum, nonselective herbicide, the concentrations of that compound and AMPA manifested a similar pattern to that of the insecticides in the horticulture impacted water body: the mean concentrations, both in the surface water and in the bottom sediments, were found to be higher in the horticultural production system. The only compound that in extensive agriculture was found at a higher detection frequency and in higher concentrations than in horticulture, was atrazine at 73% versus 17% and a concentration range of 0.009-2.113 µg·L^{-1} versus 0.013-0.044 µg·L^{-1}, respectively.

The results of the present work, together with the observations of previous investigations, lead to two noteworthy results: (1) glyphosate is a ubiquitous pollutant in agriculturally productive activities in Argentina; thus further supporting the proposal made by Bernasconi et al. (2021), who suggested glyphosate as an environmental marker of chemical-based agriculture in Argentina; (2) these types of agroproductive activities generate a form of fingerprint in the residues produced where pesticides are used, with those of herbicides—mainly atrazine—being the characteristic pollutant of extensive agriculture and those of insecticides of widespread horticulture.

4. Conclusions

No statistically significant differences were found between the concentrations of glyphosate and AMPA in the matrices analyzed with respect to the sampling sites on the tributary streams and on the main channel of the Gualeguay River. Atrazine, more closely associated with extensive agricultural production, was also frequently detected in water samples—again, without statistically significant differences with respect to the stream order of the sampling sites. This pattern denotes not only the high mobility of these compounds, after brief times and at short distances from the source, but also underscores the quantity of pesticides used in agricultural production. Despite not being so frequently detected, certain insecticides reached concentrations higher than the guidelines for the safe protection of aquatic life, even in samples from the main channel. The calculated K_d values indicated that glyphosate and AMPA had an affinity for the particulate fraction of the surface water and the bottom sediments. In spite of this tendency in the partitioning, in the water bodies studied, the soluble fraction was the main contribution to the total concentration in surface water, representing on average more than 80% of the total value. For the bottom sediments of the Gualeguay River, a relationship between the partitioning and the water composition occurred, resulting in the coefficients being correlated with the pH and the chelating capability. Finally, based on the frequencies and concentrations at which glyphosate and AMPA were detected in the matrices analyzed in the Gualeguay basin, glyphosate is proposed as a *pseudopersistent* pollutant of aquatic systems associated with agricultural production in the region. Ultimately, these findings point to an urgent need to implement policies that will definitively reduce the application of pesticides in order to eliminate the adverse consequences of such agents on these types of basins and thus maintain the productivity of the soils, especially since those same areas drain into key ecosystems, such as the Paraná delta, that are absolutely essential for the preservation of biodiversity.

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T. Mac Loughlin: Conceptualization, Investigation, Formal analysis, Writing - Original Draft.

L. Peluso: Conceptualization, Writing - Review & Editing, Supervision, Funding acquisition.

D. Marino: Conceptualization, Writing - Review & Editing, Supervision, Funding acquisition.

Declaration of Interest Statement

Figure 1. Gualeguay basin in the Province of Entre Ríos, Argentina. The *insert* to the upper left depicts the location of the basin (light blue) within the Province of Entre Ríos (surrounding dark blue), the Province of Córdoba (orange), and the Province of Buenos Aires (green), all in Argentina. In the figure, the sampling sites on tributary streams (T) are represented by circles and the sites on the main channel (M) by squares. The names of the waterways and codes are listed in **Table 1**.

Figure 2. Frequency of pesticide detection in surface-water samples. In the bar graph, the percent detection frequency is plotted on the *ordinate* for each of the sampling campaigns itemized on the *abscissa*: autumn (AUT), winter (WIN), spring (SPR), summer (SUM). Key to the pesticide codes: GLY, glyphosate; AMPA, (aminomethyl)phosphonic acid; TRF, trifluralin; ATZ, atrazine; ATC, acetochlor; BIF, bifenthrin; CYP, cypermethrin; DEL, deltamethrin; λ-CYHAL, λ-cyhalothrin; CLP, chlorpyrifos; AZX, azoxystrobin. The different bar colors represent the order of the watercourse: main channel (dark blue) and tributary (light blue).

Figure 3. Frequency of pesticide detection in bottom-sediment samples. In the bar graph, the percent detection frequency is plotted on the *ordinate* for each of the sampling campaigns itemized on the *abscissa*: autumn (AUT), winter (WIN), spring (SPR), summer (SUM). Key to the pesticide codes: GLY, glyphosate; AMPA, (aminomethyl)phosphonic acid; λ-CYHAL, λ-cyhalothrin; CLP, chlorpyrifos. The different bar colors represent the order of the watercourse: main channel (dark orange) and tributary (orange).

Figure 4. Concentration of glyphosate, AMPA, and atrazine in surface water in the different orders of watercourses sampled. In the box plot, the concentrations of the pesticides µg·L^{-1} are plotted on the *ordinate* in left axis, glyphosate [blue diagonally hatched boxes] and AMPA [light-green diagonally hatched boxes]; right axis, atrazine [solid dark-green boxes]) for the sampling-site classification indicated on the *abscissa*. In this and subsequent boxplots, the boxes represent the 25th and 75th percentiles, the whiskers the minimum maximum values, and the solid dots the median concentration.

Figure 5. Concentration of glyphosate, AMPA, and atrazine in surface water in the different sampling campaigns. In the figure, the concentrations of the pesticides in µg·L^{-1} are plotted on the *ordinate* (left axis, glyphosate [blue diagonally hatched boxes] and AMPA [light-green diagonally hatched boxes]; right axis, atrazine [solid dark-green boxes]) for each sampling campaign indicated on the *abscissa*. The boxes represent the same statistical parameters as those in **Figure 4**. The asterisk (*) indicates a statistically significant difference from the other sampling campaigns.

Figure 6. Comparison of concentrations of glyphosate, AMPA, and atrazine in surface water with the maximum concentrations previously reported for Argentina and other countries. In the figure, the concentrations of the pesticides in µg·L^{-1} are plotted on the *ordinate* (left axis, glyphosate and AMPA; right axis, atrazine) for each compound indicated on the *abscissa*. The solid symbols represent whole water and the open symbols the soluble fraction. The key to the symbols below the figure lists the references for the data that were plotted.

Figure 7. Concentration of glyphosate and AMPA in bottom sediments in the different sampling campaigns. In the figure, the concentrations of glyphosate (dark-red boxes) and AMPA (light-red boxes) in µg·kg^{-1} are plotted on the *ordinate* for each sampling campaign indicated on the *abscissa*. The boxes represent the same statistical parameters as those in **Figure 4**. The letters (*a, b, c*) indicate statistically significant differences from the values for the other sampling campaigns.

Figure 8. Water-sediment-partition coefficients of glyphosate and AMPA in different sampling campaigns. In the figure, the partition coefficients in L·kg^{-1} for glyphosate (dark-red boxes) and AMPA (light-red boxes) are plotted on the *ordinate* for each sampling campaign indicated on the *abscissa*. The boxes represent the same statistical parameters as those in **Figure 4**.

Figure 9. Comparison of pesticide concentrations during the winter sampling campaign with the guidelines for the protection of aquatic life (GPAL). In the figure, the pesticide concentrations in µg·L^{-1} are plotted on the *ordinate* on a logarithmic scale for each compound displayed on the *abscissa*. The solid black lines indicate the guidelines of the different pesticides.
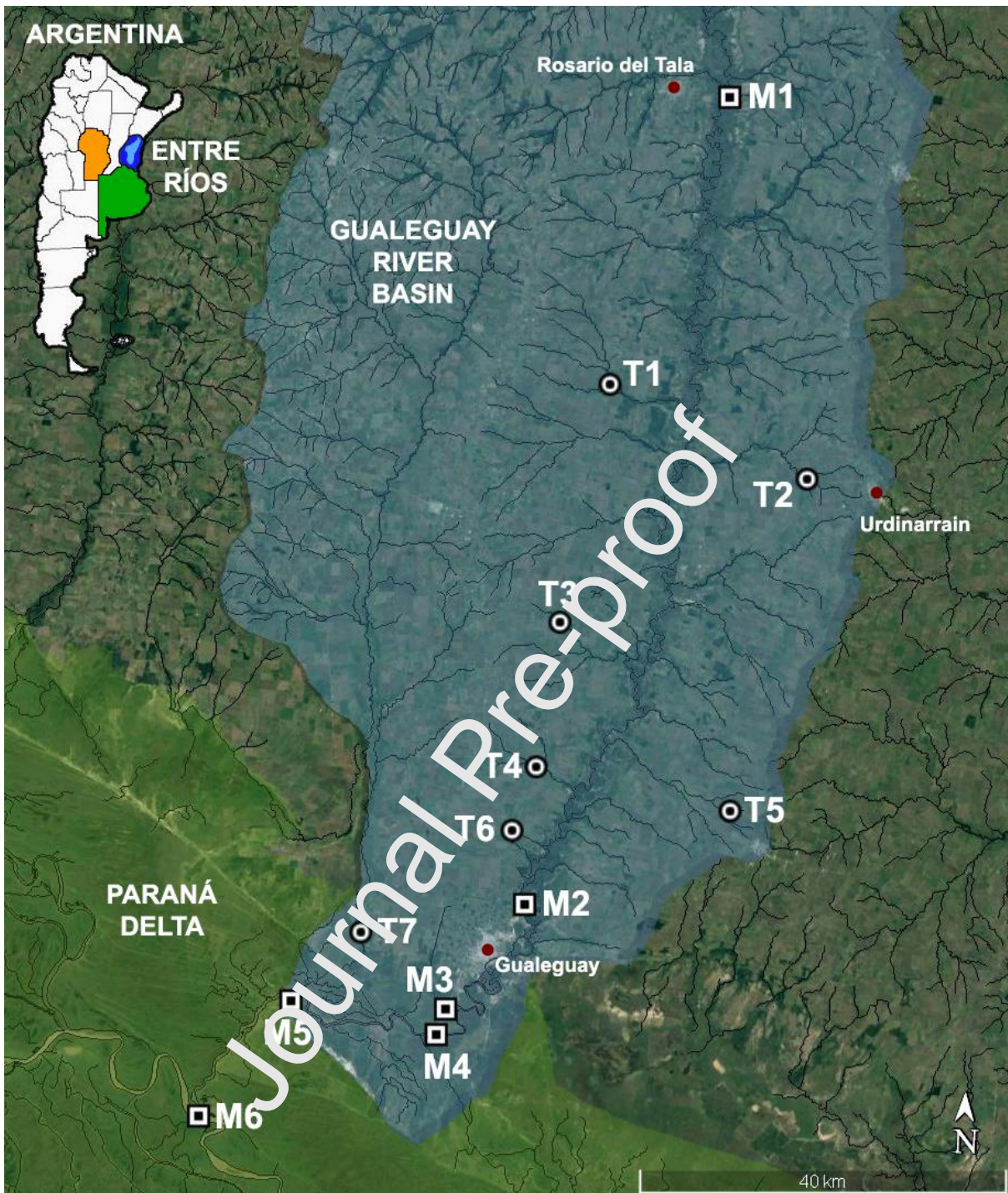
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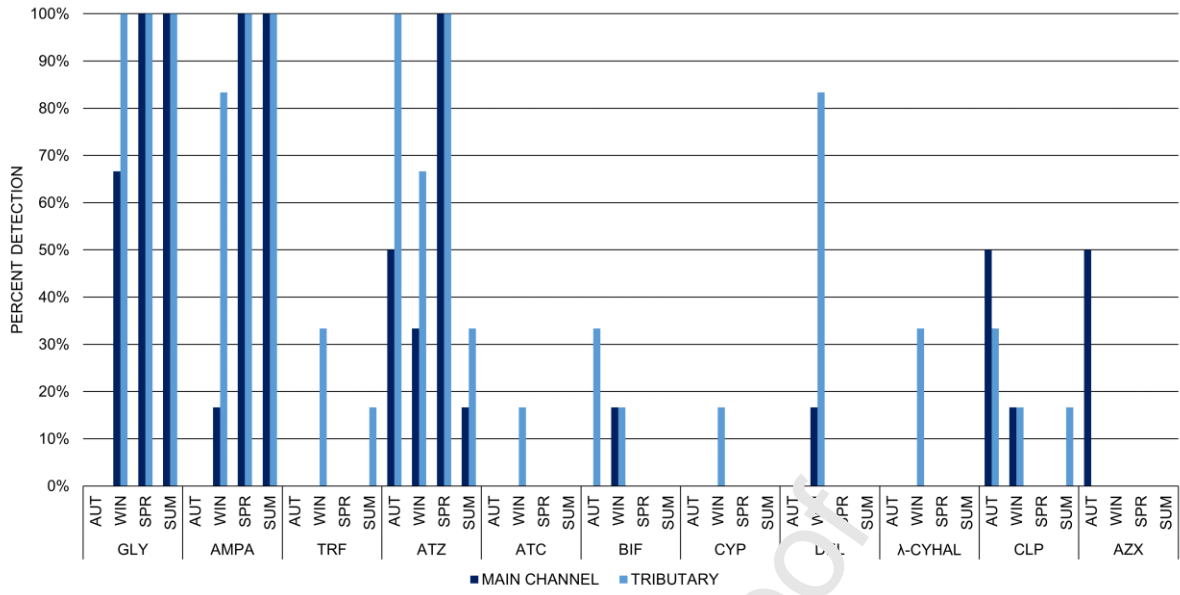
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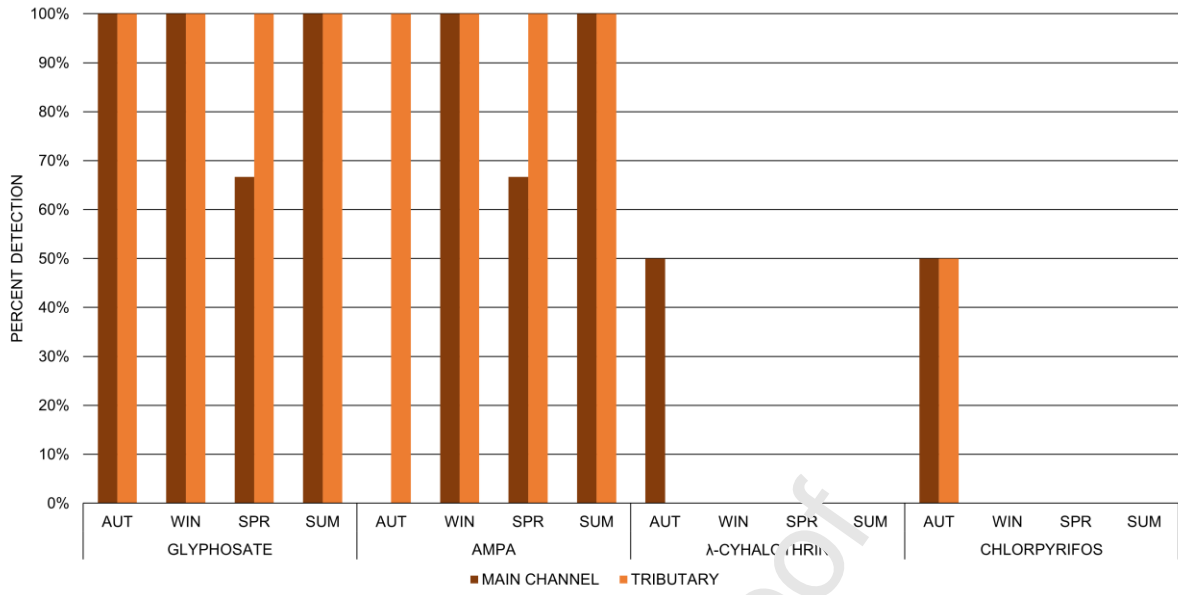
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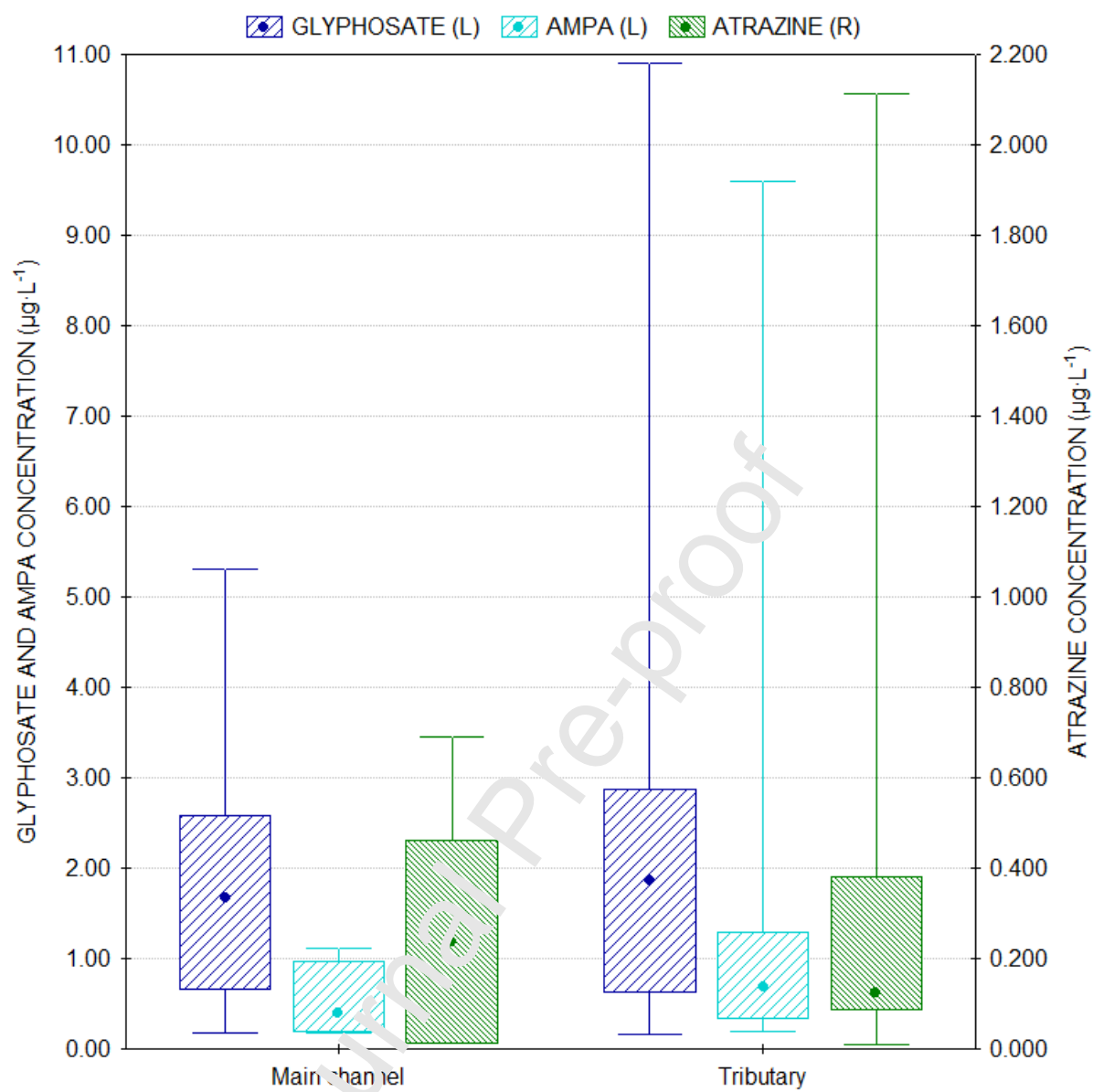
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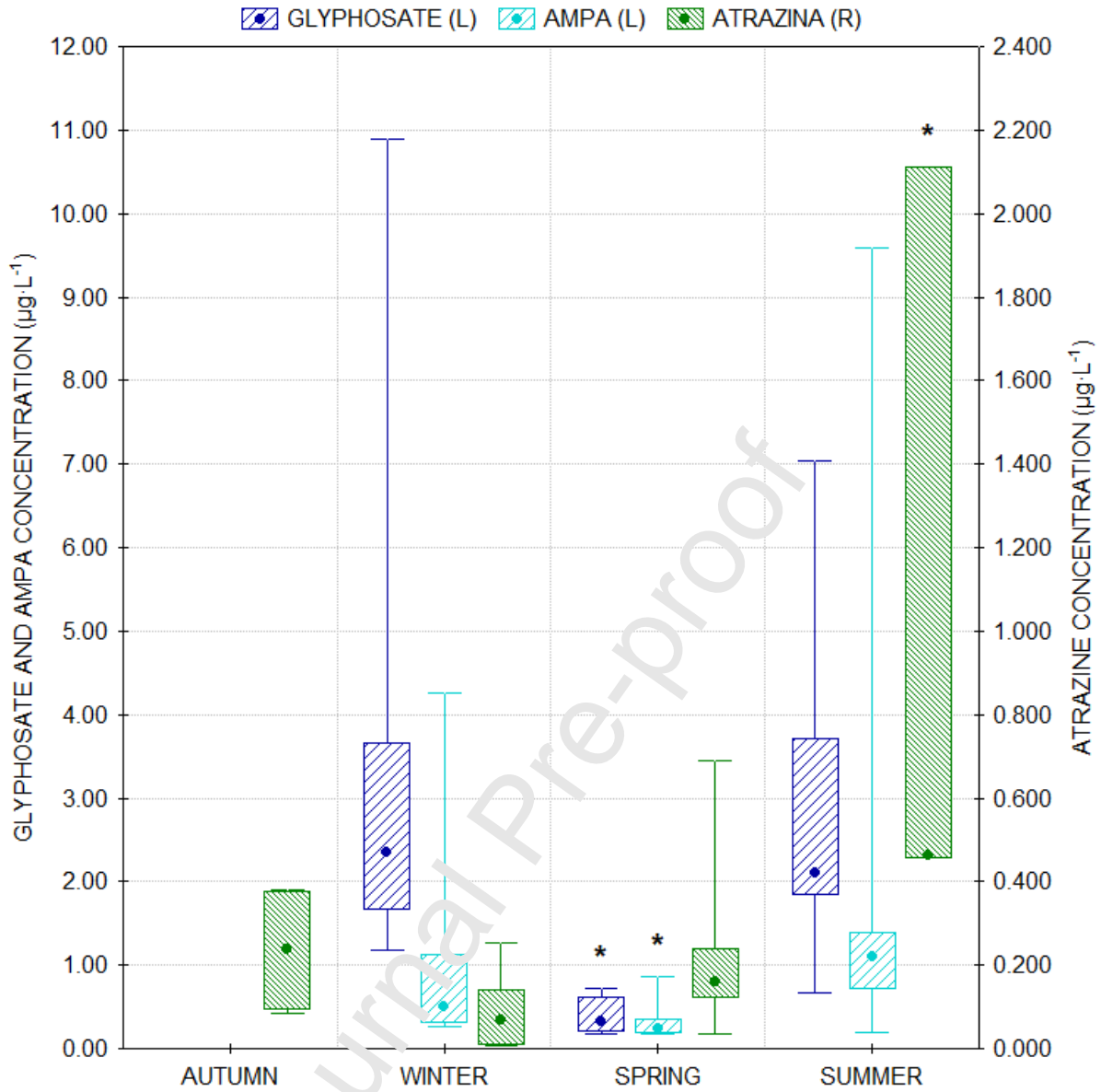
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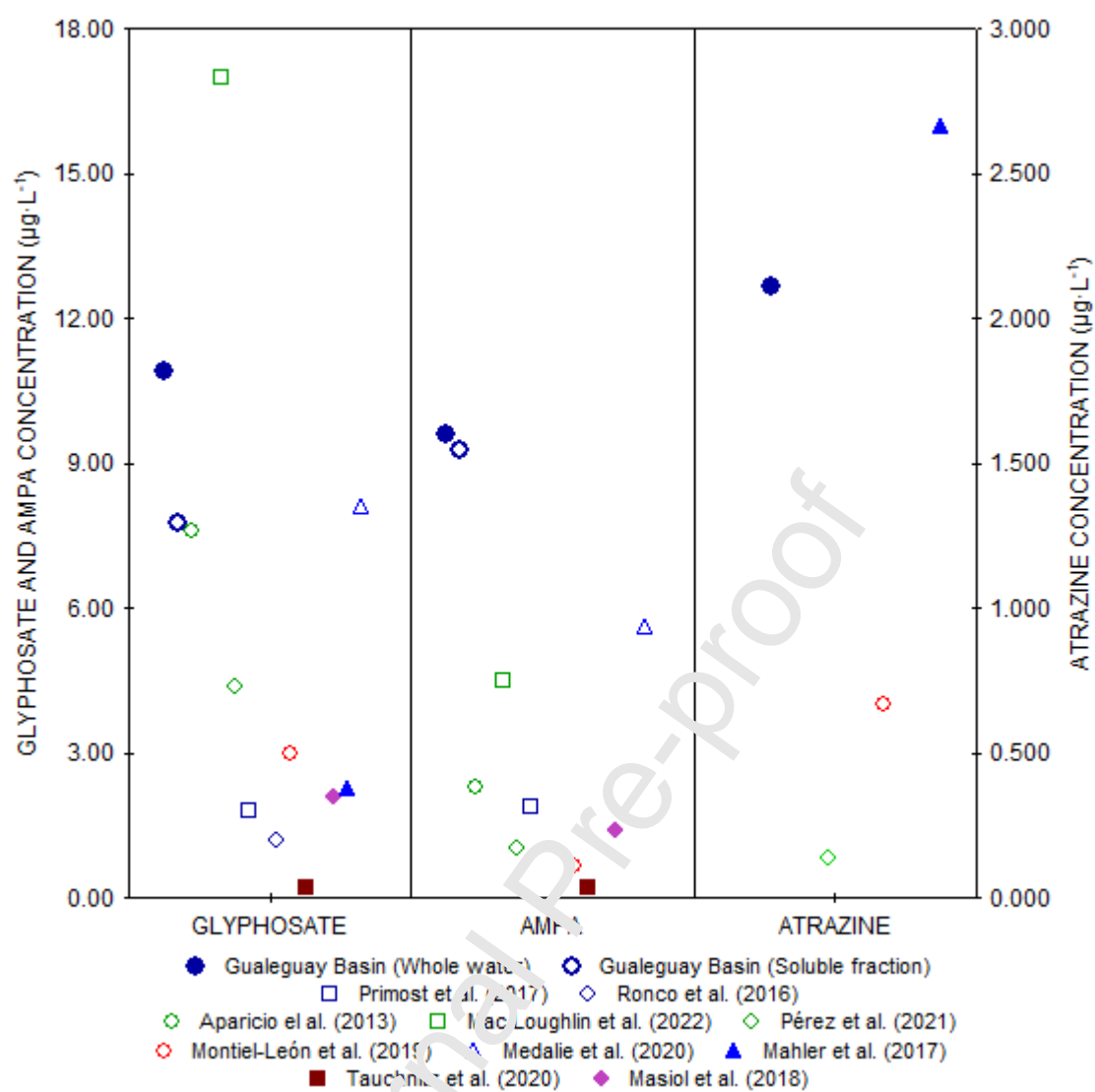
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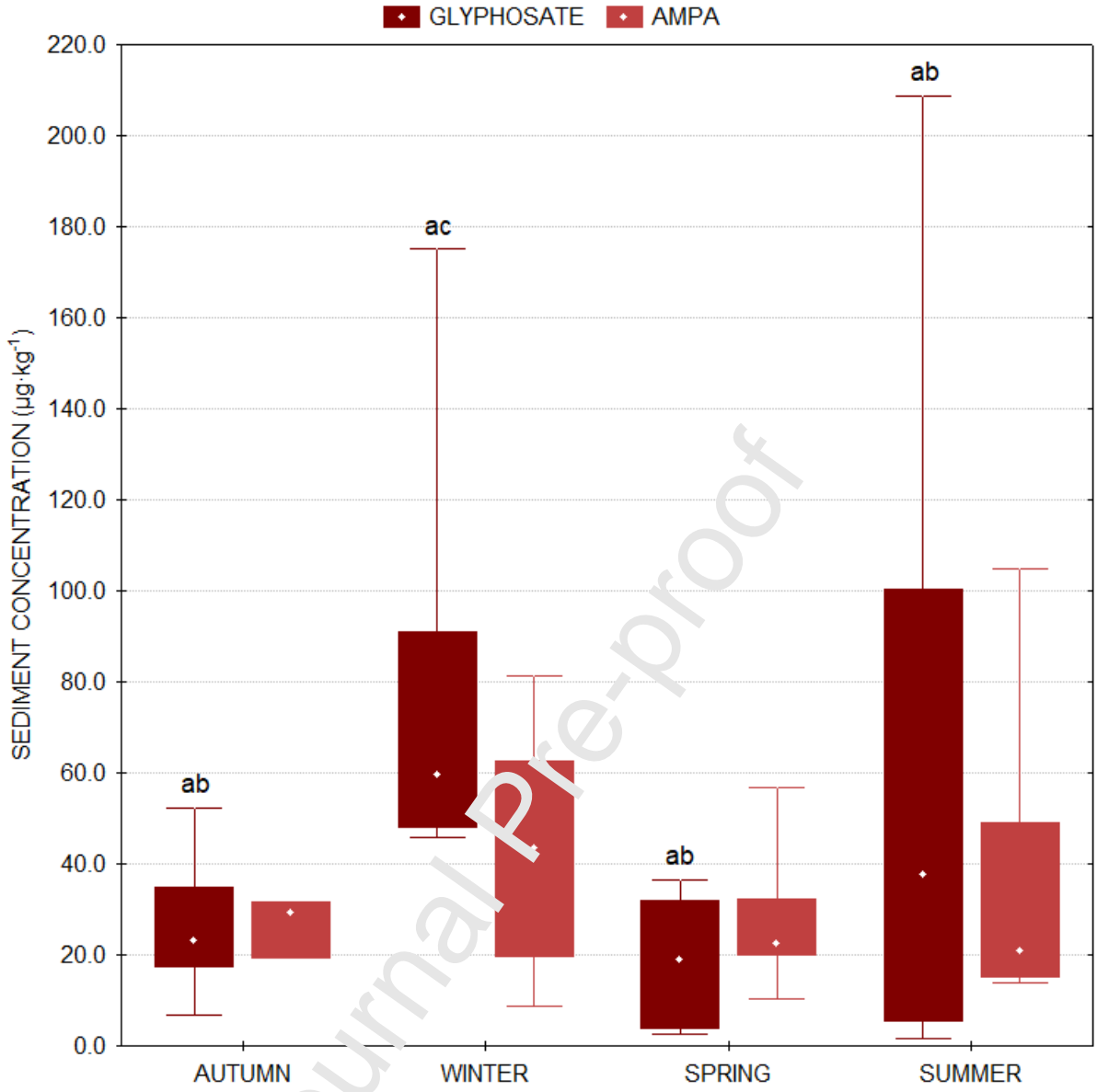
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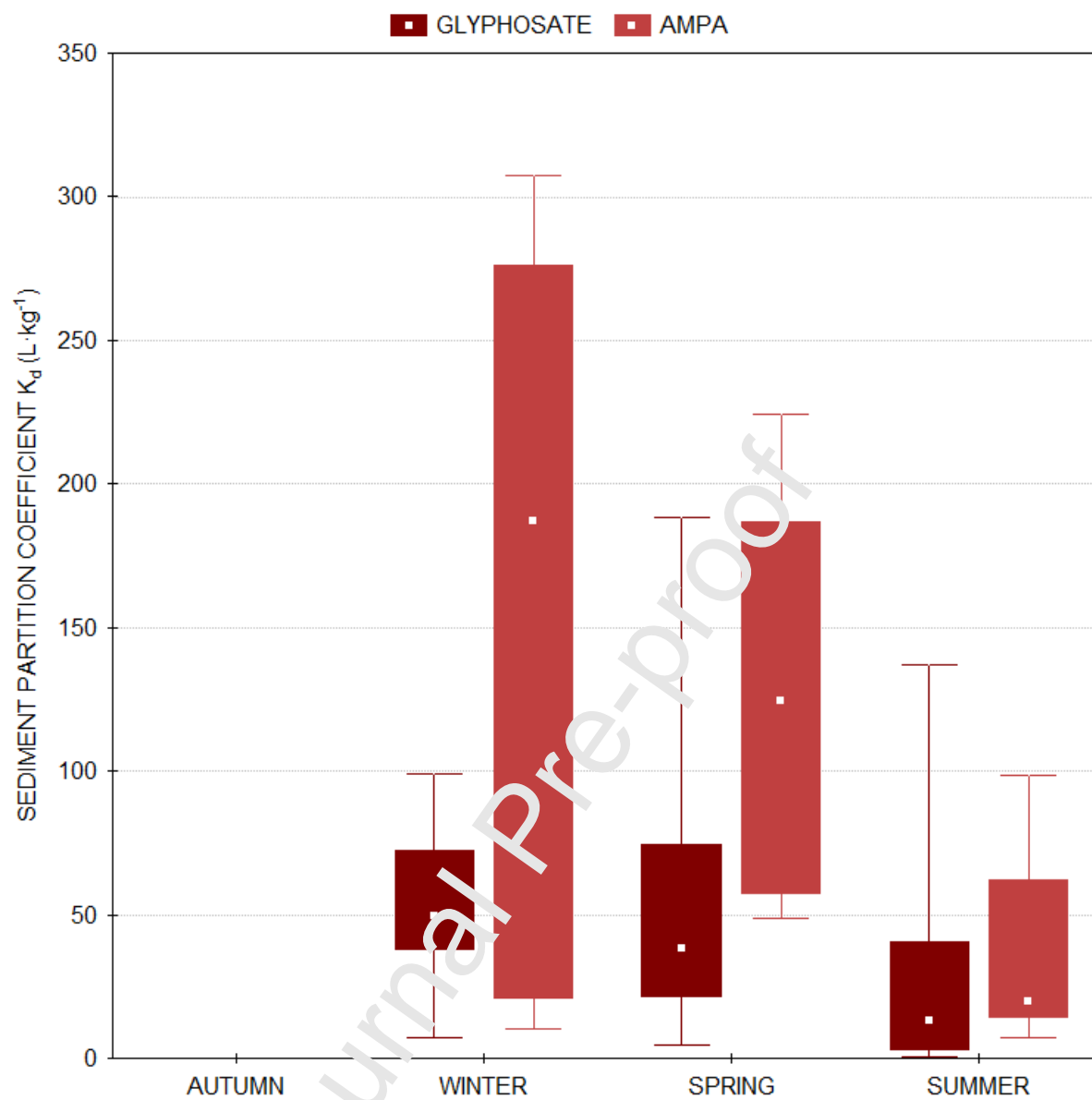
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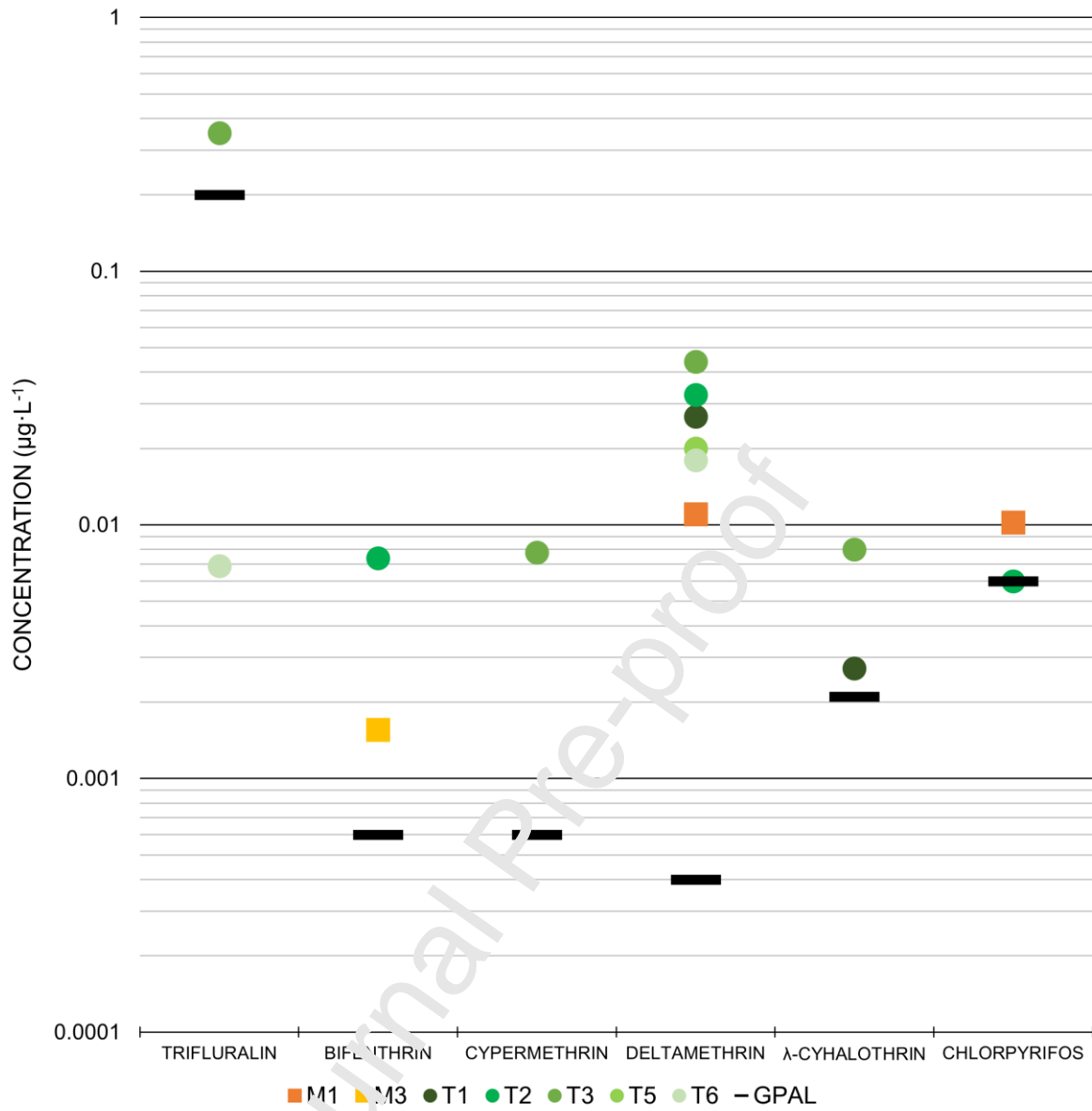
Figure 9

Table 1. Names, geographic coordinates, and codes of the sampling sites

Sampling site	Watercourse order	Coordinates	Code
Rosario del Tala (city)	Main channel	32°18'31,27"S 59° 4'35,45"W	M1
Gualeguay (city, before)	Main channel	33°5'58,06"S 59°16'12,73"W	M2
Gualeguay (city, after)	Main channel	33°12'28,01"S 59°21'8,60"W	M3
Puerto Ruiz (city)	Main channel	33°13'24.03"S 59°21'48.35"W	M4
After confluence with "Clé" Stream	Main channel	33°11'51.09"S 59°32'33.24"W	M5
Mouth of the Gualeguay River towards the Paraná delta	Main channel	33°13'20.01"S 59°38'13.38"W	M6
"El Sauce" Stream	Tributary	32°35'33,71"S 59°11'58,94"W	T1
"San Antonio" Stream (near city of Urdinarrain)	Tributary	32°40'30,13"S 58°58'1,17"W	T2
"La Vizcacha" Stream	Tributary	32°49'29,86"S 59°14'41,44"W	T3
"Arrecifes" Stream	Tributary	32°57'57,00"S 59°15'51,88"W	T4
"Del Medio" Stream	Tributary	32°59'59,76"S 59°2'14,71"W	T5
Unnamed stream (near feedlot operation)	Tributary	33° 1'42,08"S 59°17'20,07"W	T6
"Clé" Stream	Tributary	33° 7'59.37"S 59°27'29.55"W	T7

Table 2. Glyphosate and AMPA detection frequency and concentrations in the environmental matrices analyzed and reported in peer-reviewed journals

Country	Region or state	Reference	Environmental matrix	Glyphosate		AMPA	
				Detection frequency (number of samples)	Concentration	Detection frequency (number of samples)	Concentration
Argentina	Buenos Aires	(Aparicio et al., 2013)	Surface water (soluble fraction)	16%	Maximum 1.6 µg·L^{-1}	13%	Maximum 2.3 µg·L^{-1}
			Particulate matter	69%	Maximum 562.8 µg·kg^{-1}	21%	Maximum 210.4 µg·kg^{-1}
			Sediment	67%	Maximum 221.2 µg·kg^{-1}	89%	Maximum 235.0 µg·kg^{-1}
		(Pérez et al., 2017)	Surface water	84.61% (n = 31)	Mean 0.78 µg·L^{-1} Maximum 2.90 µg·L^{-1}	84.61% (n = 31)	Mean 0.32 µg·L^{-1} Maximum 2.00 µg·L^{-1}
			Sediment	78.94% (n = 57)	Mean 3.85 µg·kg^{-1} Maximum 18.50 µg·kg^{-1}	96.49% (n = 57)	Mean 6.18 µg·kg^{-1} Maximum 47.50 µg·kg^{-1}
		(Okada et al., 2018)	Surface water (stream, soluble fraction)	28% (n = 64)	Mean 0.4 µg·L^{-1} Range 0.1-8.2 µg·L^{-1}	50% (n = 64)	Mean 0.2 µg·L^{-1} Range 0.1-3.7 µg·L^{-1}
			Sediment	95% (n = 45)	Mean 7.0 µg·kg^{-1} Range 0.5-75.5 µg·kg^{-1}	100% (n = 45)	Mean 17.6 µg·kg^{-1} Range 0.5-226 µg·kg^{-1}
		(Mac Loughlin et al., 2020)	Surface water (stream, soluble fraction)	67% (n = 30)	Median 3.1 µg·L^{-1} Range 0.2-17.0	83% (n = 30)	Median 1.4 µg·L^{-1} Range 0.2-4.5

City	Reference	Matrix	Detection	Value	Detection	Value
				µg·L⁻¹		µg·L⁻¹
		Particulate matter	67% (n = 30)	Median 3,735 µg·kg⁻¹ (or 0.2 µg·L⁻¹) Range 245-35,620 µg·kg⁻¹ (or 0.0001–5 µg·L⁻¹)	83% (n = 30)	Median 662 µg·kg⁻¹ (or 0.02 µg·L⁻¹) Range 43-19,586 µg·kg⁻¹ (or 0.0006-1 µg·L⁻¹)
	(Pérez et al., 2021)	Surface water (soluble fraction)	39%	Mean 1.28 µg·L⁻¹ Range 0.50-4.36 µg·L⁻¹	78%	Mean 0.66 µg·L⁻¹ Range 0.50-1.03 µg·L⁻¹
		Sediment	72%	Mean 8.28 µg·kg⁻¹ Range 1.50-32.00 µg·kg⁻¹	83%	Mean 6.85 µg·kg⁻¹ Range 3.00-17.50 µg·kg⁻¹
	(Andrade et al., 2021)	Surface water	-	Maximum 7 µg·L⁻¹		Maximum 4 µg·L⁻¹
		Sediment	-	Maximum 4 µg·kg⁻¹		Maximum 10 µg·kg⁻¹
	(Mac Loughlin et al., 2022)	Sediment	92% (n = 29)	Median 299.6 µg·kg⁻¹ Range 11.0-1,146.5 µg·kg⁻¹	100% (n = 29)	Median 92.3 µg·kg⁻¹ Range 4.6-4,032.7 µg·kg⁻¹
Córdoba	(Bonansea et al., 2017)	Surface water (soluble fraction)	-	Maximum 125.0 µg·L⁻¹	-	Maximum 4.8 µg·L⁻¹
		Particulate matter	-	Maximum 1,570.7 µg·kg⁻¹	-	Maximum 684.9 µg·kg⁻¹
		Sediment	-	Maximum	-	Maximum 266.1

					1,882.3 µg·kg⁻¹		µg·kg⁻¹
Entre Ríos	Gualeguay Basin	(Primost et al., 2017)	Surface water (stream, whole water)	27% (3/11)	Mean 0.73 µg·L⁻¹ Maximum 1.80 µg·L⁻¹	55% (6/11)	Mean 0.53 µg·L⁻¹ Maximum 1.90 µg·L⁻¹
			Particulate matter	100% (9/9)	Mean 340.2 µg·kg⁻¹ (or 0.049 µg·L⁻¹) Maximum 584 µg·kg⁻¹	100% (9/9)	Mean 223.2 µg·kg⁻¹ (or 0.032 µg·L⁻¹) Maximum 475 µg·kg⁻¹
			Sediment	83% (5/6)	Mean 1,126 µg·kg⁻¹ Maximum 3,294 µg·kg⁻¹	100% (6/6)	Mean 2,660 µg·kg⁻¹ Maximum 7,219 µg·kg⁻¹
			Surface water (soluble fraction)	82% (n=38)	Median 1.43 µg·L⁻¹ Range 0.15-7.74 µg·L⁻¹	71% (n = 38)	Median 0.43 µg·L⁻¹ Range 0.15-9.25 µg·L⁻¹
			Surface water (whole water)	82% (n = 38)	Median 1.72 µg·L⁻¹ Range 0.17-10.90 µg·L⁻¹	71% (n = 38)	Median 0.87 µg·L⁻¹ Range 0.17-9.60 µg·L⁻¹
			Particulate matter	82% (n = 38)	Median 1,751 µg·kg⁻¹ (or 0.35 µg·L⁻¹) Range 58-41,03 µg·kg⁻¹ (or 0.005–3.16 µg·L⁻¹)	71% (n = 38)	Median 317 µg·kg⁻¹ (or 0.04 µg·L⁻¹) Range 42-50,368 µg·kg⁻¹ (or 0.007–1.59 µg·L⁻¹)
			Sediment	97%	Median	92%	Median

				(n = 37)	45.7 µg·kg^{-1} Range 1.8-208.6 µg·kg^{-1}	(n = 37)	26.5 µg·kg^{-1} Range 8.9-104.7 µg·kg^{-1}
	Paraná Basin	(Ronco et al., 2016)	Surface water (soluble fraction)	13%	Maximum 1.2 µg·L^{-1}	n.d.	n.d.
			Particulate matter	39%	Maximum 0.21 µg·L^{-1}	9%	Maximum 0.04 µg·L^{-1}
			Sediment	22%	Maximum 2,902 µg·kg^{-1}	22%	Maximum 5,374 µg·kg^{-1}
Brazil	Paraná Basin	(Mendonça et al., 2020)	Surface water	37.1% (n = 124)	Range 035-1.65 µg·L^{-1}	21.8% (n = 124)	Range 0.55-0.75 µg·L^{-1}
Canada	St. Lawrence River	(Montiel-León et al., 2019)	Surface water (soluble fraction)	84% (n = 68)	Mean 0.109 µg·L^{-1} Median 0.027 µg·L^{-1} Range <0.002-3.000 µg·L^{-1}	16% (n = 68)	Range <0.01-0.66 µg·L^{-1}
China		(Gong et al., 2021)	Surface water (soluble fraction)	14.3% (n = 196)	Median 0.23 µg·L^{-1} Midspread 0.11-0.44 µg·L^{-1} Maximum 32.49 µg·L^{-1}	15.8% (n = 196)	Median 1.29 µg·L^{-1} Midspread 1.06-1.81 µg·L^{-1} Maximum 10.31 µg·L^{-1}
Germany	Querne/Weida catchment	(Tauchnitz et al., 2020)	Surface water	8.8% (n = 59)	Range 0.03-0.20 µg·L^{-1}	7.0% (n = 59)	Range 0.12-0.21 µg·L^{-1}
Italy	Veneto region	(Masiol et al., 2018)	Surface water	-	Mean 0.17 µg·L^{-1} Maximum 2.10 µg·L^{-1}	-	Mean 0.18 µg·L^{-1} Maximum 1.40 µg·L^{-1}

|							
The Netherlands		(Geerdink et al., 2020)	Surface water	82% (n = 172)	Maximum 0.304 µg·L⁻¹	99% (170/172)	Maximum 9.900 µg·L⁻¹
Switzerland	Zürich	(Poiger et al., 2017)	Surface water	-	Median 0.11 µg·L⁻¹ 95th percentile 2.1 µg·L⁻¹	-	Median 0.20 µg·L⁻¹ 95th percentile 2.6 µg·L⁻¹
Tanzania	Kilombero Valley (Ramsar Site)	(Materu et al., 2021)	Surface water (soluble fraction)	9.5% (2/21)	Range 0.035-0.050 µg·L⁻¹	n.d.	n.d.
			Sediment	12.5% (4/32)	Range 48-240 µg·kg⁻¹	n.d.	n.d.
United States		(Battaglin et al., 2014)	Surface water (stream)	52.5% (791/1,508)	Median 0.03 µg·L⁻¹ Maximum 73 µg·L⁻¹	71.6% (1,079/1,508)	Median 0.20 µg·L⁻¹ Maximum 28 µg·L⁻¹
			Surface water (large rivers)	53.1% (169/318)	Median 0.03 µg·L⁻¹ Maximum 3.08 µg·L⁻¹	89.3% (284/318)	Median 0.22 µg·L⁻¹ Maximum 4.43 µg·L⁻¹
			Sediment	91.1% (41/45)	Median 9.6 µg·kg⁻¹ Maximum 476 µg·kg⁻¹	93.3% (42/45)	Median 18.0 µg·kg⁻¹ Maximum 341 µg·kg⁻¹
	Midwest	(Mahler et al., 2017)	Surface water (stream)	44% (n = 1,186)	Median 2.23 µg·L⁻¹	-	-
		(Medalie et al., 2020)	Surface water (stream, soluble fraction)	74%	Median 0.05 µg·L⁻¹ Maximum 8.1 µg·L⁻¹	90%	Median 0.15 µg·L⁻¹ Maximum 5.6 µg·L⁻¹
Vietnam	Red River (Hanoi)	(Vu et al., 2021)	Surface water	33% (3/9)	Maximum 0.565 µg·L⁻¹	56% (5/9)	Maximum 1.330 µg·L⁻¹

n.d. not detected

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Graphical abstract
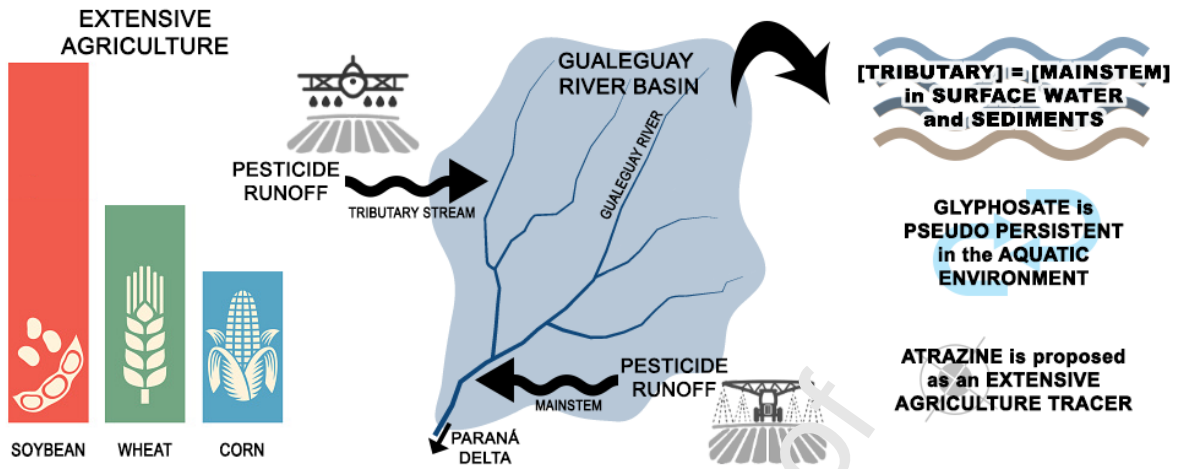
Highlights

1. Glyphosate, AMPA, and atrazine were the most frequently detected pesticides.

2. Herbicide concentrations followed crop application cycles in the region.

3. Pesticide concentrations exhibited no difference between stream orders.

4. Insecticide concentrations in water were above the recommended guidelines.

5. Atrazine can differentiate extensive agriculture from horticulture.