Article

Journal of the Brazilian Chemical Society

https://dx.doi.org/10.21577/0103-5053.20240047

J. Braz. Chem. Soc. **2024**, *35*, 9, e-20240047, 1-8

LC-FLD Determination of Glyphosate, AMPA and Glufosinate in Surface Water from the Paraná River Basin

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Natural waters from the Paraná River hydrographic basin in the Brazil-Paraguay cross-border region were analyzed by liquid chromatography coupled to a fluorescence detector (LC-FLD) after extraction of the analytes in anion exchange resin IRA-900. The method allowed good recovery (91 to 113%) of the studied species (glyphosate, (aminomethyl)phosphonic acid (AMPA) and glufosinate) precision compatible with the requirements of the National Metrology Institute (relative standard deviation < 18%) and limit of quantification (LOQ) values between 0.2 and 0.8 μg L^{-1}. In most of the samples collected between January and September 2022, it was impossible to detect the presence of herbicides, even in regions of intense agricultural activity, probably due to the high adsorption capacity of the soils of the region and due to the higher LOQ of the method. Under these conditions, the main transport route is estimated to be associated with surface runoff, which is only favored by heavy rainfall events.

Keywords: anion exchange resin IRA-900, surface water, pesticides

Introduction

In most agricultural countries, including Brazil, productivity has grown significantly without proportional growth in cultivated areas. This disparity can be explained by the notable advances in agricultural technology from the second half of the 20th century,[1] represented by the development of better practices and equipment, the introduction of more resistant species, and the use of pesticides.

Brazil is one of the largest grain producers in the world, with soy, wheat, rice, and corn harvests increasing yearly. Thus, Brazil also appears on the list of the largest pesticide consumers, with glyphosate at the top of the list of best-selling pesticides between 2009 and 2018.[2] Agricultural production of soybean, corn, and wheat crops is particularly important in the Southern region of Brazil. In the Central-West portion of the state of Paraná, for example, pesticide consumption ranges from 5 to 109 kg ha^{-1} $year^{-1}$,[3] mainly involving herbicides such as glyphosate, paraquat, atrazine and 2,4-dichlorophenoxyacetic acid (2,4-D).

Glyphosate (*N*-(phosphonomethyl)glycine, GLY) is a broad-spectrum herbicide widely used for weed control in soybean, corn and wheat crops. According to studies carried out in 1993[4] and reviewed in 2020[5] by the United States Environmental Protection Agency (USEPA), GLY is not carcinogenic to humans. While many international food safety agencies have accepted this decision, the International Agency for Research on Cancer (IARC) characterized glyphosate as a "probable risk of human cancer" in 2015.[6] Additionally, IARC admits that there is strong evidence for the genotoxicity of GLY, as well as (aminomethyl)phosphonic acid (AMPA), its major microbial metabolite.[7]

Glufosinate-ammonium (ammonium DL-homoalanin-4-(methyl) phosphinate, GLU) is a non-selective contact herbicide widely used in hybrid soybean and corn plantations. Generally, the frequency and dosage of GLU applications exceed the amounts recommended in tropical agriculture,[8] making it a pseudo-persistent pollutant in the soil. Additionally, a study have reported adverse influences of GLU on the biota and humans, particularly important in the large number of studies dealing with reproductive and developmental toxicity.[9]

For many years, the presence of glyphosate in virtually

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Editor handled this article: Maria Cristina Canela (Associate)

all environmental compartments has caused apprehension, not only because of adverse effects on the health of ecosystems but mainly concerning chronic effects on the health of the exposed population.[10,11] Thus, even though regulatory agencies certify its safety, the presence of glyphosate in drinking water[12,13] and a wide variety of foods,[14,15] including breast milk,[16] is of concern.

The dynamics of pollutants in the environment depend entirely on the physical-chemical properties of the pollutant and the characteristics of the contaminated medium. GLY is soluble in water, which favors its transport through the soil. However, GLY is strongly retained by adsorption on clay minerals, which significantly limits its mobility in the soil. Thus, the presence of GLY in surface waters is usually associated with surface runoff during heavy rainfall events, while its presence in groundwater can be explained by a colloid-facilitated transport[17] (see Figure S1, Supplementary Information (SI) section). Therefore, GLY, AMPA and GLU are frequently found in surface and groundwater samples in Brazil, usually in concentrations of tenths of μg L^{-1}.[18,19]

The analysis of glyphosate in natural waters still represents a great challenge, not only because of the usual low concentrations but also because of the impossibility of including GLY determination in multi-residue routines due to its high polarity and poor solubility in organic solvents. Thus, specific methods have been proposed for determining GLY, AMPA and GLU in natural waters, usually involving liquid chromatography tandem mass spectrometry (LC-MS/MS).[20,21] These methodologies employ solid phase extraction (SPE) preconcentration/clean-up steps allowing low LOQ (limit of quantification) values, with (LOQ = 8 ng L^{-1})[20] or without (LOQ = 25 ng L^{-1})[21] FMOC-Cl (9-fluorenylmethyl chloroformate) derivatization. Low LOQ (2.5 ng L^{-1}) has also been reported for direct injection of samples into the LC-MS/MS, after a 20-fold concentration by lyophilization.[18]

Alternative chromatographic methods have been proposed to avoid time-consuming derivatization procedures for direct aqueous determination of GLY and AMPA by LC-MS/MS. Using an ionic column, the LOQ of 30 ng L^{-1} was achieved by Yusà *et al.*[13] The determination of GLY and AMPA in freshwater through derivatization with FMOC-Cl and further liquid chromatography with fluorescence detection (FLD) was reported by Alonso *et al.*,[22] with LOQ of 250 and 1000 ng L^{-1}, respectively.

It is relevant to point out that high concentrations of GLY and AMPA were found in all the works mentioned above, in many cases reaching concentrations of the order of μg L^{-1}. This reality justifies the implementation of analytical routines that facilitate continuous monitoring programs, mainly in areas of intensive agriculture. Herein, a method was validated for determining GLY, AMPA and GLU in samples of natural waters using LC-FLD. The method was applied in a surface water monitoring program associated with the Paraná Hydrographic Basin 3 (BP3), in the cross-border of the Brazil-Paraguay region.

Experimental

Chemicals

Analytical GLY, AMPA, and GLU standards were purchased from Sigma-Aldrich (St. Louis, MO, USA) (purity > 99%). Stock solutions were prepared at 200 mg L^{-1} in ultrapure water and stored at 4 °C. Working solutions were periodically prepared at a concentration of 0.25 mg L^{-1}. High-performance liquid chromatography (HPLC)-grade acetonitrile (ACN), dichloromethane (DCM), phosphoric acid, and 9-fluorenylmethyl chloroformate (FMOC-Cl) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water, with a resistivity of 18.2 MΩ cm, was obtained through a Merck-Synergy UV purification system. The ion exchange resin Amberlite® IRA-900, with a particle size of 640 to 800 μm, was purchased from ChemCruz® (Dallas, TX, USA).

Environmental samples

In the Brazil-Paraguay cross-border region, natural water samples were collected along the Paraná Hydrographic Basin 3 (BP3). The BP3 is an extensive region located in the extreme west of the state of Paraná, comprising an area of about 8 thousand km² of tributaries of the left border of the Paraná River. Although essential cities in the state are in this region, urban areas represent a small fraction of the total area of the Basin, which is mainly dedicated to mechanized and intensive agriculture of soybean and corn crops.[3] 24 sampling points were established along the BP3, 12 on the Brazilian and 12 on the Paraguayan sides, corresponding to first, second and third-order water bodies. These sampling sites were selected based on soil occupation, being categorized as: streams heavily impacted by agricultural activity and with little riparian forest (C), streams with agricultural activity but with preservation of riparian forest (B) and streams with less agricultural activity and greater coverage of riparian forest (A) (Figure 1).

The samples were obtained from punctual collections using 1 L amber borosilicate bottles. The samples were transported in a thermal box with ice (temperature of 4 °C). At the end of the collection day, the samples were

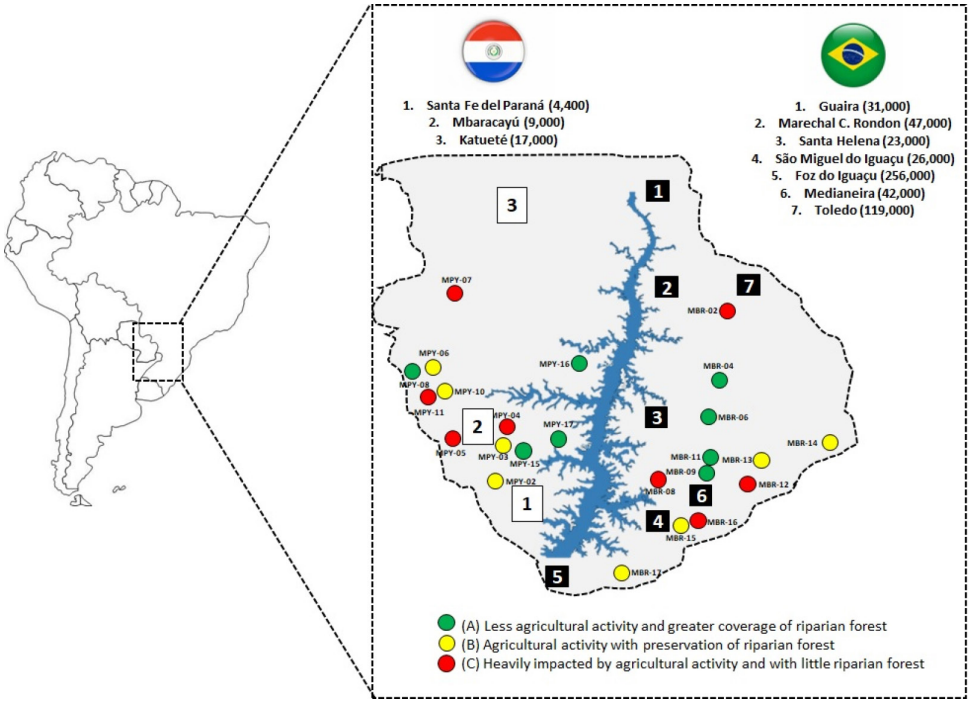

Figure 1. Representation of sampling points along the Paraná 3 River Basin. Numbers correspond to the sampling points and the city where it is located.

double-filtered through 0.7 µm glass fiber filters (GF55/F, HNM and GF/F, Whatman) and stored in a freezer (−20 °C) until analysis.

Sample preparation

Glyphosate, AMPA and glufosinate were extracted in Amberlite® IRA-900 ion exchange resin, according to procedures described in the literature.[23] The resin was hydrated under agitation for 2 h, and every 30 min, the water was renewed and, subsequently, the resin was stored in a glass bottle with water for later use. The extraction was carried out in columns mounted in 6 mL syringes containing 3 cm of resin and a flow control system. Samples (250 mL) were passed through the column at a flow rate of approximately 2.5 mL min^{-1}. Next, the system was washed with 10.0 mL of ultrapure water and eluted with 10.0 mL of 1 mol L^{-1} NaCl solution. An aliquot (2.0 mL) of the eluate was collected and submitted to the derivatization process.

The derivatization process was applied according to procedures reported by Báez *et al.*[24] To each sample (2 mL) was added 250 µL of borate buffer (pH 9, 0.040 mol L^{-1}), 500 µL of acetonitrile, and 500 µL of FMOC-Cl (160 mg L^{-1}). The mixture was stirred for 30 s and then left to stand for 30 min at room temperature. Then, excess FMOC-Cl was removed by extraction with 3.0 mL of dichloromethane. Finally, an aliquot of the aqueous phase was collected for analysis by LC-FLD.

Chromatographic analysis

Glyphosate, AMPA and glufosinate determinations were performed on a Thermo Fisher Scientific (Waltham, Massachusetts, USA) chromatograph (Dionex Ultimate 3000 series), equipped with a two-piston pump LGP-3400SD, WSP-3000 injector and fluorescence detector. Separations were performed on an ACE 5 C18 reversed-phase column (250 × 4.6 mm, 5 µm) with a guard column of the same phase.

The separation was in gradient elution mode as adapted from Mendonça *et al.*[25] Phase A was 0.05% phosphoric acid solution (pH 2.9), and phase B was ACN; the elution procedure was: 20% B for 5 min, reaching 45% of B in 15 min, maintained for 10 min in this condition; between 25 and 30 min, return to the initial condition (20% of B), keeping it for 5 min for column stabilization, totaling 35 min of the chromatographic run, with a flow rate of 1.0 mL min^{-1}. The injected volume was 20 µL and the detection of derivatized patterns was performed at wavelengths (λ) of 260 nm (excitation) and 317 nm (emission).

Calibration curves were prepared in triplicate in ultrapure water, covering the range between 2.5 and 60 µg L^{-1}.

Method validation

The method was validated according to criteria

defined by the National Metrology Institute,[26] considering parameters of selectivity, linearity, the limit of detection (LOD), the limit of quantification (LOQ), precision, and accuracy.

Selectivity was evaluated by comparing analyte retention times and the matrix effect. This last evaluation involved elaborating analytical curves with at least 5 concentration levels in triplicate (n = 3), in ultrapure water, and in the aqueous matrix.

Linearity was evaluated by creating analytical curves in the aqueous matrix in the concentration range of 0.1 to 4.8 μg L^{-1} (n = 3), containing at least 5 concentration levels. The linear fit for each analyte was expressed by the equation of the straight line and the coefficient of determination (R^2), calculated by the ordinary least squares method. Random distribution of residuals was assessed visually from the residual distribution plot, *F*-test assessed homoscedasticity, and the Durbin-Watson test assessed the independence of residuals. The LOD and LOQ were evaluated by the visual perception method, with the LOQ being the lowest concentration possible to detect with precision (30%) and accuracy (40-120%).[27] Intermediate precision (expressed as relative standard deviation, RSD) was evaluated using fortified water samples at 3 concentration levels (0.8, 1.2 and 4.0 μg L^{-1}), which were prepared by another analyst, on different days. Accuracy was assessed by the relative recovery of spiked samples at the same concentration levels as in the intermediate precision assay.

Results and Discussion

Chromatographic method

The determination of GLY, AMPA and GLU was performed by LC-FLD after derivatization with FMOC-Cl. This chloroformate inserts a fluorenylmethyloxycarbonyl group in the molecules under study, which allows its detection by fluorescence. FMOC-Cl is not very selective, being able to react even with water, which means that the derivatization reaction must be carried out with a large excess of the derivatizer, which must be removed.

The derivatization reaction has been the object of many studies,[24,28] which has provided various methods, also involving various experimental conditions. Thus, many preliminary tests were carried out to define relevant parameters, such as the amount of FMOC-Cl, the reaction time and the method used to remove the excess of FMOC-Cl. Under optimized conditions, the derivatives GLY-FMOC, AMPA-FMOC and GLU-FMOC showed retention times of 15.54, 16.67 and 17.93 min, respectively, (Figure 2a).

Calibration curves were prepared in triplicate in ultrapure water, covering the range between 2.5 and 60 μg L^{-1} (Figure 2b). From the regression data, it was possible to evaluate the linearity, LOD and LOQ of the equipment, as well as the deviation of the linear and angular coefficients. According to these results, the method showed good linearity ($R^2 > 0.99$) for all analytes, with instrumental limits of quantification of about 5 mg L^{-1}.

Precision and accuracy were evaluated in triplicate at three concentration levels. The calculated recoveries varied between 85 and 111%, whereas, except for the result for the intermediate GLY concentration, all observed deviations were less than 6% (Table S1, SI section). Thus, both parameters are in accordance with the guidelines recommended by the National Metrology Institute.[26]

Validation of the ion-exchange SPE-LC-FLD method

Initially, the selectivity of the method was evaluated based on the matrix effect, estimated by comparing the slope of the analytical curves prepared in ultrapure water and in the aqueous matrices under study. As shown in the

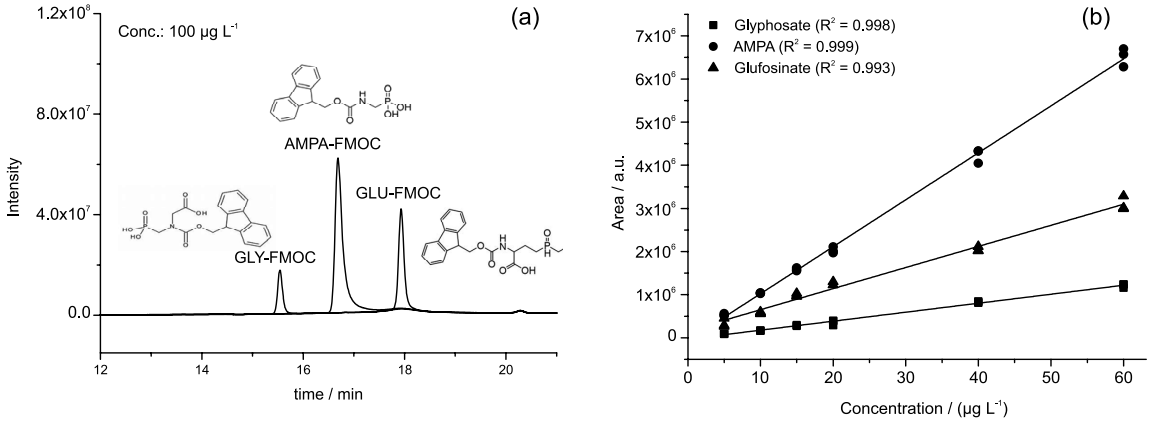

Figure 2. Chromatogram (a) and analytical curve (b) of the derivatives GLY-FMOC, AMPA-FMOC, and GLU-FMOC.

analytical curves in Figure 3, the matrix effect is relevant in samples from both sides of the reservoir. Note that for GLY, the effect is practically the same in the Brazilian (31.6%) and the Paraguayan matrix (32.8%). AMPA and GLU are influenced differently in each matrix. However, in the Brazilian matrix, the effect on AMPA (–46.3%) and GLU (–41.5%) is very close, unlike what occurs in the Paraguayan matrix, where the effect is more pronounced for AMPA (–16.6%) than for GLU (–3.6%).

The observed matrix effect is undoubtedly a function of the complexity of the samples, which is well illustrated in the chromatograms presented in Figure 3. Even when the samples are submitted to a previous extraction process, many species elute in similar retention times, contributing to the effects shown in the analytical curves.

Faced with the impossibility of elaborating an analytical curve for each sampled location, the matrix effect was minimized using analytical curves elaborated in a mixture of all samples collected from each side of the reservoir. In this way, two analytical curves were created, one for the quantification of Brazilian samples and another for Paraguayan samples. Under these conditions (Table S2, SI section), the analytical curves were linear, with satisfactory determination coefficients for the evaluated concentration range ($R^2 > 0.98$). In only one case (value highlighted in bold), the residuals were not considered homoscedastic. However, as it is an isolated point for which the Durbin-Watson test ensured the independence of the residues, it was decided to maintain this concentration level. In the residual graphs, no trend was identified, which guarantees its random distribution. Thus, it can be stated that linearity was met to determine all analytes in both analyzed matrices.

LOD and LOQ were calculated using the visual method, considering the lowest concentration that could be determined with acceptable precision and accuracy. The results show LOQ lower than 0.8 μg L^{-1} (Table 1), comparable with the values reported for similar analysis methods (Table 2).

The precision of the method was estimated in terms of intermediate precision, evaluating the relative standard deviation in triplicate determinations, carried out on different days of spiked samples in 3 concentration levels.

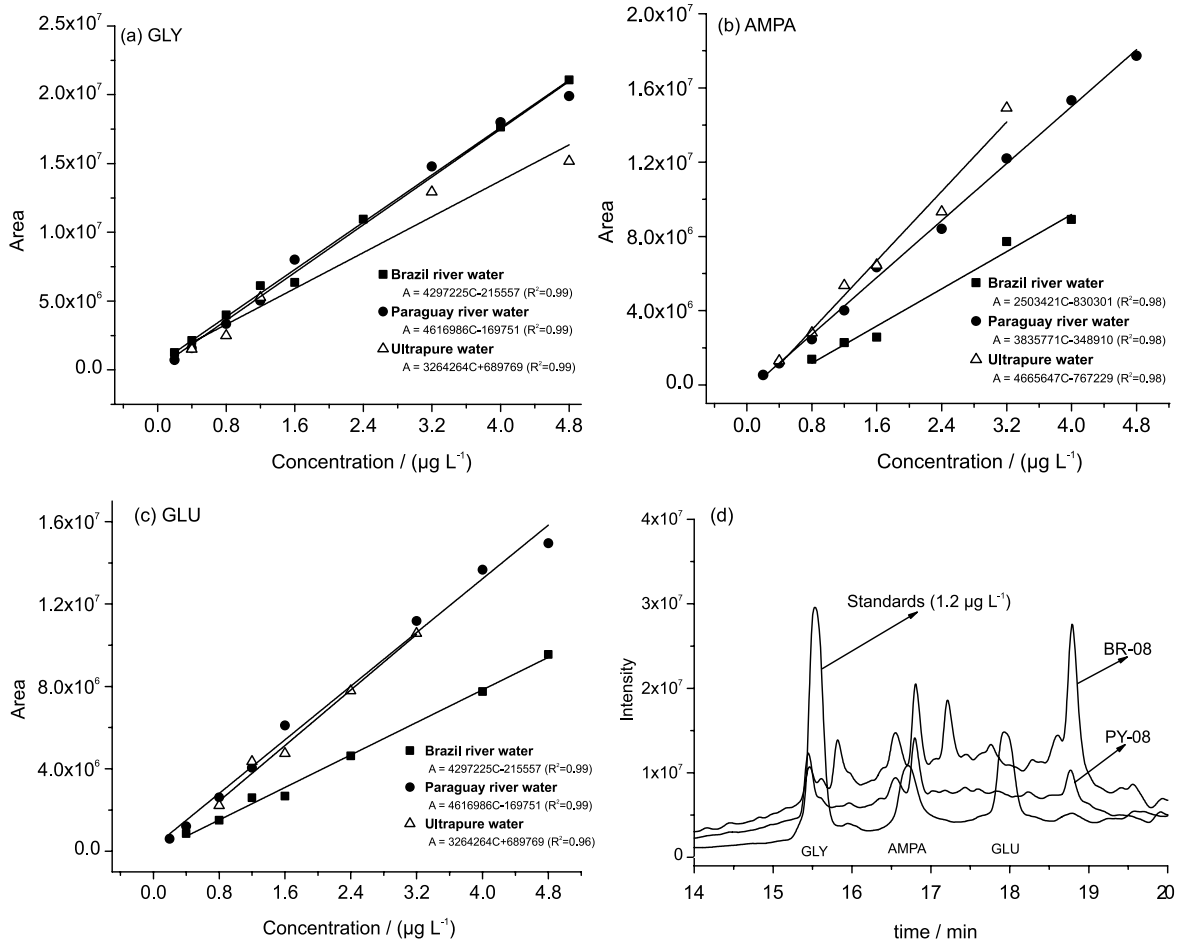

Figure 3. Analytical curves prepared in ultrapure water and in the aqueous matrices (a) GLY, (b) AMPA, (c) GLU, and (d) chromatograms of selected samples.

Table 1. LOD and LOQ obtained by the proposed method

Analyte	BR		PY	
	LOD / (μg L^{-1})	LOQ / (μg L^{-1})	LOD / (μg L^{-1})	LOQ / (μg L^{-1})
GLY	0.2	0.4	0.1	0.2
AMPA	0.4	0.8	0.1	0.2
GLU	0.2	0.4	0.1	0.2

GLY: glyphosate; AMPA: (aminomethyl)phosphonic acid; GLU: glufosinate; BR: Brazil; PR: Paraguay; LOD: limit of detection; LOQ: limit of quantification.

The results (Figure 4) reveal deviations of less than 20%, which is compatible with the acceptance criteria of the National Metrology Institute.[26]

The same samples from the previous study were used in a recovery test and the results are shown in Table 3. Recovery rates between 91 and 113% were observed, which is also in accordance with legal requirements.

Analysis of river water samples

GLY, AMPA and GLU were determined in samples collected bimonthly from January to September 2022. The analyses were carried out according to the previously described procedure, using analytical curves prepared in the mixture of the studied matrices.

The developed method did not allow the detection of GLY, AMPA and GLU in most of the analyzed samples. On the Brazilian side, GLY was only detected in the September/22 sample at points BR04 and BR16, while AMPA was detected in samples collected in January, July, and September, with its presence being particularly relevant at sampling point BR16 (January 0.85 μg L^{-1} and September 0.83 μg L^{-1}). On the Paraguayan side, only GLY was detected in July/22 (PY08) and September/22 (PY15), not being possible its quantification.

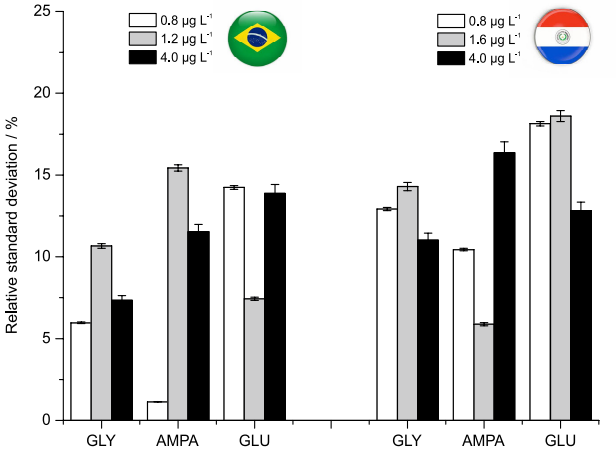

Figure 4. Relative standard deviation in the evaluation of the intermediate precision.

The presence of GLY and AMPA in samples collected in September coincides with the application of herbicides in corn crops, while the presence detected in July may be related to the wheat crop, which begins to be planted in April.[29]

As previously mentioned, soil components, particularly clay minerals, firmly retain GLY in the soil, significantly decreasing its mobility. Thus, their arrival in surface water courses is usually related to surface runoff, made possible by heavy rainfall. In the winter period (June-August), the monthly average of rainfall in the region is very low, increasing significantly from September onwards.[30] This

Table 2. Comparison of the proposed method and similar methods from recent literature for determination of glyphosate, glufosinate and AMPA

Analyte	Sample	Preconcentration	Derivatizer	Chromatographic method	LOQ / (μg L^{-1})	Reference
GLY AMPA GLU	surface and groundwater	lyophilization (×10)	post-column *o*-phtalaldehyde/ 2-mercaptoethanol	LC-FLD	0.2 0.5 0.3	18
GLY AMPA	superficial and groundwater	–	FMOC-Cl	LC-FLD	0.2 1.0	22
GLY AMPA GLU	superficial and groundwater	SPE	FMOC-Cl	LC-MS/MS	0.6 0.2 0.1	28
GLY AMPA	groundwater	–	–	LC-MS/MS	0.03	13
GLY AMPA GLU	surface water	anion exchange resin IRA-900	FMOC-Cl	LC-FLD	0.2 0.2 0.2	this work

GLY: glyphosate; AMPA: (aminomethyl)phosphonic acid; GLU: glufosinate; SPE: solid phase extraction; FMOC-Cl: 9-fluorenylmethyl chloroformate; LC FLD: liquid chromatography coupled to a fluorescence detector; LC-MS/MS: liquid chromatography tandem mass spectrometry; LOQ: limit of quantification.

Table 3. Recovery of GLY, AMPA and GLU by the proposed method in different concentration levels

	Recovery / %					
	BR			PY		
	0.8 μg L^{-1}	1.2 μg L^{-1}	4.0 μg L^{-1}	0.8 μg L^{-1}	1.6 μg L^{-1}	4.0 μg L^{-1}
GLY	104.0 ± 0.05	110.5 ± 0.14	100.2 ± 0.29	95.0 ± 0.10	110.7 ± 0.25	98.4 ± 0.43
AMPA	110.8 ± 0.01	103.7 ± 0.19	97.3 ± 0.45	91.7 ± 0.08	109.1 ± 0.10	102.2 ± 0.67
GLU	99.2 ± 0.11	112.3 ± 0.10	99.0 ± 0.55	92.8 ± 0.13	113.3 ± 0.34	103.3 ± 0.53

GLY: glyphosate; AMPA: (aminomethyl)phosphonic acid; GLU: glufosinate; BR: Brazil; PR: Paraguay.

antecedent can serve as an argument to explain the higher number of positive cases registered in September.

Due to the history of using glyphosate-based herbicides in the region, monitoring surface waters was expected to bring different results, particularly in regions with greater agricultural activity. Thus, the low number of samples in which herbicides were found may be a function of the high LOQ of the proposed procedure, as well as the recognized low mobility of these species in Brazilian soils and the facilitated dissipation of pollutants in large basins.[24] Furthermore, it is worth highlighting that in Paraguay there are few studies on the dynamics of these analytes.

Unfortunately, there are not many studies about the presence of herbicides in surface waters in the Paraná Hydrographic Basin 3 region. As far as it was possible to investigate, only two studies were published in 2016 and 2020,[25,31] showing similar results to surface water to those reported here. Ronco *et al*.[31] also evaluated the presence of glyphosate and AMPA in sediments and verified that they act as a sink for these compounds. This fact may have happened in the water bodies evaluated in this study.

Conclusions

A method was validated for determining GLY, AMPA and GLU in surface waters, using anion exchange resin extraction followed by determination by LC-FLD. The method shows sensitivity and selectivity compatible with the needs of the analysis, allowing limits of quantification much lower than the limits imposed by Brazilian legislation for the maximum glyphosate content in class I water (65 μg L^{-1}).

In general, GLY and AMPA were detected in a few samples, even in regions of high agricultural activity. This apparent inconsistency suggests the occurrence of processes that hinder the mobility of these pesticides in the soil, which also suggests that their transport to surface waters may be favored by surface runoff during heavy rainfall events.

Supplementary Information

Additional information can be found in the Supplementary Information, such as a figure of the environmental dynamics of glyphosate and tables with regression analysis and precision and accuracy parameters. Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors wish to thank Itaipu Binacional, Itaipu Technological Park Foundation (FPTI), UNILA and UFPR for financial and technical-logistical support (project 4500048483/2018).

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Submitted: November 8, 2023
Published online: April 4, 2024