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Pesticides in Ground and Surface Water from the Rio Preto Hydrographic Basin, an Important Agricultural Area in the Midwestern Region of Brazil

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Abstract: The use of pesticides in agriculture can leave residues in the treated crops. Pesticides are also potential contaminants of ground and surface water, as reported in many countries. The development of efficient analytical methods to quantify pesticides in water samples is a challenge due to the low levels present. The objective of this work was to develop and validate a method for pesticide analysis in water using sample lyophilization followed by UHPLC–MS/MS and to determine pesticide levels in samples from a Brazilian hydrographic basin. In total, 77 compounds were included, of which 28 were considered only qualitatively. The method was applied to analyze 142 water samples collected during the dry and rainy seasons of 2021–2022, of which 90 were surface and 52 were groundwater samples. In total, 19 compounds were detected in the samples (≥LOD), mainly atrazine (72.5%), atrazine-2-hydroxy (50%), fipronil (18.3%), and pirimiphos-methyl (15.5%). Most compounds (17) were detected during the rainy season regardless of the environmental compartment. Twenty-five samples had quantified levels of the compounds (≥LOQ), of which 80% were collected during the dry season, and 58.3% were groundwater samples (up to 1.045 μg L^{-1} of 2,4-D in an artesian well). The highest concentrations found in surface water were of atrazine-2-hydroxy (0.171 and 0.179 μg L^{-1}), levels that represent a potential risk to aquatic organisms (risk quotient of 1.1). This work provides an analytical method for determining pesticides in water that can be applied to other environmental pollutants. Although the levels found in the samples complied with Brazilian legislation, constant monitoring should be conducted in the region to guarantee safe levels of the pesticide in water.

Keywords: pesticides; surface water; groundwater; multiresidue method; Federal District

Academic Editor: Domenico Cicchella

Received: 21 March 2025
Revised: 11 April 2025
Accepted: 14 April 2025
Published: 15 April 2025

Citation: Pires, N.L.; Araújo, E.P.d.; Muniz, D.H.d.F.; Oliveira-Filho, E.C.; Caldas, E.D. Pesticides in Ground and Surface Water from the Rio Preto Hydrographic Basin, an Important Agricultural Area in the Midwestern Region of Brazil. *Water* **2025**, *17*, 1186. https://doi.org/10.3390/w17081186

1. Introduction

Estimates show a need to increase global food production to feed a population of approximately 9–10 billion by 2050 [1]. As an integral component of pest control practices, the use of pesticides has increased over the years to meet the demand for agricultural production [2]. According to Foley et al. [3], meeting the demand for food in the world and reducing the impact of agricultural activity on the environment is one of the biggest challenges of the current century.

Pesticides are potential contaminants of surface and groundwater and have been reported in many countries, including Brazil [4–6]. In the Federal District, located in the midwestern region of Brazil (Figure 1), pesticides were detected in Lake Paranoá [7,8], and in the Rio Samambaia hydrographic basin [9]. In previous work conducted by our research group, glyphosate, AMPA, and glufosinate were detected in the Rio Preto Hydrographic Basin (RPHB) [10], the main basin of the region surrounded by intense agricultural activity.

The development of efficient analytical methods to quantify pesticide levels in water samples is a challenge due to the low concentration of these compounds found in this compartment and the wide variety of substances used in agriculture [11,12]. The methods involve analyte extraction and sample cleanup, including liquid–liquid extraction, solid-phase extraction (SPE), and solid-phase microextraction [13]. These methods have advantages and are widely used worldwide with good performance, linearity, and adequate limits of detection/quantification; however, they require the use of consumables and organic solvents, with several analytical steps [14]. Sample pretreatment using lyophilization is a prospective technique for monitoring emerging organic contaminants present at low concentrations in water [15], including pesticides [6,10,15]. This is an autonomous operation technique, simple to perform, and allows the use of low-cost plastic containers, thus avoiding analyte losses caused by adsorption in glassware, and a very low volume of organic solvent [16].

This work aimed at developing and validating a multiresidue method for determining pesticides in water using lyophilization to pre-concentrate samples and ultrahigh-performance liquid chromatography–mass spectrometry (UHPLC–MS/MS). The method was applied to the analysis of surface and groundwater samples from the RPHB, which are the same samples previously analyzed for glyphosate, AMPA and glufosinate [10]. Furthermore, the risks to the aqueous biota from the presence of pesticides were also evaluated. To the best of our knowledge, this is the first study to report a method that uses lyophilization for sample preparation/concentration to analyze a large number of pesticides in water.

2. Materials and Methods

2.1. Study Area and Sample Collection

The RPHB is the main agricultural area in the Federal District, which uses center-pivot irrigation and is divided into seven hydrographic units (HUs), as shown in Figure 1. A total of 142 samples were collected in 2021 and 2022 in all hydrographic units of the RPHB (Figure 1). Groundwater samples were collected using a bailer-type polychloroethene sampler and surface water samples were collected approximately 15 to 30 cm deep, manually or using a van Dorn-type collector [10]. A total of 70 samples were collected during the dry season (August and September 2021) and 72 in the rainy season (January and February 2022), while 52 were groundwater samples and 90 surface water samples [10]. Groundwater samples were collected only in the Rio Jardim Sub-Basin, which is part of HU-35 (Figure 1).

The prevailing climate in the RPHB is tropical, with a well-defined seasonality pattern in the distribution of rainfall: dry winter, between April and October; and rainy summer in the remaining months of the year, with 80% precipitation during this period [17].

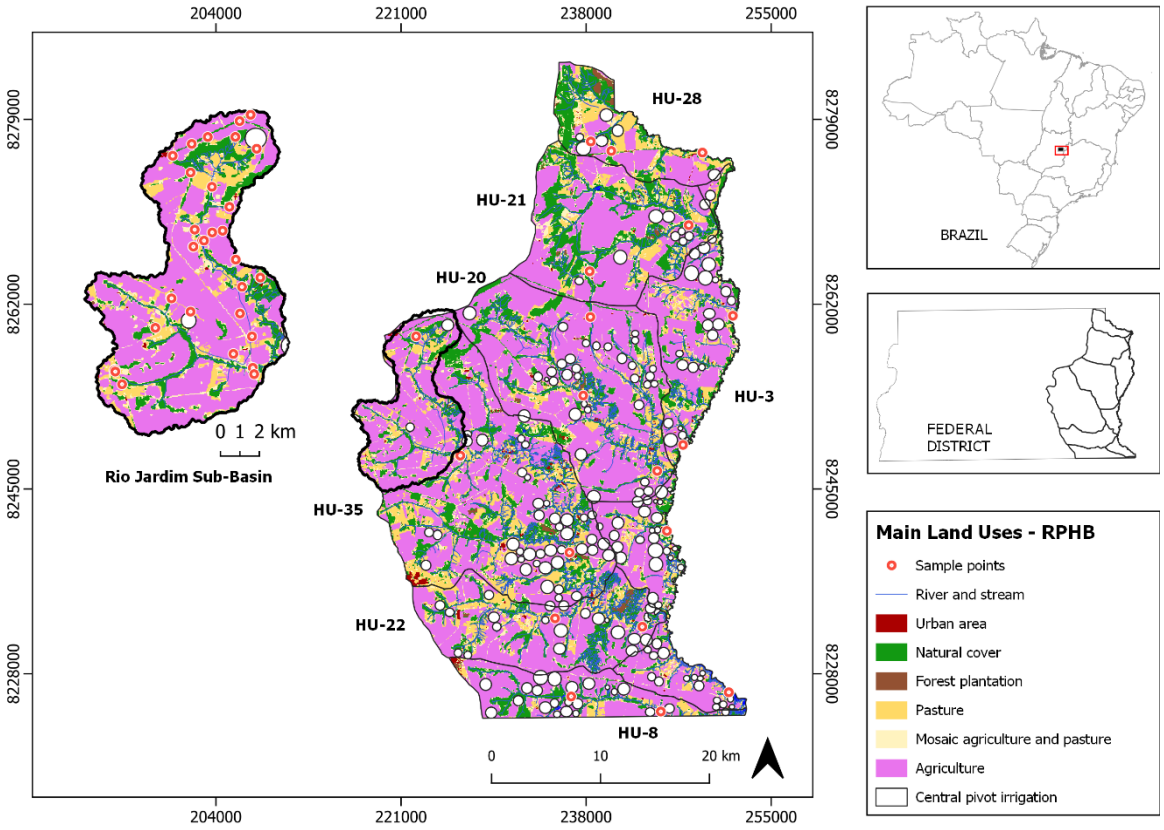

Figure 1. Rio Preto Hydrographic Basin in the Federal District of Brazil, indicating the hydrographic units (HUs) and sampling points. Groundwater samples were collected only in HU-35 (Rio Jardim Sub-Basin). Adapted from Pires et al. [10] and prepared using MapBiomas [18] and SIEG [19].

2.2. Sample Preparation

Sample preparation for pesticide analysis was previously reported for the analysis of glyphosate, AMPA, and glufosinate in water [10]. In summary, the samples were filtered with 25 mm, 0.45 µm PTFE microfibers (Millipore®, Merck KGaA, Darmstadt, Germany), and 10 mL aliquots (n = 3) were transferred to 15 mL Falcon tubes and placed in the freezer at −21 °C to be frozen and subsequently lyophilized (−70 °C, 50–80 µmHg; Liobras, K105, São Paulo, Brazil). The lyophilization bottles where the tubes were inserted were covered with aluminum foil and the lyophilized samples were kept in the freezer until analyzed, when they were resuspended in 500 µL of MeOH–water (1:1), filtered with 13 mm 0.45 µm PTFE microfibers (Millipore®), and injected into the UHPLC–MS/MS (6500+ QTRAP, AB Sciex, Framingham, MA, USA). The analysis occurred within 2 to 4 months after lyophilization, which occurred up to seven days after sample collection.

2.3. Pesticide Analysis

The selection of pesticides used in this study considered the pesticides listed in the resolutions of the Brazilian National Environmental Council for groundwater (CONAMA 396/2008) [20]) and surface water (CONAMA 357/2005) [21] and Resolution 888/2021 of the Brazilian Ministry of Health, which defines water potability standards for human consumption [22].

The 77 compounds included are listed in Table S1 (Supplementary Materials) with their respective chemical class, whether there is currently authorization for use in Brazil, and their physicochemical properties. Atrazine-2-hydroxy and zoxamide analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany), acetamiprid, atrazine, carbofuran-

3-hydoxy, fenpyroximate, and pencycuron from Sigma-Aldrich (St. Louis, MO, USA), and the other compounds were obtained from AccuStandard (New Haven, CT, USA), all with purity of at least 95%.

Stock solutions of the evaluated analytes were prepared using methanol (MeOH), acetonitrile (ACN), and ethyl acetate (AcEt), obtained from Merck (Darmstadt, Germany), or toluene (Mallinckrodt Baker, Phillipsburg, NJ, USA), HPLC grade, at a concentration of 1 mg mL^{-1}, with the exception of atrazine-2-hydroxy, which was prepared at a concentration of 0.5 mg mL^{-1} in a solution of HCl 0.1 mol L^{-1} and ACN (20:80), to allow complete solubilization of the solid standard. All solutions were stored in amber vials at ≤ -15 °C. From the stock solution of each compound, mixtures were prepared in MeOH–water (1:1) containing all the compounds. Depending on the signal strength in the UHPLC–MS/MS, the analytical curves were grouped in five concentration groups, according to Table S2.

2.4. UHPLC–MS/MS

Analyses were conducted using a Shimadzu UHPLC system (LC-20AD pumps, a SIL-20AD autosampler and CTO-20AC column oven) (Kyoto, Japan) coupled with a QTRAP 6500+ triple quadrupole mass spectrometer (AB Sciex, Framingham, MA, USA). Analyst® (version 1.6) software was used for instrument control and data acquisition. A LUNA Omega Polar C18 UHPLC column (1.6 μm $\geq$ 100 A, 100 × 2.1 mm) was used for chromatographic separation with a UHPLC C18 pre-column (fully porous polar, 2.1 mm), both from Phenomenex (Torrance, CA, USA).

The determination in the mass spectrometer was carried out with electrospray ionization (ESI) operating simultaneously in positive (ESI+) for all compounds except for 2,4-D, fipronil, and MCPA, for which the negative (ESI-) mode was used. The MS-MS was operated in multiple reaction monitoring (MRM) mode, in which two mass transitions (precursor–product) were monitored for each target compound, one for quantification and the other for confirmation. The optimized ion source conditions were 40 psi for curtain gas, medium collision gas (CAD), source temperature at 450 °C, nebulizer gas (GS1) at 65 psi, and auxiliary gas (GS2) at 50 psi. The optimized MS/MS conditions for each of the 77 compounds included in the method are shown in Table S2. The optimized conditions for chromatographic performance were: column oven temperature at 50 °C, 1 μL sample injection, and 0.3 mL/min flow rate. The mobile phases consisted of ultrapure water (A) and MeOH (B), both containing 0.1% formic acid and 5 mmol L^{-1} ammonium formate. Elution/gradient was defined as: 0.5 min at 10% B, 10% to 100% B in 10 min, maintaining at 100% B up to 12 min, and returning to 10% B in 3 min, with 15 min total run time.

2.5. Method Validation

Validation was carried out using a water control sample collected from a spring located in the study region, which was confirmed to be free of any of the analytes investigated in the study. Selectivity was assessed by checking for the presence of interferents at the same retention time, monitoring transition ions and their ratios (Table S2). Linearity was determined on an analytical curve (n = 6) prepared in MeOH–water (1:1) at five concentration levels in ranges that varied according to the analyte group (P1: 0.05 to 5 μg L^{-1}; P2: 0.20 to 10 μg L^{-1}; P3: 1.0 to 50 μg L^{-1}; P4: 10 to 100 μg L^{-1}; and P5: 50 to 500 μg L^{-1}; Table S2). This was necessary as the equipment has different sensitivities for the analytes. The linear regression was estimated using the least squares method, Cochran's Q test checked for homoscedasticity, and ANOVA determined the correlation coefficient (r) and regression significance [23]. For the heteroscedastic calibration curves, the weights ln x, ln y, $1/x$, $1/x^2$, and $1/y$ e $1/y^2$ were tested, in order to determine the best regression fit.

The matrix effect was investigated by comparing the equipment response of a analytical curve (n = 6) prepared with a lyophilized control sample and dissolved in 500 µL of MeOH:water (1:1) with a curve prepared in a control sample (no lyophilization; n = 6). The matrix effect (%ME) was calculated for each level of the calibration curve by dividing the average area of each level of the curve made in the matrix (control sample) by the average area of the curve made in MeOH–water (1:1) (without lyophilization) [24].

The repeatability and recovery of the analytical lyophilization procedure were evaluated by analyzing samples fortified at different levels, varying according to the group of each analyte, as shown in Table 1 (N1 to N5, n = 3 at each level), and considering lyophilization with a dilution factor of 20. Intermediate precision for each pesticide at each level was calculated using the validation data collected on a different day and expressed as %RSD (relative standard deviation, n = 6). The limit of quantification (LOQ) was defined as the lowest concentration level (after lyophilization) that was validated, with acceptable recovery (from 30% to 120%), repeatability and precision (≤20%) [24]. The limit of detection (LOD) was a signal/noise ratio of 3 presented in the instrument [23].

Table 1. Group (G) of compounds and their respective analytical curves and fortification levels.

G	Analytes	Analytical Curve, µg L^{-1}	Fortification Level After Lyophilization, µg L^{-1}
1	Aldicarb sulfone, ametrine, atrazine, buprofezin, carbofuran, carbosulfan, dicrotophos, difenoconazole, fipronil, malaoxon, monocrotophos, pirimiphos-ethyl, pirimiphos-methyl, trifloxystrobin	P1: 0.05 P2: 0.5 P3: 2.5 P4: 3.5 P5: 5.0	N1: 0.0125 N2: 0.025 N3: 0.125 N4: 0.175 N5: 0.25
2	Azoxystrobin, chlorfenvinphos, diazinon, dimethoate, metalaxyl-M, pirimicarb, pyraclostrobin, pyrazophos, pyridafenthion, thiabendazole, triazophos, zoxamide	P1: 0.20 P2: 2.0 P3: 5.0 P4: 7.0 P5: 10	N1: 0.05 N2: 0.10 N3: 0.25 N4: 0.35 N5: 0.50
3	Acetamiprid, atrazine–desthyl, atrazine-desisopropyl, atrazine-2-hydroxy, boscalid, carbaryl, carbofuran-3-hydroxy, chlorpyrifos-ethyl, cyromazine, EPN, epoxiconazole, ethion, fenpropathrin, fenpyroximate, fluquinconazole, flutriafol, heptenophos, imazalil, imidacloprid, linuron, malation, MCPA, methamidophos, methomyl, myclobutanil, omethoate, paraoxon-methyl, pencycuron, phentoate, profenophos, propanil, quinalphos, tebuconazole, thiamethoxam, thiobencarb, thiophanate-methyl, trichlorfon	P1: 1.0 P2: 10 P3: 20 P4: 40 P5: 50	N1: 0.05 N2: 0.50 N3: 1.0 N4: 2.0 N5: 2.5
4	Dichlorvos, fenitrothion, fenthion, cresoxim-methyl, methiocarb, metribuzim, oxyflurofem, prochloraz, prothiophos, 2,4-D	P1: 14 P2: 20 P3: 40 P4: 80 P5: 100	N1: 0.70 N2: 1.0 N3: 2.0 N4: 4.0 N5: 5.0
5	Acephate, aldicarb, aldicarb sulfoxide, chlorpyrifos-methyl	P1: 50 P2: 100 P3: 200 P4: 400 P5: 500	N1: 3.0 N2: 5.0 N3: 10 N4: 20 N5: 25

2.6. Ecotoxicological Risk Assessment

The potential risk of each quantified pesticide for aquatic biota was estimated using the risk quotient (RQ) = MEC/PNEC, where MEC (measured environmental concentration) represents the concentration quantified (≥LOQ) in the surface water sample for each pesticide. The PNEC (predicted non-effect concentration) is determined by dividing the most sensitive chronic toxicological parameter by the safety factor of 10 for representatives of three trophic levels in the aquatic ecosystem, 100 for the most sensitive chronic data found for only two trophic levels, and 1000 for the most sensitive acute toxicity data when no chronic data were available [25]. The obtained RQs were compared with the level of concern (LOC) [26], which is 0.1 for acute toxicity and 1 for chronic toxicity. RQs greater than the LOCs indicate a potential risk of causing adverse effects at different levels of aquatic biota.

3. Results

3.1. Method Validation

A total ion chromatogram of the 77 analytes at the five levels of the analytical curves is shown in Figure S1. Table S3 presents the results of the Cochran's Q test, used to test the homogeneity of variance (homoscedasticity) of the analytical curve for each analyte. Weighted linear regression ($1/x$, $1/x^2$ or $1/y^2$) was applied to analytical curves that showed heteroscedastic behavior. The coefficients of determination (R^2) were greater than 0.99 for all analytes.

The matrix effect for all analytes showed acceptable levels for all compounds at all levels (<20%), ranging from −14.4% (indicating ion suppression) to 14.9% (ion enhancement). As no significant matrix effect was observed, the analytes were quantified against an analytical curve prepared in MeOH–water (1:1).

Figure 2 summarizes the validation data for all analytes and Table S4 shows the results for each analyte. In sum, 17 of the 77 compounds included in the method showed recovery values between 70% and 100% and repeatability and intermediate precision ≤20%: acephate; acetamiprid; atrazine-desethyl; atrazine-deisopropyl; atrazine-2-hydroxy; azoxystrobin; carbofuran-3-hydroxy; cyromazine; dimethoate; flutriafol; imidacloprid; metalaxyl-M; methomyl; thiabendazole; thiamethoxan; 2,4-D e MCPA. Recovery between 30% and 70% with repeatability and intermediate precision within the acceptable range (≤20%) were found for 32 compounds: aldicarb-sulfone; aldicarb-sulfoxide; ametrine; atrazine; boscalid; carbaryl; carbosulfan; chlorfenvinphos; dicrotophos; diphenonazole; epoxiconazole; fenpyroximate; imazalil; cresoxim-methyl; linuron; methiocarb; metribuzin; monocrotophos; myclobutanil; omethoate; pencycuron; pirimicarb; prochloraz; propanil; pyraclostrobin; pyrazophos; pyridafenthion; tebuconazole; trifloxystrobin; triazophos; zoxamide and fipronil. The 49 compounds were validated and determined quantitatively, with an established LOQ [24].

For 28 compounds, the recovery was below 30% and outside the acceptable range to be considered validated: aldicarb; buprofezin; carbosulfan; chlorpyrifos-ethyl; chlorpyrifos-methyl; diazinone; dichlorvos; EPN; etion; fenitrothion; fenpropathrin; fenthion; fluquinconazole; heptenophos; malaoxon; malathion; methamidophos; oxyflurofem; paraoxone-methyl; phentoate; pirimiphos-ethyl; pirimiphos-methyl; profenophos; proteophos; quinalphos; thiobencarb; thiophanate-methyl; trichlorfon. The results for these 28 compounds were only qualitative, and no LOQ was established.

Table 2 shows the LOD for all compounds and the LOQ for the 49 compounds considered validated in the method. LOD ranged from 0.0005 to 0.75 μg L^{-1} and LOQ from 0.0125 to 3 μg L^{-1}, with the highest levels for acephate and aldicarb-sulfoxide, the only two compounds from group 5 (Table 1) that were validated.

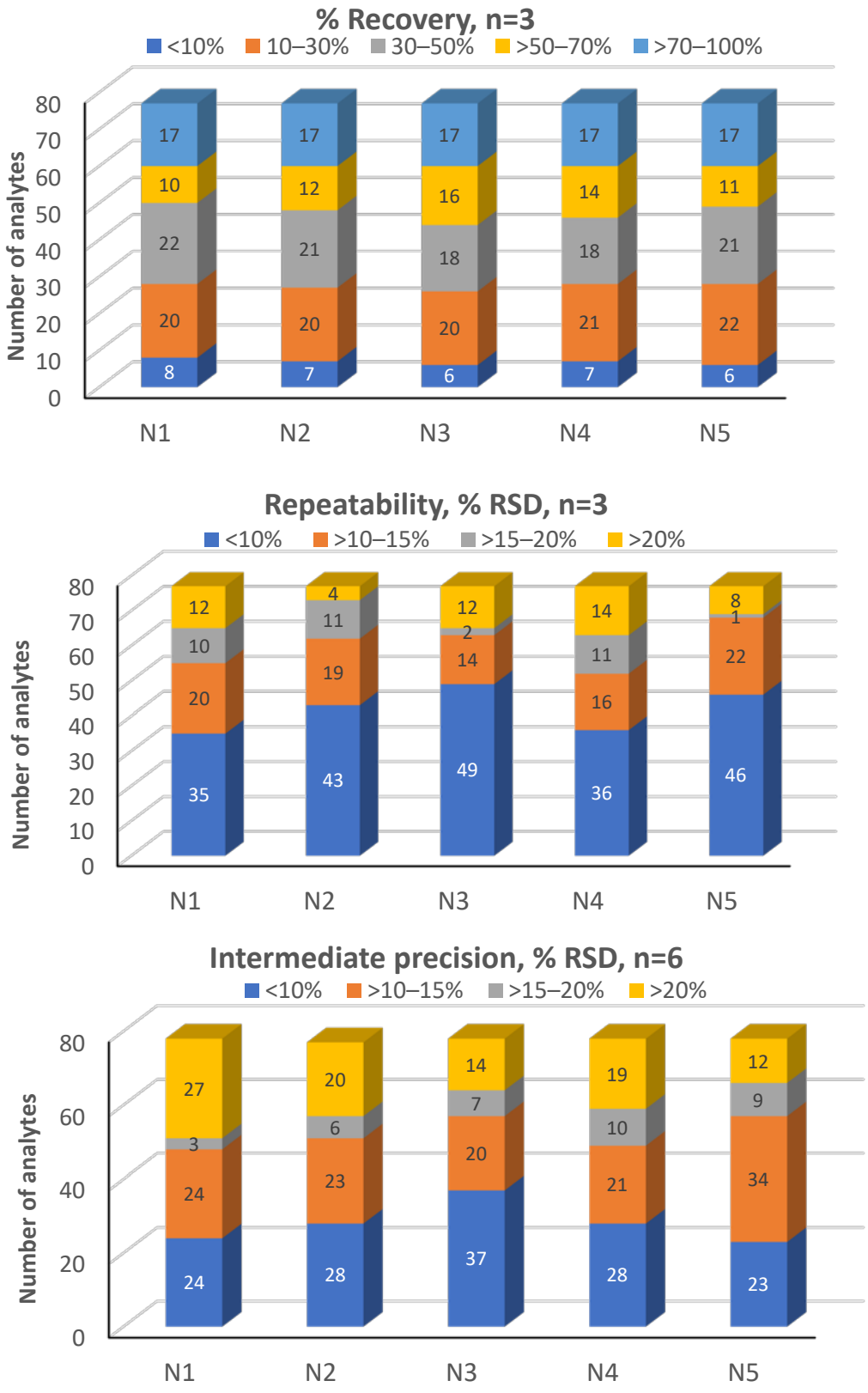

Figure 2. Summary of the validation data for the 77 compounds at 5 fortification levels (N1 to N5, Table 1). RSD = relative standard deviation. Validation data for each compound are shown in Table S4.

Table 2. Limit of detection (LOD) and of quantification (LOQ) for the 77 analytes. LOQ was only set for the 49 compounds validated in the study.

Compound	LOD, μg L^{-1}	LOQ, μg L^{-1}	Compound	LOD, μg L^{-1}	LOQ, μg L^{-1}
2,4-D	0.15	0.7	Imidacloprid	0.015	0.05
Acephate	0.75	3	Kresoxim-methyl	0.15	0.7
Acetamiprid	0.015	0.05	Linuron	0.015	0.05
Aldicarb	0.75	(a)	MCPA	0.015	0.05
Aldicarb sulfone	0.0005	0.0125	Malaoxon	0.0005	(a)
Aldicarb sulfoxide	0.75	3	Malathion	0.015	(a)
Ametryn	0.0005	0.0125	Metalaxy-M	0.003	0.05
Atrazine-desethyl	0.015	0.05	Methamidophos	0.015	(a)
Atrazine	0.0005	0.0125	Methiocarb	0.15	0.7
Atrazine-deisopropyl	0.017	0.05	Methomyl	0.015	0.05
Atrazine-2-hydroxy	0.015	0.05	Metribuzim	0.15	0.7
Azoxystrobin	0.003	0.05	Monocrotophos	0.0005	0.0125
Boscalid	0.015	0.05	Myclobutanil	0.015	0.05
Buprofezin	0.0005	(a)	Omethoate	0.015	0.05
Carbaryl	0.015	0.05	Oxyflurofem	0.15	(a)
Carbofuran	0.0005	0.0125	Paraoxon-methyl	0.015	(a)
Carbofuran-3-hydroxy	0.015	0.05	Pencycuron	0.015	0.05
Carbosulfan	0.0005	(a)	Phentoate	0.015	(a)
Chlorfenvinphos	0.003	0.05	Pirimicarb	0.003	0.05
Chlorpyrifos-ethyl	0.015	(a)	Pirimiphos-ethyl	0.0005	(a)
Chlorpyrifos-methyl	0.75	(a)	Pirimifos-methyl	0.0005	(a)
Cyromazine	0.015	0.05	Prochloraz	0.15	0.7
Diazinon	0.003	(a)	Profenophos	0.015	(a)
Dichorvos	0.15	(a)	Propanil	0.015	0.05
Dicrotophos	0.0005	0.0125	Prothiophos	0.15	(a)
Difenoconazole	0.0005	0.0125	Pyraclostrobin	0.003	0.05
Dimethoate	0.003	0.05	Pyrazofos	0.003	0.05
EPN	0.015	(a)	Pyridafenthion	0.003	0.05
Epoxiconazole	0.015	0.05	Quinalphos	0.015	(a)
Ethion	0.015	(a)	Tebuconazole	0.015	0.05
Fenitrothion	0.15	(a)	Thiabendazole	0.003	0.05
Fenpropathrin	0.015	(a)	Thiamethoxam	0.015	0.05
Fenpyroximate	0.015	0.05	Thiobencarb	0.015	(a)
Fenthion	0.15	(a)	Thiophanate-methyl	0.015	(a)
Fluquinconazole	0.015	(a)	Trichlorfon	0.015	(a)
Fipronil	0.0005	0.0125	Trifloxystrobin	0.001	0.0125
Flutriafol	0.015	0.05	Triazophos	0.003	0.05
Heptenophos	0.015	(a)	Zoxamide	0.003	0.05
Imazalil	0.015	0.05			

Note: (a) LOQ was not set as the compound was not validated and results are only qualitative.

3.2. Analysis of Water Samples

Considering all campaigns, three (HU-28) to sixteen (HU-35) (Figure 1) compounds were detected (≥LOD) in the hydrographic units. Except for the samples collected at the PN (artesian well) sampling point (HU-35), all the others had at least one positive sample per campaign. Table S5 shows the results of all samples/sampling points identified as positive (≥LOD). Out of the 142 samples analyzed, 90% contained at least one compound. About 87% of surface water samples and all groundwater samples were positive (≥LOD) for at least one pesticide. The percentage of positive samples collected during the dry and rainy seasons was similar (91.4% and 91.7%, respectively).

A total of 19 compounds were detected, mainly atrazine (71.8% of all samples), its degradation product atrazine-2-hydroxy (50%), fipronil (18.3%), pirimiphos-methyl (15.8%), atrazine-desethyl (9.2%) and chlorpyrifos methyl (4.9%). Figure 3 shows the distribution of these compounds in surface and groundwater samples during the dry and rainy seasons.

Atrazine-2-hydroxy was detected in all groundwater samples analyzed, while about 80% of surface samples contained atrazine, with no apparent impact of the season. On the other hand, fipronil, atrazine-desethyl and chlorpyrifos-methyl were mostly present in samples collected in the rainy season. Figure 4 shows the extracted ion chromatograms of two groundwater samples collected during the dry season containing multiple pesticides (atrazine, atrazine-2-hydroxy, atrazine-desethyl, acetamiprid, and 2,4-D).

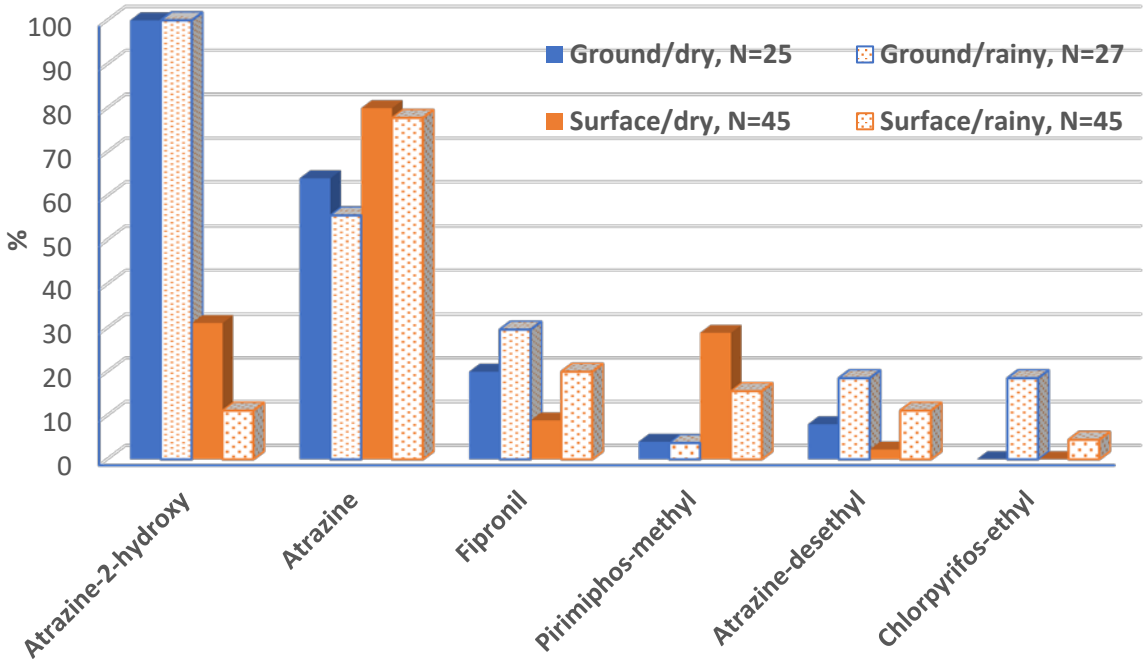

Figure 3. Pesticides most detected (≥LOD) in surface and groundwater samples during the dry and rainy seasons related to the number of samples analyzed (n).

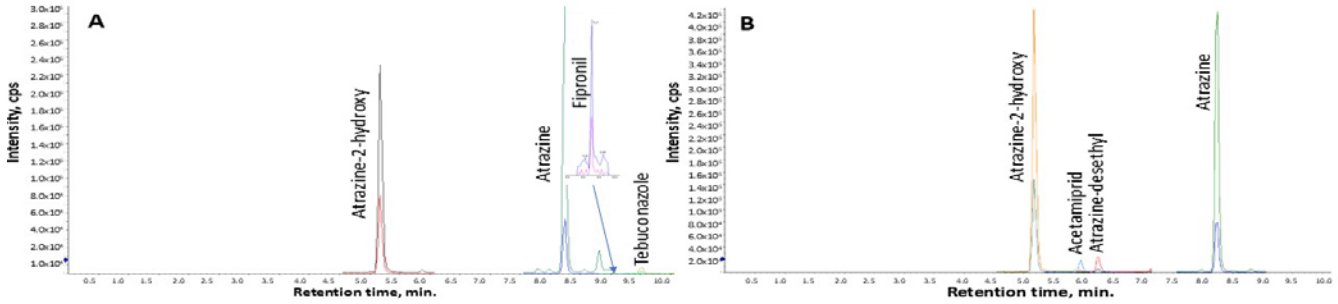

Figure 4. Extracted ion chromatograms obtained by UHPLC–MS/MS, of groundwater samples collected during the dry season: (**A**) P18GW: atrazine-2-hydroxy (0.168 µg L^{-1}), atrazine (0.159 µg L^{-1}), fipronil (<LOQ), tebuconazole (<LOQ); (**B**) P17GW: atrazine-2-hydroxy (0.291 µg L^{-1}), acetamiprid (only qualitative), atrazine-desethyl (<LOQ) and atrazine (0.305 µg L^{-1}); The two transitions are shown for each compound (Table S2).

Among the compounds validated in the method, only atrazine, atrazine-2-hydroxy, and 2,4-D had levels above the LOQ (25 samples). The results are shown in Table 3, together with the risk quotient (RQ) estimated for the aquatic organisms in the surface water samples. Atrazine was quantified in 14 samples, and was the only compound quantified in samples collected during the rainy season (5 groundwater samples). In the three groundwater samples with the highest levels of atrazine (dry season; 0.159 to 0.305 µg L^{-1}), its main metabolite atrazine-2-hydroxy was also found (0.102 to 0.291 µg L^{-1}). The compounds were also quantified in surface samples during the dry period, but only two samples of

atrazine-2 hydroxy indicated a potential risk to algae (RQ > 1.0; Table 3). 2,4-D was only detected in three groundwater samples collected during the dry season, and it had the highest quantified levels in the study (0.913 and 1.045 μg L^{-1}, in an artesian well, PT). Figure 4 shows the ion chromatograms of two dry season groundwater samples, containing atrazine and metabolites and/or 2,4-D.

Table 3. Quantitative results (≥LOQ) of surface and groundwater samples collected in the dry and rainy seasons, and the risk assessment for aquatic organisms in surface water.

Campaign, Sample (Sampling Point)	Concentration [a], μg L^{-1}	Risk Assessment End Point (PNEC)/SF	RQ
Atrazine-2-hydroxy			
A, surface, dry (P1)	0.171	Algae EC_{50} 164.2 [b]	1.04
A, surface, dry (P2)	0.179	(0.164)/1000	1.09
E, ground, dry (P11GW)	0.187		
E, ground, dry (P17GW)	0.291		
E, ground, dry (P18GW)	0.168		NA
E, ground, dry (P20)	0.109		
E, ground, dry (P46)	0.102		
E, ground, dry (P57)	0.102		
F, ground, rainy (P55)	0.153		
Atrazine			
A, surface, dry (P13)	0.039	Fish NOEAC 5 [b]	0.08
B, surface, dry (P13)	0.022	(0.5)/10	0.04
E, surface, dry (PS5)	0.016	Fish NOEAC 5 [b]	0.03
E, surface, dry (PS6)	0.017	(0.5)/10	0.03
E, ground, dry (P17GW)	0.305		
E, ground, dry (P18GW)	0.159		
E, ground, dry (P25)	0.025		NA
E, ground, dry (P46)	0.166		
E, ground, dry (P55)	0.075		
E, ground, dry (PT)	0.017		
F, ground, rainy (P10GW)	0.014		
F, ground, rainy (P25)	0.020		
F, ground, rainy (P27)	0.026		
F, ground, rainy (PT)	0.015		
2,4-D			
E, ground, dry (P54)	0.913		NA
E, ground, dry (PT)	1.045		

Note: NA = not applicable; RQ: risk quotient. RQ > 0.1 for acute risk and RQ > 1 for chronic risk present a potential risk of adverse effects. SF: safety factor. PNEC: predicted non-effect concentration. NOAEC: no observed adverse effect concentration. EC_{50}: 50% effect concentration. [a] No quantified residues were found in surface water samples from rainy season campaigns C, D and F; [b] mean of three independent samples; [a] NORMAN [27]; [b] USEPA [28].

4. Discussion

This study used lyophilization for sample preparation/concentration before UHPLC–MS/MS analysis, a technique that involves freezing the sample, reducing the pressure, and increasing the temperature to allow the frozen water in the sample to sublimate [29]. However, low analyte recovery from the water matrix was found for 28 of the 77 compounds investigated. Pesticides have different physicochemical characteristics, including polarity (log Kow) and vapor pressure, which determine how the compound behaves in the environment and in the analytical method, which may not be efficient for all compounds. One hypothesis for the low recoveries for these compounds was related to their high vapor

pressure and lower polarity. The range of vapor pressures (at 20 °C) of the compounds was quite wide, varying from 10^{-7} mPa for azoxystrobin to 65 mPa for heptenophos (Table S1), which showed recovery of less than 10% at all levels tested (Table S4). Diazinon has the second-highest vapor pressure (11.97 mPa), and also showed low recovery (13–28%). The log Kow range was also wide, ranging between −0.9 (omethoate, 51% recovery) and 7.4 (carbosulfan, 4% recovery). Inverse and significant Spearman correlations were observed between the vapor pressure and log kow with the mean recovery at all fortification levels (r = −0.5748 and −0.5094, respectively; $p = 0.001$). When the two highest vapor pressure values were removed from the data, the correlation remained significant (r = −0.5502, $p < 0.001$). These results indicate that compounds with higher vapor pressures and log Kow (less polar compounds) are more susceptible to loss during sublimation, not performing well in the lyophilization method.

Although lyophilization can lead to the loss of some analytes, the method has a low cost and is more environmentally friendly, as a very small amount of organic solvent is used during sample preparation [14]. Most methods use SPE cartridges for sample concentration, which is time-consuming, has a much higher cost, and requires a substantial amount of organic solvent [14,30].

Table 4 shows some studies that used lyophilization to prepare water samples for pesticide analysis. Sinha et al. [31] reported recoveries above 90% for eight pesticides in water, including ethion and quinalphos, for which recoveries in the present study were ≤30%, and were not considered validated. The lowest LOQ was 0.016 μg L^{-1}, within the same range as the lowest LOQ in the present study (0.0125 μg L^{-1}). Most studies also used LC–MS/MS for detection, which has the advantage of aggregating analyte identification, unlike fluorescent detectors (FL), which also requires derivatization to enhance sensitivity [32]. Most studies only analyzed glyphosate, AMPA and/or glufosinate, with LOQs ranging from 0.0025 to 0.3 μg L^{-1}.

Table 4. Application of lyophilization as concentration technique to determine pesticides and other chemicals in water samples.

Reference	Analyte (LOQ, μg L^{-1})	Sample Preparation [a]; Detection	Recovery, %
Present study	77 pesticides, validated for 49 (0.0125 to 3)	10 mL sample, resuspended in 500 μL MeOH–water (1:1), UPHLC–MS/MS	30 to 100
[31]	8 pesticides (0.016–0.171)	5 mL sample, resuspended with 1 mL ACN; HPLC–MS/MS	96–103
[16]	Glyphosate and AMPA (LOD: 0.058 and 0.108)	40 mL sample, resuspended with EDTA:FMOC-Cl; LC-FLD + MS/MS	63–69
[6]	Glyphosate (0.2) and glufosinate (0.07)	5 mL sample, resuspended with 500 μL water; HPLC-FL	72–94
[32]	Glyphosate and AMPA (0.3)	10 mL of sample, resuspended in 2 mL water/240 μL borate buffer/800 μL ACN +120 μL FMOC-Cl; UHPLC-FL	70–99
[10]	Glyphosate, AMPA and glufosinate (0.0025)	10 mL sample, resuspended in 500 μL 50 mM ammonium formate (pH 2.9); LC–MS/MS	79–111

Note: [a] resuspended after lyophilization. ACN = acetonitrile; AMPA = amino methyl phosphonic acid; EDTA = ethylenediaminetetraacetic acid; FMOC-Cl = 9-fluorenylmethyl chloroformate.

The agricultural area investigated in this study is irrigated with central pivots (Figure 1), which allows for up to three harvests per year, covering the dry and rainy seasons [33]. Samples were also collected from four water springs, all of which were surrounded by natural vegetation, with at least one analyte detected in three of them. It is possible that the contamination of these water sources comes from pesticides drifting from nearby plantations.

The samples analyzed in this study were the same as those analyzed for glyphosate, AMPA, and glufosinate in the study by Pires et al. [10], who found all 52 groundwater samples analyzed contained quantified levels of glyphosate and AMPA, while approximately 30% of the surface water samples contained these pesticides. In the present study, all the groundwater samples contained at least 1 of the 77 pesticides investigated (≥LOD), and 87% of surface samples were positive. The lower percentage of positive samples in surface water in both studies is mainly due to photodegradation of these compounds in surface water, a phenomenon that does not occur in groundwater [34].

Similarly to a previous study [10], the levels of pesticides found during the dry season were higher compared to those collected during the rainy season, consistent with findings in China [35]. While the rainy season likely increases the surface runoff of pesticides from the field into the water, concentrations decrease due to the dilution of watercourses resulting from increased precipitation volumes [36]. On the other hand, the low water volume during the dry season contributes to a higher concentration of pesticides.

With the exception of methamidophos, all detected pesticides are approved for use in soybean, maize, and/or beans [37], the main crops grown in the region [33]. Methamidophos is a degradation product of acephate, and its presence may be a consequence of acephate, which is registered for the three most relevant crops [37]. Atrazine is a broad-spectrum herbicide used worldwide, registered in Brazil for pre- and post-emergence application in soybean and maize [33]. It is commonly found in water, as are its degradation products (atrazine-desethyl, atrazine-2-hydroxy and atrazine-desisopropyl) [38]. In 2021, atrazine was the third-most commercialized herbicide in Brazil, following glyphosate and 2,4-D [39]. In a worldwide systematic review [5], atrazine was found to be the pesticide most analyzed in surface water (56% of 146 studies).

Atrazine can have different adverse effects in the biota of aquatic ecosystems, including impacting algae photosystem II, the development, reproduction, and behavior of crustacea and fish, and dysregulating their endocrine system [36]. In the present study, atrazine was the main pesticide detected in the samples (mainly in surface water) and found in quantified levels (≥LOQ) in 14 samples. Atrazine-2-hydroxy was the second analyte detected (mainly in groundwater), and also the second most quantified in the samples (nine samples). Vizioli et al. [40] summarized the results of Brazilian studies that reported atrazine and its degradation products in surface and drinking water, with levels that reached 2.9 μg L^{-1}. In Argentina, atrazine was quantified in 50% of groundwater samples at concentrations up to 1.40 μg L^{-1} [41]. These levels are much higher than the ones found in the present study (up to 0.305 and 0.039 μg L^{-1} of atrazine in ground and surface water samples, respectively), which are much lower than the maximum level (ML) established by the National Environmental Council (up to 2 μg L^{-1}) for surface water [21] and groundwater for human consumption [20]. The Ministry of Health legislation for water potability established an ML of 2 μg L^{-1} for atrazine and three degradation products (atrazine-desethyl, atrazine deisopropyl and diamino-chroro-atrazine) and a separate ML for atrazine-2-hydroxy of 120 μg L^{-1} [22], which is much higher than the highest level found in the samples (0.291 μg L^{-1} in a groundwater sample).

Montagner et al. [42] found that among 14 compounds investigated, atrazine had the highest RQ for aquatic organisms. Using national monitoring data from the Brazilian Ministry of Health from 2018 to 2021, Brovini et al. [43] found that atrazine was the most frequently quantified pesticide among 22 investigated in surface water (10.9% of the samples), at levels that could represent a risk to the aquatic system, a potential risk that was also identified by Albuquerque et al. [44]. In the present study, risk was not identified for atrazine (RQ < 1), but an RQ slightly higher than 1 was identified for its degradation

product atrazine-2-hydroxy, indicating a potential risk to aquatic organisms. This analyte was not investigated in the studies discussed in this section.

2,4-D was only detected in three samples, two of which were at quantified levels in groundwater (about 1 μg L^{-1}), which is much lower than the ML of 30 μg L^{-1} established by the Brazilian legislations [20,21]. A review reported that about 9% of 181 surface freshwater samples from Brazil contained 2,4-D, with a maximum concentration of 30 μg L^{-1} [43].

One major limitation of this study is related to the analytical method, for which about 36% of the investigated compounds had a recovery rate lower than 30%, and therefore no quantitation could be performed. However, despite this limitation, the study was able to identify the profile of compounds found in the Rio Preto Basin, which reflects the high agricultural activity in the area.

5. Conclusions

This study developed a method for the multiclass determination of 77 pesticides and degradation products in water by UHPLC–MS/MS after sample lyophilization. To the best of our knowledge, no multiresidue method with a large number of pesticides in water using lyophilization has been published in the literature.

While the levels of the pesticides quantified in the samples (atrazine, atrazine-2-hydroxy and 2,4-D) are lower than the Brazilian MLs, a potential acute risk for aquatic organisms was observed for atrazine-2-hydroxy, indicating the need for constant monitoring of its parent compound in the environmental compartments.

This is the first study to report pesticides other than glyphosate, AMPA, and glufosinate in groundwater from the Federal District in an area with high agricultural activity. This is very relevant, as contamination of surface water (springs, rivers and reservoirs) can impact aquatic organisms and groundwater (cisterns and wells), which are important sources for human consumption. Although the levels found in the samples complied with the Brazilian legislation, constant monitoring should be conducted in the region to ensure safe levels of pesticides in water.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w17081186/s1. Figure S1: Total ion chromatogram obtained by UHPLC–MS/MS of the analytical curve prepared in MeOH–water (1:1), fortified with 77 analytes at the 5 levels of the curve for each analyte; Table S1: List of the 77 compounds used in this study, with chemical class information, pesticide type, whether or not there is authorization for use in Brazil and their respective physicochemical properties. Source: ANVISA, 2024; PPDB, 2024; PubChem, 2024; Table S2: Conditions established for the system Q-trap 6500+ (SCIEX) using acquisition mode in multiple reaction monitoring (MRM; ionization ESI+ and ESI- for analysis of 77 pesticides. Table S3: Results of the Cochran test, used to test the homogeneity of variance (homoscedasticity). Table S4: Recovery, repeatability (RSD%), and intermediate precision (RSD%) for 77 pesticides in lyophilization and fortified water samples at five fortification levels (in μg L^{-1}). Table S5: Water samples collected at Rio Preto Hydrographic Basin (RPHB), midwestern region of Brazil, Federal District (DF): lyophilization, analyzed in triplicate, and identified as positive (≥LOD). P = collection point. References [37,45,46] are cited in Supplementary materials.

Author Contributions: N.L.P.: original draft preparation, conceptualization, formal analysis, investigation. E.P.d.A.: formal analysis, conceptualization. D.H.d.F.M.: formal analysis, investigation. E.C.O.-F.: funding acquisition, project administration, supervision. E.D.C.: funding acquisition, supervision, project administration, writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This project received funding from the Brazilian Ministry of Justice and Public Security (MJ; TED FDD 58/2019), the Federal District Research Foundation (FAPDF; 193.001.354/2016), and the University of Brasilia (PPGCA/PROAP 01/2021, DPG/UNB 0002 and 0004/2021).

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors thank Luciano S. Adjuto from the Brazilian Agricultural Research Corporation (EMBRAPA) for helping during the fieldwork and the students of the Toxicology Laboratory (LabTox) at the University of Brasília during sample preparation. We would like to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brazil (CAPES) for the scholarship (88882.384507/2019-01) granted to Esmeralda Pereira de Araújo.

Conflicts of Interest: Authors Daphne Heloisa de Freitas Muniz and Eduardo Cyrino Oliveira-Filho were employed by the company Agricultural Research Corporation. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest, including Esmeralda Pereira de Araújo who was a PhD student supported by the government.

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