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Detection of herbicides in water bodies of the Samambaia River sub-basin in the Federal District and eastern Goiás

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ABSTRACT

The objective of this study was to identify and quantify herbicide residues in water samples of rain, cisterns, streams, ponds, springs, semi-artesian wells, dams and a river in the Rio Samambaia sub-basin in the Federal District and eastern Goiás. A total of 287 samples were collected from 20 farms in the sub-basin in the rainy (February, summer) and dry (August, winter) seasons in 2016. Aminomethylphosphonic acid (AMPA, a glyphosate metabolite), clethodim, chlorimuron-ethyl, diuron, flazifop acid (a flazifop-p-butyl metabolite and the active ingredient), haloxyfop acid (a haloxyfop-methyl metabolite and the active ingredient), imazamox, mesotrione, metsulfuron, nicosulfuron and pendimethalin were not identified in any water sample. In the rainy season, approximately 99% of the samples contained residues at least one of the evaluated herbicides; in the dry season (, 100% of the samples contained residues of at least one of the evaluated herbicides. When considering only detection frequency, metribuzin, atrazine, clomazone and haloxyfop-methyl were the main herbicides found in the water of the Samambaia River sub-basin. In turn, based on levels higher than the limit of quantification, the main compounds detected were atrazine, clomazone, haloxyfop-methyl and glyphosate. In both seasons, the highest relative concentrations of herbicides for the rainy and dry seasons were found in spring water, 25% and 56%, respectively, and dam water, 23% and 16%, respectively.

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Environmental contamination; water source; herbicide residue

Introduction

The shift from the traditional agriculture to a more productive and modern model, coupled with population growth, has led to increased consumption of water, competition for water resources, and increased use of fertilizers and pesticides.^[1] However, this transformation has led to an increased risk of contamination of water sources. Herbicides, after reaching the soil, undergo several chemical, physical and biological processes, which control their fate and movement to different environmental compartments.^[2] Herbicides generally are rapidly degraded in soil, water and sediments, but some persist in the environment and bioaccumulate, which can impact water quality.^[3]

The physical and chemical properties of soil and of herbicides affect their behavior in the environment and their dynamics of their transformation. In another study, characterizing adsorption and absorption, degradation, drift, volatilization, leaching, surface flow, and especially the interaction between these processes influence fugacity and make the study of herbicide molecules in the environment very complex.^[4] In addition, the author emphasizes the variety of structures and properties of the chemical substances, which along with meteorological conditions, composition of soil microorganism populations, presence or absence of plants, location of the soil within the surrounding topography and farm management practices, make it difficult to monitor and

determine of environmental fate of applied plant protection products. Thus, the intrinsic characteristics of each region determine the dynamics of the pesticides used, and, in most cases, the final destination of the products are water bodies.^[5]

In addition to the evaluation of the herbicides present in water bodies, the ability of the molecules to be retained in the sediments of rivers, lakes or streams, where they accumulate and become potential contaminants after disturbances, is also relevant.^[6] Another determining factor is local rainfall, as rains are responsible for transporting the product vertically and horizontally in the soil, toward reservoirs or rivers. Precipitation also condenses herbicide molecules suspended in the air, returning them to the soil or depositing them in lakes.^[7] The authors found that 0.6% of atrazine and 0.4% of alachlor, known to be slightly (vapor pressure of 3.9×10^{-5} Pa) and moderately (vapor pressure of 2.9×10^{-3} Pa) volatile, and applied to corn crops, were found in rains far from the application site.

Many studies have reported concerning herbicide concentrations in aquatic environments ^[1,2,8–15], especially in groundwater, since it is often a direct source of potable water. Groundwater is mainly recharged by rainfall and is an important source of surface water, which moves and spreads along the flow paths of springs, streams, marshes, lakes and ponds.^[3] Pesticides concentrations in groundwater depend on the vulnerability of groundwater to pollution,

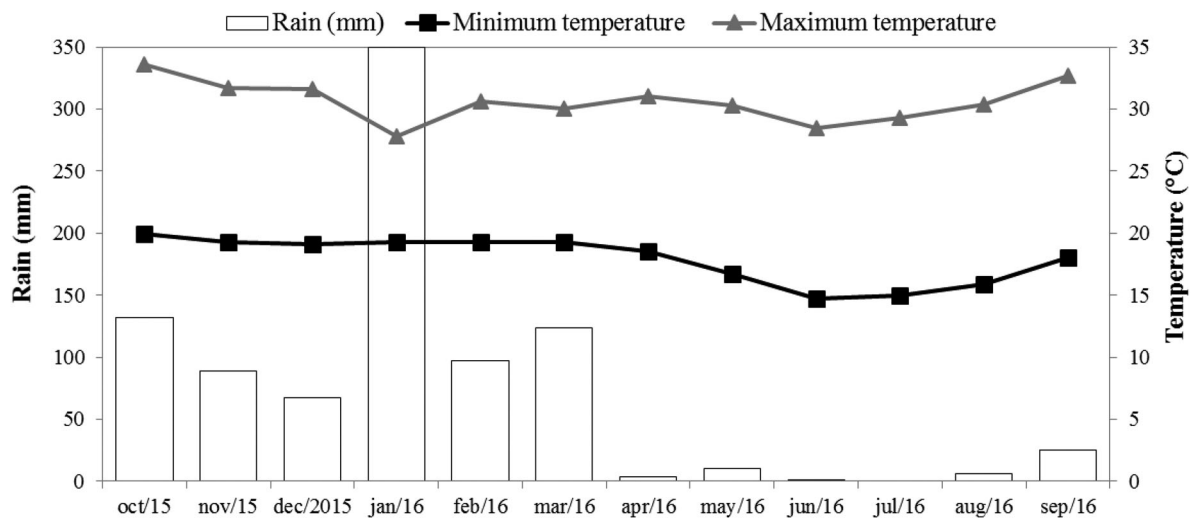


Figure 1. Rainfall (total monthly) and average (monthly), minimum, and maximum air temperatures recorded in the Samambaia River sub-basin - October 2015 to September 2016. Data obtained from the Agroclimatological Station of the Agricultural Cooperative of the Federal District Region (COOPADF), Brasília, DF, Brazil.

which is determined mainly by land use, as well as other factors such as aquifer recharge, groundwater depth, geological characteristics of the environment, and characteristics of the unsaturated zone.^[14] Understanding the environmental behavior of pesticides is essential for the development of measures to mitigate or eliminate the risk of water contamination by products such as herbicides.^[2]

The Samambaia River sub-basin is part of the São Marcos hydrographic basin, which empties into the Paranaíba River and encompasses many farms where streams, ponds, dams and wells are found. Center pivot irrigated intensive agriculture is practiced from the source of the Samambaia River, in the region of the Federal District Organized Settlement Program (Programa de Assentamento Dirigido do Distrito Federal - PAD-DF), to where it empties into the São Marcos River, in the municipality of Cristalina, Goiás (GO). Of the 68,400 hectares occupied by pastures and crops, 19,700 hectares are irrigated by 233 pivots, with 73 man-made reservoirs (or dams).^[16] The water of the dams is used only for irrigation.

The crops produced under center pivot irrigation include garlic, potatoes, coffee, onions, carrots, beans, corn (sweet, green and seed), tomatoes and wheat; rainfed crops include cotton, citrus, eucalyptus, corn (grain and silage), soybeans and sorghum.

The objective of this study was to identify and quantify herbicide residues in samples of water from rain, cisterns, streams, ponds, springs, wells (artesian and semi-artesian), dams and a river in the Samambaia River sub-basin in the Federal District and eastern Goiás.

Materials and methods

Most of the soil of the Samambaia River sub-basin is classified as Red Yellow Latosol (Brazilian Soil Classification System) or Oxisol (US Soil Taxonomy) and has a clayey texture, relatively flat relief with approximately 3% slope. The lowest point of the sub-basin is located 998 m above sea level, and the highest point is at 1,021 m.^[17] The local climate is Aw (hot and humid) according to Köppen

classification, with mean annual rainfall between 1,400 and 1,700 mm, maximum and minimum temperatures of 35 °C and 4 °C, respectively, and mean temperatures on the range of 20 to 23 °C.^[17,18] Rainfall (total monthly) and average (monthly), minimum, and maximum air temperatures recorded in the Samambaia River sub-basin, October 2015 to September 2016, are presented in Figure 1.

During April and May 2015, twenty farms located in the Samambaia River sub-basin were visited to collect information on the history of the herbicides applied in the previous two years, the agricultural crops grown and the water bodies present on the properties. Based on the information obtained, the herbicides to be analyzed were determined, and the distribution of sampling points and placement of rainwater collectors were defined, which were identified by global coordinates. The agricultural area of the twenty farms evaluated totalized 47,026 hectares; 39.2% of this area is irrigated and the remainder is rainfed.

The evaluated compounds and their physicochemical characteristics are shown in Table 1. Crops, planting systems (no-tillage or conventional tillage), irrigation conditions (irrigated or rainfed) and herbicide applications in the seasons (spring/summer or autumn/winter) in the Samambaia River sub-basin, can be observed in Table 2.

The water samples were collected in a period of intense rains (3, 4, 5, 10, 11, 12 and 25 February 2016) and repeated at the same collection points in the dry season (2, 3, 5, 8, 9, 10 and 11 August 2016). Rainwater was collected only in the rainy season. Thus, two water sampling seasons (rainy and dry) were evaluated in cisterns (6), streams (13), ponds (17), springs (28), wells (14), dams (48) and the river (13), totaling 139 samples in the rainy season and 138 in the dry season (one sample was missing because the dam was dry). With the addition of 10 rainwater samples, the total number of water samples collected and analyzed in the study was 287.

For rainwater collection, prior to forecasted rain events, a 10-L bucket (0.25 m in diameter and 0.22 m high) was set on the ground so that the water would enter directly therein. When the water volume reached approximately

Table 1. Compounds analyzed in water bodies of the Samambaia River sub-basin, in the Federal District and eastern Goiás, and water solubility (S), vapor pressure (VP), partition coefficient normalized for soil organic carbon (K_{OC}), octanol-water partition coefficient (K_{OW}), ionization constant - pK and classification 1, a and half-life ($t_{1/2}$) values in soil (lab or field) and aqueous photolysis² studies (aq photo).

Compounds	S (mg L ⁻¹)	VP (mPa)	K_{OC} (mL g ⁻¹)	K_{OW}	pK, classification	$t_{1/2}$ (days)	
						Soil	Aq photo
AMPA ³	1466561	–	2002	0.02342	0.9-10.2 wa	121.4	–
Atrazine	35	3.9×10^{-2}	100	0.0541	1.7 wb	75	2.6
Bentazon	7112	1.7×10^{-1}	55.3	0.347	3.51 wa	20	4
Carfentrazone-ethyl	29.3	7.2×10^{-3}	866	5010	0 np	1	8.3
Chlorimuron-ethyl	1200	4.9×10^{-7}	106	1.29	4.2 wa	40	st
Clethodim	5450	2.08×10^{-3}	–	13800	4.47 wa	0.55	5.45
Clomazone	1212	2.7×10^{-1}	300	380	0 np	22.6	st
Diclosulam	6.32	6.67×10^{-10}	90	7.08	4 wa	49	st
Diuron	35.6	1.15×10^{-3}	680	741	0 np	146.6	43
Fluazifop ⁴	40.5	–	205	1510	3.12 wa	25	15
Fluazifop-p-butyl	0.93	1.2×10^{-1}	3394	31600	0 np	1	6
Flumioxazin	0.786	3.2×10^{-1}	889	355	0 np	21.9	1
Fomesafen	50	4×10^{-3}	50	0.0631	2.83 wa	86	st
Glyphosate	10500	1.31×10^{-2}	1424	0.000631	2.34 wa	15	69
Haloxifop ⁵	1.6	1.33×10^{-3}	75	–	2.9 wa	9	12
Haloxifop-methyl	7.9	5.5×10^{-2}	–	10000	0 np	0.5	20
Imazamox	62600	1.33×10^{-2}	–	229000	2.3-10.8 wa	200.2	0.2
Linuron	63.8	5.1×10^{-2}	842.8	1000	0 np	57.6	st
Mesotrione	1500	5.7×10^{-3}	122	1.29	3.12 wa	19.6	89
Metribuzin	10700	1.21×10^{-1}	–	56.2	1.3-12.8 wa	7.1	0.2
Metsulfuron-methyl	2790	1.4×10^{-8}	–	135	3.75 wa	10	st
Nicosulfuron	7500	8×10^{-7}	30	4.07	4.78-7.58 wa	86	202
Paraquat	620000	1×10^{-2}	1000000	0.0000316	0 np	3000	st
Pendimethalin	0.33	3.34	491	251000	2.8 wa	182.3	21
S-metolachlor	480	3.7	–	1.120	0 np	51.8	146
Sulfentrazone	780	1.30×10^{-4}	43	9.79	6.56 wa	541	st
Tembotrione	71000	1.1×10^{-5}	–	0.0813	3.18 wa	14.5	56.3

¹Classification: wa - weak acid, wb - weak base, np - nonpolar

² $t_{1/2}$ aq photo: st - stable

³Aminomethylphosphonic acid, a glyphosate metabolite

⁴Fluazifop-p-butyl metabolite

⁵Haloxifop-methyl metabolite; - missing data.

Source^[19]

3.0 L or less, depending on the rainfall intensity, a sample of 0.5 L was taken from the collector and stored in polyethylene amber bottles. Rainwater samples were collected at then sites in the rainy season.

When collecting water from a stream, the collector (an amber bottle attached to the end of a 2.0-m long bamboo stick) was placed on the surface and at the point of greatest flow velocity against the flow and filled to approximately 0.5 L, five times at the same point, totaling 2.5 L. The five samples were mixed in a bucket, and a 0.5-L composite sample was then removed and placed in storage as described previously. A similar procedure was used for collecting in ponds and dams, where the composite samples were obtained after placing the collector on the surface, five times at the same point, 0.5 m away from the edge of the water body, with a collection of 2.5 L and separation of 0.5 L.

Water was collected from springs at a maximum radius of 0.5 m from the center, five samples were drawn at the same point, reserving 0.5 L for storage. For water collection in cisterns and wells, 2.5 L of water was suctioned, and 0.5 L was placed in an amber bottle. The cisterns were 5 to 14 m deep, and the wells, semi-artesian, from 15 to 190 m.

All 0.5-L composite samples in amber bottles were transported in coolers containing ice to the Laboratory of Weed Science of Embrapa Vegetables in Brasília, Federal District (DF), placed into freezers and kept frozen at -20°C .

Subsequently, the material was transported frozen to the laboratory of the Advanced Weed Science Research Center (Núcleo de Pesquisas Avançadas em Matologia - NUPAM) at the School of Agronomic Sciences, Paulista State University UNESP), Botucatu Campus, São Paulo, where the chromatographic analyses were performed.

After thawing, the water samples were filtered using 3-mL plastic syringes equipped with a Millex - HV filter (0.45 μm PVDF membrane, 13.0 mm diameter) into 2.0-mL vials. The herbicides were quantified using a liquid chromatography with tandem mass spectrometry (LC-MS/MS) system comprising a high efficiency liquid chromatograph (HPLC) (UFLC Prominence, Shimadzu), two pumps (LC-20AD), an autoinjector (SIL-20AC), degasser (DGu-20A5), controller system (CBM-20A) and oven (CTO-20AC). A 4500 triple quadrupole mass spectrometer (Applied Biosystems) was coupled to the HPLC.

To develop the chromatographic method and the calibration curves, analytical standards (Merck Germany) with high degrees of purity (above 99%) were used, and different compositions of the mobile phase for chromatographic separation were tested in different compositions and flow rates. The reaction mode used was multiple reaction monitoring (MRM), which is the standard quantitative mode used for target metabolite identification, and has the main advantages of high sensitivity and reproducibility, low noise and simultaneous measurement of up to 100 compounds.

Table 2. Crops, planting systems (no-tillage or conventional tillage), irrigation conditions (irrigated or rainfed) and herbicide applications in the seasons (spring/summer or autumn/winter) in the Samambaia River sub-basin.

Herbicide	Crops	Planting systems	Irrigation condition	Herbicides applications (in the seasons)
Atrazine	Corn (sweet, green and seed)	No-till	Irrigated	Autumn/winter
	Corn (grain and silage)	No-till	Rainfed	Autumn/winter
	Sorghum	No-till	Rainfed	Autumn/winter
Bentazon	Bean	No-till	Irrigated	Autumn/winter
Carfentrazone-ethyl	Citrus	No-till	Rainfed	Spring/summer
	Coffee ¹	No-till	Irrigated Rainfed	Spring/summer
	Soybean	No-till	Rainfed	Spring/summer
Chlorimuron-ethyl	Bean	No-till	Irrigated	Autumn/winter
	Soybean	No-till	Rainfed	Spring/summer
Clethodim	Carriot, garlic, onion, potato, tomato	Conventional	Irrigated	Autumn/winter
	Bean	No-till	Irrigated	Autumn/winter
Clomazone	Cotton	Conventional	Rainfed	Autumn/winter
	Eucalyptus	Conventional	Rainfed	Spring/summer
Diclosulam	Soybean	No-till	Rainfed	Spring/summer
Diuron	Cotton	Conventional	Rainfed	Autumn/winter
Fluazifop-p-butyl	Carriot, garlic, onion, potato, tomato	Conventional	Irrigated	Autumn/winter
	Bean	No-till	Irrigated	Autumn/winter
Flumioxazin	Citrus	No-till	Rainfed	Spring/summer
	Coffee	No-till	Irrigated Rainfed	Spring/summer
	Garlic	conventional	Irrigated	Autumn/winter
	Soybean	No-till	Rainfed	Spring/summer
	Tomato	conventional	Irrigated	Autumn/winter
Fomesafen	Bean	No-till	Irrigated	autumn/winter
Glyphosate	Citrus	No-till	Rainfed	Spring/summer
	Coffee	No-till	Irrigated Rainfed	Spring/summer
	Corn (grain and silage)	No-till	Rainfed	Autumn/winter
	Eucalyptus	Conventional	Rainfed	Spring/summer
	Soybean	No-till	Rainfed	Spring/summer
Haloxifop-methyl	Carriot, garlic, onion, potato, tomato	Conventional	Irrigated	Autumn/winter
	Bean	No-till	Irrigated	Autumn/winter
	Soybean	No-till	Rainfed	Spring/summer
Imazamox	Bean	No-till	Irrigated	Autumn/winter
Linuron	Carrot	Conventional	Irrigated Rainfed	Autumn/winter
				Spring/summer
Mesotrione	Corn (grain and silage)	No-till	Rainfed	Autumn/winter
Metribuzin	Carrot	Conventional	Irrigated Rainfed	Autumn/winter
				Spring/summer
Metsulfuron-methyl	Potato, tomato	Conventional	Irrigated	Autumn/winter
	Wheat	No-till	Irrigated	autumn/winter
Nicosulfuron	Corn (grain and silage)	No-till	Rainfed	autumn/winter
Paraquat ²	Citrus	No-till	Rainfed	Spring/summer
	Coffee	No-till	Irrigated Rainfed	Spring/summer
	Potato	Conventional	Irrigated	autumn/winter
	Soybean	No-till	Rainfed	Spring/summer
	Bean	No-till	Irrigated	autumn/winter
Pendimethalin	Garlic, onion	Conventional	Irrigated	Autumn/winter
	Potato, tomato	Conventional	Irrigated	autumn/winter
S-metolachlor	Potato, tomato	Conventional	Irrigated	autumn/winter
Sulfentrazone	Tomato	conventional	Irrigated	autumn/winter
	Soybean	No-till	Rainfed	Spring/summer
Tembotrione	Corn (grain and silage)	Conventional	Rainfed	autumn/winter

¹The sub-basin has coffee areas irrigated and rainfed;

²Paraquat is used for desiccation of potato and soybean crops.

To optimize the mass spectrometer conditions, direct injections were carried out with standard analytical solutions of 1 mg L⁻¹ for each compound individually. From the injections, the source ionization mode (ESI - electrospray ionization) was chosen, which produces analyte ions in the liquid phase before entering the mass spectrometer. For each compound, the ionization mode that allowed higher signal intensities was chosen. The chromatographic conditions used to quantify glyphosate, AMPA and other molecules are shown in Table 3.

The analytical curve was determined^[20] and submitted to linear regression analysis: $y = ax + b$, where b is the intercept of the analytical curve, and a is the slope of the line. The analytical curves for the compounds were constructed in the concentration ranges described in Table 4. All

analytical curve R² values were 0.99 or above except for diuron. The minimum limit of quantification was determined according to ICH guidelines.^[21]

Due to the dynamics of the factors influencing the contamination of water bodies by herbicides, the results were expressed as frequency of detection of the residues, lowest and highest values, in addition to the sum of total residues, considering, in this case, only values higher than or equal to the limit of quantification (LOQ).

Results and discussion

In the rainy season, approximately 99% of the samples contained residues of some of the evaluated herbicides.

Table 3. Chromatographic conditions used to quantify glyphosate and AMPA and the other molecules.

Compounds	Analytical column	Gemini 5 μ C18 110 Å (150 mm x 46 mm)
Glyphosate and AMPA	Mobile phase (pH 7.0)	Phase A (PA) = 5 mM ammonium acetate in water; Phase B (PB) = 5 mM ammonium acetate in methanol
	Gradient	0 – 1 minute = 10% PB and 90% PA; 1 – 4 minutes = 95% PB and 5% PA; 4 – 8 minutes = 95% PB and 5% PA; 8 – 10 minutes = 10% PB and 90% PA; 12 - Stop
	Flow rate	0.800 mL min ⁻¹
Other molecules	Analytical column	Synergi 2.5 μ Hydro-RP 100 Å (50 mm x 4,6 mm)
	Mobile phase (pH 2.5)	Phase A (PA) = 0.5% acetic acid in water; Phase B (PB) = 0.5% acetic acid in methanol
	Gradient	0 – 2 minute = 20% PB and 80% PA; 2 – 4 minutes = 95% PB and 5% PA; 4 – 10 minutes = 95% PB and 5% PA; 10 – 13 minutes = 20% PB and 80% PA; 15 - Stop
	Flow rate	0.600 mL min ⁻¹

Table 4. Parameters of the analytical curves and concentration ranges for each analyzed compound.

Compound	Retention time (min)	Linear equation	r ²	Linear Interval	LOQ(1)	LOD ⁽²⁾
				(μ g L ⁻¹)		
AMPA	2.08	y = 397.36x + 61.723	0.9998	1.17 – 600	3.0616	1.0103
Atrazine	5.46	y = 773630x – 30828	0.9998	0.1 – 12.5	0.2153	0.0710
Bentazon	5.37	y = 2E + 06x + 103972	0.9998	0.1 – 6.25	0.2148	0.0709
Carfentrazone-ethyl	5.73	y = 19576x + 1203.5	0.9992	0.1 – 12.5	0.8492	0.2802
Chlorimuron-ethyl	5.52	y = 220675x – 62768	0.9961	0.1 – 25	0.4906	0.1619
Clethodim	5.57	y = 12123x – 3707.2	0.9983	0.1 – 50	0.6485	0.2140
Clomazone	5.57	y = 134344x – 16217	0.9935	0.1 – 25	0.1573	0.0519
Diclosulam	5.24	y = 102075x + 24832	0.9960	0.1 – 50	0.4311	0.1422
Diuron	5.46	y = 4664x – 3811.6	0.9838	1.56 – 12.5	7.5083	2.4778
Fluazifop	5.57	y = 281928x + 93830	0.9920	0.1 – 50	0.4561	0.1505
Fluazifop-p-butyl	5.92	y = 154700x + 10368	0.9973	0.1 – 12.5	0.5848	0.1930
Flumioxazin	5.41	y = 11901x + 7702	0.9964	0.1 – 50	1.5584	0.5143
Fomesafen	5.99	y = 185578x – 3099.3	0.9999	0.1 – 6.25	0.2276	0.0751
Glyphosate	2.08	y = 2249.7x – 1917.4	0.9998	1.17 – 150	1.1509	0.3798
Haloxifop	5.79	y = 84758x + 11908	0.9996	0.1 – 12.5	0.7410	0.2445
Haloxifop-methyl	5.84	y = 133541x + 234851	0.9975	0.2 – 50	1.6200	0.5346
Imazamox	4.86	y = 118066x – 3954.4	0.9998	0.1 – 50	0.0906	0.0299
Linuron	5.57	y = 9587.7x + 544.57	0.9953	0.1 – 12.5	1.3145	0.4338
Mesotrione	5.06	y = 23231x + 4870.3	0.9996	0.1 – 25	0.2034	0.0671
Metribuzin	5.24	y = 53628x – 23285	0.9912	0.2 – 50	2.3755	0.7839
Metsulfuron-methyl	5.13	y = 92087x – 2827.3	0.9970	0.1 – 50	0.4671	0.1541
Nicosulfuron	5.08	y = 80158x + 5401.8	0.9943	0.1 – 50	0.4998	0.1649
Pendimethalin	5.90	y = 520.58x + 250.48	0.9995	0.39 – 50	8.8694	2.9269
S-metolachlor	5.73	y = 1E + 06x + 109454	0.9996	0.1 – 12.5	0.0889	0.0293
Sulfentrazone	5.14	y = 25585x + 1263.6	0.9997	0.1 – 12.5	0.8572	0.2829
Tembotrione	5.49	y = 646046x + 154804	0.9947	0.1 – 12.5	0.3716	0.1226

¹Limit of quantification.²Limit of detection.

However, concentrations were very low, and only in 10.7% were they higher than the limit of quantification of the molecules (Table 5). When considering only the presence of the compound at concentrations higher than LOQs, metribuzin was detected in 73.2% of the samples, followed by atrazine at 42.9%, clomazone at 32.9% and haloxyfop-methyl at 15.4%. Although found in a significant number of samples measured concentrations were very low, at 0%, 3.1%, 6.1% and 8.7% of the samples, respectively for those herbicides, that had concentrations higher than the LOQs. The herbicide glyphosate was detected in 3.4% of the samples; however, none of them had a concentration greater than the LOQ.

In the dry season, 100% of the samples had some detectable herbicide residues, but only 12.3% had concentrations higher than the LOQs of the compounds (Table 6). The most frequently detected herbicide during this season was haloxyfop-methyl (98%), followed by clomazone (62%), metribuzin (56%), fluazifop-p-butyl (48%) and atrazine (41%), and only 0.7%, 9.4%, 0%, 0%, and 1.8% of the samples,

respectively, for the herbicides mentioned above had concentrations higher than the LOQs.

Many of the investigated compounds, however, were not detected in any of the water samples taken either during the rainy or dry season, and these included AMPA (glyphosate metabolite), clethodim, chlorimuron-ethyl, diuron, fluazifop (fluazifop-p-butyl metabolite), haloxyfop (haloxyfop-methyl metabolite), imazamox, mesotrione, metsulfuron, nicosulfuron and pendimethalin (Tables 5 and 6). Tembotrione was detected in a single water sample in the rainy season but with a concentration lower than the LOQ. The physical and chemical characteristics of the compounds, and their less intense use in the sub-basin compared to other products, can explain the absence of detection of these molecules in the water samples.

The number of samples with herbicide residues, considering concentrations lower and higher (or equal) to the LOQ and the total concentration, detected in the water bodies of the Samambaia River sub-basin during the rainy and dry seasons are shown in Table 7.

Table 5. Concentrations (lowest and highest values), limits of quantification (LOQs), and numbers of samples with concentrations below and above (or equaling) the LOQ and total concentration of each product evaluated in the water samples of the Samambaia River sub-basin in the rainy season.

Product	Concentration ($\mu\text{g L}^{-1}$)			Number of samples		
	Lowest	Highest	LOQ	<LOQ	\geq LOQ	Total
AMPA	–	–	3.0616	0	0	0
Atrazine	0.0080	1.7484	0.2153	62	2	64
Bentazon	0.0058	0.8310	0.2148	2	1	3
Carfentrazone-ethyl	0.0021	0.0325	0.8492	3	0	3
Chlorimuron	–	–	0.4906	0	0	0
Clethodim	–	–	0.6485	0	0	0
Clomazone	0.0011	4.0621	0.1573	43	6	49
Diclosulam	0.0000	0.1040	0.4311	1	0	1
Diuron	–	–	7.5083	0	0	0
Fluazifop	–	–	0.4561	0	0	0
Fluazifop-p-butyl	0.0206	0.0387	0.5848	2	0	2
Flumioxazin	0.0008	0.0828	1.5584	16	0	16
Fomesafen	0.0000	0.0040	0.2276	1	0	1
Glyphosate	0.6078	1.0628	1.1509	5	0	5
Haloxifop	–	–	0.7410	0	0	0
Haloxifop-methyl	0.0459	3.8859	1.6200	21	2	23
Imazamox	–	–	0.0906	0	0	0
Linuron	0.0406	0.0599	1.3145	5	0	5
Mesotrione	–	–	0.2034	0	0	0
Metribuzin	0.0017	0.8217	2.3755	109	0	109
Metsulfuron-methyl	–	–	0.4671	0	0	0
Nicosulfuron	–	–	0.4998	0	0	0
Pendimethalin	–	–	8.8694	0	0	0
S-metolachlor	0.1420	1.7800	0.0889	0	5	5
Sulfentrazone	0.0852	0.8471	0.8572	4	0	4
Tembotrione	0.0390	–	0.3716	1	0	1

Table 6. Concentrations (lowest and highest values), limits of quantification (LOQs), and number of samples with concentrations below and above (or equaling) the LOQ and total concentration of each product evaluated in the water samples of the Samambaia River sub-basin in the dry season.

Product	Concentration ($\mu\text{g L}^{-1}$)			Number of samples		
	Lowest	Highest	LOQ	<LOQ	\geq LOQ	Total
AMPA	–	–	3.0616	0	0	0
Atrazine	0.0130	0.5914	0.2153	56	1	57
Bentazon	0.0561	0.2500	0.2148	2	1	3
Carfentrazone-ethyl	0.0020	0.0364	0.8492	5	0	5
Chlorimuron	–	–	0.4906	0	0	0
Clethodim	–	–	0.6485	0	0	0
Clomazone	0.0011	2.8621	0.1573	72	13	85
Diclosulam	0.0001	0.0224	0.4311	8	0	8
Diuron	–	–	7.5083	0	0	0
Fluazifop	–	–	0.4561	0	0	0
Fluazifop-p-butyl	0.0172	0.0595	0.5848	67	0	67
Flumioxazin	0.0000	0.0078	1.5584	1	0	1
Fomesafen	0.0000	0.0126	0.2276	1	0	1
Glyphosate	0.8048	11.3328	1.1509	2	2	4
Haloxifop	–	–	0.7410	0	0	0
Haloxifop-methyl	0.0159	2.6759	1.6200	135	1	136
Imazamox	–	–	0.0906	0	0	0
Linuron	0.0015	0.0109	1.3145	2	0	2
Mesotrione	–	–	0.2034	0	0	0
Metribuzin	0.0007	0.2897	2.3755	78	0	78
Metsulfuron-methyl	–	–	0.4671	0	0	0
Nicosulfuron	–	–	0.4998	0	0	0
Pendimethalin	–	–	8.8694	0	0	0
S-metolachlor	0.0129	0.8430	0.0889	4	3	7
Sulfentrazone	0.0000	0.1421	0.8572	1	0	1
Tembotrione	–	–	0.3716	0	0	0

In both seasons, the highest relative concentrations of herbicides were detected in spring and dam water, those being 25% and 23%, respectively, in the rainy season and 52% and 17%, respectively, in the dry season (Table 8). In

Table 7. Number of samples with herbicide residues, considering concentrations below and above (or equaling) the limits of quantification (LOQs) and total concentrations detected in the water bodies of the Samambaia River sub-basin during the rainy and dry seasons.

Site	Number of samples	Rainy season			Dry season		
		Number of samples with residue					
		<LOQ	\geq LOQ	Total	<LOQ	\geq LOQ	Total
Rain	10	9	0	9	–	–	–
Cistern	6	6	1	6	5	1	6
Stream	13	10	3	13	13	0	13
Pond	17	12	5	17	16	1	17
Spring	28	24	3	28	22	6	28
Well	14	13	1	14	12	2	14
Dam	48/471	47	3	48	40	7	47
River	13	13	0	13	12	1	13
Total	149	135	16	148	121	17	138

¹48 in the rainy season and 47 in the dry season.

addition, the total absolute concentration in the dry season, considering only values higher than the LOQ of each compound, was 12.9% higher than in the rainy season. This result can be explained by the higher water availability in the water sources, which resulted in dilution of the herbicides and, consequently, reduction in their concentration in the rainy season.^[22] Moreover, it should be considered that agricultural activity in the sub-basin does not stop in the autumn-winter period; including production of both perennial or annual irrigated or rainfed crops such as grain corn and sorghum.

Atrazine, bentazon, clomazone, haloxifop-methyl and s-metolachlor were the only herbicides detected in the rainy season with quantities larger than LOQs and presented relative concentrations of 19.2%, 11.4%, 17.7%, 41.8% and 9.7%, respectively, relative to the total concentration analyzed in that season ($20.98 \mu\text{g L}^{-1}$) (Table 9). The same occurred in the dry season for atrazine, bentazon, clomazone, glyphosate, haloxifop-methyl and s-metolachlor, which had relative concentrations of 5.4%, 2.3%, 4.2%, 58.9%, 24.3% and 4.9%, respectively. Although atrazine had the fourth-most detections in the dry season (57), only one were above the LOQ. Thus, when only considering levels exceeding LOQ, the main herbicides detected were atrazine, clomazone and haloxifop-methyl in the rainy season and haloxifop-methyl and glyphosate in the dry season.

Nine of the ten rainwater samples had residues of the herbicides metribuzin, atrazine, clomazone, flumioxazin and haloxifop-methyl, with frequencies of 70%, 60%, 50%, 10% and 10%, respectively. However, for all of them, the concentrations were lower than the LOQ of each herbicide (data not shown).

Atrazine was among the most commonly used herbicides on the farms, being used in almost 100% of them. It is an important product for corn and sorghum crops, applied mainly in the autumn/winter period, which is the growing season of these crops in the sub-basin. Grain corn, silage corn, green corn, sweet corn and seed corn are grown in the agricultural areas of the basin, and in the case of the last two, due to their high sensitivity to many other herbicides registered for the crops, weed control is performed almost exclusively with atrazine or in some cases with atrazine combined with tembotrione. Transgenic cultivars are

Table 8. Number of samples and concentrations (absolute in $\mu\text{g L}^{-1}$ and relative in %) of the products detected in the water bodies of the Samambaia River sub-basin during the rainy and dry seasons, considering only concentrations exceeding or equaling the limits of quantification.

Site	Number of samples	Concentration		
		Absolute total	Mean per point	Relative total
		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	(%)
Rainy season				
Cistern	1	0.1420	0.1420	2.0394
Stream	3	3.7840	1.2613	18.1151
Pond	5	5.9879	1.1976	17.1994
Spring	3	5.3191	1.7730	25.4640
Well	1	1.0100	1.0100	14.5055
Dam	3	4.7370	1.5790	22.6773
Total	16	20.9801	6.9629	100.0007
Dry season				
Cistern	1	0.5261	0.5261	10.4106
Stream	0	0.0000	0.0000	0.0000
Pond	1	0.2301	0.2301	4.5533
Spring	6	15.8524	2.6421	52.2826
Well	2	1.2621	0.6311	12.4884
Dam	7	6.0481	0.8640	17.0971
River	1	0.1601	0.1601	3.1681
Total	18	24.0789	5.0535	100.0000

Table 9. Number of samples and concentrations (absolute in $\mu\text{g L}^{-1}$ and relative in %) of the evaluated products in the water samples of the Samambaia River sub-basin in the rainy and dry seasons, considering only concentrations exceeding or equaling the limits of quantification.

Product	Number of samples	Concentration		
		Absolute total	Average per point	Total Relative
		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	(%)
Rainy season				
Atrazine	2	2.7969	1.3985	19.2446
Bentazon	1	0.8310	0.8310	11.4357
Clomazone	6	7.7333	1.2889	17.7368
Haloxypop-methyl	2	6.0819	3.0410	41.8477
S-metolachlor	5	3.5370	0.7074	9.7348
Total	16	20.9801	7.2668	99.9998
Dry season				
Atrazine	1	0.5914	0.5914	5.3770
Bentazon	2	0.2500	0.2500	2.2730
Clomazone	13	5.9737	0.4595	4.1778
Glyphosate	2	12.9556	6.4778	58.8966
Haloxypop-methyl	1	2.6759	2.6759	24.3295
S-metolachlor	3	1.6320	0.5440	4.9461
Total	21	23.4872	10.9986	100.0000

available for grain and silage corn, in which atrazine and glyphosate are applied in mixture.

As for the physical and chemical characteristics of the molecule, atrazine has relatively low volatility, has low water solubility, intermediate polarity, a relatively long half-life in soil of approximately 140 days^[8] and shows moderate adsorption to soil, which is influenced to the content and quality of organic matter^[15] and pH.^[23–25] In the literature there are many reports of atrazine detections in water sources,^[1,2,8–14] and it is considered one of the most commonly found herbicides in water bodies. It has been banned in other countries like Australia, Canada and in the European Union.

Metribuzin and clomazone, although often detected in the sub-basin water samples, are used on less than 20% of the farms, which is lower than for many of the other evaluated herbicides.

The clomazone sprayed in the agricultural areas of the sub-basin is applied prior to cotton sowing and eucalyptus planting. This herbicide has high water solubility, moderate adsorption to soil, intermediate polarity, a half-life in water of over 30 days and is moderately volatile.^[26,27] The volatility of the molecule might have contributed to its distribution throughout the sub-basin and presence in many samples, including to areas not treated with the herbicide. In this context, the higher the volatility of a product, the higher its capacity of escape to the atmosphere, representing a potential danger to not-target organisms, since the product can be absorbed as gas or even condensate at favorable conditions, reaching the surface when transported by rains.

Other studies have also reported the presence of clomazone in groundwater and surface water samples.^[22,27,28] The high frequency of detection of clomazone in groundwater in both shallow and deep wells may be explained by its high leaching potential due to the low soil absorption coefficient and high water solubility as well as relatively long half-life in soil.^[27]

Metribuzin has relatively low volatility, low soil adsorption, intermediate polarity and very high water solubility. Its physical and chemical characteristics favor leaching and water source contamination more than those of atrazine. Another study also reported high detection frequencies of this herbicide in groundwater and surface water samples from the Primavera do Leste region of Mato Grosso, Brazil.^[9]

In the sub-basin metribuzin is used for tomato and potato crops, usually at a dose of 480 g ha⁻¹ and almost exclusively before planting. Even without registration, some carrot fields in the sub-basin and other producing regions of Brazil, also receive metribuzin applications. However, in this case, in the post-emergence period, doses of 96 to 144 g ha⁻¹ were used once or twice until crop closure to complement the action of the registered herbicide (linuron). The production areas of these vegetables are characterized by exhaustive mechanical soil preparations such as plowing, harrowing and rotary-hoeing (for potatoes and carrots). These practices involve the movement of significant quantities of soil and combined with herbicide applications made directly to the soil, they can favor loss of herbicides, mainly through surface runoff and leaching, resulting in the contamination of water bodies, as observed in the present study.

Leaching refers to the in-depth transport through the soil profile of the fraction of solids dissolved in the soil solution.^[29] In turn, surface runoff is the horizontal movement of water, soil and crop residues on the soil surface. The herbicide dissolved in the water or retained in the clay or organic matter will follow the flow of water, potentially reaching a surface water reservoir. Surface runoff occurs in the field in situations of heavy rain due partly to rapid saturation of the surface soil with water, a dense soil structure slowing water infiltration as found in fields with a lack of conservation practices such as no-till planting under dead cover (straw), and the construction of terraces. These practices favor water infiltration into the soil, reducing soil erosion.^[29] The no-tillage system is a common practice in

Brazil for wheat, corn and soybean crops. Thus, herbicide losses from the field due to surface runoff depend, among other factors, on the time interval between applications and the occurrence of the next intense rainfall.^[2] Detected concentrations of metribuzin were lower than its LOQ, indicating that, despite frequently found, concentrations found were usually very low.

Despite detection in only four samples, with two values lower and two values higher than the LOQ, glyphosate was the herbicide with the highest relative and absolute concentrations in the dry season, accounting for 62% of the total herbicide mass detected in this season. In a single sample, the analyzed value was $11.33 \mu\text{g L}^{-1}$, corresponding to 48% of the total. This sample was of spring water, and the concentration found may be explained by direct contamination from application of the herbicide, as the spring was not protected and was near a road.

Glyphosate was the herbicide most commonly used on the farms, is used multiple times in some crops, and is applied at higher doses than all other herbicides used on the farms. Due to its physical and chemical characteristics, it is environmentally safe, provided that good agricultural practices are followed in handling and application. It is a nonvolatile, hydrophilic compound with extremely high solubility in water, very strong adsorption to soil, and a half-life of 47 days in soil. Although its water solubility is extremely high, the strong adsorption to the soil does not allow the molecule to remain in the soil solution, and thus it is prone to losses by leaching and surface runoff attached to soil colloids. In the total 287 samples evaluated, glyphosate was detected in nine, and in only two, were the concentrations higher than the LOQ of the compound.

Although glyphosate is considered nontoxic to humans, its presence in water bodies, either by run-off and/or leaching, is a potential risk to human health and to the biota that inhabit these ecosystems.^[30] A study conducted in Mexico detected the herbicide glyphosate in the urine of local farmers, in drinking water and in groundwater of the Yucatán Peninsula, which will require monitoring over time to evaluate the impacts of the herbicide on the environment and human health.^[30]

The herbicides haloxyfop-methyl and fluazifop-p-butyl are used in the agricultural areas of the sub-basin especially for post-emergence control of grasses in beans and vegetables (garlic, potatoes, onions, carrots and tomatoes) and were used in 60% and 25% of farms, respectively. In addition, haloxyfop-methyl is also applied in soybeans fields infested with glyphosate-resistant sourgrass (*Digitaria insularis*) populations. In these cases, application is performed before and after sowing. The two ACCase-inhibiting belong to the same chemical group, aryloxyphenoxypropionates, but differ in their physical and chemical characteristics, especially in soil half-lives, 15 days for fluazifop-p-butyl and 55 days for haloxyfop-methyl, and in soil adsorption very strong for fluazifop-p-butyl (K_{oc} 5700) and much weaker for haloxyfop-methyl (K_{oc} 75).^[26]

The two herbicides are classified as having low volatility and very low water solubility. Haloxyfop-methyl is

lipophilic, and fluazifop-p-butyl varies from hydrophilic (at neutral pH) to lipophilic (neutrally charged at acidic pH). All these characteristics regulate the availability and persistence of an herbicide in the soil and are important for measuring the hazard posed by the molecules to the environment.

Conclusions

Aminomethylphosphonic acid (AMPA, a glyphosate metabolite), clethodim, chlorimuron-ethyl, diuron, fluazifop (a fluazifop-p-butyl metabolite), haloxyfop (a haloxyfop-methyl metabolite), imazamox, mesotrione, metsulfuron, nicosulfuron and pendimethalin were not identified in any water sample.

Considering only the frequencies of detection of the compounds in the samples, metribuzin, atrazine, clomazone and haloxyfop-methyl were the main analytes detected in the Samambaia River sub-basin. In turn, based on levels higher than the limits of quantification, the main herbicides detected in the rainy season were atrazine, clomazone and haloxyfop-methyl, and those in the dry season were haloxyfop-methyl and glyphosate.

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