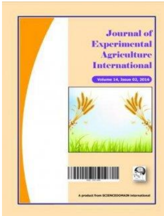

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Occurrence of Waste Herbicides in Surface Water from North of São Paulo (Brazil)

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The incorrect use of herbicides can cause the contamination of soil and aquatic ecosystems. In this study, we evaluated the contamination of surface water samples from the northern state of São Paulo, Brazil. Samples were collected from rain, streams and lakes in three seasons in different agricultural areas. Liquid chromatography coupled with high performance mass spectrometry was used to analyze water contamination by the following herbicides: ametryn, amicarbazone,

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clomazone, diclosulam, diuron, hexazinone, imazapic, imazapyr, isoxaflutole, s-metolachlor, sulfentrazone, sulfometuron-methyl and tebuthiuron. According to the method, the limits of quantification were 3.13 μg L^{-1} for diuron and 0.391 μg L^{-1} for the other herbicides. It was observed that 82% of all the samples contained at least one herbicide, and clomazone was the most common product. The highest quantized values were found for streams: s-metolachlor (10.2 hg L^{-1}), diuron (7.65 and 5.49 μg L^{-1}) and hexazinone (4.3 μg L^{-1}). The results indicate that surface water from the north of São Paulo contains residual herbicides in quantifiable levels.

Keywords: Leaching; LC-MS / MS; sorption and sugar cane.

1. INTRODUCTION

Brazil is currently the largest consumer of pesticide in the world, followed by USA. Among pesticides, herbicides are the most widely used [1]. This is because the country is the largest producer of sugar cane, various tropical fruits, and biodiesel [2]. Herbicides, when applied in pre- or post-emergence weeds, directly or indirectly reach the soil, and may cause damage to succeeding crops, soil flora and fauna, or contaminate surface and groundwater. Products which are considered volatile can easily be lost into the atmosphere and have been detected in precipitation, especially in tropical conditions [3].

Among the herbicides most frequently detected in the surface water of lakes and streams in Brazil are ametryn, clomazone, diuron, hexazinone, sulfentrazone and tebuthiuron [3,4,5], which are used, together, in important crops such as peanuts, rice, coffee, sugar cane, corn and soybeans. These products are highlighted in ranking models of the detection risks of molecules in water samples, due to their physicochemical characteristics, particularly solubility, sorption into the soil and their half-life [6,7].

Despite the large area of agricultural land in Brazil, the amount of herbicides applied, fluvial system and different forms of agricultural management, there are few studies on the detection of these products in water samples, especially in rainfall. The water authorities in many other countries have monitoring programs for the presence of pesticides, but in Brazil, the law only limits the presence of six herbicides in freshwater [8]. The detection of herbicides in water bodies can help define the potential contaminants of different products and strategies to mitigate the problem. Thus, the aim of this study was to verify herbicide contamination of water samples collected from rainfall, streams and lakes, in an agricultural region of southeastern Brazil.

2. MATERIALS AND METHODS

The study was conducted in the catchment of Córrego Rico, an area controlled by the Mogi Guaçu River Basins Committee and present in the territorial area of Jaboticabal, Monte Alto, Santa Ernestina, Taquaritinga and Guariba municipalities, in the northern state of São Paulo, Brazil. Approximately 95% of the area is occupied by sugarcane all year round; however; they are also found in small farm with peanuts, citrus, corn, guava, soybeans and vegetable crops. Regarding land use, the site is characterized by rugged terrain, and most of the soil has high sand content. There is a great deal of soil movement resulting from activity to prepare the soil for sugarcane and vegetables grown, especially during the rainfall onset [9,10].

2.1 Sampling

Water samples were collected over three periods: November 26 to 30, 2010; February 02 to 06, 2011; and May 15 to 18, 2011. The samples were chosen according to the agricultural activities in the area and precipitation indexes (Fig. 1). All the sampling points were recorded using geographic coordinates (Table 1).

For rain water collection, before the first expected precipitation of the day (after 8:00 AM), a stainless steel sink with a capacity of 9.0 L and of 28 cm diameter was placed on the floor, so that water could flow directly into this container. When the volume of water was approximately 1.0 L, a 0.2 L aliquot was collected. The procedure was performed three times and, together, the three samples generated a sample of 0.6 L. Rain samples were collected at four points in the first and second period, and two points in the third period, when there was less rain. Ten samples were therefore collected.

For collections from streams, the container was placed at the stream surface at the point of the water's greatest velocity, and three samples of 1.0 L each were collected. Each sample was withdrawn at aliquot of 0.2 L and the three aliquots generated a sample of 0.6 L. The samples were taken at 28 points, for a total of 84 samples from the streams.

A container was positioned 0.5 meters from the edges of ponds. Surface water was collected from 18 ponds, totaling 54 sample points. We adopted the same procedure as used in streams. Finally, all composite samples were placed in amber vials and immediately transported on ice to the laboratory where they were frozen at -20°C until analysis.

2.2 Chromatographic Analysis

For the quantification of pesticides, the direct injection method of samples was used, with modifications according to [11].

Multiresidue analysis by liquid chromatography coupled to high performance mass spectrometry (LC-MS / MS) was the method used. After thawing at room temperature, the samples were stirred and 2.0 mL was filtered, using a syringe and 0.45 µm filters (Millipore), and a 13 mm membrane, after which the sample was placed directly in the amber vial (FlowSupply) for injection into the chromatograph.

The sample analysis was performed on a HPLC system Shimadzu Proeminence UFLC model, C18 column (Synergi, RP-Fusion 250 mm x 4.6 mm id, 4 mm particle size). The chromatographic conditions involved a mobile phase consisting of methanol and water with 0.5% acetic acid, flow 0.4 mL min^{-1} and 30 µL injection volume. The gradient started at 20:80 (methanol / water) to 8 minutes, by 8 to 12 minutes changed to 95:5 remaining at this rate until 15 minutes, returning to 20:80 in the final 4 minutes. The detector used was a mass spectrometer, model 3200 QTRAP (Applied Biosystems) with hybrid triple quadrupole.

After analysis, the results were analyzed by occurrence frequency and higher concentration determined.

2.3 Statistical Analysis

For the presentation of the obtained results, a statistical analysis was performed through the analysis of variance, however, there was no significance of the parameters. Thus, the data were analyzed and presented in frequency form. In the creation of the graphs, the excel software was used.

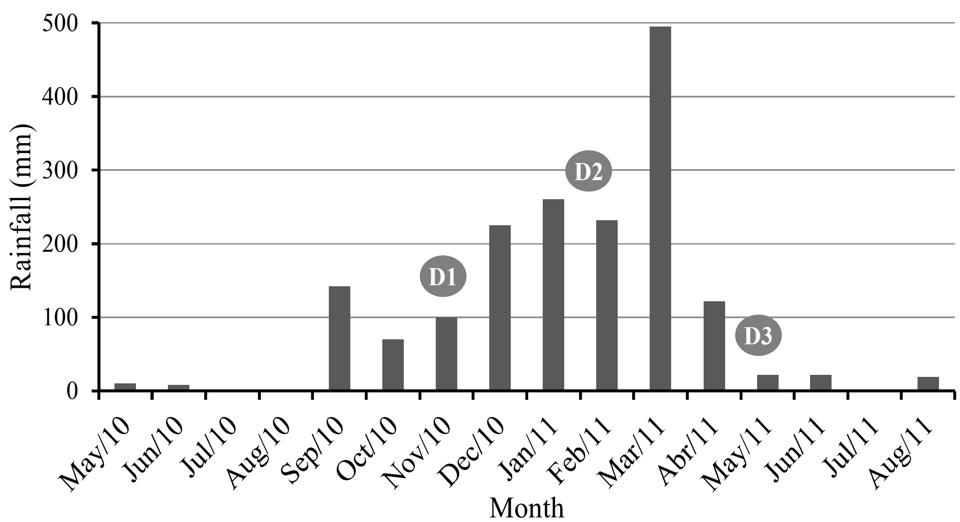

Fig. 1. Monthly rainfall accumulation in the catchment of Córrego Rico (SP) where water samples were collected for herbicide detection. Sampling dates: D1: November 26 to 30, 2010, D2: February 02 to 06, 2011, D3: May 15 to 18, 2011. Jaboticabal, SP.

Table 1. Identification, by geographical coordinates, of localities where the rain (RA), stream (ST) and lakes (LA) water samples were taken to assess the presence of herbicides in the watershed of Córrego Rico. Jaboticabal, SP, Brazil

Point	Coordinate		Point	Coordinate	
	South	West		South	West
			Rains		
RA1	21° 17' 00.40"	48°22' 00.77"	RA3	21° 17' 42.71"	48°25' 29.09"
RA2	21° 16' 24.49"	48°23' 48.53"	RA4	21° 17' 21.77"	48°26' 04.36"
			Streams		
ST1	21° 16' 33.52"	48°21' 09.91"	ST15	21° 16' 34.75"	48°24' 59.38"
ST2	21° 16' 37.65"	48°21' 24.82"	ST16	21° 17' 46.75"	48°25' 26.98"
ST3	21° 17' 41.75"	48°23' 15.97"	ST17	21° 19' 06.56"	48°24' 07.64"
ST4	21° 19' 01.29"	48°24' 34.55"	ST18	21° 19' 07.42"	48°24' 06.56"
ST5	21° 17' 55.85"	48°22' 31.65"	ST19	21° 16' 33.27"	48°20' 53.97"
ST6	21° 17'46.91"	48°25' 46.95"	ST20	21° 18' 04.13"	48°21' 27.34"
ST7	21° 17'46.21"	48°26' 30.05"	ST21	21° 19' 03.04"	48°17' 33.14"
ST8	21° 18'45.52"	48°26' 55.82"	ST22	21° 19' 20.05"	48°16' 24.43"
ST9	21° 16' 17.92"	48°23' 49.63"	ST23	21° 18' 37.35"	48°19' 25.69"
ST10	21° 15' 27.43"	48°23' 55.58"	ST24	21° 17' 42.99"	48°15' 52.08"
ST11	21° 15' 39.16"	48°23' 50.77"	ST25	21° 17' 21.12"	48°15' 38.47"
ST12	21° 16' 53.60"	48°24' 56.70"	ST26	21° 17' 02.26"	48°15' 25.25"
ST13	21° 16' 09.16"	48°24' 47.58"	ST27	21°16' 44.53"	48°15' 35.56"
ST14	21° 16' 35.56"	48°24' 58.62"	ST28	21° 16' 42.95"	48°15' 06.11"
			Lakes		
LA1	21° 16' 38.80"	48°21' 26.23"	LA10	21° 16' 20.15"	48°23' 48.40"
LA2	21°16' 49.77"	48°22' 03.40"	LA11	21° 15' 34.31"	48°23' 52.78"
LA3	21° 16' 56.11"	48°22' 00.07"	LA12	21° 15' 31.44"	48°23' 54.80"
LA4	21° 16' 57.70"	48°22' 08.43"	LA13	21° 15' 41.22"	48°26' 53.04"
LA5	21° 18' 59.29"	48°23' 29.98"	LA14	21° 16' 41.56"	48°25' 00.92"
LA6	21° 17' 33.34"	48°23' 12.10"	LA15	21° 16' 07.11"	48°24' 47.98"
LA7	21° 17' 33.39"	48°23' 12.26"	LA16	21° 16' 34.04"	48°24' 57.60"
LA8	21° 16' 13.24"	48°23' 02.41"	LA17	21° 18' 38.71"	48°25' 13.87"
LA9	21° 16' 46.27"	48°22' 40.35"	LA18	21° 17' 41.10"	48°25' 26.19"

3. RESULTS AND DISCUSSION

3.1 Features of Herbicides in Chromatographic Analysis

The limit of quantification was 3.13 μg L^{-1} for diuron, and 0.391 μg L^{-1} for all other herbicides. The analytical curve was prepared from herbicide standards of purity to 99.8%. The other parameters relating to the characterization of herbicides are shown in Table 2.

3.2 Detection Frequency of Herbicides

At least one herbicide was detected in 82% of the samples collected (Table 3). The highest frequency herbicide detection in the samples was in October 2010 (98%), followed by May 2011 (88%) and February 2011 (60%). Many herbicides were detected in the May samples, which is when the cane sugar harvest began. Products with residual effects are applied in order to remain in an active form in the soil, and to control weeds that germinate after cutting. At the beginning of the rainy season (from September), the volume of herbicides applied is greater, when they are used to control pre- and post-emergence weeds in sugar cane, corn, citrus, guava, and peanuts, among other crops.

The residual herbicides detected at different times of the year were probably due to a combination of recent applications and residual herbicides applied in previous months. The highest frequencies in October and May, compared to February, may also be related to more intense rainfall in February (Fig. 1), when the large volume of water decreases the concentration of the product and consequently detection, as also reported by other authors regarding agriculture in the state of São Paulo [12].

Table 2. Parameters for the analysis of herbicides (H) by LC-MS / MS in water samples collected in the catchment of Córrego Rico. Jaboticabal, SP

Herbicide	Retention time[1]	Linearity equation	CC[2]	Molecular mass (g mol^{-1})			
				H	F[3]1	F 2	F 3
ametryn	8.53	y = 20700x - 2880	99.5	228.13	186.1	68.1	96.2
amicarbazone	7.85	y = 15900x - 9610	99.3	505.31	165.3	264.2	183.3
clomazone	9.12	y = 11200x + 3810	99.4	240.20	125.1	89.1	99.1
diclosulam	8.13	y = 4040x + 176	99.5	405.94	160.9	90.2	125.1
diuron	8.98	y = 191x + 158	99.2	234.03	72.0	73.1	174.0
hexazinone	8.28	y = 12100x - 411	99.6	253.30	171.2	71.2	85.2
imazapic	6.96	y = 1690x - 530	95.2	276.14	163.2	69.1	86.1
imazapyr	6.18	y = 810x - 57,5	99.6	262.12	78.2	69.2	86.2
isoxaflutole	8.53	y = 5990x + 849	99.5	360.05	251.2	220.2	144.0
s-metolachlor	9.77	y = 10100x + 3010	99.7	284.21	252.3	176.2	91.1
sulfentrazone	8.02	y = 1250x + 2000	99.2	386.95	110.2	146.1	273.1
SMM[4]	7.85	y = 3800x - 111	99.6	365.08	150.2	107.1	67.2
tebuthiuron	8.25	y = 10500x - 959	99.0	229.25	172.3	116.1	62.0

Table 3. Frequency (%) of water samples contaminated by herbicides, collected in three periods: P1: October 26 to 30, 2010, P2 February 2 to 6, 2011 and P3: May 15 to 18, 2011 in the watershed of Córrego Rico, Jaboticabal, SP, Brazil

Herbicides	-------- Rain --------			------- Stream --------			-------- Lakes ---------		
	P1	P2	P3	P1	P2	P3	P1	P2	P3
ametryn	50	-	50	-	4	-	-	6	-
clomazone	100	100	50	71	14	61	56	17	33
diclosulan	-	-	-	-	4	-	-	-	-
diuron	-	-	-	50	43	-	67	28	11
hexazinone	25	-	-	39	18	57	22	17	44
imazapic	-	-	-	7	-	-	11	-	-
imazapyr	-	-	-	-	4	-	-	-	-
s-metolachlor	-	-	50	39	4	43	39	6	44
sulfentrazone	75	-	50	11	4	57	44	6	33
tebuthiuron	-	-	50	7	-	-	11	-	-

At the start of the rainy season, it is common for the soil to be prepared for planting. This soil movement causes plant residue and particulate material, which contains herbicides, to move towards streams. Similarly, most ground exposure, which allows the herbicide to be lost into the atmosphere, particularly in situations of low relative humidity, [13,14] favors the detection of these products also in rainfall. All these factors optimize the entry of products to bodies of surface water, because there is a lack of soil protection practices in the study area [9] and the main agricultural activity is sugarcane, responsible for intensive agricultural implements use and large soil losses [10].

Of all the rain samples, 83% of samples from streams and 76% of samples from lakes contained at least one herbicide. Out of the 13 products evaluated, six were detected in rain samples, 13 in stream samples and eight in samples collected from lakes. Whenever detected in rain, herbicides were also detected in streams and lakes and, with the exception of diclosulan and imazapyr, all herbicides occurring in streams also occurred in lakes, including the same collection season (Table 3).

Agricultural activities in a watershed can be harmful to water sources and, in most cases, the first component of achievement for pesticides residues is the network of streams. This network, which converges into ponds or rivers, is the most exposed waterway by occupying large areas and receiving eroded material, especially in places where there are no protection activities, such as the preservation of riparian forests, contour preservation or other conservation soil practices [15].

It should be noted that herbicide detection in water samples means technical inefficiency in the use of plant protection products. The main determinants of the arrival of products in water are soil permeability, water body topography and position of the water in relation to the herbicide application site [16]. In the case of the study area, many agricultural fields are on high slopes, bounded by streams or containing ponds, and classified as susceptible to erosion [9,10]. Technical problems during the application of herbicides thus promote body-of-water contamination.

Another factor in the detection of herbicides in rainfall is the straw formed after harvesting sugarcane. The large volume of waste (30 t ha^{-1}) has a direct influence on the dynamics of herbicides applied during the dry season [17]. This period lasts around four months in the study region and, once in straw, the products may be lost into the atmosphere, mainly due to vapor pressure, and the relative humidity, winds and temperature of the environment [6,14].

It was observed when evaluating the individual herbicides that the most commonly found product was clomazone. Clomazone was detected in all rain water samples from the first and second sample periods, and one of the two third period samples (Table 3). The highest detection of this product may be related to the greater probability of its loss to the atmosphere, due to its vapor pressure, and to the large number of crops for which the product is registered (Table 4), justifying its greater use and consequent high frequency in non-target environments.

Clomazone has been identified in surface water in Brazil and reported in others papers [4,12,18]. This product can cause toxic effects in cultures after dry or wet deposition, including when it is in the atmosphere [6]. Despite the detection in most of the samples collected in Córrego Rico watershed, the product was not detected in measurable levels according to the analysis method.

The herbicide hexazinone was detected in measurable levels in most of the samples, especially those originating from streams and lakes (Table 3 and Fig. 2). This detection and quantification are related to its use in the culture of sugar cane, which is the main agricultural activity in the region [10]. The dosage used for pre- and post-emergent management, is approximately 500 g ha^{-1}. Low sorption to the soil and a long residual period (Table 4) are other factors related to water contamination by this product. Depending on the physical and chemical characteristics desired, for herbicide applications recommendation on the sugar cane straw, mainly solubility (Table 4), hexazinone is used in a mixture with diuron and clomazone, and registered in Brazil 34 commercial products with this active ingredient.

Diuron, which is the product with the highest registered users in Brazil (Table 4), was detected in quantifiable levels and at maximum concentrations of 7.65 µg L^{-1} (Fig. 2). This product is recognized worldwide as an effective tool in the management of hundreds of weeds, but also as one of the main contaminants of surface water. According to the high Koc, the dynamics are closely related to organic soil matter, in this sense; the loss of material into streams can be considered the main factor related to the quantification of the product in water [6,7,14].

Among the most important herbicides, found in the Córrego Rico watershed streams, is s-metolachlor (Table 3 and Fig. 2). This herbicide was found at the highest concentrations in relation to other products, and its detection in the area is related to sugar cane, beans, corn and soybeans crops (Table 4). Concentrations equivalent to 10.2 µg L $^{-1}$ were detected in a sample from coordinates 21° 17' 46.75" S and 48° 25' 26.98" O. During the second sample collection, intensive soil preparation for planting was noted, even in the face of intensive rainfall, which may have caused the product to enter in the stream at high concentrations.

The level of pesticides in the aquatic environment is unstable, due to their dilution in water, degradation by biotic and abiotic agents, absorption or adsorption of the soil components and application in the fields [6]. The high concentrations of s-metolachlor and sulfentrazone herbicides detected may thus be related to recent applications, and losses resulting from drift may be responsible for the presence of the product in environments.

Table 4. Physico-chemical characteristics of herbicides evaluated in water, wells and spring samples in the watershed of Córrego Rico, Jaboticabal, SP, Brazil

Herbicide[1]	$t_{1/2}$[2]	Koc[3]	SW[4]	VP[5]	GUS[6]	Registered in Brazil to
ametryn	53	300	200	$3.7x10^{-4}$	5.98	Pineapple, cotton, bananas, coffee, sugar cane, citrus, cassava, corn and grapes.
amicarbazone	150	30	4600	$1.3x10^{-6}$	3.34	Sugar cane and corn.
clomazone	24	150	1.100	$1.9x10^{-2}$	2.1	Cotton, Rice, potato, sugar cane, tobacco, cassava, corn, bell pepper and soybean.
diclosulan	75	90	6.3	$4.0x10^{-9}$	3.46	Sugar Cane and soybean.
diuron	372	480	42	$9.2x10^{-6}$	3.38	Non-agricultural, pineapple, alfalfa, cotton, bananas, cocoa, coffee, sugar-cane, citrus, corn, rubber, soybeans, wheat and grapes.
hexazinone	222	54	33.000	$3.0x10^{-5}$	2.8	Sugar cane.
imazapic	180	80	2.200	$1.0x10^{-7}$	3.87	Peanut, rice, sugar cane and corn.
imazapyr	60	100	11.300	$1.0x10^{-7}$	3.90	Rice, sugar cane, eucalyptus, beans, corn, pine and rubber.
isoxaflutole	18	134	6.2	$1.0x10^{-6}$	0.59	Cotton, potatoes, sugar cane, cassava, corn and pine.
s-metolachlor	33	200	488	$1.3 x 10^{-6}$	1.94	Cotton, sugar cane, beans, corn and soybeans.
sulfentrazone	548	43	490	$1.3x10^{-7}$	6.48	Pineapple, coffee, sugar-cane, citrus, eucalyptus, tobacco and soybeans.
SMM[7]	30	85	70	$5.4x10^{-16}$	2.86	Sugar cane
tebuthiuron	1220	80	2500	$2.7x10^{-4}$	6.31	Sugar cane and pastures.

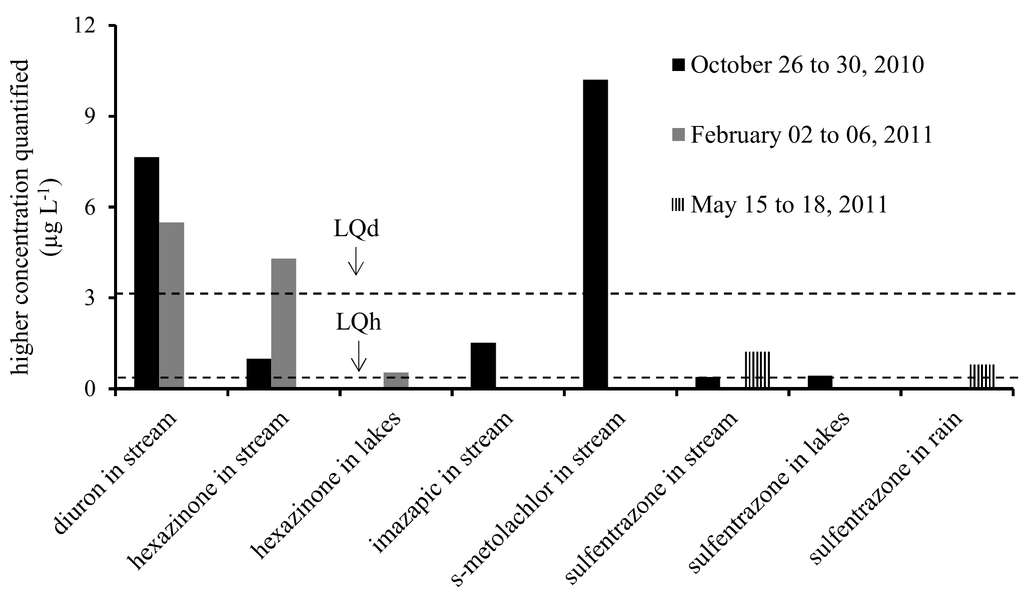

Fig. 2. Residual maximum of herbicides, quantified by LC-MS / MS in water samples collected on three occasions under three matrices (rain, streams and lakes), in the watershed of Córrego Rico, Jaboticabal, SP, Brazil. Limit of quantification for diuron (LQd) and other herbicides (LQh)

Another factor to consider in the use of sulfentrazone is its persistence in the soil. This herbicide is used at a dosage of 1.4 kg ha^{-1} at pre-emergence on sugar cane. Because of its high $t_{1/2}$ life, it is classified as the most likely contaminant of water bodies among the herbicides evaluated (Table 4), but as a result of successive applications added to this soil concentration, a large amount of product is adsorbed to the particles. It is emphasized that in the study area, the reduction in rainfall and high temperatures in May, the winds and the intense work of soil preparation, meant that a great amount of clay is suspended in the atmosphere, material that probably contains the herbicide, and it can reach the soil via the rain [19,20].

The herbicide ametryn was detected in three rain samples, one stream sample and one lake sample, at non-measurable concentrations. This herbicide is widely used in sugarcane crops, in mixtures with atrazine, diuron, tebuthiuron, trifoxysulfuron-sodium and 2,4-D. Due to their adsorption in soil colloids, it remains, for the most part, on the surface, where there is greater microbial activity primarily responsible for degradation [6]. Despite its use, smaller quantities of this product are present in the environment, in relation to the other herbicides.

Investigating the factors related to the loss of herbicides to water bodies, there are several studies related to the physical and chemical characteristics of products. The most common herbicide in the water samples (clomazone) in this study is classified as less dangerous to the environment than other herbicides. S-metolachlor, which was also detected in high concentrations, is also classified as low risk (Table 4).

Diclosulan, imazapic, imazapyr and tebuthiuron herbicides were detected less frequently than others, but they are classified as highly leachable (Table 4), as are amicarbazone and sulfometuron-methyl, which were not detected in any sample. Isoxaflutole is not classified as a probable contaminant in water bodies and was not detected. Characteristics related to the loss of these products are related, despite the physical-chemical characteristics of these herbicides, to application and environmental conditions.

4. CONCLUSION

According to the methods of analysis used, 82% of water samples collected from the rain, streams and lakes of the Córrego Rico watershed were contaminated with at least one herbicide. Residues of diuron, hexazinone, imazapic, s-metolachlor and sulfentrazone were detected in quantifiable levels, and ametryn, clomazone, diclosulan, imazapyr and tebuthiuron in unquantifiable levels. Finally, this results show the importance of the proper use of these herbicides, and the need for constant monitoring of waters in agricultural areas in Brazil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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