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Investigation into the occurrence of herbicide residues in the rivers of the Acaú-Goiana extractive reserve

Brazil is the world's largest consumer of pesticides and numerous studies have reported damage to both human health and the environment due to exposure and the toxicity of these agrochemicals. Sugarcane crops present the highest herbicide consumption, leaving the margins of large watersheds. In this study, we have investigated the occurrence of herbicides in the surface waters of three different catchment areas, the rivers: Tracunhaém, Três Bocas and Capibaribe Mirim, all located in Goiana, Pernambuco, in a region outstanding for its intense agroindustrial activity, coastal marine biome and areas of shrimp farming. These rivers supply the domestic, industrial and agricultural consumption of around 26 municipalities of the North region of the Zona da Mata in the state of Pernambuco, and has a population of 465,549. Twelve herbicides were investigated in the waters of the Goiana River using the ultra-efficient liquid chromatography technique coupled with triploquadrupole mass spectrometry (UPLC-MS/MS). The study was conducted from March to August 2019 and detected the presence of residues from the herbicides Ametryn, Atrazine, Diuron and Tebuthiuron during March, April and May, in concentrations ranging from 10 to 150 µg L-1. The results indicate the need to monitor surface water contamination, as current agricultural practices have an unprecedented impact on water quality and consequently on ecosystems and human health.

Keywords: Pesticides; Environmental Contamination; Surface Water; Sugarcane; UPLC-MS/MS.

Investigação da ocorrência de resíduos de herbicidas em rios da reserva extrativista Acaú-Goiana

exposição e a toxicidade desses agroquímicos. A cultura de cana-de-açúcar apresenta o maior consumo de herbicidas, ficando as margens de grandes bacias hidrográficas. Neste trabalho, foi investigada a ocorrência de herbicidas nas águas superficiais de três áreas de captação diferentes: Rio Tracunhaém, Três Bocas e Rio Capibaribe Mirim, todos localizados no município de Goiana, Pernambuco, em uma região que se destaca pela intensa atividade agroindustrial, pelo seu bioma marinho costeiro e por áreas destinadas à carcinicultura. Estes rios abastecem o consumo doméstico, industrial e agrícola de cerca de 26 municípios da Zona da Mata Norte de Pernambuco e apresenta uma população de 465.549 habitantes. Foram investigados 12 herbicidas nas águas do Rio Goiana, utilizando-se a técnica de cromatografia líquida de ultra eficiência acoplada à espectrometria de massa triploquadrupolo (UPLC-MS/MS). O estudo foi realizado nos meses de março a agosto de 2019 e detectou a presença de resíduos dos herbicidas Ametrina, Atrazina, Diurom e Tebutiurom nos meses de março, abril e maio, em concentrações que variaram de 10 a 150 µg L-1. Os resultados indicam a necessidade de realizar o monitoramento da contaminação de águas superficiais, uma vez que as práticas agrícolas atuais tem um impacto sem precedentes na qualidade da água e consequentemente nos ecossistemas e na saúde humana.

Palavras-chave: Pesticidas; Contaminação Ambiental; Água Superficial; Cana-de-açúcar; UPLC-MS/MS.

Topic: **Desenvolvimento, Sustentabilidade e Meio Ambiente**

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INTRODUCTION

Brazil is the world's largest consumer of pesticides, due to the extensive planting area across the country, increased food production and the improved quality of agricultural production. To maintain such production, this sector uses vast amounts of chemical inputs such as fertilizers and pesticides (PIGNATI et al., 2017).

Herbicides belong to the world's most consumed class of pesticide, of which glyphosate is the most widely used. In 2017, around 173,000 tons of glyphosate products were sold in Brazil (ANVISA, 2019). Herbicides may be dispersed into the environment due to rainfall runoff, since they inhibit photosynthesis in marine ecosystems, causing several ecotoxicological effects (MASTERS et al., 2013).

According to Pignati et al. (2017), sugarcane crops correspond to 38% of the planted area in the state of Pernambuco, thereby establishing itself as a crop with high herbicide application, increasing the contamination of surface water and groundwater.

The municipality of Goiana hosts large industries, such as blood products and automotive, and is a center for glass, cement and shrimp farming. In addition, the cultivation of sugarcane predominates within the region (ARAÚJO et al., 2016). Water resources are contained within a scenario of negative impacts from the sugar and alcohol plants, which dominate the region, and from the large surrounding industries (ARAÚJO et al., 2016).

Considering the importance of Resex Acaú-Goiana for both the local population and the environment, it is necessary to monitor herbicides in river waters, generating reliable data so that the competent agencies may assess the risks to the environment and human health. Thus, this study aims to investigate the occurrence of herbicides in surface waters of the Goiana River, originating from sugarcane cultivation at Resex.

MATERIALS AND METHODS

The Goiana River basin supplies 26 municipalities in the Pernambuco North Zona da Mata and is located on the border between the states of Pernambuco (PE) and Paraíba (PB), in the municipalities of Pitimbu (PB), Caaporã (PB) and Goiana (PE), as well as being part of the Acaú-Goiana Extractive Reserve (Resex), a protected area of the Chico Mendes Institute for Biodiversity Conservation (ICMBio/IBAMA).

In the present study, surface water samples were collected from three different catchment areas, the rivers: 1) Tracunhaém, 2) Capibaribe Mirim, and 3) Três Bocas (Figure 1).

The Tracunhaém and Capibaribe Mirim Rivers form the Goiana River, and their sources are, respectively, in the municipalities of Bom Jardim and São Vicente Férrer (CPRH, 2016), while the area called Três Bocas refers to the stretch of river where the surface waters of the Tracunhaém River and the Goiana watercourse meet.

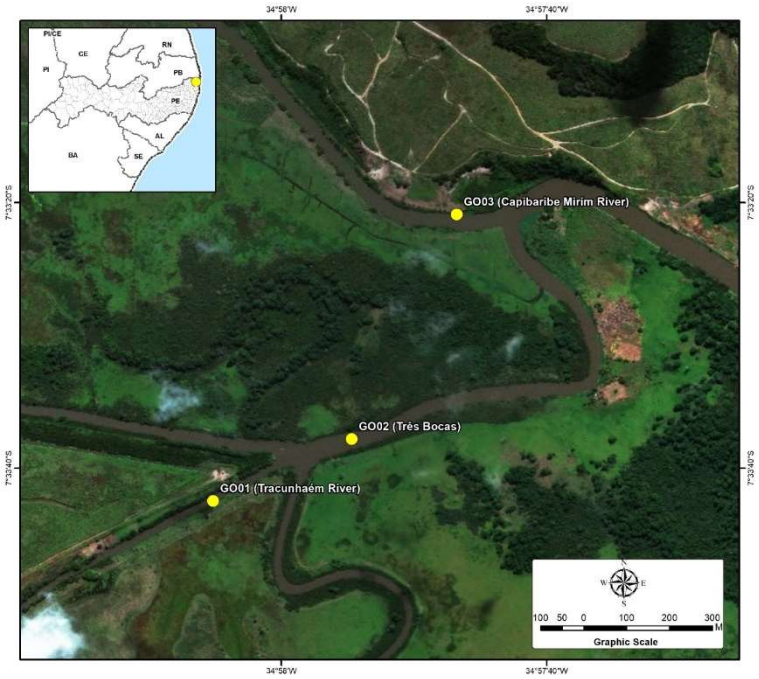

Figure 1: Map of surface water collection points on the Goiana River/PE.

These three collection points were adjusted to the Datum WGS84 geographic coordinate system (Table 1), selected for receiving agroindustrial, industrial and agricultural effluents from the region and to assess the occurrence of herbicides.

Table 1: Location of Goiana River water collection points, PE.

Collection points	Geographic coordinates	Reference
GO01 (Tracunhaém River)	L 7 33 42.480 N 34 58 5.160	Near the urban area of Goiana-PE
GO02 (Três Bocas)	L 7 33 37.800 N 34 57 54.720	Goiana watercourse
GO03 (Capibaribe Mirim River)	L 7 33 20.880 N 34 57 46.800	Near the sugarcane plantation

Water was collected from March to August (rainy months) 2019, with 36 samples obtained at each collection point, totaling 108 samples.

Water samples were collected at a depth of 50 cm, approximately one liter per sample, in plastic containers so as to avoid interaction with glass surfaces, and placed in Styrofoam boxes containing ice and then, taken to the Center for Pharmaceutical and Cosmetic Development (NUDFAC) at the Universidade Federal de Pernambuco.

The herbicides studied are widely used in sugarcane cultivation: Glysophate, AMPA, 2,4 D, Alachlor, Atrazine, Ametryn, Diuron, Tebuthiuron, Simazine, Metribuzim, Hexazinone e Sulfentrazone, all produced by Dr. Ehrenstorfer GmbH (Augsburg, Germany), except for AMPA, by Spex (CertiPrep, US).

In order to determine the herbicides in the Goiana River water samples, processing consisted of filtering 1 mL of the samples using a nylon filter (0.22 µm) and 1% acetic acid. The methodology employed in the analysis of herbicide residues was the ultra-efficient liquid chromatography technique coupled with triploquadrupole mass spectrometry (UPLC-MS/MS).

Initially, the analytical procedure was optimized and validated to evaluate the efficiency of the

method according to the analytical criteria (SANTE, 2017), such as obtaining the limits of detection, quantification, linearity and precision.

During optimization of the method, as well as the validation steps, the samples used as analytical control presented an absence of the investigated compounds, in order to assure reliability of the results and efficiency of the method through the recovery evaluation (accuracy and precision).

For the limits of detection (LOD) and quantification (LOQ) of the method, a mixture of herbicide standards with concentrations of 10 μg L^{-1} was used for UPLC-MS/MS. From 1 mg mL^{-1} stock solutions successive dilutions were prepared of the individual herbicides in methanol with 1% acetic acid.

Accuracy and recoveries were determined within two days by analyzing fortified blank samples (n = 6) at levels of 10, 25 and 50 μg L^{-1}. The LOD and LOQ of the method was experimentally estimated by injecting samples with decreasing concentrations and determined by analyte concentrations that provide a signal to noise ratio (S/N) of three and ten, respectively. In addition, a statistical analysis was performed using the statistical program Statistica®.

RESULTS AND DISCUSSION

The method for the determination of herbicides had a limit of detection (LOD) of 10 μg L^{-1} and a limit of quantification (LOQ) of 25 μg L^{-1} for the 12 compounds analyzed. The precision of the method for the compounds was estimated between 87.3 and 116.8%, and the precision between 1.8 and 14.8%. These values meet the acceptability range for recovery (70 and 120%) and accuracy (<20%) according to Sante (2017).

With regard to the period of application, it may be stated that herbicides are generally used during pre-emergence or post-emergence, and are effective against weeds. The main triazines are: Atrazine, Ametryn, Hexazinone, Simazine and Metribuzim, and its main action characteristics are apoplastic translocation. The mechanism of action of Alachlor is related to inhibiting protein synthesis and cell division. Glyphosate and AMPA inhibit amino acid synthesis. Sulfentrazone is a membrane distributor herbicide. 2,4 D is a plant growth regulating herbicide. Diuron and Tebuthiuron are photosynthesis-inhibiting herbicides (Table 2) (VICTORIA FILHO et al., 2004).

Table 2: Herbicides used in sugarcane cultivation.

Herbicides	Commercial name	Chemical group	Season of application
Gliphosate	Roundup	Glicina	Postemergence
AMPA	Roundup	Glicina	Postemergence
2,4 D	DMA BR	Ácido ariloxialcanóico	Post and Preemergence
Alachlor	Agimix	Cloroacetanilida	Preemergence
Atrazine	Gesaprim	Triazina	Post and Preemergence
Ametryn	Gesapax	Triazina	Post and Preemergence
Diuron	Karmex	Uréia	Post and Preemergence
Tebuthiuron	Combine	Uréia	Preemergence
Simazine	Gesatop	Triazina	Post and Preemergence
Metribuzim	Sencor	Triazinona	Post and Preemergence
Hexazinone	Velpar K	Triazinona	Post and Preemergence
Sulfentrazone	Boral	Triazolona	Preemergence

The herbicides Ametryn, Atrazine, Diuron and Tebuthiuron were detected in water samples collected

in the Goiana River from March to May. Studies conducted along the Jiménez River Basin, in Costa Rica and the Guadalquivir River, in Spain, confirm the results obtained due to herbicide contamination along the river banks affecting ecosystems (ECHEVERRÍA-SÁENZ et al., 2012; HERMOSIN et al., 2013).

Similar studies were reported by Azevedo et al. (2004), Paraíba do Sul River (RJ), where the herbicide Atrazine was detected at an average concentration of 0.231 µg L^{-1} in areas close to sugarcane fields, where the herbicide is widely used. Jacomini et al. (2010), evaluated the contamination of the Sapucaí, Pardo and Mogi-Guaçu Rivers and the presence of Ametryn in a concentration of 0.05 µg L^{-1}, near sugarcane cultivation sites.

In a study by Ferreira et al. (2016), in the Ipojuca River Basin, Pernambuco, Diuron and Ametryn were observed in the water samples, at levels ranging from 0.01 to 1.4 µg L^{-1}, with higher levels during the rainy season.

According to Britto et al. (2012), the presence of Diuron and Ametryn was reported in the Poxim River, in the state of Sergipe, during the rainy season, at levels ranging from 0.03 to 0.9 µg L^{-1} and 0.03 to 0.5 µg L^{-1}, respectively. Muendo et al. (2012), investigated the presence of Diuron in the waters of the Kuywa River, Kenya, near areas of sugarcane cultivation at levels ranging from 0.44 to 1.75 µg L^{-1} during heavy rainfall.

The highest level of Atrazine was observed in the area where collection point GO03 is located and the highest level of Diuron was observed in the area where collection point GO02 is located, thereby demonstrating significantly higher levels of these herbicides in the month of April.

Although the lack of seasonal variation was observed, the detected levels of Ametryn ranged from 10 to 60 µg L^{-1} (March-May/2019), Tebuthiuron levels ranged from 10 to 40 µg L^{-1} (March-May/2019), Diuron levels ranged on average from 10 to 140 µg L^{-1} (March-April/2019) and the Atrazine level was 150 µg L^{-1} (April/2019) (Figure 2).

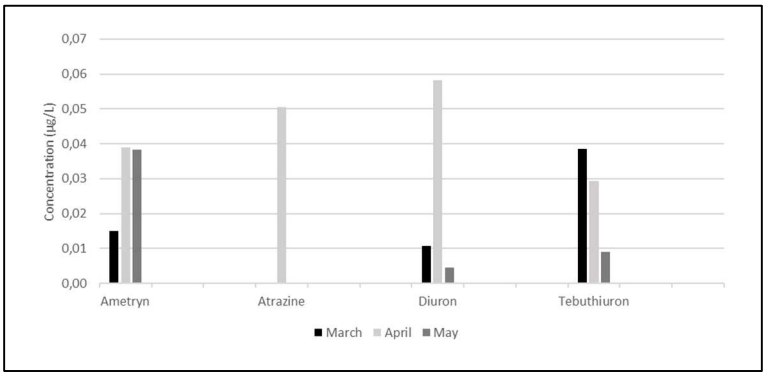

Figure 2: Variation of Ametryn, Atrazine, Diuron and Tebuthiuron concentrations in the waters of the Goiana River, PE, from March to May 2019

The occurrence of Atrazine, Ametryn, Diuron and Tebuthiuron in the Goiana River waters was more evident in the first months of sugarcane cultivation, during the region's rainy period. Corroborating the results obtained with the present study, Dores et al. (2001) reported that the concentration of pesticides in water is low due to the dilution effect and the fact that they are poorly soluble in water. However, there is a

possibility of high concentrations due to certain factors, such as pesticide application at high concentrations after heavy rainfall.

Given the above, the herbicides Ametryn, Atrazine, Diuron and Tebuthiuron are photosynthesis inhibitors, which are partially water soluble, whereby Atrazine is the most frequently used and the most frequently detected, because it has a broad spectrum of action, is selective and has a leaching power that is able to reach groundwater (ROMAN et al., 2005).

In the present study, we have observed the relationship between rainfall and the levels of pesticide detected in the water samples, with the highest concentration of Ametryn during the months of April and May and the highest concentration of Tebuthiuron in March and April, which may also be attributed to runoff and leaching capacity.

Given the exposure to reflexes involving climate change, the study conducted by Santos et al. (2013), observed that the months with the highest rainfall on the basin are: March, April, May, June, July, August and September and that the difference in runoff may be justified due to the availability of water in the second half of the year in relation to the first.

According to a study by Oliveira et al. (2013), the detection of herbicides in groundwater and surface water is due to their mobility and biodegradation in the water-soil system, in addition to the characteristics of organic matter.

In general, the higher the solubility of the molecules, the easier it is for the herbicide to be transported to the river courses. In tropical regions, the occurrence of rainfall at certain periods makes it possible for herbicides to be easily carried, thereby increasing the potential for environmental contamination (MARCHESAN et al., 2010).

However, based on the observed results, environmental monitoring is required to assess herbicide contamination in Goiana river waters due to their toxicity and high agricultural activity.

CONCLUSIONS

The results reported herein have demonstrated surface water contamination in samples collected in the three points: Tracunhaém, Três Bocas and Capibaribe Mirim. The herbicides Ametryn, Atrazine, Diuron and Tebuthiuron were detected due to their frequent use and their characteristics of mobility and persistence.

A higher contamination of Atrazine residues was observed in the Capibaribe Mirim River and Diuron in Três Bocas in April, while the lowest levels were observed during the rest of the period. However, contamination by Amethrin and Tebuthiuron was observed only from March to May, mainly related to this being the rainy season and the physical-chemical characteristics of the water. In the collection of samples from June to August, residues of the studied herbicides were no found.

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