Pesticide residues in the Formoso River: a threat to biodiversity in the Cerrado of the Tocantins State, Brazil

Resíduos de pesticidas no Rio Formoso: uma ameaça à biodiversidade no Cerrado do Estado do Tocantins, Brasil

Residuos de plaguicidas en el Río Formoso: una amenaza para la biodiversidad en el Cerrado del Estado de Tocantins, Brasil

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Patricia M. Guarda
ORCID: https://orcid.org/0000-0003-0937-6779
Federal University of Tocantins, Brazil
E-mail:patriciaguarda@uft.edu.br
Larissa da S. Gualberto
ORCID: https://orcid.org/0000-0002-7335-1771
Federal University of Tocantins, Brazil
E-mail:larissagualberto.eng@gmail.com
Danylo B. Mendes
ORCID: https://orcid.org/0000-0002-2115-9796
Federal University of Tocantins, Brazil
E-mail:danylo@uft.edu.br
Magale Karine Diel Rambo
ORCID: https://orcid.org/0000-0003-2529-9574
Federal University of Tocantins, Brazil
E-mail:magalerambo@uft.edu.br
Emerson A. Guarda
ORCID: https://orcid.org/0000-0003-0227-3881
Federal University of Tocantins, Brazil
E-mail:emersonprof@uft.edu.br
José Expedito Cavalcante da Silva
ORCID: https://orcid.org/0000-0002-8776-389X
Federal University of Alagoas, Brazil
E-mail:jose.silva@penedo.ufal.br

Abstract
Cerrado biodiversity has been threatened by the increase in agricultural production in the state of Tocantins and the increase in the use of pesticides. This work was carried out in the Formoso do Araguaia region, on the banks of the Formoso River, which is home to about 1,825 indigenous people and is one of the largest indigenous lands in the state of Tocantins, Brazil. The presence of pesticides of the imidazolinone and strobirulin classes was verified, analyzed by UHPLC-MS/MS from April 2018 to February 2019, to assess the impacts of these pesticides on the biodiversity of the study site. After the analyses, five active principles (azoxystrobin, phenamidone, imazethapyr, tricyclazole and trifloxystrobin) were detected in the water matrix, two active principles (azoxystrobin and tricyclazole) in the soil matrix, but no active principle was detected in the sediment matrix. Contamination in the region, where riverine and indigenous people use this water for cultivation, hygiene and food, which is worrying, are exposed to these substances.
Keywords: Pesticides; Water; Soil; Sediment; Tocantins.

Resumo
A biodiversidade do Cerrado tem sido ameaçada pelo aumento da produção agrícola no estado do Tocantins e pelo aumento do uso de agrotóxicos. Este trabalho foi realizado na região de Formoso do Araguaia, as margens do Rio Formoso, que abriga cerca de 1.825 indígenas e é uma das maiores terras indígenas do estado do Tocantins, Brasil. Foi verificada a presença de agrotóxicos das classes imidazolinonas e estrobirulinas, analisadas por UHPLC-MS/MS no período de abril de 2018 a fevereiro de 2019, para avaliação dos impactos desses agrotóxicos na biodiversidade do local de estudo. Após as análises, cinco princípios ativos (azoxistrobina, fenamidona, imazetapir, triciclazol e trifloxistrobina) foram detectados na matriz hídrica, dois princípios ativos (azoxistrobina e triciclazol) na matriz do solo, mas nenhum princípio ativo foi detectado na matriz sedimento. A contaminação na região, onde ribeirinho e

indígenas utilizam essa água para cultivo, higiene e alimentação, o que é preocupante, estão expostas a essas substâncias.
Palavras-chave: Agrotóxicos; Água; Solo; Sedimento; Tocantins.

Resumen
La biodiversidad del Cerrado se ha visto amenazada por el aumento de la producción agrícola en el estado de Tocantins y el aumento en el uso de pesticidas. Este trabajo se llevó a cabo en la región de Formoso do Araguaia, a orillas del río Formoso, que alberga a unos 1.825 indígenas y es una de las tierras indígenas más grandes del estado de Tocantins, Brasil. Se verificó la presencia de pesticidas de las clases imidazolinona y estrobirulina, analizados por UHPLC-MS/MS desde abril de 2018 hasta febrero de 2019, para evaluar los impactos de estos pesticidas en la biodiversidad del sitio de estudio. Tras los análisis, se detectaron cinco principios activos (azoxistrobina, fenamidona, imazetapir, triciclazol y trifloxistrobina) en la matriz de agua, dos principios activos (azoxistrobina y triciclazol) en la matriz del suelo, pero ningún principio activo se detectó en la matriz del sedimento. La contaminación en la región, donde ribereños e indígenas utilizan esta agua para cultivos, higiene y alimentación, lo cual es preocupante, están expuestos a estas sustancias.
Palabras clave: Plaguicidas; Agua; Suelo; Sedimento; Tocantins.

1. Introduction

The largest biodiversity on the planet is found in Brazil in six different biomes, namely the Amazon, Cerrado, Atlantic Forest, Caatinga, Pantanal, and Pampa (Magalhães, 2018). Each biome has different physical, chemical and biological characteristics according to soil, climate, vegetation, animals, and microorganisms. Biodiversity loss is one of the biggest threats to the global ecosystem, as it can change the functioning of biological processes, agricultural productivity and environmental sustainability (Monteiro, 2007). In this context, the conservation of these Brazilian biomes has been a matter of concern due to extinction threats mainly influenced by agricultural deforestation (Abujaile et al., 2011).

The growth of agriculture in the Cerrado of Tocantins also increases the number of foreign substances added to the environment, which reach the environmental compartments of water bodies in different ways. Such increase is not only in the amount used, but also in the variety of substances used for different types of crops. This poses a threat to all diversity still existing in these aquatic environments.

Some aspects have caused water quality problems in the main Tocantins watersheds, such as the lack of efficient planning of use of water resources, the disorderly advance of agricultural frontiers, industrial, urban and agricultural pollution, climate variability such as droughts, among others (SEPLAN, 2016). In addition, changes in the Cerrado resulting from land use due to agrarian development, characterized by the conversion of native areas into pastures and agricultural areas, may be affecting the different communities within this biome (Mesquita, 2011).

Biodiversity is supported by species diversity, genetic diversity and ecosystem diversity. This triad has been affected by physical pressures, degradation or loss of habitats, chemical pressures, the action of contaminants in the environment, biological pressures, introduction of exogenous substances, and/or trophic chain disruption, and elimination of key species in ecological communities (Alho, 2005). The frequency of exposure also affects the toxicity of chemical compounds. An acute exposure to a single concentration may result in an immediate adverse effect on an organism; two successive cumulative exposures equal to a single acute exposure may have little or no effects due to organism metabolism between exposures or organism acclimatization to the compound (Rand & Petrocelli, 1985).

The biological cycle of a pesticide includes bioconcentration in plants and animals, and incorporation into the food chain is by water or soil (Oliveira & Silva, 2013). Bioaccumulation is the process by which living beings absorb and retain substances in their organisms. Biomagnification is the increase in the concentration of a substance in organisms as the trophic level increases (Isherwood, 2000). This bioamplification of the concentration in the body tissues of organisms may reach concentrations above those of the environment in which these organisms inhabit (De Geronimo et al., 2014).

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Much of the territory of the state of Tocantins is located within the Cerrado biome (Carvalho et al., 2018). This biome comprises a set of ecosystems in Central Brazil. It has a large biodiversity of endemic species (Mesquita, 2011) and is the habitat of 160,000 species of animals, plants and fungi (Coba, 2012). However, the expansion of agricultural territory called MATOPIBA (Maranhão, Tocantins, Piauí, and Bahia) has decreased the native area of this biome and increased the conversion of natural into agricultural areas (Silva, 2012). Biodiversity is greatly affected by human activity and the relationship between it and the functioning of the ecosystem has become the focus of studies in recent decades (Zhang et al., 2017).

Only with scientific knowledge about the Cerrado can the reduction, loss, change or degradation of habitats strongly influenced by anthropic actions be avoided. These studies can propose actions that ensure the preservation of the biodiversity of this biome (Azevedo et al., 2016).

In the region of Formoso do Araguaia, it is home to around 1,825 indigenous people and is one of the largest indigenous territories in the state of Tocantins. According to Mattos et al. (2013), the region of the Indigenous Lands of Parque do Araguaia, shelter the Javaé, Karajá and Avá Canoeiro peoples, who use this water for cultivation, hygiene and food, which is worrying.

Considering the expansion of agriculture in the Legal Amazon region, growth of the planted area in Tocantins and in the Rio Formoso Agricultural Project and the increase in the use of pesticides, which accompanies the increase in the planted area, this study on the determination of pesticides of the classes imidazolinones and strobirulins was carried out in environmental compartments of Rio Formoso to verify the influence of the agricultural project on the contamination of this environment.

2. Methodology

According to Pereira et., (2018) the work methodology was calculated, since all numerical data were processed and processed, generating results. All tests in this study were performed in the laboratory and all bibliographic research was performed by narrative literature review.

The samples were collected at seven points of the Formoso River within the Rio Formoso Agricultural Project in Formoso do Araguaia, TO, Brazil. The choice of points focused on verifying the influence of the project on river contamination. A point was selected on the river before it passed the agricultural project (P1), five points along the project (P2 to P6), and one point after the project (P7), as shown in Figure 1. The four campaigns were held in April (Campaign 1-C1) in the rainy season, July (Campaign 2- C2), October (Campaign 3- C3), conducted in the dry season of 2018, and February 2019 (Campaign 4- C4) in the rainy season. Monitoring was carried out from February 2018 to October 2019.

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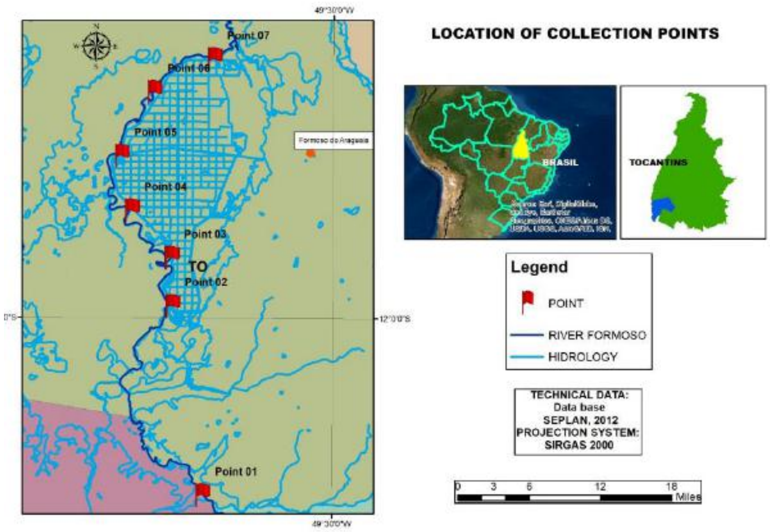
Figure 1. Image with sample area and collection points.



Source: SEPLAN (2012).

The rainfall conditions on the days of collection were 11.4 mm in C1, 0 mm in C2 and C3, and 0.6 mm in C4. The depth of the river reflects these climatic conditions. Only two points (P1 and P5) have depth data, as they have real-time monitoring. In C1, 830 cm in P1 and 650 cm in P5; in C2, 275 cm in P1 and 183 cm in P5; in C3, 233 cm in P1 and 158 cm in P5; and in C4, 413 cm in P1 and 249 cm in P5 (SEMARH, 2017; SEMARH, 2018a; SEMARH, 2018b; SEMARH, 2018c; SEMARH, 2018d).

The collection period for each campaign lasted 48 hours. The collection was carried out by boat following the same collection time in each point. The rainy season sampling was carried out without strong rains.

Although it is known that the active ingredients selected in this work may not be those most used in the studied region, the selection of pesticides was due to data availability, since an inventory of substances used was not carried out in the studied region. Data on the use and sales of products in the region were not obtained from regulatory agencies. The state of Tocantins, as many states in Brazil, does not have a database on substances used.

Pesticides were analyzed by a UHPLC-MS/MS from Waters (USA), namely imazamoxy, imazapyr, imazapic, imazethapyr, imazaquin, phenimidone, azoxystrobinam methyl cremoxim, piraclostrobin, trifloxystribin, and tricyclazole (Kemmerich, 2017). For the analysis of the pesticides, soil, sediment and water, samples were collected and stored according to Filizola et al. (2016) and CETESB (2011) and analyzed within 48 hours after collection.

For soil samples, approximately 2 kg of the surface layer were collected up to 20 cm deep, 5 to 10 m from the riverbank, in a composite sampling. For sediment samples, approximately 2 kg of the surface layer were collected 5 to 10 m from the riverbank, in a composite sampling, with a modified Petersen stainless steel collector. Water samples were collected from the surface of the water body 5 to 10 m from the riverbank due to a large difference in river depth at different collection times. Simple sampling was performed, and samples were packed in 500-mL amber flasks.

Sediment and soil samples were prepared for extraction analysis using the modified QuEChERS method. The method used acidified acetonitrile as extraction solvent; for the partition step, the salts used were magnesium sulfate and sodium chloride. The extracts were cleaned by dispersive solid phase extraction (d-SPE). For the d-SPE step, magnesium sulfate and octadecylsilane (C18) and secondary primary amine (PSA) solvents were used. The extracts were then stirred, centrifuged and filtered. Prior to UHPLC-MS/MS analysis, samples were diluted five times in ultrapure water (Prestes, 2009).

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For pesticide analysis in water samples, a solid phase extraction (SPE) was performed. For the SPE procedure, Oasis® HLB cartridges were used, 100 mL of sample were percolated and eluted with the acidified mixture MeOH:MeCN (1:1, v/v). Before chromatographic injection, samples were diluted twice in ultrapure water (Donato, 2015).

The analyses were performed by ultra-high performance liquid chromatography coupled with a UHPLC-MS/MS serial mass spectrometry equipped with liquid chromatograph; triple quadrupole MS detector, Xevo TQ; electrospray ionization interface/source; peak nitrogen generator; solvent controller system (binary pump system) for high pressure gradient operation; Acquity UPLC® BEH C18 analytical column (50 × 2.1 mm, 1.7 µm) manufactured by Waters (USA); and data acquisition system using the *MassLynx* 4.1 software (Waters, USA). The monitoring of selected reactions was used for quantification and identification of analytes. The mobile phase was (A) water: methanol (98:2, v/v) and (B) methanol, both containing 5 mmol L^{-1} of ammonium formate and 0.1% formic acid (v/v); flow rate of 0.225 mL min^{-1} and 10 µL injection volume. A gradient elution mode [time (min), %A, %B] was used: [0.95, 5], [0.25, 95, 5], [7.75, 5, 95], [8.5, 5, 95], [8.51, 95, 5], [10, 95, 5], respectively (Kemmerich, 2017).

The calibration curves were prepared in the solvent and in the white extract of the matrix with adequate linearity and coefficient of determination values greater than 0.99.

The limit of quantification (LOQ) and limit of detection (LOD) for water analysis with satisfactory precision, recovery between 70 and 110 %, and relative standard deviations below 19.7 %. For soil and sediment analyses, the recovery values were between 70 and 120 %, the relative standard deviations below 20 %. The limit of quantification (LOQ) and limit of detection (LOD) are described in the discussion section.

In each analysis, analytical quality control of the method was performed, who obtained different LOD and LOQ depending on the collection campaign and the active ingredient analyzed.

3. Results and Discussion

After the monitoring study for a period of one year, the ingredients found are shown in Table 1 below.

Table 1 - Pesticides detected and/or quantified and not detected in the study.

Pesticides detected and/or quantified	**Pesticides not detected**
Azoxystrobinam, Phenimidone, Tricyclasol, Trifloxystribin, Imazethapyr	Methyl Cremoxim, Imazamoxy, Imazapic, Imazapyr, Imazaquin, Piraclostrobin,

Source: Authors.

After analysis of sediment samples, all results found were below the limits of detection (LOD) and the limits of quantification (LOQ), thus considering that the active principles were not present in the sediment samples.

In the soil, only the active principles azoxystrobin and tricyclazole were found with values below the LOQ of the method, which was 0.008 mg Kg^{-1}.

In campaigns C2 and C3, at points P5 and P4, azoxystrobin was found. Tricyclazole was found in C3 at P4 and P5, and in C4 at P5, according to table 2. At these points, there was no riparian forest protecting the Formoso riverbed, which may be one of the factors that led to contamination. For all active principles in soil analysis, the LOD and LOQ values of the method were 0.003 mg Kg^{-1} and 0.008 mg Kg^{-1}, respectively, for all pesticides studied, except for methyl cremoxim, which had values of 0.010 and 0.033 mg Kg^{-1}, respectively, in C2. There is no legislation in Brazil establishing levels of pesticide contamination in the soil.

Table 2 - Pesticides detected in the soil, in the different sampled points and in different sampling campaigns.

	Campaign 1	Campaign 2	Campaign 3	Campaign 4
P4			azoxystrobinam, tricyclasol* (<LOQ)	
P5		Azoxystrobinam*(<LOQ)	Tricyclasol* (<LOQ)	Tricyclasol* (<LOQ)

*LOD 0,003 mg $Kg^{-}1$ and LOQ 0.008 mg Kg^{-1}. Source: Authors.

Some active ingredients were not detected in the water: imazamoxy, imazapic, imazapyr, imazaquin, cremoxim methyl, and piraclostrobina.

For all active principles in waters analysis, the LOD and LOQ values of the method were 0.006 µg L^{-1} and 0.020 µg L^{-1}, respectively, except for methyl cremoxim, imazapir and imazamoxi, which had values of 0.012 µg L^{-1} and 0.040 µg L^{-1}, respectively, in C2, as can be seen in Table 3

Table 3 - Pesticides detected and/or quantified in the water, in the different sampling points and in different sampling campaigns.

	Campaign 1	Campaign 2	Campaign 3	Campaign 4
P1			Azoxystrobin (<LOQ) Phenimidone (<LOQ) Tricyclasol (<LOQ) Trifloxystribin (<LOQ)	
P2			Azoxystrobin (<LOQ) Phenimidone (<LOQ) Trifloxystribin (<LOQ)	
P3			Trifloxystribin (<LOQ)	Tricyclasol (<LOQ)
P4	Tricyclasol (<LOQ)		Trifloxystribin (<LOQ) Imazethapyr (0,021 µg L^{-1})	Tricyclasol (<LOQ)
P5	Tricyclasol (<LOQ)		Tricyclasol (<LOQ) Trifloxystribin (<LOQ)	
P6	Tricyclasol (<LOQ)		Tricyclasol (<LOQ) Trifloxystribin (<LOQ)	Tricyclasol (0,022 µg L^{-1})
P7	Tricyclasol (<LOQ)		Tricyclasol (<LOQ)	Tricyclasol (<LOQ)

LOD 0,006 µg L^{-1} and LOQ 0.020 µg L^{-1}. Source: Authors.

In C1, which was performed at the end of the region's rainy season, only tricyclasol was found from P4 to P7, with a value below the LOQ of the methods (0.020 µg L^{-1}), indicating that contamination arises in the river when it passes along the margin of the agricultural project.

The C3 was performed in the dry season in the region. In this campaign, at P1 and P2, a lower concentration than the LOQ of the method was found for fenamidone and azoxystrobin. The contamination by these active ingredients were already detected at P1 before the river passed along the agricultural project, indicating that contamination by these substances occurs even before its influence. By evaluating the results for these substances, we found that they dilute along the river and are no longer detected from P3.

At P5 and P6, tricyclazole and trifloxystrobin were found; at P7, tricyclazole had values lower than the LOQ. Contamination by these active principles arises within the agricultural project and continues until the river passes along it. Tricyclazole contamination remained in the C4 at P4, P5 and P7 (concentration lower than LOQ). In this campaign, it was quantified with a concentration of 0.022 µg L^{-1} at P6. Contamination by these substances is constant in the Formoso River if we consider the region studied and arise within the agricultural project.

The imazethapyr was quantified in C3 at P4 with a concentration of 0.021 µg L^{-1}. After analyzing all data, the most critical points of contamination are from P4 because they are points where most of the active ingredients were found, both in water and on the riverbank soil, in most campaigns. The Formoso River, when passing the margin of the agricultural project, is being impacted by it.

After the study, the dry season in the region where the river is lower is the most critical period for threat to biodiversity.

In total, five active ingredients were found in water, namely tricyclazole, trifloxystrobin, imazethapyr, fenamidone and azoxystrobin.

Tricyclazole is currently one of the fungicides recommended for the treatment of diseases in irrigated rice. Wandscheer et al, (2017) indicates that the application of the tricyclazole fungicide leads to an increase in the genotoxic activity in the rice crop water, through the appearance of chromosomal abnormalities. This substance appears to have adversely effects on reproductive tissues and hormone levels (Fattahi, 2015).

Reimche et al. (2015) in study of the imazethapyr in zooplankton community, show that there is a selecrive impact on zooplankton community. Overall, the herbicide caused a rapid stimulation of cladocers, copepods and copepod (nauplius) population. On the other hand, rotifer population decreased, with recovery at the end of the experimental period.

All detected substances are authorized for use in Brazil. Tricyclazole and imazethapyr are not authorized in the European Union and are classified as with a medium to high toxicity. Despite the common occurrence of pesticide mixtures, legislation generally assesses the risk of a substance individually, but all compounds can contribute to the toxicity of the overall mixture even if they occur individually at concentrations that are not harmful to freshwater biota (Di Lorenzo et al., 2018).

While some active ingredients were not detected in the monitoring period and others were not found in all campaigns, this sporadic detection does not indicate that these substances are not contaminating the water body, as the detection of pesticides in natural environments (uncontrolled) is difficult because several dynamic processes are involved in these environments (dilution, dispersion, decomposition, hydrolysis, photolysis) (Calheiros et al., 2018).

The mobility and persistence of pesticides in the environment are related to water runoff intensity, rainfall and environmental temperature (Azevedo et al., 2016). The effects of dilution and low solubility of pesticides in water are responsible for their low concentration. However, after heavy rainfalls, high concentrations may occur when high doses have been applied (Dores and Lamonica, 2001). The Table 4 presents some physicochemical, environmental and contamination properties of the pesticides found in the region.

Table 4 - Identification, classification, physical chemical properties and potential for contamination of pesticides found in the water of the Rio Formoso.

Identification	Physical Chemical Property	Environmental behavior	Contamination potential
AZOXISTROBINA $C_{22}H_{17}N_3O_5$ Nº CAS 13860-33-8 (strobirulin) Fungicide	Sol_W: 6.7 mg L^{-1} Log K_{ow}: 2.5 K_{oc}: 589 KH: 7.4x10^{-9}Pa m^3 mol^{-1} $T_{1/2\ water}$: estável $T_{1/2\ soil}$: 78 days $T_{1/2\ sediment}$: 205 days	Low water solubility Low bioaccumulation Moderately .mobile on the ground non volatile persistent in water Moderate persistence in soil Slow degradation in the sediment	GUS: (2.532) Leaching Potential EPA: Contaminant Potential Both: Contaminant Potential GOSS $_{sediment}$: Medium GOSS $_{Dissolved}$: High
FENIMIDONA $C_{17}H_{17}N_3O_5$ Nº CAS 161326-34-7 (imidazolinone) Fungicide	Sol_W:7.8 mg L^{-1} Log K_{ow}: 2.8 KH: 5.0x10^{-6} Pa m^3 mol^{-1} $T_{1/2\ water}$: 411 days $T_{1/2\ soil}$: 6.9 days $T_{1/2\ sediment}$: 97 days	Low water solubility Moderate Bioaccumulation mobile on the ground non volatile persistent in water Not persistent in soil Moderate degradation in sediment	GUS: (1.28) No leaching EPA: Inconclusive Both: Inconclusive GOSS sediment: Inconclusive Calculated GOSS: Inconclusive
IMAZETAPIR $C_{13}H_{15}N_3O_3$ 81334-34-1 (imidazolinone) Herbicide	Sol_W:9740 mg L^{-1} Log K_{ow}: 0.11 K_{oc}: 30 KH: 3.0x10^{-7}Pa m^3 mol^{-1} $T_{1/2\ water}$: 180 days $T_{1/2\ soil}$: 79 days $T_{1/2\ sediment}$: 2 days	High solubility in water Low bioaccumulation mobile on the ground moderate volatility persistent in water Moderately persistent in soil Rapid degradation in the sediment	GUS: (3.65) Leaching Potential EPA: Contaminant Potential Both: Contaminant Potential GOSS $_{sediment}$: Medium GOSS $_{Dissolved}$: High
TRICICLASOL $C_9H_7N_3S$ Nº CAS 41814-78-2 (Benzimidazol) Fungicide	Sol_W: 596 mg L^{-1} Log K_{ow}: 1.4 K_{oc}: 169 KH: 5.86x10^{-7} Pa m^3 mol^{-1} $T_{1/2\ water}$: Estável $T_{1/2\ soil}$: 450 days $T_{1/2\ sediment}$: 453 days	Moderate water solubility Low bioaccumulation Moderately mobile on the ground non volatile persistent in water persistent in soil stable in sediment	GUS: (3.89) Potential Contamination EPA: NE Both: NE GOSS $_{sediment}$: NE GOSS $_{Dissolved}$: NE
TRIFLOXISTROBINA $C_{20}H_{19}F_3N_2O_4$ Nº CAS 141517-21-4 (strobirulin) Fungicide	Sol_W: 0.61 mg L^{-1} Log K_{ow}: 4.5 K_{oc}: 2377 KH: 2.3x10^{-3} Pa m^3 mol^{-1} $T_{1/2\ water}$: 40 days $T_{1/2\ soil}$: 7 days $T_{1/2\ sediment}$: 2.4 days	Low water solubility High bioaccumulation Slightly mobile on the ground non volatile Moderately persistent in water Not persistent in soil Rapid degradation in the sediment	GUS: (0.15) No leaching EPA: Non Contaminant Both: Not Contaminant GOSS $_{sediment}$: Medium GOSS $_{Dissolved}$: Medium

SolW – water solubility at 20°C, Log Kow – octanol partition coefficient water at pH 7 and 20°C, Koc- adsorption coefficient, KH- Henry's constant at 25°C, T1/2 water- hydrolysis half-life in water at pH 7 and 20°C, T1/2 soil – half-life in soil, T1/2- half-life water/sediment, environmental toxicology- ANVISA, NE- not found. Source: Adapted from MARTINI et al 2012; GAMA et al, 2013; PPDB, 2020

Although pesticide residue concentrations are often low and within the values recommended by aquatic life and human safety legislation, there are two mechanisms of pesticide absorption within aquatic ecosystems, i.e., bioaccumulation and biomagnification, which increase their toxic potential (Upadhi and Wokoma, 2012). The effects of an active ingredient may also be potentiated in the presence of others synergistically. Studies on this and on the cumulative effects of pesticides are limited (Calheiros et al., 2018).

In Table 5, we can see that trifloxystrobin, due to its high toxicity for algae, trifloxystrobin for fish, imazethapyr and, for aquatic plants, trifloxystrobin for aquatic invertebrates, while azoxystrobin, presents a high ecotoxicological risk for aquatic crustaceans.

Table 5 - Ecotoxicity of pesticides found in the monitoring of the Formoso River.

Identification	Effective and lethal concentration	Ecotoxicity
AZOXYSTROBIN	Algae EC_{50} 0.36 mg L^{-1}	Moderate
	Fish LC_{50} 0.47 mg L^{-1}	Moderate
	Aquatic plants EC_{50} 3.2 mg L^{-1}	Moderate
	Aquatic invertebrates 0.23 mg L^{-1}	Moderate
	Aquatic crustaceans LC_{50} 0.055 mg L^{-1}	High
FENAMIDONE	Algae CE_{50} 3.84 mg L^{-1}	Moderate
	Fish LC_{50} 0.74 mg L^{-1}	Moderate
	Aquatic plants EC_{50} 0.88 mg L^{-1}	Moderate
	Aquatic invertebrates 0.19 mg L^{-1}	Moderate
	Aquatic Crustaceans CL_{50}	-
TRICYCLASOL	Algae CE_{50} 8.2 mg L^{-1}	Moderate
	Fish LC_{50} 7.3 mg L^{-1}	Moderate
	Aquatic plants CE50 -	-
	Aquatic invertebrates 34 mg L^{-1}	Moderate
	Aquatic Crustaceans CL_{50} -	-
TRIFLOXYSTROBIN	Algae EC_{50} 0.0053 mg L^{-1}	High
	Fish LC_{50} 0.022 mg L^{-1}	High
	Aquatic plants EC_{50} 1.93 mg L^{-1}	Moderate
	Aquatic invertebrates 0.011 mg L^{-1}	High
	Aquatic Crustaceans CL_{50} -	-

Algae EC_{50} (72h), Fish LC_{50} (96h), Aquatic plants EC_{50} (7 days), Aquatic Invertebrates EC_{50} (48h), Aquatic Crustaceans LC_{50} (96h), Sediment-living animals LC_{50} (96h). Source: PPDB (2020).

When we have mixtures of toxic substances, additive effects can be verified, when the toxicity of the mixture is equal to the sum of the individual toxicities of each substance alone, or synergistic effect, when the toxicity of the mixture is greater than the sum of the toxicities of the substances alone (Costa et al, 2008).

The occurrence of these effects will depend on the type of mixture, as well as on the mode of interaction between the components of the mixture.

There are not many studies to compare with this work on the quantification of pesticides in different environmental compartments in the northern region of Brazil, more specifically in the Cerrado of Tocantins.

Guarda et al. (2020a, 2020b, 2020c), detect the presence of pesticides of the class of carbamates, environmental, of the different classes of carbamates, benzimidazoles, among others in the region, therefore, studies in the state are numerous.

The availability of existing information is greater for other regions, although still scarce. They report on places with biomes different from those of this study. The lack of information on quantitative data can be justified by the fact that there is no analytical infrastructure in the state of Tocantins to determine the levels of these substances, in addition to the logistics for sending samples to other regions. This is a difficulty for studies conducted in Tocantins.

4. Conclusion

Thus, according to the results, it is evident that the threat to the biodiversity of the Tocantins Cerrado is increasing every day. This is because, after the study, two contaminated environmental compartments (soil and water) were found, with five substances of medium to high toxicological classes.

The degradation of the Cerrado biome is threatened by the agricultural expansion of the studied region. This concern increases as indigenous peoples who live in the region and feed on the resources of this river may be exposed to these substances.

Therefore, it is necessary that the monitoring continues, increasing the number of substances analyzed, and studies on the toxicity of these substances in the different types of organisms that inhabit the different environmental compartments of the Rio Formoso.

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