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THAÍS PAULA MARTINS NUNES

CONCENTRATION AND DISTRIBUTION OF PESTICIDES, ELEMENTS, AND PHYSICOCHEMICAL PARAMETERS IN THE SURFACE WATERS OF THE URUÇUÍ PRETO RIVER DURING A COMPLETE HYDROLOGICAL CYCLE

Bom Jesus – PI
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Doctoral thesis submitted to the Graduate Program in Agricultural Sciences - PPGCA, Professora Cinobelina Elvas *Campus* - CPCE, Federal University of Piauí - UFPI, in the area of concentration Soil Science, as a requirement for the degree of Doctor of Agricultural Sciences.

Advisor: Prof. Dr. Cácio Luiz Boechat
Co-advisor: Prof. Dr. Ozeas da Silva Costa Junior

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To my son, who, even in the moments when I was absent, was my greatest strength and inspiration. Every step of this journey was for you and because of you

Dedicated.

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God is good all the time; all the time, God is good.

ABSTRACT

The increasing intensification of agricultural activities has directly influenced the processes that regulate the quality of water resources, especially in basins subject to agricultural expansion. In the Cerrado of Piauí, within the MATOPIBA region, agricultural expansion is a key factor in understanding the dynamics that affect the quality of surface waters, since management practices can alter the natural concentrations of elements and favor the presence of pesticide residues in aquatic ecosystems. In this context, this study aimed to evaluate the spatial and temporal distribution of pesticide compounds and chemical elements in the surface waters of the Uruçuí Preto River basin, considering the influence of seasonality and land use and land cover. Water samples were collected at 10 points for pesticide analysis over four representative months (February, March, April, and August) and at 19 points for the determination of physicochemical variables and elements between January and December 2021. Pesticides were determined by Solid-Phase Microextraction (SPME) and Liquid Chromatography coupled with Mass Spectrometry (LC-MS/MS), whereas Ca, Mg, P, K, Mn, Zn, Fe, and Cu were determined by atomic absorption spectrometry. The results showed the detection of different chemical groups of pesticides, with emphasis on Clomazone, which was present at all sampling points in August, a period characterized by drought. This suggests that dry-season conditions favor the concentration and persistence of residues in water bodies. In the rainy months, lower concentrations of the compounds were observed, although some molecules remained detectable. For the elements, precipitation played a determining role in their concentrations, reinforcing the influence of seasonality on elemental transport, dilution, and input processes. Canonical correlation analysis demonstrated that different land-use classes, especially agricultural areas and pastures, were associated with the observed chemical variations, although, overall, water quality was not significantly compromised during the evaluated period. The results highlight the influence of anthropogenic activities and show that both the occurrence of pesticides and the hydrogeochemical variability reflect the interaction between agricultural management practices and precipitation. Therefore, continuous monitoring, combined with the adoption of environmentally conscious land-use practices, is essential to mitigate potential environmental impacts and ensure the maintenance of water quality in river basins subject to rapid agricultural expansion.

Keywords: Agricultural expansion, Land use, Land cover, Pesticides, Water quality.

RESUMO

A crescente intensificação das atividades agropecuárias tem exercido influência direta sobre os processos que regulam a qualidade dos recursos hídricos, especialmente em bacias sujeitas à expansão agrícola. No Cerrado piauiense, na região MATOPIBA, o avanço da agricultura constitui um fator determinante na compreensão das dinâmicas que afetam a qualidade das águas superficiais, uma vez que práticas de manejo podem alterar as concentrações naturais de elementos e favorecer a presença de resíduos de pesticidas nos ecossistemas aquáticos. Nesse contexto, objetivou-se avaliar a distribuição espacial e temporal de compostos de pesticidas e elementos químicos nas águas superficiais da bacia hidrográfica do rio Uruçuí Preto, considerando a influência da sazonalidade e do uso e ocupação do solo. Foram realizadas coletas de água em 10 pontos para análise de pesticidas ao longo de quatro meses representativos (fevereiro, março, abril e agosto) e em 19 pontos para determinação de variáveis físico-químicas e elementos entre janeiro e dezembro de 2021. Os pesticidas foram determinados por Microextração em Fase Sólida (SPME) e Cromatografia Líquida acoplada à Espectrometria de Massas (LC-MS/MS), enquanto Ca, Mg, P, K, Mn, Zn, Fe, Cu, foram determinados por espectrometria de absorção atômica. Os resultados evidenciaram a detecção de diferentes grupos químicos de pesticidas, com destaque para o Clomazone, presente em todos os pontos de coleta no mês de agosto, período caracterizado pela seca, sugerindo que condições de estiagem favorecem a concentração e persistência de resíduos nos corpos hídricos. Nos meses chuvosos, observou-se menor concentração dos compostos, embora algumas moléculas continuassem detectáveis. E para os elementos, verificou-se que a precipitação exerce papel determinante em suas concentrações, reforçando a influência da sazonalidade sobre processos de transporte, diluição e aporte de elementos. A análise de correlação canônica demonstrou que diferentes classes de uso da terra, especialmente áreas agrícolas e pastagens, estão associadas às variações químicas observadas, ainda que, de modo geral, a qualidade da água não tenha sido significativamente comprometida ao longo do período avaliado. Os resultados revelam a influência das atividades antrópicas e demonstram que tanto a ocorrência de pesticidas quanto a variabilidade hidrogeoquímica refletem a interação entre práticas de manejo agrícola e precipitação. Portanto, o monitoramento contínuo, aliado à adoção de práticas conscientes de uso do solo, é fundamental para mitigar potenciais impactos ambientais e assegurar a manutenção da qualidade da água em bacias hidrográficas sujeitas à rápida expansão agrícola.

Palavras-chave: Expansão agrícola, Ocupação do solo, Pesticidas, Qualidade da água, Uso do solo.

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1 GENERAL INTRODUCTION

Monitoring water quality is essential for understanding the complex dynamics of aquatic ecosystems, assessing the impact of human activities on these systems, and ensuring the use of water resources for drinking, recreation, and transportation (Coraggio *et al*., 2022). Estimates indicate that by 2050 the global demand for water will increase by 20–30% across all sectors, and part of the population may lack access to clean water (Baggio; Qadir; Smakhtin, 2021). This scenario results from the growing demand for water, declining water availability, and increasing pollution levels, driven by population and economic growth (Capoane *et al*., 2014).

Certain land-use practices can contribute significantly to the degradation of aquatic ecosystems. These practices are primarily associated with the demand for food production, livestock, and urban expansion. When such activities occur near aquatic ecosystems, they can negatively affect water quality by increasing the input of nutrients, metals, organic pollutants, pharmaceuticals, and hormones into water bodies (Frascareli *et al*., 2015; Daripa *et al*., 2022; Krithiga *et al*., 2022; Chaturvedi *et al*., 2021; Ojoghoro; Scrimshaw; Sumpter, 2021).

Agricultural activity can also contribute to the introduction of agrochemicals into aquatic environments. Although agriculture is essential for human survival, especially as population growth demands increasingly higher food production, the use of chemical products to control diseases, pests, and weeds becomes necessary to achieve significant yields (Souza *et al*., 2020). These compounds may reach environments other than their target organisms, including the atmosphere, soil, and surface and groundwater, through runoff, leaching, and spray drift (Meftaul *et al*., 2020).

Studies on aerial drift resulting from pesticide application in crop fields indicate that up to 10% of all applied products may disperse into the environment (Tudi *et al*., 2021). These losses may increase when rainfall occurs shortly after application, and the presence of these compounds can have adverse effects depending on their concentration and exposure time (Guo *et al*., 2023).

The Uruçuí Preto River basin is located within the last agricultural frontier in Brazil, which is notable for the expansion of grain cultivation, livestock, and cotton production in Cerrado areas—one of the main economic activities in northeastern Brazil (Silva *et al*., 2021). The hypothesis of the present study is that the surface waters of the Uruçuí Preto River basin have been impacted by land use and management practices, resulting in increased concentrations of chemical elements and the presence of pesticides. Therefore, the objective of this study was to determine the spatial and temporal distribution of pesticides in surface waters

during the dry and rainy seasons in the Uruçuí Preto River Sub-basin (PI), and to characterize the spatial and temporal elemental distribution throughout an entire hydrological cycle in the surface waters of the Uruçuí Preto River**.**

2 EXPERIMENTAL STRATEGY

To achieve the objectives of this study, the research was conducted in three consecutive and interdependent stages: the first corresponding to pre-field planning, the second to field sampling activities, and the third to laboratory analyses.

In the first stage, the study area was defined as the Uruçuí Preto River basin (PI), selected due to changes observed in land use and land cover over recent decades. This was followed by the establishment of 19 sampling points for the analysis of chemical elements and 10 points for pesticide analyses. The selection of sampling sites considered factors such as the inflow of water into the main stem from its tributaries and the presence of bridges that allowed for safe access to collect samples from the central portion of the river.

The second stage began in January 2021 with water sampling. In each campaign, specific containers were used to separate the portions of water destined for physicochemical, elemental, and pesticide analyses. The samples were stored in thermal boxes throughout the sampling process to preserve their original properties. Some physicochemical parameters were measured directly in the field using portable equipment.

The third stage was carried out after returning from each field excursion. The analyses of chemical elements were performed at the laboratory of the Federal University of Piauí (UFPI), whereas pesticide analyses were conducted at the Pesticide Residue Analysis Laboratory (LARP) of the Department of Chemistry at the Federal University of Santa Maria (UFSM).

3 CHAPTER 1

THEORETICAL REFERENCE

3.1 Northeastern Cerrado

Historically, the lands of the Cerrado were considered unsuitable for agricultural and livestock production, since the natural soil conditions, including the relief, which is characterized by flat or gently undulating, indicated nutrient-poor and acidic soils (Silva *et al*., 2023). However, with the development of agronomic research conducted in the region, technologies capable of correcting soil acidity and establishing adequate fertilization levels were made available, among other advances, making it possible to exploit the agricultural potential of this phytogeographic domain (Frederico *et al*., 2024).

The historical processes of occupation of these areas are not recent; beginning in the 1970s, the first public-sector investments were allocated to the northeastern economy (Canedo *et al*., 2020), promoting agricultural development and identifying Cerrado areas with favorable characteristics for cultivating various species (Rodrigues *et al*., 2021). With the discovery of the agricultural potential of the Cerrado and the arrival of farmers, landowners, and producers, new crops such as soybean, sunflower, castor bean, cassava, maize, and other monocultures were introduced, fostering growing urbanization in nearby towns and increasing employment opportunities (Silva *et al*., 2023).

The Cerrado areas of Piauí cover 8.5 million hectares, representing approximately 30% of the total Brazilian Cerrado (Albuquerque; Zucherato, 2023). Considering that the state of Piauí is one of the last agricultural frontiers in Brazil, it is essential to adopt conservationist management systems to prevent soil, water, and nutrient losses (Frederico *et al*., 2024). This region, located within the Northeastern Cerrado, follows the increasing expansion of agricultural activity, which has driven the advancement of agricultural frontiers in the state. Consequently, the region known as MATOPIBA—an acronym formed from the states of Maranhão, Tocantins, Piauí, and Bahia—has emerged, where agricultural production is rapidly expanding (Agostinho *et al*., 2023).

The region stands out in Brazil's agricultural sector as one of the country's major agricultural frontiers. Its topographic characteristics, deep soils, and climate favorable to the cultivation of various crops have enabled its growth, making it a significant agricultural producer (Nepomoceno; Carniatto, 2022). The occupation and use of Cerrado soils has been

justified by the depletion of agricultural lands in other regions of the country, along with lower land prices in the region. As a result, the southern region of Piauí has undergone an accelerated process of land occupation driven by agricultural and livestock activities (Rocha; Nascimento, 2021).

With the rapid expansion of agriculture, there has been an increasing need for soil amendments, fertilizers, and pesticides in an effort to improve soil quality in the Cerrado and increase crop productivity. However, some of these agricultural inputs do not reach only the intended areas; due to their mobility, they may be transported to a variety of environments, including aquatic systems.

3.2 Fresh surface water

Water is a natural resource of great importance and necessity for all human activities (Jayalakshmi; Saritha; Dwarapureddi, 2017; Mishra, 2023b). For human consumption and for meeting essential needs, water must be of high quality, that is, pure and safe, free from chemical substances, suspended materials, color, taste, odor, and microorganisms harmful to health (Saleh; Hassan, 2021).

Surface waters are those that do not infiltrate the soil but instead accumulate on the surface, flow, and give rise to rivers, lakes, streams, and creeks (ANA, 2020). Monitoring this matrix is extremely important, particularly to assess changes in water quality, since these waters are among the main sources of potable water on the planet (Soares; Souza., 2020; Chow *et al*., 2020).

Each year, freshwater has increasingly become the subject of debate due to factors such as global population growth, changing consumption patterns, rising demand from new economic activities, and climate change (Granziera, 2022; Mishra, 2023a). According to UNESCO, global water use has increased by approximately 1% per year since the 1980s, and worldwide water demand is expected to continue rising at a similar rate until 2050, corresponding to a 20–30% increase compared to current levels (UNESCO, 2023).

Agriculture, including irrigated cropland, livestock, and aquaculture, is the largest consumer of freshwater, accounting for 69% of annual global water withdrawals. This is followed by industry (19%) and domestic use (12%) (Ibrahim *et al*., 2023; Verdegem *et al*., 2023).

In Brazil, CONAMA Resolution No. 357 (CONAMA, 2005) establishes the conditions for the classification of water bodies and effluent discharge standards. According to this

resolution, freshwater is classified into: special class, and classes 1, 2, 3, and 4. Special-class waters are intended for human consumption after disinfection, for the preservation of aquatic community balance, and for the protection of aquatic environments in conservation units. Class 1 waters may be used for human consumption after simplified treatment, for the protection of aquatic communities, for recreation such as swimming, water skiing, and diving, and for the irrigation of vegetables. Class 2 waters may be used for human consumption after conventional treatment and have the same purposes as Class 1. Class 3 waters may be used for human consumption after conventional or advanced treatment, as well as for irrigation of tree and forage crops, amateur fishing, and secondary-contact recreation. Class 4 waters are intended for navigation and landscape harmony (CONAMA, 2005).

In Brazil, water is considered potable when it meets the requirements established by the Ministry of Health's Consolidation Ordinance No. 5/2017, which regulates the control and surveillance of drinking water quality and its potability standards (ANVISA, 2017). For this reason, concern regarding the conservation of water quality in water bodies is continuous, as population growth increases freshwater demand and intensifies urbanization, raising the likelihood of contamination in river basins.

The peculiar hydrological regime of the Cerrado biome in Piauí State—characterized by prolonged droughts alternating with short periods of rainfall with low annual volume, high irradiation and evaporation rates, and long-term urbanization—has posed a threat to biodiversity, causing changes in the dynamics of natural environments and affecting all communities that depend on or live within these water bodies (Oliveira *et al*., 2020; Cantonati *et al*., 2020).

3.3 Alterations in water bodies

From the mid-20th century onward, concerns regarding the impacts of human activities on the environment have increased significantly (Huhle, 2022; Caradonna, 2022). The acceleration of scientific and technological development, coupled with rapid urbanization and intense population growth, has resulted in rising health problems associated with negative environmental effects (Silva *et al*., 2020; Zhang *et al*., 2022).

Under natural conditions, the quality of surface water is influenced by surface runoff, infiltration, and the interaction between water, rocks, and soil resulting from atmospheric precipitation (Cheng *et al*., 2022; Akhtar *et al*., 2021). Under anthropogenic conditions, water

quality can be affected by domestic, industrial, and agricultural discharges (Libânio; Sardinha, 2020; Madhav *et al*., 2020; Zahoor; Mushtaq, 2023).

Environmental impacts are largely associated with the persistent and ubiquitous nature of many pesticides used in the agricultural sector (Sharma; Mohanty, 2024). Pesticides that are not easily degraded accumulate in soils or are mobilized from one location to another as degraded products, and even at low concentrations, they may be amplified through the food chain (bioaccumulation and biomagnification), potentially causing toxicity to human health (Rani *et al*., 2021; Ghosh *et al*., 2022).

Although soil often acts as a reservoir for pesticides due to the high affinity of agrochemicals for soil particles, pesticide contamination of surface water resources, such as streams, estuaries, and lakes, as well as groundwater, remains a risk because of the close interconnection between soil and water bodies (Rasool; Rasool; Gani, 2022; Gavrilescu, 2021).

Pesticides reach water bodies through point and diffuse sources. Point sources originate from fixed locations and include chemical runoff during storage, loading, and improper disposal (Syafrudin *et al*., 2021; Ray; Shaju, 2023). Diffuse sources involve the movement of pesticides from extensive areas across watersheds, eventually reaching water bodies over time (Xu *et al*., 2023; Xue; Wang; Zhang, 2022). Diffuse pesticide sources typically originate from agricultural fields, triggered by runoff and erosion events, leading to the gradual leaching of pesticides into soil and surface waters (Kreutz *et al*., 2023; Hussain *et al*., 2025).

A substantial threat to aquatic ecosystems and drinking-water resources arises from water bodies contaminated with pesticide residues. Water pollution occurs when water bodies are negatively impacted by the addition of large quantities of external constituents (Rajmohan *et al*., 2020; Madhav *et al*., 2020).

Another recurring problem identified in some reservoirs in the Northeastern region of Brazil is the process of eutrophication, which corresponds to the increase in nutrient concentrations in water (Santos; Medeiros, 2023; Mishra, 2023a). This process promotes the growth of phytoplankton biomass, leading to reduced water transparency and altering the physical and chemical structure of aquatic ecosystems, ultimately creating favorable conditions for cyanobacterial blooms (Oliveira *et al*., 2020; Geletu, 2023).

3.4 The input of nutrients into waters

Surface-water environments are easily accessible sources for general use and are, therefore, more susceptible to pollution (Varol, 2020; Syeed *et al*., 2023). As productive land

decreases, the agricultural sector has a growing need to apply pesticides, soil amendments, and fertilizers to maintain crop growth rates and yields, leading to the runoff, transport, and leaching of nutrients into surface waters (Cheng *et al*., 2022; Lang *et al*., 2022).

Although studies already exist on measuring and predicting the impacts of land use and agricultural activities, other land-use types may also contribute to nutrient inputs into surface waters, including urban areas, pasturelands, forestry plantations, road networks, and mining activities, through processes such as surface runoff, soil erosion, wastewater discharge, and atmospheric deposition. (Cheng *et al*., 2022). This contribution is common in areas subject to human activities, including large urban centers, industry, mining, and others (Finér *et al*., 2021; Li *et al*., 2021). These activities directly affect water quality, as nutrients, metals, pharmaceuticals, and toxic substances are carried from these areas into aquatic environments (Fadhullah *et al*., 2020; Akhtar *et al*., 2021).

Although nutrients are essential for sustaining life, their absence or low availability may alter ecosystem dynamics; conversely, when present in excess, they may become pollutants and trigger eutrophication (Mishra, 2023a; Lan *et al*., 2024). Anthropogenic practices have the potential to contribute to the excessive input of nutrients into rivers, lakes, and consequently watersheds, leading to eutrophication and impairing aquatic life (Häder *et al*., 2020; Penuelas *et al*., 2020).

Eutrophication is a process of both natural and anthropogenic origin, ranging from the natural aging of a water body to a eutrophic state (Sonarghare *et al*., 2020; Pannard *et al*., 2024). This transition may occur over long geological time scales or through a rapid increase in nutrient levels as a result of human activities (Zhang *et al*., 2023; Akinnawo, 2023). However, point-source discharges and non-point nutrient loads introduced into aquatic ecosystems by human activities have accelerated the rate and magnitude of eutrophication, with consequences for drinking-water sources, aquatic life, and recreational water bodies (Akinnawo, 2023; Kakade *et al*., 2021).

Thus, eutrophication becomes a harmful factor that results in the pollution of water bodies (Chang *et al*., 2022), threatening the continued existence of aquatic organisms due to algal proliferation resulting from nutrient enrichment. This enrichment is attributed to society's strong dependence on fertilizers, agrochemicals, and soil amendments for food production (Zhang, 2022; Kapsalis; Kalavrouziotis, 2021).

3.5 Use of chemical pesticides

Pesticides are commonly used to protect crops from diseases, pest damage, weed growth, and vector-borne diseases that affect human life (Sharma; Sharma; Chopra, 2020; Taghilou *et al*., 2024). The beneficial results associated with pesticides make them an important tool for maintaining and improving global global food production. An average of 2 million tons of pesticides are used globally each year to control weeds, insects, and pests (Syafrudin *et al*., 2021).

The demand for pesticides and similar compounds has increased due to their accessibility and broad efficacy against various pests. According to the Food and Agriculture Organization (FAO) database, global pesticide use in agriculture has an average application rate of 1.8 kg per hectare of arable land and remained stable at 2.7 million tons of active ingredients in 2020 (FAO, 2022).

Approximately two million tons of pesticides are produced and used worldwide each year. Of this total, 24% is consumed by the United States, 45% by European countries, and the remaining 25% by other regions of the world (Rajmohan *et al*., 2020; Hedlund *et al*., 2020). These values reflect global population growth, which demands increasingly higher food production (Neves *et al*., 2020).

In Brazil, several states (MG, SP, PE, PR, ES, CE, and RJ) have policies that encourage the commercialization of these agrochemicals, granting significant reductions in the Tax on the Circulation of Goods and Services (ICMS), which may reach up to 100% in certain periods (Soares; Souza, 2020). According to the National Union of the Plant Defense Products Industry (Sindiveg), Brazil is one of the largest consumers of pesticides in the world (Souza *et al*., 2023).

An estimated one-third of agricultural products rely on pesticide application; without these compounds, yield reductions would reach 78% in fruits, 54% in vegetables, and 32% in cereals. (Tudi *et al*., 2021; García *et al*., 2022). Thus, the importance of pesticides becomes evident for increasing crop productivity and sustaining the world population.

3.6 Risks to human health

Access to clean and safe water is a basic human right, yet much of the world's surface water remains unsuitable for human consumption (Ahmad, 2020). Numerous pathogens, including bacteria, viruses, and yeasts, can proliferate in water, leading to substantial health

risks. In addition, several toxic pollutants such as pesticides, heavy metals, and dyes worsen this problem (Saravanan *et al*., 2021; Taghilou *et al*., 2024).

Many studies have already highlighted the long-term effects of pesticides and the impact of lethal chemical substances discharged into water bodies (Chow *et al*., 2020; Mukhles *et al*., 2022). Due to their rapid fat solubility and their tendency to bioaccumulate, pesticides can affect the respiratory, nervous, and reproductive systems and may lead to various types of cancer and infant methemoglobinemia (Qi *et al*., 2022; Ray; Shaju, 2023). The increasing occurrence of cancers and other chronic diseases over the past 50 to 60 years may not be attributed solely to population growth but also to pesticide chemicals that act as catalysts for carcinogens (Rajmohan *et al*., 2020; Intisar *et al*., 2022). Recent studies show that chronic respiratory dysfunctions such as asthma result from long-term exposure to these harmful pesticide compounds (Lima *et al*., 2022; Tewari, 2024). Pesticide exposure can worsen asthma through irritation, inflammation, immunosuppression, and endocrine disturbances (Rajmohan *et al*., 2020; Pathak *et al*., 2022).

The misuse of pesticides, including uncontrolled applications, improper disposal, the absence of protective equipment, and the use of illegal or counterfeit pesticides, contributes to the contamination of water and soil (Calista *et al*., 2022). It also causes adverse effects on human health as well as implications for food safety related to chronic exposure to lipophilic and bioaccumulative active substances (Lykogianni *et al*., 2021; Ali *et al*., 2021).

Acute pesticide poisoning is characterized by symptoms that appear shortly after contact with a toxic substance (Boedeker *et al*., 2020; Faluomi *et al*., 2022). This type of poisoning is responsible for a large number of deaths each year worldwide, and the vast majority of these deaths, approximately 99 percent, occur in developing countries (Karunarathne *et al*., 2020; Karunarathne *et al*., 2021). The vulnerability of these countries is attributed to less stringent health, safety, and environmental regulations, which are often weakly enforced (Agostinetto *et al*., 2020; Jepson *et al*., 2020).

3.7 Classification of pesticides

A pesticide is primarily categorized according to the type of function it performs. Based on its mode of action against insects, weeds, and fungi, pesticides are classified as insecticides, herbicides, and fungicides, respectively (Tudi *et al*., 2021; Nayak; Solanki, 2021). According to toxicity level, pesticides are classified as extremely toxic, highly hazardous, moderately

hazardous, slightly toxic, and unlikely to cause acute harm (Table 1). There are also pesticides that remain unclassified due to the lack of information provided by manufacturers.

The categorization established by ANVISA (2017) allows for defining and classifying the risks and hazards of chemical products, establishing standardized communication elements on product labels, and prescribing safety measures against risks to human health.

Table 1 - Toxicological classification of pesticides (ANVISA, 2017).

Toxicological Classification	LD_{50} range (mg kg^{-1} of body weight)	Description
Extremely Toxic	Less than 5	Substances with a high potential to cause harm. Small amounts are lethal to humans or animals.
Highly Hazardous	From 5 to 50	Substances that, if ingested, inhaled, or absorbed through the skin, can cause serious health damage or even death.
Moderately Hazardous	From 50 to 500	Substances that may cause serious health effects but require a larger amount to cause death or significant harm.
Slightly Toxic	From 500 to 5000	Substances that present a lower risk to human health but may still cause adverse effects depending on exposure and the amount absorbed.
Unlikely to Cause Acute Harm	Greater than 5000	Substances that, even in large amounts, pose minimal risk of causing immediate harm to health.

Pesticides can also be classified based on their nature, toxicity level, and target application. The most widely used approach for classifying pesticides is based on their chemical properties and target characteristics. Pesticides are categorized according to their chemical structure and composition (Figure 2) into organochlorines, organophosphates, carbamates, pyrethroids, triazines, and chloroacetamides (Rajmohan *et al*., 2020; Ahmad *et al*., 2024).

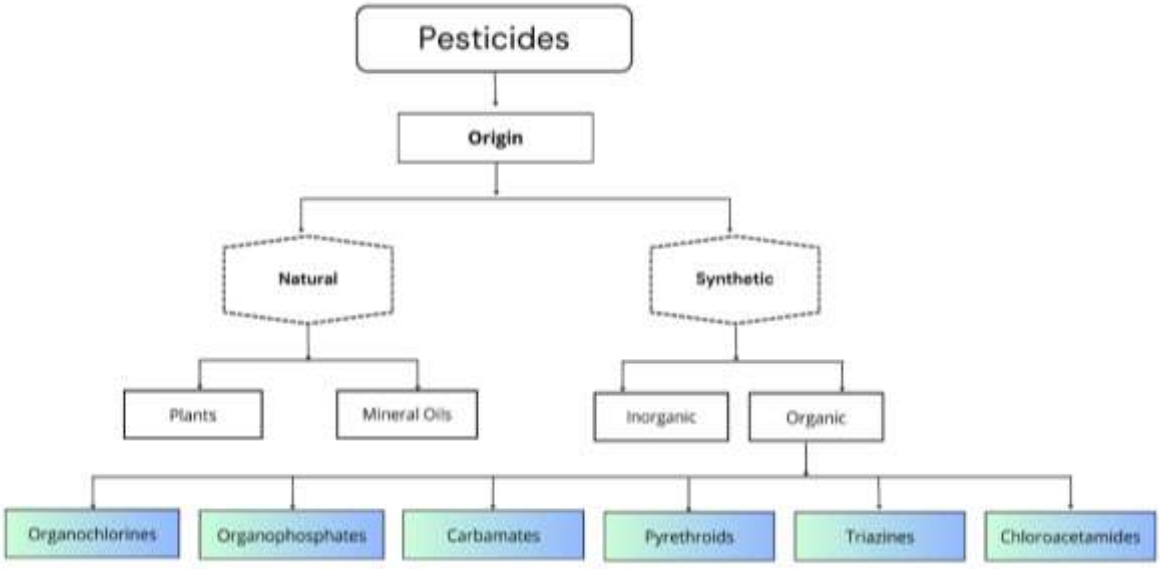


Figure 1 - Classification of pesticides. Adapted from Hassaan and Nemr (2020).

Pesticides are also classified according to their origin, which may be natural or synthetic. Natural-origin pesticides may be plant-based or derived from mineral oils, whereas synthetic-origin pesticides may be inorganic or organic, such as organochlorines, organophosphates, carbamates, and pyrethroids (Hassaan; Nemr, 2020).

3.7.1 Organochlorines

Organochlorine pesticides are stable chemical substances that are highly persistent in the environment and have the potential to accumulate in adipose tissue. Structurally, organochlorines are divided into the following groups: DDT (dichlorodiphenyltrichloroethane) and its analogs, including dichlorodiphenyldichloroethylene (DDE); dichlorodiphenyldichloroethane (DDD); hexachlorocyclohexane (HCH); toxaphene; mirex and chlordecone (Hassaan; Nemr, 2020).

Organochlorines were among the first pesticides to be developed. Their chemical composition includes carbon, hydrogen, and chlorine, and they are characterized by low reactivity, low solubility in water, low vapor pressure, and high chemical stability (Nascimento; Melnyk, 2016).

DDT was the most widely used pesticide in the world during the 20th century, and most of this product was applied in agriculture (Tudi *et al*., 2021). Its popularity in Brazil was such that it gave rise to the verb “dedetizar” in the Portuguese language. Despite its historical importance, due to its persistence and toxicity, its use is now restricted and recommended only for malaria control in some developing countries in Africa and Asia (Nascimento; Melnyk, 2016). DDT has a half-life of approximately 15 years (Ahmad *et al*., 2024)

DDE is a metabolite with low toxicity to insects and has not been used as a pesticide. In the environment, DDT tends to undergo conversion to its metabolites DDE and DDD. This transformation can occur through photolysis and biological metabolism (Hinz *et al*., 2021). In the oxidative pathway, the DDT molecule loses one chlorine atom and one hydrogen atom, resulting in the formation of DDE. In the reductive pathway, one chlorine atom is replaced by hydrogen, producing DDD (Dang *et al*., 2022).

HCH is a compound that is relatively soluble in water and highly volatile, and during agricultural application it is largely lost to the atmosphere. In Brazil, HCH was widely used in coffee, soybean, and cotton crops, as well as in the control of Chagas disease (Noblat *et al*., 2021). The technical product was commercialized as a mixture of eight HCH isomers (Attaullah *et al*., 2021). Its average chemical composition was as follows: 65 percent α-HCH, 9 percent β-

HCH, 12 percent γ-HCH, 8 percent δ-HCH, 2 percent ε-HCH, and 4 percent other isomers (Amirbekov *et al*., 2024).

In 2009, the α-HCH, β-HCH, and γ-HCH isomers were added to the Stockholm Convention list of Persistent Organic Pollutants (POPs) for elimination. Although α-HCH and β-HCH do not exhibit toxicity to insects, they are toxic to various non-target organisms, including mammals (Noblat *et al*., 2021; Vijgen *et al*., 2022).

Toxaphene is a mixture containing more than 670 compounds, whose chemical compositions may vary from C10H18−nCln to C10H16−nCln, with each molecule containing between five and twelve chlorine atoms. This pesticide was extensively used in the United States in crops such as cotton and maize. In Brazil, its use was registered for agricultural purposes and in household pest control products (Matosinhos *et al*., 2023; Kumari *et al*., 2024).

Mirex is a pesticide used for the control of ants and termites. It is a highly persistent compound in the environment and in biological tissues, and it is slowly eliminated by living organisms due to its resistance to metabolism (Bhuvaneswari *et al*., 2021).

Chlordecone is a pesticide analogous to mirex, also known by the commercial name Kepone, and was widely used in banana and tobacco crops. In Brazil, this compound was never registered for use. Despite its efficiency, chlordecone is highly resistant to aerobic degradation, extremely persistent in the environment, and has low mobility (Cabral *et al*., 2022; Kumari *et al*., 2024).

3.7.2 Organophosphates

Organophosphates are insecticides that contain a phosphorus atom in their chemical structure. They are esters of phosphoric acid and belong to the category of insecticides. After the ban of organochlorines, organophosphate pesticides have been widely used in agriculture and are among the main chemical products employed for pest control today (Costa, 2018; Kaushal; Khatri; Arya, 2021) and among the most commonly used agrochemicals in Brazil.

They fall into a category of high toxicity and act by inhibiting the enzyme acetylcholinesterase, which is responsible for degrading acetylcholine. This inhibition prevents the termination of nerve impulses, leading to a condition known as cholinergic crisis (Sarailoo *et al*., 2022). Due to this mechanism, prolonged exposure to these compounds results in a series of neurological damages. In humans, their mode of action affects the central nervous system by blocking acetylcholine activity. Symptoms of intoxication vary and may include dizziness, nausea, headache, and, in severe cases, death (Moura *et al*., 2020).

However, despite their toxicity, organophosphates have lower environmental persistence compared to other agrochemical groups, such as organochlorines. They decompose within days or weeks and are therefore rarely detected in the food chain (Tzanetou; Karasali, 2022).

3.7.3 Carbamates

Some organic ester compounds derived from dimethyl N-methylcarbamic acid are used as herbicides, insecticides, nematicides, and fungicides, and are referred to as carbamates (Mdeni *et al*., 2022). The toxicity of carbamate compounds varies according to their molecular structure, but in general they have a shorter persistence than organophosphates and organochlorines (Ranjan; Jindal, 2022). This class of chemical products is known for not leaving persistent residues in the environment or in mammalian species, due to their rapid hydrolysis into less toxic metabolites that are easily excreted by the organism (Moreira *et al*., 2022). However, because of their lack of species selectivity and their lipophilicity, chronic exposure represents a number of threats to environments and to human health (Sun *et al*., 2022).

Of the carbamate compounds used in the agricultural sector, only a portion reaches the target organisms. The remainder is distributed throughout the environment, affecting non-target areas and species (Shahid *et al*., 2021). Processes such as leaching, adsorption, runoff, and volatilization contribute to the distribution and persistence of these compounds in the environment (Malhotra *et al*., 2021).

The growing global use of carbamate pesticides in food production, commercial activities, and domestic applications has generated numerous environmental problems. These products are harmful to the environment even though they are used to protect economically important edible crops from pests and diseases (Mdeni *et al*., 2022). Nevertheless, due to their versatility, this chemical group is widely used in various sectors, with the advantage of having a shorter half-life and reversible effects compared to organophosphates (Martins *et al*., 2021).

This type of compound acts on the nervous system of target and sometimes non-target pests by preventing the inactivation of acetylcholine, a chemical mediator necessary for the transmission of nerve impulses between neurons (Mdeni *et al*., 2022). This leads to continuous transmission of nerve impulses and a wide variety of symptoms, including weakness, gastrointestinal disturbances, salivation, and others (Xia *et al*., 2024).

3.7.4 Pyrethroids

Pyrethroid pesticides are derived from pyrethrins, which are chemical compounds found in natural pyrethrum extracted from chrysanthemum flowers (Ahamad; Kumar, 2023). They are a type of organic insecticide that has been used worldwide since the 1980s due to their high efficiency and lower toxicity when compared with organophosphate and carbamate groups (Ribeiro *et al*., 2022). Pyrethroids are more effective at lower concentrations, which is one of the reasons they have surpassed the use of previous pesticide groups (Ravula; Yenugu, 2021).

In general, they exhibit low toxicity to birds and mammals and high toxicity to arthropods, and only very low doses are required to control insects. However, they are not effective at penetrating soil to kill subterranean pests because they bind strongly to soil particles and organic matter (Santos *et al*., 2023).

Pyrethroids make up a class of insecticides used worldwide and account for more than 30 percent of the global agrochemical market (Liu *et al*., 2024). Due to the increasing use of these products, several environmental issues have been reported, including soil and surface-water contamination, food contamination, and toxicity to aquatic arthropods, bees, and fish (Ribeiro *et al*., 2022).

Compared with traditional pesticides, pyrethroids have lower potential to pollute the environment, but they may still enter organisms through food chains (Tang *et al*., 2018). Due to the lipophilicity of these compounds, they are difficult to eliminate once they enter an organism. Long-term exposure, even at low doses, may lead to chronic diseases and toxic effects on the nervous, immune, and cardiovascular systems (Huang *et al*., 2023).

3.7.5 Triazines

Triazines are heterocyclic compounds containing nitrogen. They possess a planar aromatic six-membered ring in which three carbon atoms are substituted by nitrogen atoms (Verma *et al*., 2023). These compounds are used as herbicides in different crops with the purpose of controlling the growth of herbaceous weeds by inhibiting the photosynthetic electron transport chain in plants (Matias *et al*., 2021).

According to ANVISA (2018), triazines fall under Class III (moderately toxic) within the toxicological classification system. These compounds stand out as chemical pollutants because of their widespread use in the agricultural sector, being applied in many crops such as maize, soybeans, wheat, and others (Manousi; Kabir; Zachariadis, 2022). In addition, they are

used in pre- and post-emergence applications for controlling weeds in various crops, including maize, sorghum, and sugarcane (Ahmad *et al*., 2023).

Despite the usefulness of the triazine group in agriculture, their use must always be carried out consciously, as they have high toxicity and long environmental persistence (Zeng *et al*., 2024). These compounds exhibit relatively low adsorption in soil, resulting in their migration through soil layers into surface waters, which can lead to negative environmental impacts (Wang *et al*., 2021).

3.7.6 Chloroacetamides

The chloroacetamide group functions by inhibiting the synthesis of nucleic acids and proteins. These compounds control pre-emergent grass weeds in crops such as soybean, bean, sugarcane, maize, and others. They also control seedlings of many annual grasses and some dicotyledonous species before or shortly after emergence (Cai *et al*., 2023). Chloroacetamides have low to moderate mobility in soil, which is an important characteristic because compounds with high mobility tend to exhibit greater environmental dispersion, potentially contaminating non-target environments such as surface waters (Roman *et al*., 2005).

The selectivity of this herbicide is related to its target metabolic rate, as tolerant plants rapidly metabolize chloroacetamides compared with less tolerant species. As a result, tolerant plants are able to metabolize these compounds in sufficient quantities to prevent their accumulation and persistence at phytotoxic levels (Kang *et al*., 2023).

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4 CHAPTER 2

SPATIOTEMPORAL OCCURRENCE AND DISTRIBUTION OF CURRENT-USE PESTICIDES IN SURFACE WATERS OF THE URUÇUÍ-PRETO RIVER BASIN LOCATED IN ONE OF THE LAST AGRICULTURAL FRONTIERS IN BRAZIL

ABSTRACT

The intensification of agricultural activities, driven by population growth, has resulted in significant impacts on the quality and availability of water resources. This expansion increases the likelihood of pesticide contamination, affecting the water quality of aquatic ecosystems. In regions of intensive agricultural production, such as the Cerrado of Piauí (MATOPIBA region), crop management practices require careful attention due to the potential presence of pesticide residues in surface waters. In this context, the present study aimed to assess the spatial and temporal distribution of pesticides in surface waters of the Uruçuí-Preto River basin during the dry and rainy seasons. Sampling was conducted at 10 points over four representative months (February, March, April, and August), encompassing distinct climatic conditions. Pesticide residues were determined using Solid-Phase Microextraction (SPME) followed by analysis via Liquid Chromatography–Tandem Mass Spectrometry (LC-MS/MS). The results revealed the presence of several chemical groups of pesticides, with notable emphasis on Clomazone, which was detected at all sampling points in August, the month characterized by the absence of rainfall. The higher concentrations observed during this period suggest that reduced precipitation favors the accumulation of residues in water bodies. Conversely, during the rainy months, a dilution effect was observed, although occasional pesticide detection persisted. Overall, the findings highlight the influence of seasonality and agricultural practices on water quality, underscoring the need for continuous monitoring and policies that promote the safe management of agrochemicals in the region.

Keywords: Agrochemicals, Human-impacted environment, Surface water, Water quality.

4.1 Introduction

The continuous growth of the global population has increased the demand for food. In the pursuit of more efficient agricultural systems to meet current needs, the use of pesticides

for pest and disease control has intensified (Souza *et al*., 2020). Although this production model has contributed to expanding food availability, it has also raised environmental and public health concerns, as the recurrent use of these substances increases the risk of contamination of aquatic and terrestrial ecosystems (Brito *et al*., 2020; Abuqamar *et al*., 2024).

Over the past ten years, the global population has increased by nearly 11%, rising from approximately 7.3 billion in 2015 to 8.2 billion in 2025 (ONU, 2024), thereby intensifying pressure on agricultural systems to ensure sufficient food production. In response, the Brazilian agricultural sector has expanded in an effort to increase productivity and meet both domestic and international market demands.

To achieve higher yields, pesticides have become one of the primary tools for managing and controlling pests and diseases (Dallegrave *et al*., 2018; Khan *et al*., 2023). According to the Ministry of the Environment, Brazil is currently one of the world's largest consumers of pesticides (FAO, 2023; MMA, 2024). However, as a consequence of intensive pesticide use, residues may contaminate soils, biota, the atmosphere, and surface and groundwater resources (Kariyanna *et al*., 2024).

Studies on aerial drift resulting from pesticide spraying indicate that up to 90% of the applied volume may disperse into the environment (Elhamalawy *et al*., 2024). This dispersion can reach non-target areas such as soils, neighboring crops, and even native vegetation fragments, and its effects may intensify along the borders of agricultural fields. These losses may be even greater if rainfall occurs shortly after pesticide application (Punniyakotti *et al*., 2024). Brazil has extensive areas under intensive agriculture, and the Cerrado biome, particularly the portion within the MATOPIBA region, is currently a major agricultural production center, covering approximately 1,983,017 km², or 23.3% of Brazil's territory (MMA, 2024), of which about 16% is occupied by croplands (MAPA, 2022).

Historically, Cerrado soils were considered unsuitable for agricultural production due to their natural characteristics, including flat to gently undulating relief and acidic, nutrient-poor soils (Rodrigues; Lopes; Silva, 2022). However, agronomic research in the region has developed technologies capable of correcting soil acidity, establishing adequate fertilization regimes, and improving other limiting factors, thus enabling the large-scale agricultural exploitation of this phytogeographical domain (Albuquerque; Zucherato, 2023).

As a result, agriculture has rapidly expanded in southwestern Piauí, particularly with the growth of soybean cultivation. The Uruçuí-Preto River basin is located in one of Brazil's last agricultural frontiers and stands out due to the expansion of grain production, mainly soybeans

and corn, which currently represents one of the major economic activities in the MATOPIBA region (Souza *et al*., 2019; Boechat *et al*., 2020; Vieira *et al*., 2021; Rego *et al*., 2024).

Pesticide levels in freshwater systems can be influenced by multiple factors. Extensive field and modeling studies have shown that commonly used agricultural pesticides tend to infiltrate nearby surface and groundwater bodies, posing risks to drinking water sources (Meite *et al*., 2018; Barizon *et al*., 2022; Elhamalawy *et al*., 2024; Rego *et al*., 2024). Consequently, pesticide use in agriculture emerges as a major upstream factor contributing to freshwater contamination. Environmental regulations, particularly water quality standards for pesticides in surface and groundwater, play a crucial downstream role in preventing freshwater contamination (Huang; Li, 2025).

Given this context, our hypothesis is that the surface waters of the Uruçuí-Preto River basin have been affected by agricultural expansion, resulting in the presence of pesticide residues in surface waters. Therefore, the objective of this study was to identify and characterize the spatial and temporal distribution of pesticides in surface waters during the dry and rainy seasons in the Uruçuí-Preto River basin.

4.2 Material and methods

4.2.1 Study area

The Uruçuí-Preto River basin is one of the main tributaries of the Parnaíba River in the state of Piauí and represents an important source of freshwater for human consumption, particularly in rural areas. The basin covers approximately 16,000 km² and is drained by the Uruçuí River and its tributaries, including the Ribeirão dos Paulos, Castros, Colheres, and Morro d'Água streams, as well as the Estiva and Corrente creeks. The river extends for 300 km and encompasses 25 municipalities within the state (Medeiros *et al*., 2022). The Uruçuí-Preto River originates along the boundaries of the municipalities of Santa Filomena and Gilbués, fed by two major streams, and its mouth is located 12 km from the city of Uruçuí, Piauí.

The basin is situated in a rapidly developing region with strong economic activity driven by agribusiness, which has expanded quickly across the Cerrado biome (Figure 2). This region is a leading producer of major agricultural crops such as soybeans and corn.

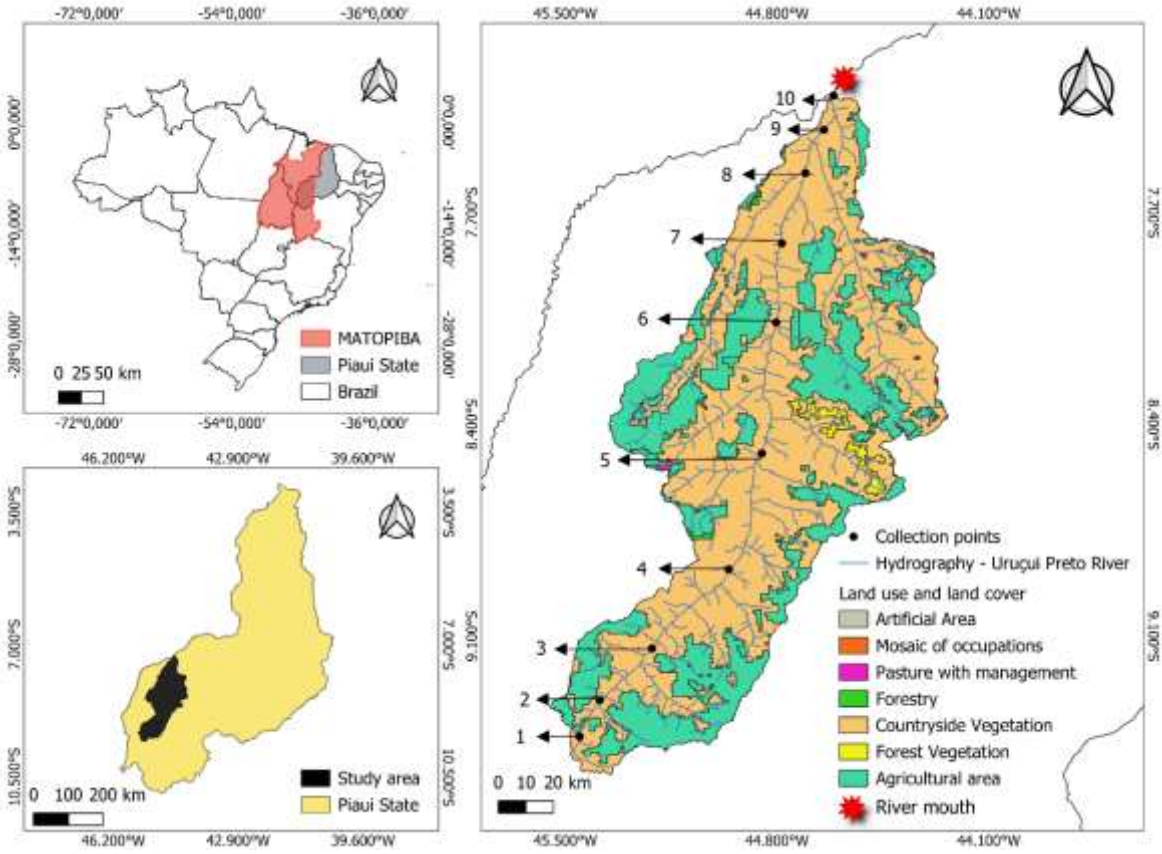


Figure 2 - Area of study, land use and land cover and location of the sampling points in the Uruçuí-Preto River basin.

Within the basin, two climatic types can be distinguished: Aw — tropical hot and humid, with summer rainfall and a dry winter; and BSh — hot semi-arid, with summer rains and a dry winter (Köppen). The region has an average temperature of 31.6 °C, with recorded maxima of 39 °C and minima of 16.9 °C. Annual precipitation reaches 913.9 mm, with the rainy season beginning in November and extending until mid-April (Medeiros *et al*., 2022). The soils that make up the basin's drainage area are predominantly Yellow Oxisols (Latossolos Amarelos), in addition to Entisols, Quartzipsamments (Neossolos Quartzarênicos), and hydromorphic soils (Santos *et al*., 2018). The defining characteristic of these soils is the high percentage of resistant minerals, with over 90% of the smaller than 2 mm grains made up of quartz and similarly insoluble minerals (IUSS Working Group WRB, 2022). They are also known for their sandy texture, high microporosity, and saturated hydraulic conductivity (Zech; Schad; Hintermaier-Erhard, 2022). Because they consist mostly of inert quartz and have very low clay and organic matter content, these soils are typically acidic, have low natural fertility, a low cation exchange capacity, and a very low volume of available water for plants (Oliveira *et al*., 2023).

Land use and land cover data were obtained from the IBGE database (2022). The predominant land cover types in the region are countrysid vegetation (65.36%) and agricultural areas (31.44%) (Appendix Figure 1). Grassland vegetation is characterized by the predominance of sparsely distributed shrubs over a grassy–woody layer and includes savannas, steppes, savanna–steppe formations, pioneer formations, and ecological refuges (IBGE, 2022). Agricultural areas include temporary, semi-perennial, and perennial crops, irrigated or non-irrigated, used for producing food, fibers, fuel, and other raw materials (IBGE, 2022). Other land-use classes also occur within the basin's drainage area and account for slightly more than 3% of the total area. These include artificial areas, characterized by anthropogenic surfaces; managed pasture for grazing cattle and other livestock; and forestry, referring to forest cultivation through agricultural management practices (IBGE, 2022).

The cultivation of these crops occurs under rainfed conditions between November and March, a period that coincides with the regional rainy season (Appendix Figure 2). Precipitation data for each sampling point were obtained from NASA POWER estimates (NASA, 2023), which generate climate data based on geographic coordinates and the selected time period.

4.2.2. Sample collection

During the 2021 hydrological year, surface-water samples were collected in duplicate during the last two months of the rainy season (February and March) and during two months within the dry season (April and August). Water samples were collected at 10 sampling points distributed along the Uruçuí-Preto River (Figure 2), taking into account the presence of tributaries, accessibility conditions, and river crossings such as bridges (ANA, 2011), totaling 40 river water samples.

During sampling campaigns, 5.0-L samplers were used and submerged at 0.00–0.10 m below the water surface for sample collection. Before each sampling event, the samplers were washed with 2.0 M HCl solution and Milli-Q water (18.2 MΩ·cm) (CETESB, 2012). Samples were stored in 1.0-L amber glass bottles and kept at 4 ± 2 °C (ANA, 2011).

At the end of each campaign, samples were transported to the Pesticide Residue Analytical Laboratory (LARP) in Santa Maria - RS, for the analysis of 150 pesticide residues. Electrical conductivity (EC), temperature (T), and dissolved oxygen (DO) of river water were measured in situ using a multiparameter probe (AKSO – Ak87).

4.2.3 Laboratory analyses

The pesticides evaluated in this study (Table 2) were selected because they appear on the lists of national and international regulatory agencies, including the Brazilian Health Regulatory Agency (ANVISA), the National Environmental Council (CONAMA), the U.S. Environmental Protection Agency (USEPA), and the European Union (EU).

Table 2 - Detection and quantification limits for the 150 pesticide residues investigated in this study.

Compounds	LOD (µg L^{-1})	LOQ (µg L^{-1})
Acetamiprid. ametryn. azaconazole. azamethiphos. atrazine. azoxystrobin. buprofezin. carbaryl. carbendazim. 3-hydroxycarbofuran. carbofuran. carboxin. clomazone. chloramphenicol. chlorimuron-ethyl. chlorpropham. cyazofamid. cyproconazole. chlorfenvinphos. clothianidin. diazinon. dimethoate. demeton-S-methyl sulfone. diclosulam. dicrotophos. dimoxystrobin. diuron. epoxiconazole. ethoprophos. fenpropimorph. fipronil. fluquinconazole. flutolanil. fenamidone. fenamiphos. fenhexamid. fenitrothion. fenoxycarb. flutriafol. flusilazole. phosalone. phosmet. furathiocarb. imazalil. imidacloprid. iprovalicarb. imazamox. imazapic. imazapyr. imazaquin. imazethapyr. indoxacarb. mecarbam. mepronil. metalaxyl. methamidophos. metconazole. methiocarb sulfone. mevinphos. myclobutanil. monosodium methanearsonate (MSMA). monolinuron. mephosfolan. methidathion. methiocarb. methoxyfenozide. metribuzin. nicosulfuron. oxyfluorfen. pyraclostrobin. pyrazophos. pyridafenthion. pyrimethanil. pirimicarb. pirimiphos-methyl. prochloraz. profoxydim (lithium salt). propiconazole. propoxur. parathion-ethyl. penthiopyrad. penconazole. picoxystrobin. piperonyl butoxide. pirimiphos-ethyl. pyriproxyfen. procymidone. prometon. quinoxyfen. quinalphos. quizalofop-p-ethyl. saflufenacil. simazine. tebuconazole. tetraconazole. thiacloprid. thiamethoxam. thiodicarb. triadimefon. triazophos. trifloxystrobin. triflumezopyrim. tebufenpyrad. thiabendazole. thiobencarb. tricyclazole. diflubenzuron. vamidothion.	0.006	0.020
Aldicarbe. azinfós-etílico. azinfós-metílico. bitertanol. bromoconazol. cimoxanil. cresoxim-metílico. difeconnazol. diniconazol. etoxisulfurom. fenarimol. linurom. melationa. metomil. metsulfurom-metílico. oxadixil. penoxsulam. propanil. tebufenozida. tolifluanida. trifloxissulfurom.	0.012	0.040
Diflubenzuron. fenthion. molinate. monocrotophos. nuarimol (nuarimol permanece igual). oxamyl. paraoxon-methyl. profenofos. quinclorac.	0.024	0.080
Boscalid. cyanazine. dichlorvos. EPN. famoxadone. fluroxypyr. tolclofos-methyl. triadimenol.	0.060	0.200
2.4-D.	0.120	0.400

LOD = Limit of detection of the method; LOQ = Limit of quantification of the method.

The determination of pesticide residues was performed using Solid-Phase Microextraction (SPME) followed by Liquid Chromatography–Tandem Mass Spectrometry (LC-MS/MS), conducted on a LC/APGC Xevo TQXS system. The Headspace Solid-Phase

Microextraction (SPME) technique is the most widely applied sample preparation method for the multiresidue analysis of pesticides in water, whereas LC–MS/MS is an analytical technique that involves the physical separation of target compounds followed by their detection and quantification by tandem mass spectrometry (Donato *et al*., 2012).

Samples were filtered through PTFE syringe filters, and the selected volumes were transferred to the SPME cartridges using PTFE tubing and a collector. The analytical method was developed using 10.0 mL stock solutions of each pesticide prepared in MeOH, except for carbendazim, which was solubilized in acetonitrile/HCl 0.1 mol L^{-1} (8% v/v).

The liquid chromatography system was coupled to a triple-quadrupole mass spectrometer (320 MS) equipped with a ProSat 410 autosampler and a column oven (Thermo Scientific). The system was fitted with a UPS Pursuit C18 column (50 × 3.0 mm i.d., 2.4 µm particle size). The mobile phase consisted of 5.0 mmol L^{-1} aqueous ammonium formate (solvent A) and methanol (solvent B), delivered at a flow rate of 150 µL min^{-1}.

The proposed method was validated by evaluating several parameters, including linearity, matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery), and precision (in terms of repeatability and intermediate precision). All validation parameters met international guidelines for pesticide residue analysis using chromatographic methods. Linearity was assessed using the determination coefficient (R^2) of calibration curves constructed at seven concentration levels: 10, 25, 50, 75, 100, 200, and 250 µg L^{-1}. Calibration solutions were prepared using the mobile phase consisting of 5 mmol L^{-1} aqueous ammonium formate and methanol (1:1, v/v) for LC–MS/MS. The matrix effect was calculated by comparing the slope of solvent-based curves with that of blank-matrix extracts (Donato *et al*., 2012).

Precision was evaluated through recovery assays at three concentration levels (0.5, 1.5, and 4.0 µg L^{-1}). Repeatability and intermediate precision were assessed based on the relative standard deviation (RSD) of recovery values for each fortification level. For dieldrin, aldrin, and chlordane, an additional lower-level fortification (0.02 µg L^{-1}) was included, following the regulatory limits for drinking water in Brazil. Six replicates were extracted and injected once into the chromatographic system for each concentration level.

LOD and LOQ were estimated using the signal-to-noise method. The LOD was defined as the lowest concentration at which the analytical signal could be reliably distinguished with an S/N ratio of 3:1, while the LOQ corresponded to the lowest concentration giving an S/N ratio of 10:1 with acceptable accuracy and precision.

4.2.4 Statistical analyses

Statistical analyses were performed using a descriptive approach based on the observed pesticide concentration values across the different sampling points and periods. Concentrations were organized by site and sampling season, enabling the identification of occurrence patterns, distribution trends, and potential seasonal influences. Comparisons between observed concentrations and the environmental quality standards established by Brazilian regulations, such as CONAMA Resolution No. 357/2005, were used to assess environmental compliance. Data organization and descriptive analyses were carried out using R software (version 4.3.0). For the Principal Component Analysis (PCA), pesticide concentrations, chemical parameters, and sampling months were included to evaluate associations among variables. Spearman correlation analyses were performed due to the non-normal distribution of data, and were conducted separately for the dry and rainy seasons using Python programming language (version 3.11).

4.3 Results

Five pesticides were quantified in surface water samples, with concentrations (μg L^{-1}) ranging from 0.107 to 0.194 for clomazone, 0.045 for chlorantraniliprole, 0.048 for 2,4-D, 0.031 for picoxystrobin, and 0.022 for atrazine (Figures 3 and 4). Additional compounds were detected below the limit of quantification (LOQ), including clothianidin, procymidone, imidacloprid, cyproconazole, carbendazim, diuron, chlorimuron-ethyl, and metsulfuron-methyl.

Clomazone was detected at all sampling points (n = 10), presenting the highest concentrations among the quantified compounds (0.107–0.194 μg L^{-1}). Chlorantraniliprole was quantified in one sample (n = 1; 0.045 μg L^{-1}). Picoxystrobin was quantified in one sample (0.031 μg L^{-1}) and detected below the LOQ in eight additional samples. Atrazine was quantified in one sample (0.022 μg L^{-1}) and detected below the LOQ in four additional samples. The herbicide 2,4-D was detected in seven samples (n = 7), with quantification in one sample (0.048 μg L^{-1}).

Other pesticides detected below the LOQ included clothianidin (TI-435; n = 1; 0.006 μg L^{-1}), procymidone (WP; n = 7; 0.006 μg L^{-1}), imidacloprid (IMI; n = 1; 0.006 μg L^{-1}), cyproconazole (CIPRO; n = 1; 0.006 μg L^{-1}), carbendazim (CBZ; n = 1; 0.006 μg L^{-1}), diuron

(n = 1; 0.006 μg L^{-1}), chlorimuron-ethyl (n = 1; 0.006 μg L^{-1}), and metsulfuron-methyl (MSM; n = 1; 0.012 μg L^{-1}).

The highest number of pesticide detections by sampling point was observed at P03, P04, and P06 (n = 6), followed by P02, P05, and P09 (n = 5), P07 and P01 (n = 4), and P10 (n = 3). Regarding sampling periods, August 2021 presented the highest number of detections (n = 32), followed by February 2021 (n = 9), March 2021 (n = 4), and April 2021 (n = 3). Recorded precipitation during the sampling periods was 401.5 mm in February, 136.6 mm in March, 125.8 mm in April, and 7.4 mm in August (Figures 2 and 3).

Sampling points P1, P2, and P3 presented the occurrence of procymidone, picoxystrobin, clomazone, and atrazine. Picoxystrobin was detected at nine sampling points in August and at one point in February. Clomazone was detected at all sampling points in August and was not detected in February and March. Atrazine was detected at four sampling points in August and at one point in March. In February, 2,4-D was detected at points P2, P3, P4, P5, and P7. At sampling point P5, clomazone and procymidone were detected in August, while chlorantraniliprole was detected in April.

Correlation analysis among pesticide compounds showed grouping patterns based on co-occurrence at sampling points and sampling periods (Figure 5a). Analysis of sampling months indicated differentiation among February, March–April, and August (Figure 5b). Spearman correlation analysis showed distinct correlation patterns between dry and rainy periods (Figure 6)

4.4 Discussion

4.4.1 Occurrence of pesticides in surface waters

The classification and concentration of the pesticides detected in this study, considering measured concentrations (μg L^{-1}), were as follows: clomazone (0.107–0.194), chlorantraniliprole (0.045), 2,4-D (0.048), picoxystrobin (0.031), and atrazine (0.022). Other compounds were detected but remained below the LOQ: clothianidin, procymidone, imidacloprid, cyproconazole, carbendazim, diuron, chlorimuron-ethyl, and metsulfuron. The detection of multiple pesticides, including those found below the limit of quantification (LOQ), underscores the complexity of the contamination scenario. Although many were present at low concentrations, their analytical confirmation demonstrates that the input of these molecules into the surface water network is not sporadic (Figures 3 and 4).

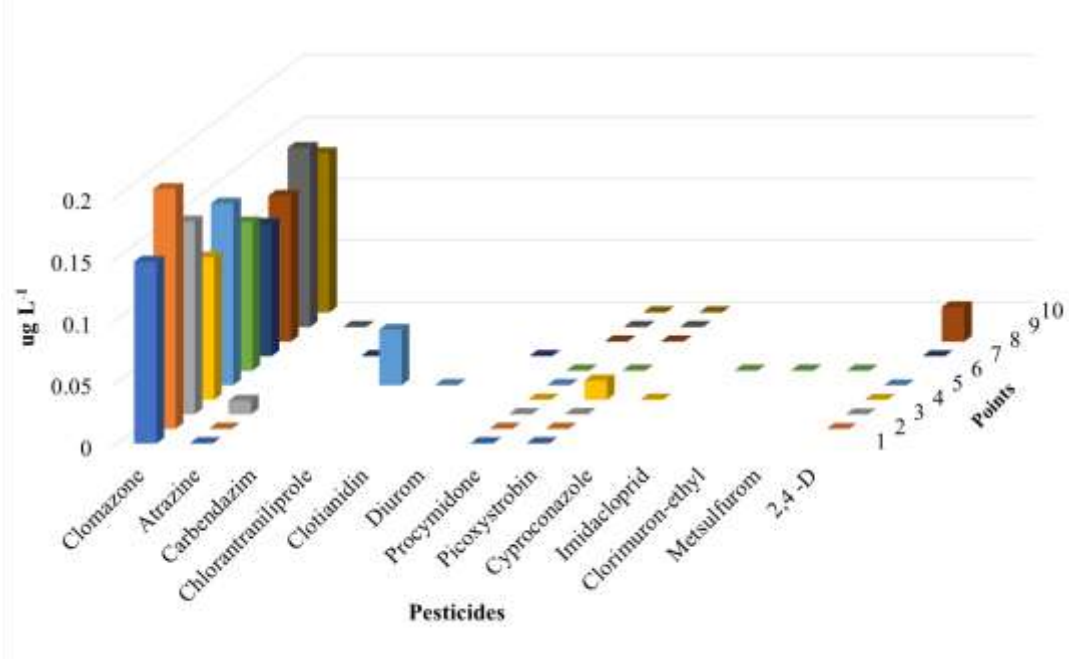


Figure 3 - Pesticide concentrations at different sampling points in the Uruçuí-Preto River Basin.

Clomazone (CLO) showed the highest concentrations and was detected at all sampling points (n = 10), with values ranging from 0.107 to 0.194 µg L^{-1} (Figure 3). This result indicates the widespread use of this molecule in the basin, as clomazone is a globally used herbicide for weed control in soybean, wheat, and rice crops, and its mobility in soil favors transport to aquatic systems (Zimdahl, 2018; Escoto *et al*., 2019).

Chlorantraniliprole (IRAC 28) was identified in only one sample (n = 1), with a concentration of 0.045 µg L^{-1}, suggesting a punctual application due to its low water solubility (Ding *et al*., 2024). Although its isolated detection implies a lower risk of diffuse contamination, chlorantraniliprole is increasingly used in agriculture owing to its high efficiency, low toxicity, long persistence, and low residue levels, warranting continued monitoring (Du *et al*., 2018; Song *et al*., 2019).

Picoxystrobin (PXS) was quantified in one sample (0.031 µg L^{-1}) and detected below the LOQ in eight additional samples, confirming its presence in the basin's surface waters (Figure 3). Although the quantified value falls within acceptable regulatory limits, its detection frequency indicates that this active ingredient exhibits both mobility and environmental persistence under the region's edaphoclimatic conditions (Scheel; Tarley, 2020). Strobilurin fungicides, such as picoxystrobin, may reach water bodies through spray drift and leaching from treated seeds (Gao *et al*., 2019).

Atrazine (ATZ) was quantified in one sample (n = 1; 0.022 μg L^{-1}) and detected below the LOQ in four additional samples (Figure 3). Atrazine is widely applied in pre- and post-emergence herbicide treatments (Hansen *et al*., 2019). Its presence in surface waters may be associated with its high potential for transport by surface runoff (Bachetti *et al*., 2021), a common behavior in areas under intensive soil management, such as the Uruçuí-Preto River Basin (Appendix Figure 1) (Alonso *et al*., 2018).

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) was detected in seven samples (n = 7), with quantification in only one sample (0.048 μg L^{-1}). Its recurrent presence may be related to applications during pre-planting, coinciding with the onset of the rainy season (Appendix Figure 2), which favors transport to water bodies (Silva *et al*., 2020). Although highly soluble, 2,4-D can persist in the environment after long-term and continuous use (Chen *et al*., 2018; Serbent *et al*., 2019).

Other pesticides detected at concentrations below the LOQ included: clothianidin (TI-435), n = 1 (0.006); procymidone (WP), n = 7 (0.006); imidacloprid (IMI), n = 1 (0.006); cyproconazole (CIPRO), n = 1 (0.006); carbendazim (CBZ), n = 1 (0.006); diuron, n = 1 (0.006); chlorimuron-ethyl, n = 1 (0.006); and metsulfuron-methyl (MSM), n = 1 (0.012). Although the concentrations were low, their detection demonstrates the diversity of molecules in circulation and the cumulative effects of intensive pesticide use (Figure 2).

The occurrence of substances with different chemical classes and modes of action reflects the direct influence of agricultural practices on water quality (Zahoor; Mushtaq, 2023). Thus, it is essential to consider the spatial and temporal distribution of these molecules, as factors such as land use, management practices, rainfall intensity, and seasonality may significantly influence the presence and behavior of pesticides in surface waters.

4.4.2 Spatial and temporal distribution of pesticides

The sampling points with the highest number of pesticide occurrences were P03, P04, and P06 (n = 6) > P02, P05, and P09 (n = 5) > P07 and P01 (n = 4) > P10 (n = 3). The sampling campaign with the highest number of detections was August 2021 (n = 32) > February 2021 (n = 9) > March 2021 (n = 4) > April 2021 (n = 3). These results correspond to precipitation levels: February 2021 (401.5 mm) > March 2021 (136.6 mm) > April 2021 (125.8 mm) > August 2021 (7.4 mm) (Figures 2 and 3). This pattern may explain the relationship between precipitation and the concentration or dilution of pesticides in aquatic environments, as well as their potential for leaching (Pérez-Lucas *et al*., 2018; Zhua *et al*., 2021). During the period of lowest precipitation

in August (Appendix Figure 2), pesticide concentrations and detection frequencies were higher, suggesting that the basin's water volume influences pesticide detectability in surface waters (Wang *et al*., 2022).

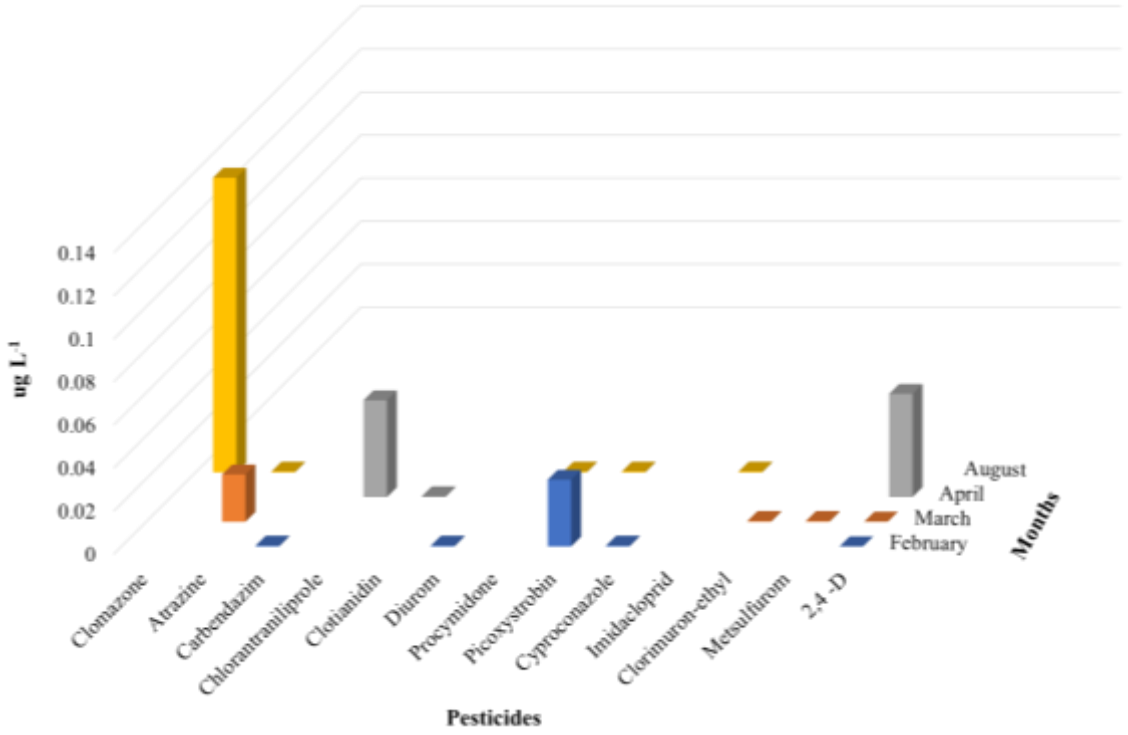


Figure 4 - Pesticide concentrations during sampling periods (February and March - wet season; April and August - dry season) in the Uruçuí-Preto river basin.

Sampling points 1, 2, and 3 exhibited the presence of four compounds, procymidone, picoxystrobin, clomazone, and atrazine (Figure 4), which may reach water bodies through point or diffuse sources. Their proximity to agricultural areas suggests that these pesticides were transported by diffuse runoff originating in crop fields (Figure 1), triggered by erosion or surface flow processes that promote gradual leaching into soil and surface waters (Jakobsen *et al*., 2019; Syafrudin *et al*., 2021).

These pesticides were identified at these points during August, corresponding to the dry season, which suggests that reduced basin water volume may increase compound concentrations (Liu *et al*., 2025). The potential for transport to surface waters is determined by pesticide properties such as half-life, solubility, and adsorption capacity. As most pesticides are organic compounds, they typically degrade through microbial, photochemical, or chemical reactions (Meite *et al*., 2018).

Procymidone is an organophosphorus fungicide used in both preventive and curative applications, commonly applied by spraying (Özdoğan *et al*., 2018). It may have been applied

in agricultural fields near the basin before or after planting, in seed treatments, or during pre- and post-harvest operations, depending on the target crop (Kapukıran *et al*., 2019). Its soil half-life ranges from 14.3 to 21.4 days, depending on soil type and moisture (Zhang *et al*., 2021), suggesting that residues may reach aquatic environments long after application. Its low water solubility (2.46 mg L^{-1} at 20 °C) and high leaching potential index (University of Hertfordshire, 2025) indicate that it may persist in aquatic systems even after rainfall events.

Strobilurins are among the most widely used classes of fungicides in modern agriculture. However, when they reach non-target environments, they may exert toxic effects on unintended organisms, especially in aquatic ecosystems (Zhao; Zhao; Hu, 2020). Picoxystrobin, a strobilurin fungicide, was detected at nine sampling points in August (dry period) and at only one point in February, the month with the highest precipitation (Figure 3; Appendix Figure 2). Intensive use of this fungicide may pose environmental risks, as it can enter water bodies via spray drift, leaching, and surface runoff (Li *et al*., 2018). Previous studies show that elevated picoxystrobin concentrations in water often occur following rainfall events after application (Guo *et al*., 2017), which is consistent with the results of this study. In February, the highest picoxystrobin concentration (0.031 μg L^{-1}) was recorded, likely due to mobilization of soil residues (Figure 3). Picoxystrobin residues tend to persist in agricultural soils, favoring transport by leaching (Jia *et al*., 2018). The compound has moderate water solubility (3.1 mg L^{-1}) and can persist for extended periods in environments with limited light exposure, with aquatic half-lives ranging from 39 to 83 days depending on oxygen availability and microbial activity (University of Hertfordshire, 2025).

Similarly, clomazone was detected at all sampling points in August (Figure 4), whereas it was not detected in the rainy months (February and March). This distribution may be explained by environmental mechanisms that influence the mobility and persistence of clomazone. Clomazone exhibits relatively high-water solubility, approximately 1,100 mg L^{-1}, indicating potential mobility in soils with low organic matter content (Cao *et al*., 2025). Its half-life in surface waters is about 30 days, and the compound remains stable at pH 4.65 and 7.0, which aligns with the conditions of this study, where pH varied from 5.65 to 6.45 during the sampling period. This stability contributes to its persistence in the water column over long periods (Miranda *et al*., 2025). In soils, clomazone half-life can range from 28 to 84 days under aerobic conditions, depending on soil type and climate (Cao *et al*., 2025). During the rainy season, the compound is expected to be diluted more rapidly and transported through surface runoff and percolation, reducing its concentration in the water column and hindering its detection in point samples collected from rivers or streams (Correia *et al*., 2020). Its high

mobility, combined with incorporation into sediments or dispersion by flow, can make its presence transient and often below detection limits (Schreiber *et al*., 2017).

Atrazine, a triazine herbicide widely used in crops such as maize, soybean, and sugarcane, was detected at four sampling points in August, the dry season with only 7.4 mm of rainfall, and at a single point in March, part of the rainy season, which recorded 136.6 mm of precipitation (Figure 4). This temporal distribution highlights the strong influence of meteorological conditions on the mobility of this compound, which is known for its high environmental persistence (Barcellos *et al*., 2022; Chang *et al*., 2022). Its more frequent occurrence in August, despite low precipitation, may be explained by reduced dilution, allowing residues from earlier applications to remain in aquatic microhabitats (Figure 4). In March, intense rainfall (136.6 mm) may have promoted rapid dilution, transport, and dispersion of atrazine, resulting in concentrations below detection limits at most sampling points (Appendix Figure 2). Nonetheless, its occurrence, even sporadic, reinforces its potential for mobilization under heavy rainfall, especially in areas near agricultural zones, as well as its prolonged environmental persistence (Barcellos *et al*., 2022). Atrazine has a water solubility of approximately 33 mg L^{-1} at 25 °C and low soil adsorption, enabling its mobility via surface runoff and leaching, particularly in soils with low organic matter content (Deng *et al*., 2024). Its half-life in soil ranges from 18 to 148 days, and in aquatic systems it may persist from 30 to 100 days (Hong *et al*., 2022), which contributes to its detection even during dry periods.

In February, the month with the highest rainfall in the study (401.5 mm), the herbicide 2,4-D was detected at points 2, 3, 4, 5, and 7 (Figure 4; Appendix Figure 2). The presence of this compound is directly linked to its high environmental mobility, given its high-water solubility (approximately 900 mg L^{-1} at 25 °C) and low soil adsorption capacity, especially in soils with low organic matter (Magnoli *et al*., 2020). These characteristics favor leaching and transport via surface runoff, phenomena that are intensified during rainy periods (Meftaul *et al*., 2020).

At sampling point 5, clomazone and procymidone were detected during August. In April, when precipitation reached 136.6 mm, chlorantraniliprole was detected, suggesting potential mobilization of this compound through surface runoff. Although point 5 is located in grassland vegetation, its proximity to agricultural areas suggests possible transport into surface waters (Figure 1).

Among the compounds detected at levels close to the LOQ, procymidone (WP) stands out, occurring in nine samples and frequently observed during the rainy season at points P2, P4, P7, and P9 (Figure 3). This pattern may indicate diffuse contamination from agricultural

applications, as well as its slow degradation. The other pesticides, clothianidin (TI-435), imidacloprid (IMI), cyproconazole (CIPRO), carbendazim (CBZ), diuron, chlorimuron-ethyl, and metsulfuron-methyl (MSM), were detected individually (n = 1) and at very low concentrations, reflecting a pattern of sporadic contamination, possibly associated with recent application events or long-distance transport via drift or drainage.

4.4.3 Correlation among pesticides, environmental variables, and seasonality

Pesticides may exhibit correlations with environmental variables such as precipitation, land use and land cover, as well as their specific physicochemical properties (Einsiedel *et al*., 2024). The correlation analysis among pesticides (Figure 5a) groups them according to patterns of environmental occurrence, indicating that certain compounds tend to appear together at the same sampling points and during the same periods. Also, a clear separation between herbicides and fungicides, suggesting that agronomic class influences their presence across points and sampling periods, as these products are typically applied during distinct agricultural cycles (Figure 5).

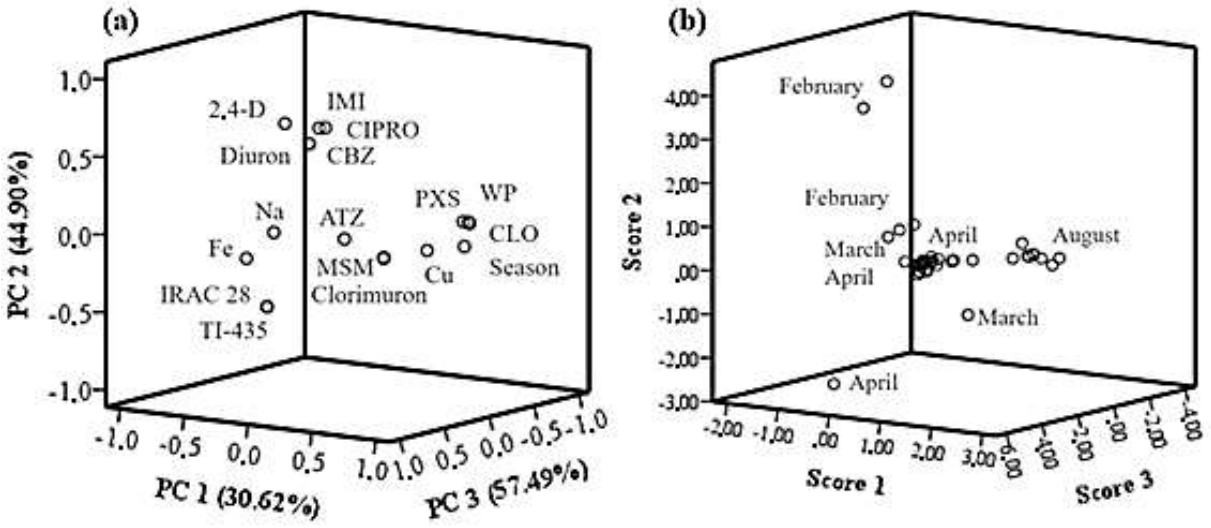


Figure 5 - Correlation among pesticide compounds, seasonality, and physicochemical variables; (b) correlation among the different sampling months. 2,4-dichlorophenoxyacetic acid (2,4-D), Diuron, Imidacloprid (IMI), Cyproconazole (CIPRO), Carbendazim (CBZ), Chlorantraniliprole (IRAC 28), Clothianidin (TI-435), Atrazine (ATZ), Metsulfuron (MSM), Clorimuron-ethyl (Clorimuron), Clomazone (CLO), Season, Picoxystrobin (PXS), Procymidone (WP).

February appears more isolated from the other months, reflecting the effect of the high precipitation characteristic of this period (Figure 4b; Appendix Figure 2). This intense rainfall

regime alters the mechanisms of transport and dispersion of nutrients and pesticides within the watershed, enhancing processes such as surface runoff and leaching (Schönenberger *et al*., 2022). Its proximity to March and April indicates that the persistence of rainfall during these months results in more similar hydrological conditions among them.

August, on the other hand, marked by very low precipitation, also appears isolated, representing the typical conditions of the dry season (Figures 4 and 5; Appendix Figure 2). In this month, a higher number of pesticides was detected across sampling points compared to the other months, which is associated with reduced water volume and the persistence of more stable molecules in the environment (Liu *et al*., 2025; Wang *et al*., 2025a), justifying its separation in the clustering.

4.4.4 Effect of seasonality on the correlation between pesticides and physicochemical parameters of the water

The Spearman correlation analysis (Figure 6) revealed marked differences between the dry and rainy seasons, underscoring the crucial role of seasonality in shaping pesticide behavior within the watershed. During the dry period (Figure 6a), positive correlations predominated among physicochemical variables such as electrical conductivity (EC), temperature, Na, and K, indicating concentration effects related to lower discharge and increased evaporation. These conditions suggest that reduced dilution and enhanced evaporative concentration promote the accumulation of dissolved ions in surface waters (Li *et al*., 2022).

During the rainy period (Figure 6b), correlations distinct from those observed in the dry season were identified, reflecting the influence of greater water availability and enhanced element mobilization on pesticide dynamics within the watershed. Positive correlations among pH, Na^+, and K^+, as well as between Ca and EC, indicate cation mobilization during hydrological recharge. This behavior is associated with increased mineralization of surface waters, which may result from the leaching of soil salts and the diffuse input of sodium- and potassium-based fertilizers applied in agricultural areas of the basin (Oliveira *et al*., 2021; Stewart *et al*., 2022).

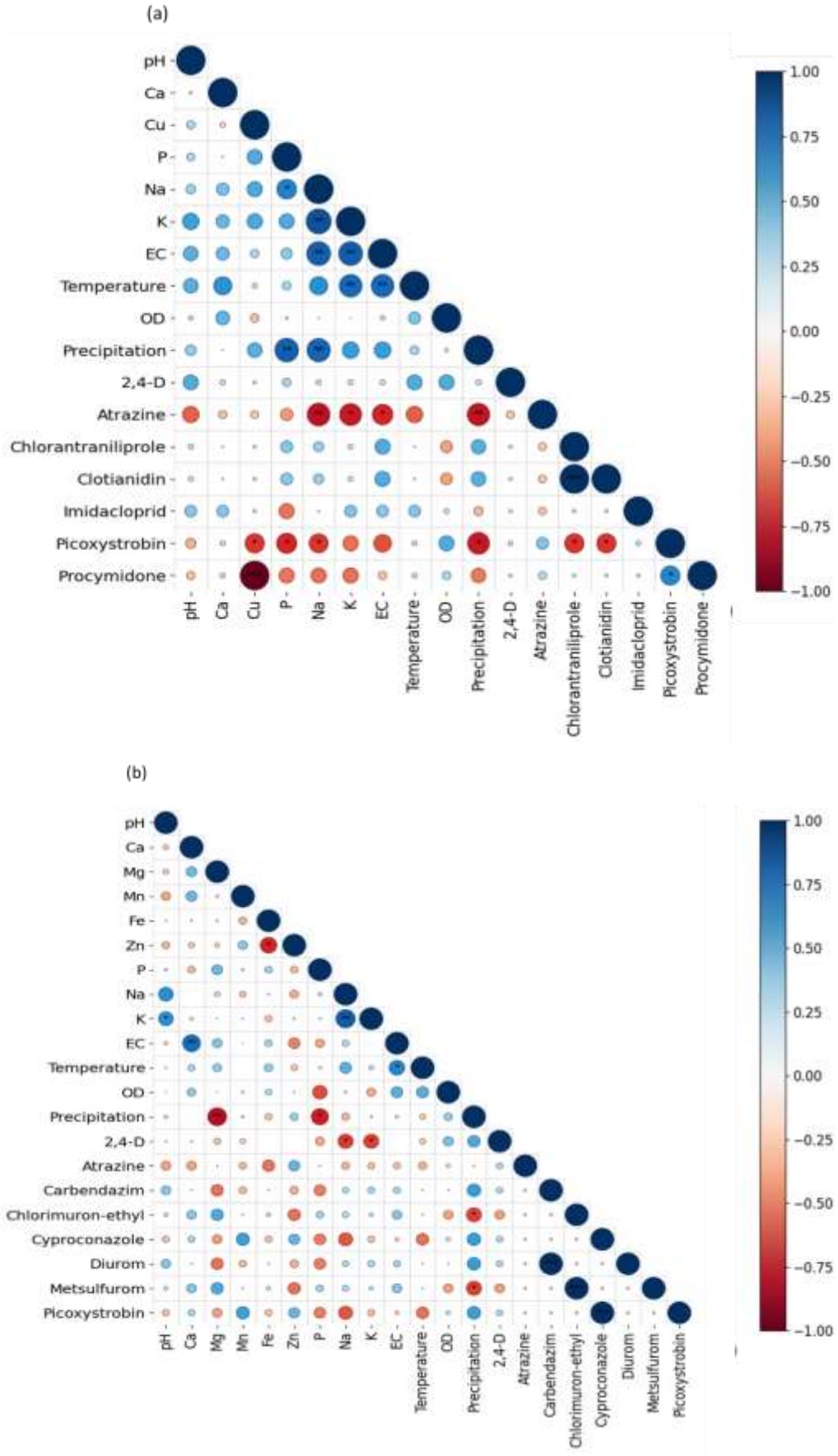


Figure 6 - Spearman correlation matrix between pesticides and physicochemical water variables during the (a) dry and (b) rainy period.

Positive correlations were also observed among pesticide compounds, such as diuron and carbendazim, and between metsulfuron and chlorimuron-ethyl, suggesting that these compounds may originate from common application sources or share similar environmental behavior (Figure 6b). Additionally, a positive correlation between cyproconazole and picoxystrobin indicates that these fungicides are often applied together or mobilized under similar hydrological conditions, possibly associated with intensified phytosanitary management during planting periods (Porter; Collins, 2025).

On the other hand, negative correlations between precipitation, Mg, and P indicate that increased discharge leads to dilution of these elements within the watershed, reducing their concentrations (Wang *et al*., 2025b). A negative correlation was also observed between 2,4-D, Na, and K, indicating that this herbicide tends to show higher concentrations when Na and K ions are at lower levels, which may reflect its greater persistence in the aqueous phase under conditions of reduced mineralization. This behavior is consistent with studies showing that the environmental fate of 2,4-D is strongly influenced by chemical conditions, including ionic strength, which affects its sorption and mobility (Blachnio *et al*., 2023).

Furthermore, the negative correlations between chlorimuron-ethyl and precipitation, as well as between metsulfuron and precipitation, suggest that these compounds are more susceptible to dilution during intense rainfall events, possibly because they are rapidly transported to other compartments or undergo faster degradation in environments with higher water input (Puczko; JekatierynczuK, 2020).

4.5 Conclusion

This study demonstrated the occurrence of multiple pesticides in the surface waters of the Uruçuí-Preto River Basin, with clear spatial and temporal variations. The findings show that pesticide dynamics and occurrence are closely linked to climatic seasonality, land use and land cover, and the physicochemical properties of the detected compounds.

During the rainy season, higher concentrations and greater diversity of pesticides were observed, particularly in areas influenced by agricultural activities. In the dry season, although overall concentrations decreased, different compounds were still detected at all sampling points, indicating that contamination is not limited to immediate rainfall events and that some pesticides may persist in the environment. Multivariate analysis reinforced these patterns by grouping compounds according to similarities in persistence, solubility, and application period, highlighting environmental behaviors across agronomic classes.

The results emphasize the need for continuous monitoring of water quality in the basin, especially considering the intense agricultural activity and recurrent pesticide use. The adoption of environmentally responsible agricultural management practices and mitigation strategies aimed at reducing drift and surface runoff is essential to prevent contamination of non-target areas. Although the concentrations observed did not exceed the maximum limits established by current Brazilian legislation, the recurrent presence of multiple pesticides indicates a potential cumulative risk and reinforces the importance of ongoing surveillance and monitoring of these compounds.

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5 CHAPTER 3

FACTORS CONTROLLING THE GEOCHEMISTRY OF THE URUÇUÍ-PRETO RIVER WATER IN THE NORTHEASTERN BRAZILIAN CERRADO DURING A COMPLETE HYDROLOGICAL CYCLE

ABSTRACT

The agricultural expansion in the Cerrado biome is characterized by rapid human occupation and intensified economic activities associated with the conversion of native vegetation into extensive cropland for grain production. This study examines the physicochemical parameters and elemental distribution in surface waters of the Uruçuí-Preto River during the dry and rainy seasons in a watershed located within Brazil's last agricultural frontier, where land-use intensification poses significant risks to water resources. Surface water samples were collected at 19 points along the river's main channel over a complete hydrological year (January to December 2021). Physicochemical analyses, pH, electrical conductivity (EC), temperature, and dissolved oxygen (DO), and the determination of Ca, Mg, P, K, Mn, Zn, Fe, and Cu were conducted to evaluate the influence of seasonality and land-use/land-cover changes. The results indicate that local climatic conditions strongly influence the concentration of these elements. Water quality in the watershed was not substantially compromised despite its proximity to agricultural areas. Canonical correlation analysis revealed that different land-use types, including croplands and pastures, were associated with several water variables, such as physicochemical parameters (pH, EC, and DO) and specific elements (e.g., Ca, P, and Zn). The study concludes that continuous water-quality monitoring is essential to mitigate the negative impacts of excessive agricultural inputs and urban pollution. Spatial and temporal variability analyses proved effective for ensuring the sustainability of water resources in the Uruçuí-Preto River watershed. Overall, the findings highlight the importance of adopting sustainable management practices to safeguard water quality in regions vulnerable to environmental degradation.

Keywords: Agricultural expansion, Climatic conditions, Spatio-temporal changes, Water elements, Water quality.

5.1 Introduction

Population growth and global demand for food have driven the rapid expansion of agricultural lands in the last century. Since the 1980s, agriculture has expanded more rapidly in the Global South (Fuglie *et al*., 2024), directly impacting ecosystem functions. Land-use changes can affect these functions within watersheds, altering systems, water flow, and reducing water quality (Baggio *et al*., 2021; Getirana *et al*., 2021). In this context, freshwater quality has become a concern due to increasing urbanization, agricultural expansion, prolonged droughts, inadequate treatment infrastructure, and industrialization, which lead to excessive water use for various daily activities (Ustaoğlu *et al*., 2021; Santos; Laranja, 2024; Bojer *et al*., 2025).

Different types of land use pose risks to water resources, with urban and agricultural areas being the most significant contributors to global water quality degradation (Akhtar *et al*., 2021; Nascimento *et al*., 2023). Moreover, well-managed soils enhance water infiltration, improve groundwater recharge, and reduce surface runoff, thus mitigating river pollution. Agricultural and urban effluents are also sources of diffuse pollution in freshwater systems. However, interactions between the tropical climate, soil types, vegetation, and land management practices result in varying impacts on water quality (Mello *et al*., 2018; Mello *et al*., 2020; Salomão *et al*., 2023).

Currently, Brazil ranks as the third-largest grain producer globally, being a top-5 producer of 34 agricultural commodities (Valdes, 2022). Also, holds the largest volume of water resources among all nations (Getirana *et al*., 2021). However, water scarcity has become a growing issue (Mello *et al*., 2020), driven by prolonged droughts, increased consumption, and inadequate treatment infrastructure. These factors, compounded by population growth and intensive land use, contribute to the degradation of water quality, affecting its natural properties.

In the country, the primary drivers of land-use changes and their consequent effects on water quality include the conversion of tropical forests into agricultural or urbanized areas. This trend is evident in the Cerrado biome, where native vegetation is replaced by agricultural fields, representing a significant cause of water quality risks in the biome's rivers (Dias, 2024). The Cerrado is home to numerous springs and critical recharge zones, playing a vital role in the hydrological processes of watersheds in the region.

This study focuses on a watershed in northeastern Brazil, located in the southern region of Piauí and within the Cerrado biome, considered one of Brazil's last agricultural frontiers. Numerous studies on soil quality (Amorim *et al*., 2020; Sousa *et al*., 2023), soil pollution (Brito

et al., 2020), agricultural productivity, and management systems (Sousa *et al*., 2019; Pires *et al*., 2020) have been conducted, driven by the cultivation of crops, particularly soybeans and corn. Conversely, research in other regions has shown that land-use changes and soil degradation are contributing to water scarcity, reduced reservoirs, and declining water quality (Ingrao *et al*., 2023). However, due to insufficient observational data, issues related to water resources in the northeastern Cerrado remain unresolved.

In this context, nutrients are essential for sustaining life in both soil and water, but when present in excess, they act as pollutants, leading to eutrophication and water quality deterioration. Similarly, the absence or low levels of nutrients can disrupt ecosystem dynamics (Wroblescki *et al*., 2021). Thus, maintaining a balance in land-use practices is crucial, especially near watersheds, where excessive fertilizer application represents a major source of diffuse water pollution.

The Uruçuí-Preto River watershed stands out for its expanding grain cultivation, which is one of the main economic activities in northeastern Brazil (Souza *et al*., 2023). This study hypothesizes that specific land-use types, particularly agricultural areas under intensive cultivation, are the primary drivers of changes in nutrient concentrations in the surface waters of the Uruçuí-Preto River watershed, with the highest concentrations expected during the rainy season due to enhanced runoff and nutrient mobilization. The objective of this study was to characterize the spatial and seasonal (dry and rainy periods) variation of physical–chemical parameters and the concentrations of calcium (Ca), magnesium (Mg), zinc (Zn), iron (Fe), copper (Cu), manganese (Mn), and available phosphorus (P) in the surface waters of the Uruçuí-Preto River watershed, and to evaluate how specific land-use types, particularly intensive agricultural areas, drive changes in these variables across climate seasons.

5.2 Material and methods

5.2.1 Study area

The Uruçuí-Preto River basin, located in the state of Piauí (Figure 7), is one of the main tributaries of the Parnaíba river. The basin is located between the coordinates 7° 18′ 16″ to 9° 33′06″ south and 44° 15′ 30″ to 45° 31′ 11″ west with a surface of 15,777 km^2. The watershed is drained by the Uruçuí-Preto River and its tributaries, Ribeirão dos Paulos, Castros, Colheres and Morro d'Água, in addition to the Estiva and Corrente streams. The river is 300 km long and covers 25 municipalities distributed throughout the basin (Medeiros, 2022). The river originates

on the border of the municipalities of Santa Filomena and Gilbués, with its headwaters coming from two large streams, and its mouth is located 12 km from the city of Uruçuí, Piauí.

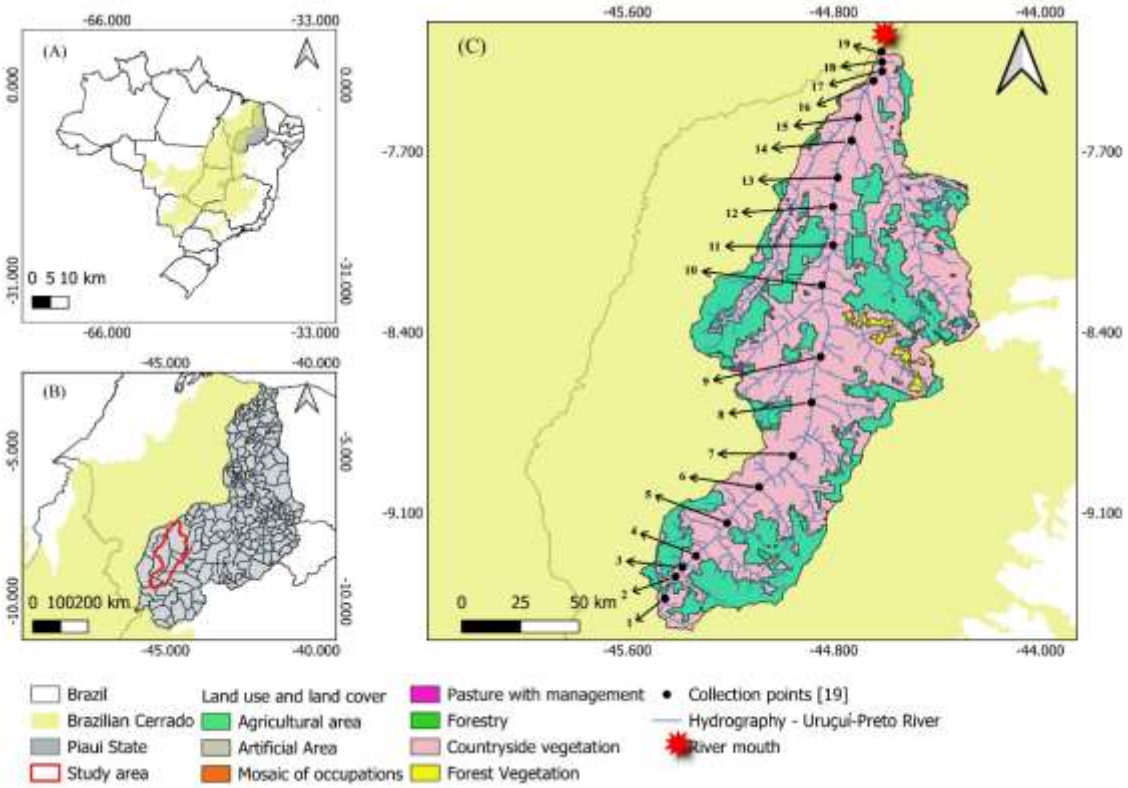


Figure 7 - Location map of the study area in Cerrado biome (A), Uruçuí-Preto River basin (B) and land use and land cover and location of sampling points.

In Brazil, water quality standards are described in CONAMA Resolution No. 357 (CONAMA, 2005), which classifies surface waters according to biological, chemical, and physicochemical parameters and their intended use for each water body (Galhardi; Bonotto, 2016). According to this resolution, the Uruçuí-Preto River watershed is classified as Class II, which allows for the following uses: human consumption after simplified treatment, protection of aquatic communities, recreational activities, aquaculture, and irrigation (CONAMA, 2005).

The region's average temperature is 31.6 °C, with an annual maximum of 39.0 °C in October and a minimum of 16.9 °C in July. Along the basin, two climatic types can be distinguished: Aw, tropical hot and humid, wet summer and dry winter and BSh, hot semi-arid (Köppen). The average total annual precipitation is 913.9 mm, with a monthly maximum of over 200 mm usually in March, in a rainy season that extends from November to mid-April (Medeiros *et al.*, 2022). The main soil types found in the Uruçuí-Preto River basin are Oxisols, which dominate the area, as well as Entisols (Soil Survey Staff, 2014).

The Uruçuí-Preto River has an average, maximum, and minimum annual discharge of 28.81, 62.37, and 19.19 $m^3 s^{-1}$, respectively (Souza *et al.*, 2019), with average depth ranging from 1.5 m (near the headwaters) to approximately 6.0 m (during the dry season).

Data on land use was obtained from the IBGE (2022). Native grassland vegetation (65.36%) and agricultural areas (31.44%) are the predominant land use (Figure 7). Grassland vegetation is characterized by the predominance of sparsely distributed shrubs over a grassy-woody stratum, including Savannas, Steppes, Savanna-Steppes, Pioneer Formations, and Ecological Refuges (IBGE, 2022). Agricultural areas are characterized by temporary, semi-perennial, and permanent crops, irrigated or not, used to produce food, fibers, fuels, and other raw materials (IBGE, 2022). Other land use types contribute slightly more than 3% of the basin's area and are subdivided into developed areas, managed pastures, intended for grazing cattle and other animals; and forestry, which is the cultivation of managed forests for a variety of purposes (IBGE, 2022). Figure 8 shows the dominant land use in the sub-watersheds for each of the 19 sampling sites.

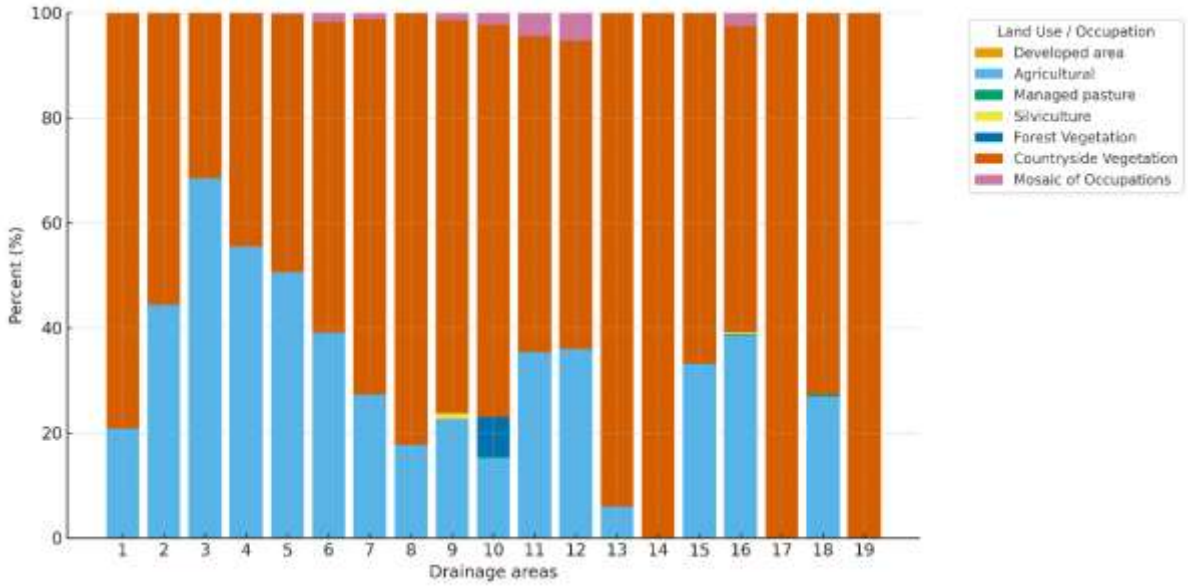


Figure 8 - Distribution of land use and land cover (%) across the Uruçuí-Preto River basin at the 19 sampling sites.

The basin is situated in a prosperous agricultural region that has rapidly expanded within the Cerrado biome, a leading region in the production of agricultural crops such as soybeans and corn. These crops are cultivated between November and March, a period that coincides with the region's rainy season (Figure 8).

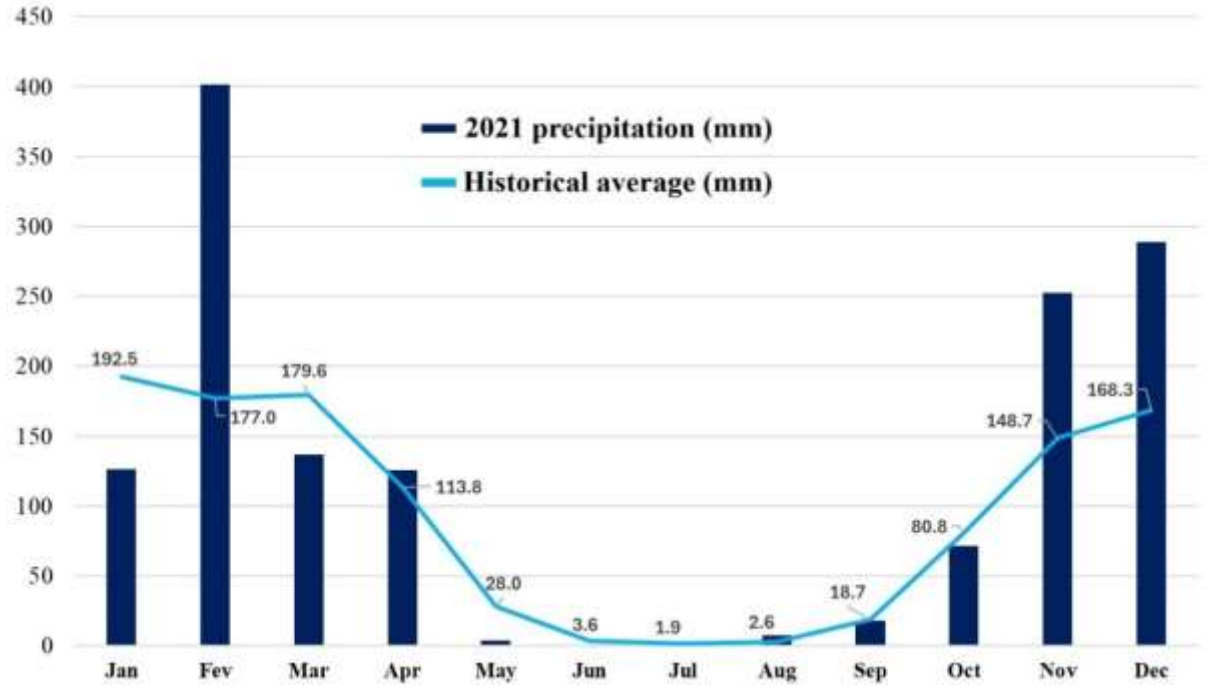


Figure 9 - Average monthly precipitation (mm) recorded from January 2021 to December 2021 in the Urucuí-Preto river basin (NASA, 2023). Historical average is calculated from data available at the World Bank Climate Change Knowledge Portal (https://climateknowledgeportal.worldbank.org/) covering the period of 1901-2020.

5.2.2 Sample collection

During the hydrological year from January to December 2021 (Figure 9), covering the dry season (April to October) and rainy season (November to March), water samples were collected monthly at 19 points distributed along the Uruçuí-Preto River. Factors used in the selection of sampling sites included the presence of tributaries and ease of access, according to guidelines from the Brazilian National Water Agency (ANA, 2011).

Polyethylene plastic samplers with a volume of 5 L were used, placed at a depth of 0.0 - 0.10 m below the water surface to collect surface water samples (Figure 10A and 10B). Before each collection, the samplers were washed with a 2 N HCl solution and Milli-Q 18.2 MΩ cm water (CETESB, 2011).

Portable field meters were used for the measurement of physical-chemical parameters (Figure 4D). The pH of the water samples was measured using a Tecnal pH-meter (model Tec-3MP). Electrical conductivity (EC) was measured using a Hanna conductivity meter (model HL98303). Water temperature (T), and dissolved oxygen (DO) were measured using an AKSO digital water quality meter (model Ak87). All instruments were calibrated before each field campaign using calibration solutions recommended by the manufacturers. After filtration, the

original sampled volume was separated into subsamples and stored in sterile 25 mL pre-identified containers (Figure 4C), stored at a temperature of 4 ± 2 ºC (ANA, 2011) and sent to a laboratory for analysis.



Figure 10 - Sample collection (A, B), sample identification (C), sample filtration in the field and measurement of physical-chemical parameters using field meters (D).

5.2.3 Laboratory analyses

Using a pipette, 0.10 mL of water (sub-samples) was diluted and homogenized with 4.9 mL of lanthanum solution (1 g L^{-1}) (Parron, 2011) for the determination of calcium (Ca), and magnesium (Mg). Only filtered water (sub-samples) were used for zinc (Zn), iron (Fe), copper (Cu), and manganese (Mn). Concentrations were determined using a rapid sequential atomic absorption spectrophotometer (Agilent, Model 240FS AA®, Hainesport, NJ, USA).

Available phosphorus (P-available) was determined by colorimetric analysis. In this method, 5.0 mL of water was pipetted, 10 mL of diluted ammonium molybdate acid solution was added, and approximately 30 mg of ascorbic acid was included. Then, the reading was taken on a UV-Vis spectrophotometer (Even, Model ESPEC-UV-5100®) at a wavelength of 660 nm. To determine potassium (K), 20 mL of water solution (sample) was pipetted, and the reading was performed on a flame photometer (Analyzer, Model 910®) after calibration with distilled water (Parron, 2011).

5.2.4 Statistical analyses

Data were organized into matrices, and descriptive statistics were used to calculate mean values, standard deviations, and maximum and minimum values. Spatial and temporal

distributions were represented by boxplots (median and upper and lower limits). To compare nutrient concentrations between points, the Kruskal-Wallis test ($p < 0.05$) was used.

The differences among land-use types were evaluated using Canonical Variable Analysis (CVA), implemented through the Canonical Variable function from the {Multivariate Analysis} package (Azevedo, 2025). CVA is a multivariate procedure analogous to Canonical Discriminant Analysis, aiming to identify linear combinations of environmental variables that maximize separation among groups (levels of the factor Land Use). Prior to analysis, all continuous environmental variables were standardized (mean = 0; standard deviation = 1) to avoid scale differences among units of measurement. The model included the factor Land Use, comprising categories such as Agriculture, Grassland, Pasture, Forestry, Mosaic, among others. The CV1 and CV2 axes were used to represent the multivariate separation among groups, while the vectors of environmental variables indicated their contribution to discrimination among land-use types.

All analyses were performed in the R environment (R Core Team, 2024), using the {MultivariateAnalysis}, {tidyverse}, and {ggplot2} packages.

5.3 Results

The concentrations and spatial–temporal distribution of the studied elements and physicochemical parameters are presented in Figures 11 and 12. Differences between dry and rainy periods were observed, with median, minimum, and maximum values represented for each variable (Figure 11). Based on precipitation data, the months of January, February, March, April, November, and December were classified as the rainy season, while the period from May to October corresponded to the dry season (Figure 8).

Calcium concentrations varied along the watershed among sampling points, with no statistically significant difference between the dry and rainy periods (Figure 11A). Magnesium showed lower concentrations during the dry season and higher concentrations during the rainy period (Figure 11B). Potassium concentrations were higher during the rainy season compared to the dry season at most sampling points (Figure 11C). Phosphorus exhibited higher concentrations during the dry period (Figure 11D).

Sodium concentrations varied between seasons and among sampling points (Figure 11E). Manganese presented low concentrations during the dry season, with increased concentrations during the rainy season at sampling points 3, 4, 7, 12, 14, 15, 17, and 19 (Figure

11F). Zinc and iron concentrations were low at all sampling points during the dry period and increased during the rainy period (Figures 11G and 11H).

Physicochemical parameters, including pH, electrical conductivity, temperature, and dissolved oxygen, showed spatial and seasonal variability within the watershed (Figure 12). Water pH values ranged from 4.65 to 7.85 across both seasons, with average values above 6.0 (Figure 12A). Electrical conductivity values remained below the limits established by CONAMA Resolution No. 357/05 and showed an increasing trend from the headwaters toward the river mouth across all sampling periods (Figure 12B). Water temperature values were higher during the dry period (Figure 12C). Dissolved oxygen concentrations exceeded 5.0 mg L^{-1} during the dry period and were equal to or below 4.0 mg L^{-1} during the rainy period (Figure 12D).

Spatial variability in surface water quality was observed among sampling points, influenced by climate conditions, land use and land cover, and the location of the sites (Tables S1 and S2). Calcium, potassium, and sodium concentrations varied among sampling points (Figure 13). The highest potassium concentration was recorded at sampling point 1, located near the river source. Sodium concentrations increased longitudinally from the headwaters toward the river mouth (Figure 13).

Canonical correlation analysis (CCA) was used to evaluate relationships among physicochemical parameters, climatic variables, and land use and land cover (Figure 14). The first canonical axis explained more than 84% of the correlation structure. This axis included associations among physicochemical parameters and land-use categories such as developed areas, managed pasture, agricultural land, occupation mosaics, grassland vegetation, silviculture, and forest vegetation.

5.4 Discussion

5.4.1 Seasonal variability in water quality

The concentrations and distribution of studied elements and physicochemical parameters are presented in Figures 11 and 12. These results show greater correlation with the precipitation during the months of January, February, March, April, November, and December, defining the rainy season, while the months from May to October characterize the dry season (Figure8). Differences between dry and rainy periods are observed, with the median and maximum and minimum values represented (Figure 11). In three lentic environments rounded

by agriculture activities in a conservation unit of Brazil were observed the same results with high differences in the nutrients concentrations influenced by seasons and rainy period (Santos; Laranja, 2024).

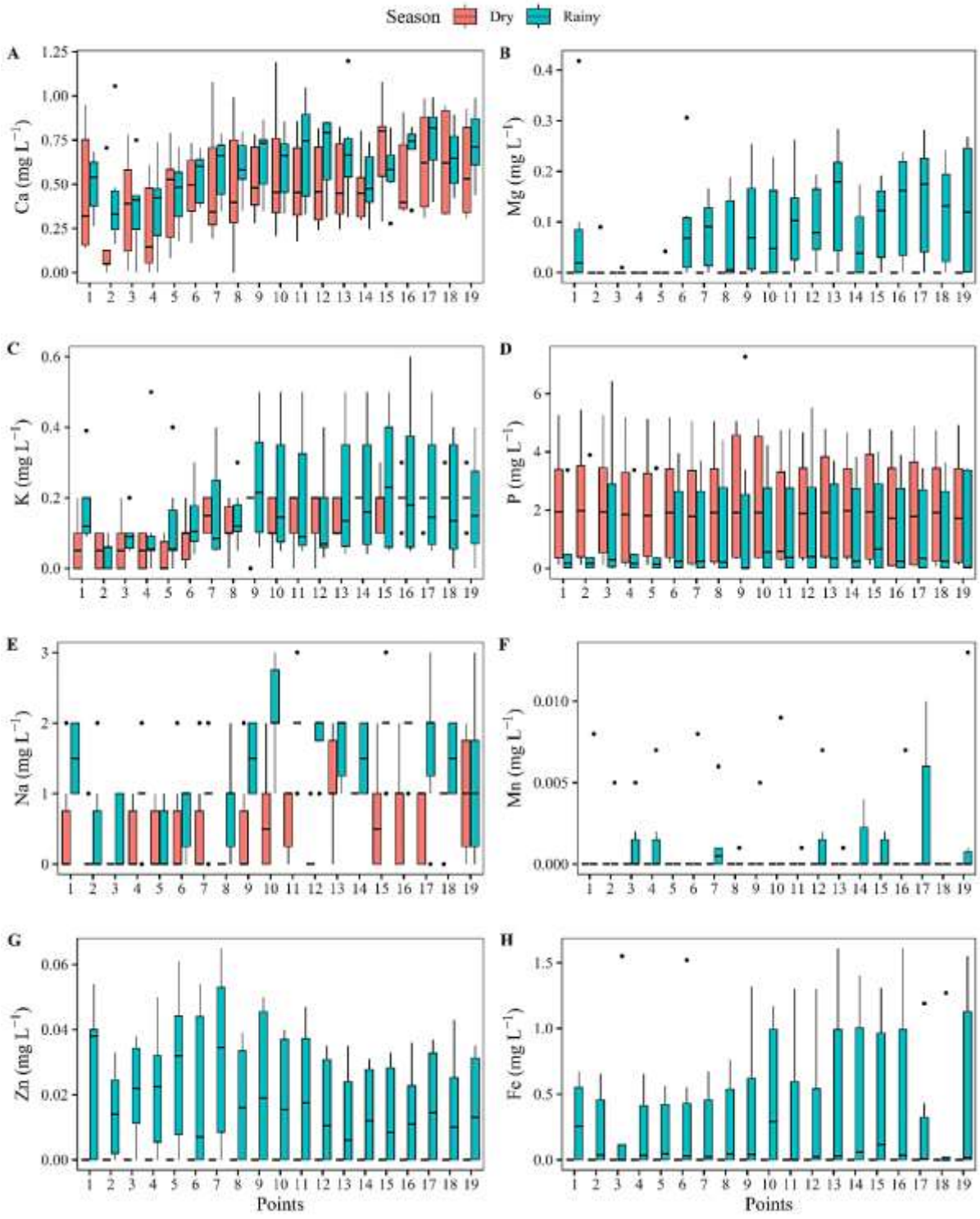


Figure 11 - Spatio-temporal variability of the concentration of Ca (A), Mg (B), K (C), P (D), Na (E), Mn (F), Zn (G), and Fe (H), during the dry and rainy periods in surface waters of the Uruçuí-Preto River, Piauí, Brazil.

It is noted that calcium showed variations along the watershed, at different collection points, but the difference between the two analyzed periods was not significant (Figure 11A). The concentration of calcium in the water is associated with plant respiration and organic matter decomposition (Colin *et al*., 2006). Water is enriched with dissolved CO_2 (Stefano *et al*., 2019) due to respiration and organic matter decomposition within the watershed, and through the mineralization process, calcium is released into surface waters. Also, Mg and Ca are nutrients commonly applied through dolomitic limestone to correct soil acidity in Cerrado systems (Brito *et al*., 2020; Veloso *et al*., 2020), and their introduction into the watershed may occur through leaching from soils into adjacent aquatic environments.

The element Mg had its lowest concentration in water during the dry season, but its concentration significantly increased during the rainy period (Figure 11B). This increase can be attributed to natural or anthropogenic sources, considering that the basin area is close to production regions. With rain, Mg becomes more mobile, manifesting at specific points (Khanoranga; Khalid, 2019), and is transported from agricultural areas, which use it in soil correction, to the surface waters of the watershed.

K showed higher concentrations during the rainy season compared to the dry season at most points (Figure 11C), suggesting that this element is transported by rainwater from different areas (Galhardi; Bonotto, 2016), increasing its concentration in the watershed's surface waters. This increase is more pronounced at points near agricultural areas, as the basin receives water from several tributaries, which becomes more intense during the rainy period (Figure 7).

Phosphorus (P) showed a higher concentration in the dry period (Figure 10D), in agreement with results found by Benassi *et al*. (2012), Rocha *et al*. (2018), and Tilahun *et al*. (2024). This element is a critical factor in determining water quality (Tilahun *et al*., 2024). Prolonged droughts in semi-arid regions, and the consequent decrease in river water volume, can promote eutrophication, affecting water quality by increasing total phosphorus concentrations (Carvalho *et al*., 2022).

Sodium showed considerable variation between the two periods (Figure 11E). At some points, Na concentrations were higher during the rainy season This behavior is to be expected, due to the lower volume of water and consequently a lower dilution power. (Nascimento *et al*., 2023). Also, sodium concentrations were higher in all areas with a history of land-use change compared to secondary forest. In agricultural land, excessive fertilizers and soil erosion can lead to an increase in ions in the water body (Mello *et al*., 2018; Nascimento *et al*., 2023). On the other hand, during the rainy season, sodium ions are dispersed due to the rise in water levels caused by precipitation (Fig 11E).

Manganese had very low concentrations during the dry season, with noticeable increases during the rainy season at points 3, 4, 7, 12, 14, 15, 17 and 19 (Figure 11F). These points are located near production regions, which may have influenced Mn presence during the rainy period, as fertilizers used in these areas can be transported by rainwater. Although Mn is essential for agriculture, excessive amounts can be harmful to human health (Hou *et al*., 2020).

Similarly, Zn and Fe concentrations were very low at all points during the dry season, but these concentrations increased during the rainy period (Figure 11G, H). The rise in Fe may be explained by the types of soils that make up the basin, which contain significant amounts of iron oxides, leading to the transport of this nutrient into the water. Zn is essential for organisms but can be toxic in high concentrations (Desaulty; Petelet-Giraud, 2020). Despite the higher occurrence of Zn during the rainy season, its levels are within those established by CONAMA (Brazil, 2005). The presence of this nutrient in the watershed may be related to fertilizer disposal containing Zn, as well as to burning and vehicle combustion that contribute to Zn dispersion in the environment. This metal is leached by rain, forming elevated concentrations that accumulate in rivers and ultimately reach watersheds (Desaulty; Petelet-Giraud, 2020).

Physicochemical parameters such as pH, electrical conductivity, temperature, and oxygen demand varied within the basin and were influenced by precipitation (Figure 12). Water pH in the Uruçuí-Preto River watershed ranged from 4.65 to 7.85 during both seasons (Figure 12A), with an average pH consistently above 6.0, classifying it as water within acidity standards according to CONAMA Resolution 357/05. Higher pH values were observed during the dry period, though there was no statistically significant difference between periods. The pH tends to decrease with increased rainfall, which may be related to the input of dissolved leached material (Conceição *et al*., 2020). River water pH can also be influenced by terrestrial inputs, as most soils in the humid tropics are acidic. This pattern is consistent with soils from the Uruçuí River basin, which range from pH 3.6 to 6.3, with an average of 4.7 (Boechat *et al*., 2020; Silva *et al*., 2021; Tanaka *et al*., 2021).

The electrical conductivity (EC) values of the Uruçuí-Preto River surface water are below the minimum standard levels established for this parameter by Resolution nº 357 (CONAMA, 2005), which is consistent with the chemical characteristics of the regional soils, as they also exhibit low EC. However, an exponential increasing trend in EC was observed from the river's headwaters to its mouth across all sampling periods (Figure 12B).

Water temperature was higher during the dry period (Figure 12C), as expected, due to increased surface heating driven primarily by conductive heat transfer. This process is influenced by factors such as solar irradiance, cloud cover, humidity, and topography (Muniz;

Caracristi, 2021). Temperature is one of the most important ecological variables, as many physical, chemical, and biological processes depend on it (Hamid *et al*., 2020). For the dissolved oxygen (DO) parameter, mean values above 5.0 mg L^{-1} (Class 2) were observed during the dry period, whereas values equal to or below 4.0 mg L^{-1} (Class 3) occurred during the rainy period (Figure 11D). However, these values are higher than those reported for water bodies in northern Brazil under different land-use and management conditions (Nascimento *et al*., 2023).

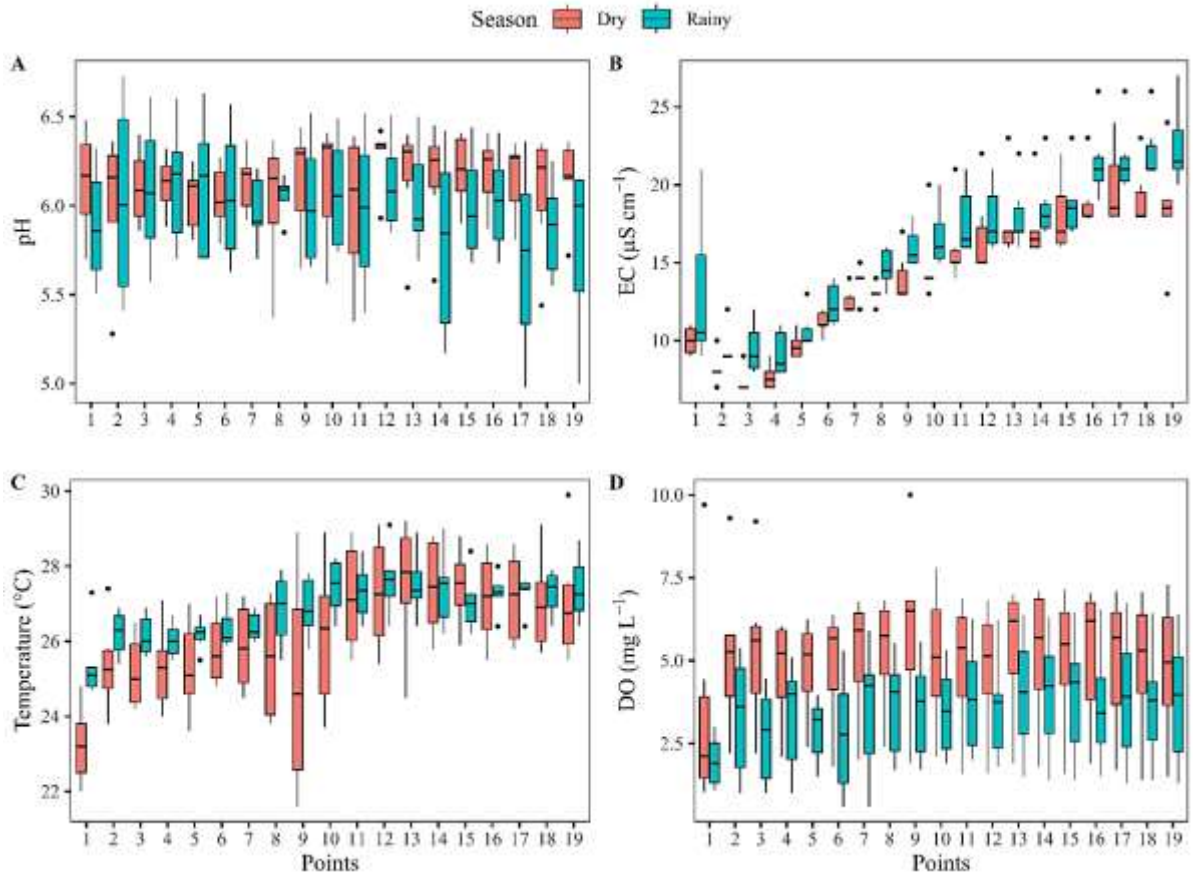


Figure 12 - Spatio-temporal variability of physicochemical parameters—pH (A), electrical conductivity (B), temperature (C), and dissolved oxygen (D), during the dry and rainy periods in surface waters of the Uruçuí-Preto River, Piauí, Brazil.

This pattern in the Uruçuí-Preto River may be related to precipitation, which dilutes organic matter and leads to lower DO concentrations during the rainy season (Rodrigues, 2023). Dissolved oxygen is also highly sensitive to seasonal variations in river discharge (Liu *et al*., 2020). Despite this, substantial variability was observed in both periods, as some sampling points are located in areas with dense vegetation or near diffuse pollution sources, both of which may influence DO levels (Tanaka *et al*., 2021).

5.4.2 Spatial variability in surface water quality

Climate conditions, land use and land cover, and the spatial location of the sampling points contribute to the variability in element concentrations, resulting in significant differences among sites (Tables S1 and S2).

Calcium, in the form of $CaCO_3$, is one of the main inputs used to correct soil acidity (Veloso *et al*., 2020), especially in Cerrado soils, which generally have high acidity (Brito *et al*., 2020). The different concentrations of this element are related to different land uses, as higher values are found near production areas where this element is used as a soil amendment in liming. In the Uruçuí-Preto River basin, the point with the highest concentration of K was point 1 (Figure 13), located near the river's source. This occurs because this point is close to areas where K is applied in fertilizers, which are transferred to other areas due to surface runoff and leaching. Despite the presence of this nutrient at all points, the values are within the limits recommended by CONAMA (2005) and do not pose risks to the health of organisms.

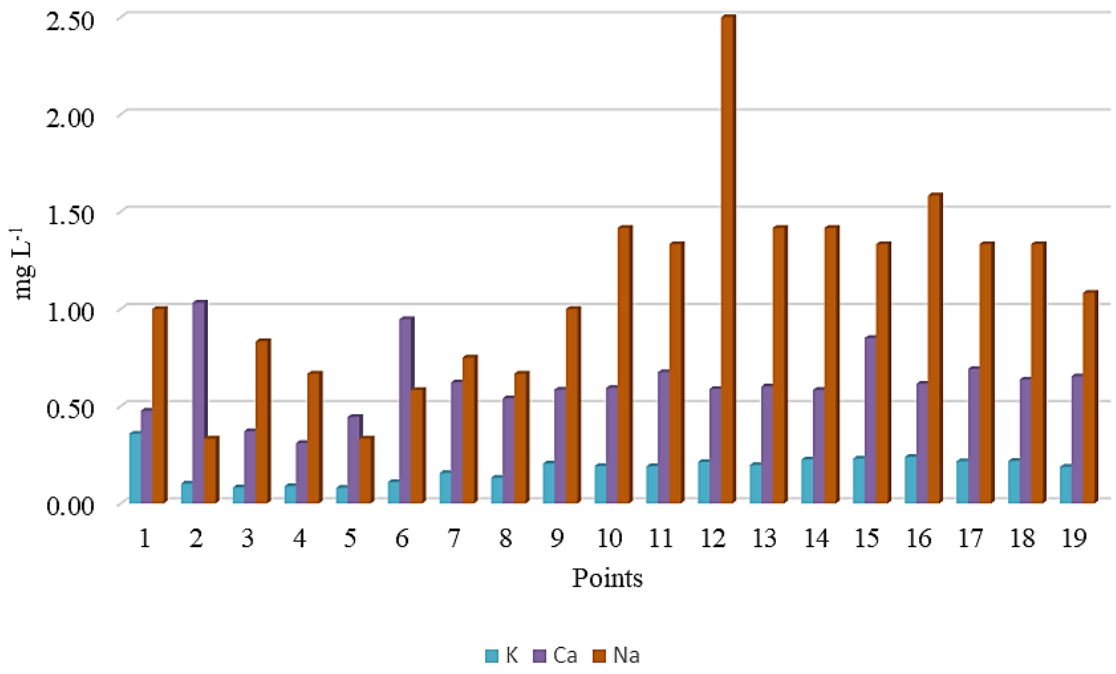


Figure 13 - Spatial variability of the concentration of Ca (A), K (B), and Na (C) in the surface waters of the Uruçuí-Preto River, Piauí, Brazil.

Regarding Na, a clear longitudinal pattern was observed, with lower concentrations near the headwaters and increasing values toward the river mouth (Figure 13). Sodium can enter surface waters through mineral deposits, sewage effluents, and sodium-containing chemical products (Mondal *et al*., 2019). However, Cerrado soils, including those in Piauí, are naturally

acidic and characterized by low organic matter content and low levels of micronutrients such as Mo (Sousa *et al*., 2019; Brito *et al*., 2020). Sodium molybdate is an important fertilizer in Cerrado regions of Piauí due to its role in nitrogen metabolism and biological nitrogen fixation in legumes, and it may represent the main source of this element in the surface waters of the Uruçuí-Preto River. Despite the observed variation, sodium concentrations remained well below the limits established by CONAMA (2005).

5.4.3 Effect of land use and occupation on the concentration of elements in water

As shown in figure 1, the spatial location of the sampling points influences the chemical and physical parameters of the watershed. In addition, climatic factors such as precipitation and temperature act as key drivers of nutrient mobilization and transport within watersheds (Coffey *et al*., 2019). The canonical correlation analysis (CCA) allowed us to examine the relationships among physicochemical variables, climatic conditions, and land use/land cover (Figure 14).

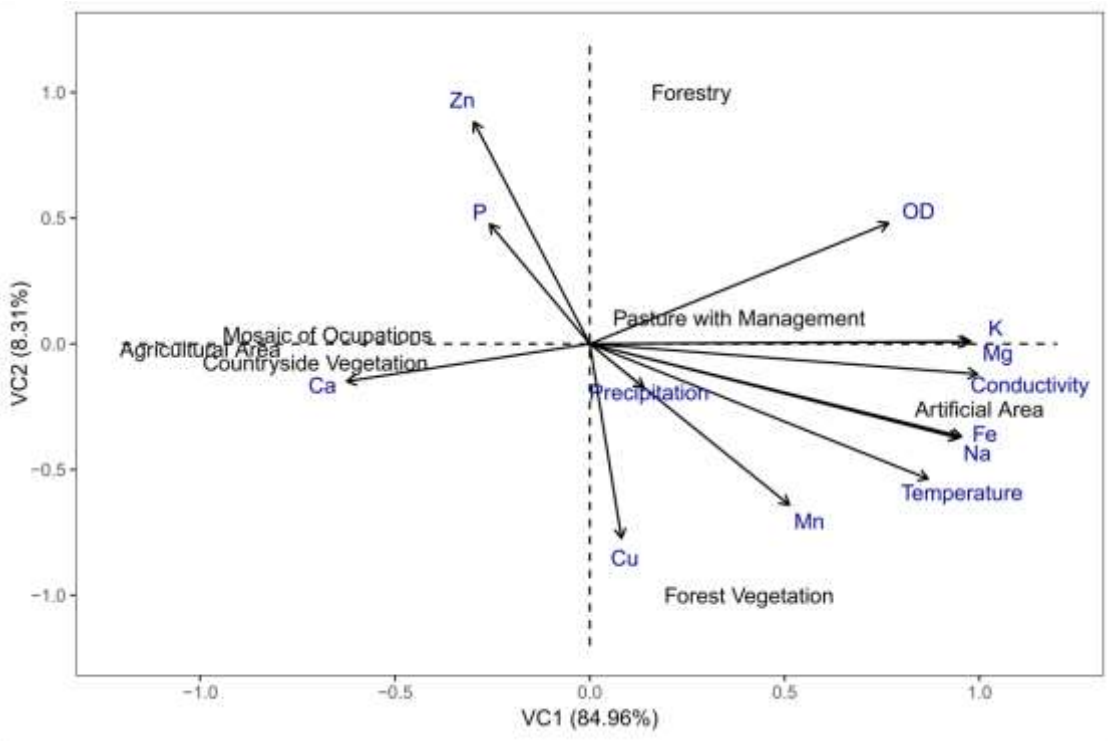


Figure 14 - Canonical correlation of land use and cover, climatic factors and the chemical and physical parameters in the surface waters of the Uruçuí-Preto River, Piauí, Brazil.

The first canonical axis accounted for more than 84% of the explained correlation structure. This axis integrates physicochemical parameters and land-use categories, including developed areas, managed pasture, agricultural land, occupation mosaics, grassland vegetation,

silviculture, and forest vegetation, whose associations reflect their underlying environmental characteristics (Figure 13).

Managed pasture and forestry correlate with dissolved oxygen (Figure 14). Managed pasture, despite the correlation, shows little influence on this variable. Forestry, a type of land use characterized by areas designated for reforestation or commercial purposes, presents anthropogenic interferences (IBGE, 2020). This contributes to the decrease in DO, because organic matter decomposition proceeds more rapidly in tropical waters and bacterial respiration increases DO consumption (Tanaka *et al*., 2021).

Artificial land use, characterized by anthropic non-agricultural surfaces (IBGE, 2020), correlates with nutrients like Mg, Fe, and Na, as well as temperature and conductivity (Figure 14). Electrical conductivity of water represents its capacity to transmit electrical current due to the presence of dissolved substances that dissociate into cations and anions, such as Na concentrations, which justify the correlation between these variables (Gama *et al*., 2023).

Mg and Ca are nutrients commonly applied through dolomitic limestone to correct soil acidity in Cerrado systems (Brito *et al*., 2020; Maltoni *et al*., 2020; Veloso *et al*., 2020), and their introduction into the watershed may occur through leaching from soils into adjacent aquatic environments. Although Mg concentrations in the river water were low, rainfall can mobilize and transport elements from upland areas into water bodies, particularly when surface runoff interacts with nutrient-enriched sources such as recently fertilized fields or organic residues, thereby enhancing their mobilization and delivery (Coffey *et al*., 2019).

Fe, despite its correlation with developed areas, is predominant in the watershed, which predominate the soil class of Oxisols, soils rich in iron oxides (Brito *et al*., 2020; Embrapa, 2021). Tributaries and surface runoff transport this element into the watershed.

Land uses categorized as occupation mosaics, including mixed occupation of agricultural areas, temporary, semi-perennial, and permanent crops, and grassland vegetation, characterized by different shrub vegetation categories (IBGE, 2020), correlated with Ca. Ca is commonly applied through dolomitic limestone to correct soil acidity in Cerrado systems, which frequently have a deficiency of this nutrient. The use of lime, which contains calcium carbonate (Brito *et al*., 2020; Maltoni *et al*., 2020; Pires *et al*., 2020; Veloso *et al*., 2020), contributes to the leaching and transport of Ca into the aquatic environment.

There is a correlation between manganese, copper, and forest vegetation land use. Mn is introduced into aquatic environments through the dissolution of soil compounds and the transport of this element, like Cu (Melo *et al*., 2019). Despite its presence in the Uruçuí-Preto River watershed, Mn and Cu concentrations are relatively low and do not exceed the limits

recommended by CONAMA (2005). Similarly, Zn and P nutrients are correlated. Phosphorus plays an important role in the fate and transport of zinc (Shen *et al*., 2020), and an inversely proportional correlation is observed (Figures 11D, G and 14). P is in higher concentration during the dry season, while Zn predominates in the rainy season. The application of leaf micronutrients and phosphate fertilizers contributes to the influx of both elements into watersheds, as observed in the Uruçuí-Preto River watershed (Stackpoole *et al*., 2019; Pires *et al*., 2020; Jalal *et al*., 2024).

5.5 Conclusion

The analysis of the physicochemical parameters and the dynamics of elements in the surface waters of the Uruçuí-Preto River demonstrates the direct influence of precipitation, land use and land cover, and the environmental characteristics of the watershed on water quality. The results show that the rainy season promotes a significant increase in the concentrations of elements such as copper, manganese, sodium, and iron when compared to the dry season, indicating that rainfall plays a decisive role in the transport, mobilization, and input of these constituents into the water body. Additionally, the proximity to agricultural areas alters the concentrations of calcium, phosphorus, and zinc, showing that management practices employed in grain-producing regions and managed pastures contribute to chemical modifications within the aquatic system.

Despite the strong anthropogenic influence, the concentrations of the evaluated elements remained within the limits established by CONAMA Resolution nº 357/2005, indicating that no immediate risks to human health or local biodiversity were identified during the study period. However, the observed relationship between land use and land cover and the physicochemical parameters, such as pH, electrical conductivity, and oxygen demand, demonstrates that agricultural expansion and landscape alterations can consistently modify the environmental conditions of the river, reinforcing the need for more sustainable agricultural practices.

In this context, the implementation of continuous monitoring actions becomes essential, as they allow the detection of spatial and temporal variability in surface water quality across the watershed. Such a strategy is crucial for identifying trends, preventing degradation processes, and mitigating potential impacts arising from both agricultural inputs and urban expansion. Therefore, systematic monitoring, combined with conscious soil and water

management, constitutes an indispensable tool for ensuring the conservation of water resources and the environmental sustainability of the Uruçuí-Preto River.

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6 FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES

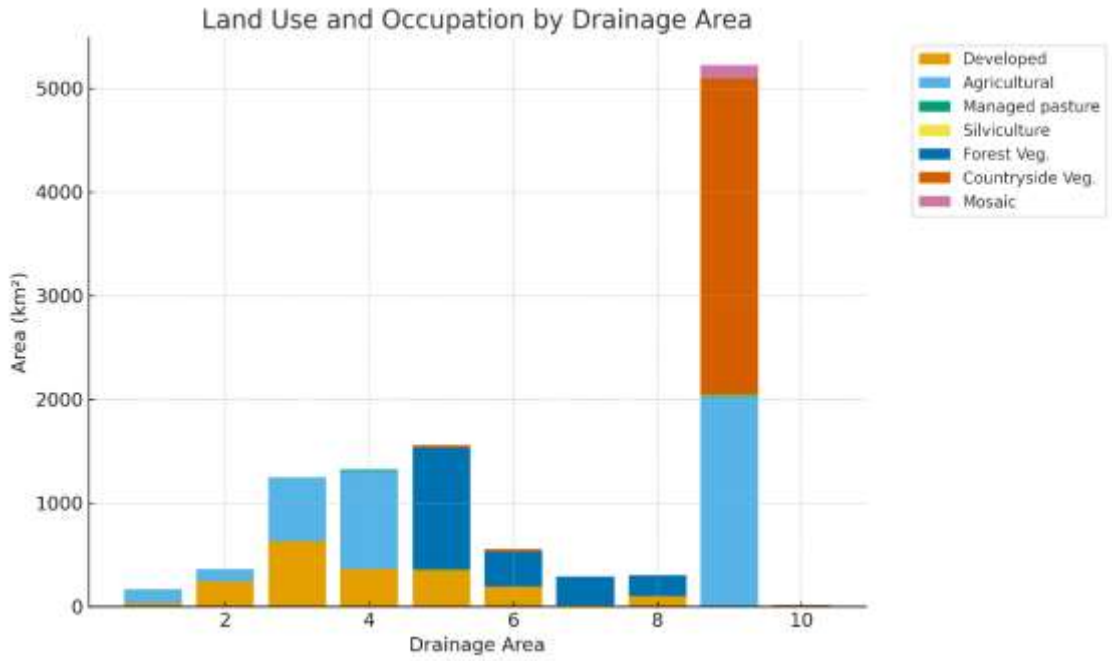
The results obtained in this research demonstrate that the Uruçuí-Preto River watershed exhibits an environmental dynamic strongly influenced by seasonality and by agricultural land use, both of which are characteristic features of the Cerrado in the state of Piauí. From a hydrogeochemical perspective, the contrast between the rainy and dry seasons plays a decisive role in shaping the concentrations of pesticides, elements, and the physicochemical parameters of the water.

The integrated analysis of the results indicates that the watershed shows signs of environmental vulnerability, requiring continuous attention to land-use practices and the management of agricultural inputs. The detection of pesticides reinforces the need to strengthen preventive strategies and systematic monitoring, particularly in areas exposed to the expansion of the agricultural frontier, such as the MATOPIBA region.

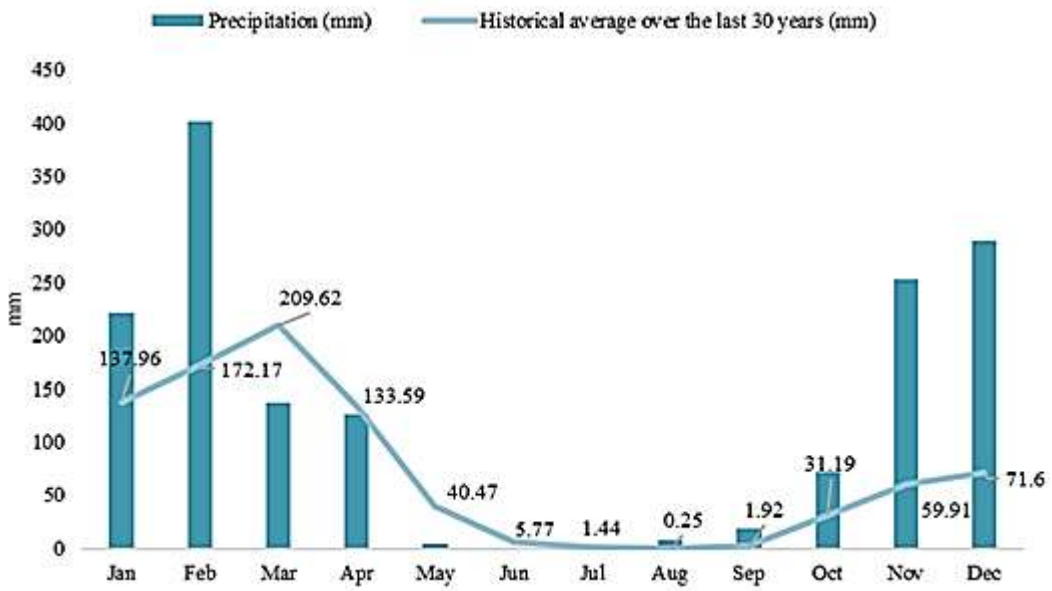
The findings of this study are expected to contribute to advancing knowledge on hydrogeochemical dynamics and pesticide occurrence in agricultural watersheds of the Cerrado, enhancing the understanding of how seasonality and land use influence the quality of surface waters.

Furthermore, it is expected that future research in the region will explore topics such as the mobility and environmental fate of pesticides, the interactions between chemical elements and emerging contaminants, and the cumulative effects of these substances on aquatic ecosystems. Continued investigations may also support improvements in environmental management and monitoring policies, especially in areas affected by agricultural expansion, facilitating the identification of potential risk scenarios.

APPENDICES



Appendix Figure 1 - Land use and land cover at the 10 surface-water sampling sites in the Uruçuí-Preto River basin (IBGE, 2022).



Appendix Figure 2 - Monthly mean precipitation (mm) recorded from January to December 2021.

Appendix Table 1 - Kruskal-Wallis test to compare nutrient content between points ($p<0.05$).

Element	X^2	DF	p
Ca	29.084419	18	0.0474*
Cu	5.9743021	18	0.9960^{ns}
Fe	0.3031163	18	1.0000^{ns}
K	40.28853	18	0.0019*
Mg	14.972868	18	0.6640^{ns}
Mn	8.280385	18	0.9740^{ns}
Na	46.139561	18	0.0002*
P	2.8819064	18	1.0000^{ns}
Zn	5.4480464	18	0.9980^{ns}

X^2 = chi-squared, DF = degrees of freedom, p = level of significance.

Appendix Table 2 - Kruskal-Wallis test to compare nutrient content between points ($p<0.05$).

Sampling point	Ca	K	Na
1	0.48 (96.58) a	0.36 (104.71) ad	1 (115.67) ab
2	1.03 (74.17) a	0.1 (66.88) cd	0.33 (65.92) b
3	0.37 (75.88) a	0.08 (74.38) bd	0.83 (69.25) b
4	0.31 (63.25) a	0.09 (67.33) cd	0.67 (92.42) ab
5	0.44 (90.58) a	0.08 (63.79) d	0.33 (67) b
6	0.95 (113.96) a	0.11 (94) ad	0.58 (85.79) ab
7	0.62 (118.88) a	0.16 (115.58) ad	0.75 (97.96) ab
8	0.54 (113.75) a	0.13 (111) ad	0.67 (87.42) ab
9	0.59 (123) a	0.2 (138.38) ab	1 (115.67) ab
10	0.59 (120.75) a	0.19 (123.21) ad	1.42 (138.79) a
11	0.67 (131.08) a	0.19 (122.12) ad	1.33 (137.17) a
12	0.59 (124) a	0.21 (125.92) ad	2.5 (136.25) a
13	0.6 (121.75) a	0.2 (127.79) ad	1.42 (146.62) a
14	0.58 (110.04) a	0.23 (144.96) a	1.42 (144.88) a
15	0.85 (141.42) a	0.23 (139.54) ab	1.33 (136.08) a
16	0.62 (130.83) a	0.24 (143.08) ab	1.58 (148.75) a
17	0.69 (149.75) a	0.22 (138.42) ab	1.33 (133.25) a
18	0.64 (136) a	0.22 (140.54) ab	1.33 (138.25) a
19	0.65 (139.83) a	0.19 (133.88) abc	1.08 (118.38) ab

Letters in the column indicate significant differences according to the Dunn test with FDR correction ($p < 0.05$).