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NOTA TÉCNICA

Atrazine, 2,4-D and carbendazim: occurrence in freshwater and removal eficiency in water treatment plants in a city in northeast Brazil

Atrazina, 2,4-D e carbendazim: ocorrência em água doce e eficiência de remoção em estações de tratamento de água em uma cidade do nordeste do Brasil

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ABSTRACT: In Brazil, the use of pesticides in the agricultural sector is one of the main causes of river pollution. The aim of this study is to detect and measure the levels of the pesticides atrazine, 2,4-D, and carbendazim in two Water Treatment Plants (WTP) that supply water to a metropolitan region in northeast Brazil. Additionally, the study aims to assess the removal efficiency of these substances in the WTPs. Three samples were collected at both inlet (raw surface water) and outlet (drinking water) of WTP1 and WTP2. The target compounds were extracted using solid phase extraction (SPE), and the analysis was done using high-performance liquid chromatography with ultraviolet detection (HPLC/UV). The method was validated by determining linearity, recovery, limit of detection, and limit of quantification. In the raw water at the WTP1, the maximum concentrations of atrazine, 2,4-D, and carbendazim were 86.00 ng L^{-1}, 171.94 ng L^{-1}, and 730.89 ng L^{-1}, respectively. In the treated water, the concentrations were 15.70 ng L^{-1}, 8.10 ng L^{-1}, and 31.96 ng L^{-1} for atrazine, 2,4-D, and carbendazim, respectively. However, none of the pesticides detected exceeded the limits set by CONAMA 357/2005 for raw surface waters and Brazilian Ministry of Health Ordinance 888/2021 for drinking water. None of the three contaminants were detected at the inlet or outlet of the WTP2.

Keywords: Emerging Contaminants; Pesticides; Water Treatment Plants; Water Pollution.

RESUMO: No Brasil, o uso de pesticidas no setor agropecuário é uma das principais causas da poluição dos rios. O objetivo deste estudo é detectar e medir os níveis dos pesticidas atrazina, 2,4-D e carbendazim em duas Estações de Tratamento de Água (ETA) que abastecem uma região metropolitana no Nordeste do Brasil. Além disso, o estudo busca avaliar a eficiência de remoção dessas substâncias nas ETAs. Foram coletadas três amostras tanto na entrada (água superficial bruta) quanto na saída (água tratada) das ETA1 e ETA2. Os compostos-alvo foram extraídos por extração em fase sólida (SPE) e analisados por cromatografia líquida de alta eficiência com detecção por ultravioleta (HPLC/UV). O método foi validado por meio da determinação da linearidade, recuperação, limite de detecção e limite de quantificação. Na água bruta da ETA1, as concentrações máximas de atrazina, 2,4-D e carbendazim foram de 86 ng L^{-1}, 171,94 ng L^{-1} e 730,89 ng L^{-1}, respectivamente. Na água tratada, as concentrações foram de 15,70 ng L^{-1}, 8,10 ng L^{-1} e 31,96 ng L^{-1} para atrazina, 2,4-D e carbendazim, respectivamente. No entanto, nenhum dos pesticidas detectados excedeu os limites estabelecidos pela Resolução CONAMA 357/2005 para águas superficiais brutas e pela Portaria GM/MS nº 888/2021 para água potável. Nenhum dos três contaminantes foi detectado na entrada ou saída da ETA2.

Palavras-chave: Contaminantes Emergentes; Pesticidas; Estações de Tratamento de Água; Poluição Hídrica.

INTRODUCTION

Agricultural production in Brazil has gained global prominence, resulting in an increase in pesticide use, generally without sufficient consumption control (Chrisman et al., 2009; Chiarello et al., 2017). This situation raises concerns about potential impacts on aquatic ecosystems, soil biota, and human health (Chrisman et al., 2009).

In 2022, Brazil was one of the largest consumers of pesticides in the world. Sales reached 800,652 tons of active ingredients, corresponding to an 11% increase compared to the previous year. The

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pesticide commercialization report for 2022, published by the Brazilian Institute of the Environment and Renewable Natural Resources (IBAMA), highlights glyphosate as the top-selling active ingredient, followed by 2,4-D and atrazine. In 2022, 47,660 tons of atrazine were sold, making it the third most-traded active ingredient in the country (Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis, 2024). On the other hand, due to the environmental persistence of atrazine and its potential for groundwater contamination, this compound was removed from the list of approved products in the European Union in 2004 (Matias et al., 2021). Adverse effects on human health and the environment associated with atrazine are reported by Hayes et al. (2010) and Munif et al. (2011).

The pesticide 2,4-D, belonging to the aryloxyalkanoic acid group, is widely used in various crops. In 2022, it was the second most commercialized active ingredient in Brazil, reaching 65,360 tons (Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis, 2024). Another prominent pesticide is carbendazim, which is a broad-spectrum fungicide widely used in agriculture to protect cereal and fruit crops against fungal diseases (Pan et al., 2012; Singh et al., 2016). It has been classified as mutagenic and considered toxic to reproduction and development by leading international regulatory authorities (European Food Safety Authority, 2014; Agência Nacional de Vigilância Sanitária, 2024; United States Environmental Protection Agency, 2014). In Brazil, carbendazim is among the 20 top-selling pesticides. It is authorized for agricultural use in the foliar form in several crops, such as cotton, sugarcane, barley, citrus, beans, apples, corn, soybeans, and wheat. In addition, it is approved for application in seeds in cotton, rice, beans, corn, and soybean crops (Agência Nacional de Vigilância Sanitária, 2024). Adverse effects on human health and the environment associated with carbendazim are reported by Silva et al. (2014).

The use of pesticides is the second leading cause of contamination of Brazilian rivers, ranking only behind the discharge of untreated domestic sewage. However, concentrations in public water supplies generally remain below the maximum limits set by legislation (Chiarello et al., 2017). Farto et al. (2021) reported that atrazine was the most researched herbicide in surface water bodies and public water supplies in Brazil. The concentrations of this compound ranged from 171.30 to 10.40 ng L^{-1} in surface waters and from 3.00 to 687.00 ng L^{-1} in public water supplies.

Despite this, it is difficult to assess the risks associated with chronic exposure due to the lack of sufficient data on acceptable doses for this type of exposure. Therefore, pesticides have become a priority in water quality and security agendas in Brazil. It is essential to monitor these compounds in aquatic environments; World Health Organization, 2017; Montiel-León et al., 2019).

In this context, as a measure to protect public health, countries have established guidance levels for some pesticides in drinking water. In the European Union (2020), for example, the individual limit concentration of any pesticide in drinking water is 0.1 µg L^{-1}, and the sum of them should not exceed 0.5 µg L^{-1}. In Brazil, Ministry of Health Ordinance 888/2021, legislates 54 compounds in drinking water standard, including pesticides and their metabolites (Brasil, 2021). The limit concentrations of atrazine, 2,4-D, and carbendazim are 2, 30, and 120 µg L^{-1}, respectively.

Regarding to the removal of micropollutants in WTP, Thuy et al. (2008) emphasized that during coagulation-sedimentation it occurs through their adsorption onto natural substances present in the water. This is in agreement with Benner et al. (2013), who stated that micropollutants that can be adsorbed onto suspended particles and coagulation flocs surfaces can be removed during the settling process, constituting the primary mechanism for removing micropollutants in coagulation-sedimentation stage. Jatoi et al. (2021) state that advanced treatment processes like biological activated carbon, ozonation, advanced oxidation, and membrane filtration are effective in the removal of pesticides in drinking water treatment plants.

Tao et al. (2024) reported that the total concentrations of pesticides in the effluent of the three water treatment plants (WTP) employing full-cycle treatment (coagulation-flocculation, clarification, filtration, ozonation, chlorination) were 59.0 ng/L, 22.8 ng/L, and 51.2 ng/L, with an average removal rate of 78.3%.

In this context, Tao et al. (2024) emphasize that the efficacy of pesticide removal depends not only on the treatment method but also on factors such as the distribution of pesticides in water, the physicochemical properties of specific pesticide substances and the process parameters and performance of specific treatment units, and that, therefore, the selection of pesticide treatment methods in WTP still requires a comprehensive and specific evaluation, including comparisons among different approaches.

Despite their recognized environmental and public health relevance, there is still a lack of information regarding the presence of pesticides in water sources used for public supply and in water treatment plants in the Northeast Region of Brazil. In this region, there is little information about the presence of pesticides in water sources used for public supply and in water treatment plants. In this context, the objective of this work is to quantify the pesticides atrazine, 2,4-D, and carbendazim in two WTP (WTP1 and WTP2) responsible for supplying a metropolitan region in Northeast Brazil and to evaluate the removal efficiency of these substances in the WTPs.

MATERIALS AND METHODS

Characteristics of the study area

The study was carried out in two WTPs serving a metropolitan region in Northeast Brazil. Both WTPs are full-cycle, including coagulation/flocculation, clarification, sand and anthracite bed filtration, and chlorine disinfection. WTP1 started operation in 1991 and presently can treat a flow rate of up to 1917 L.s^{-1}, while WTP2 started operation in 1952 and presently can treat a flow rate of up to 1000 L.s^{-1} (Farto, 2024). Both water supply systems (WTP1 and WTP2) are partially integrated and serve a population of about 1 million people.

The study area comprises four watersheds, whose water is abstracted for treatment at WTP1 and WTP2. To optimize water production in these WTPs, there may occur transfers of water between these four watersheds during some month in the year, and thus, these WTPs receives water from an integrated area. The boundaries of this area are illustrated in Figure 1.

Figure 2 depicts the land use and occupation within the integrated water catchment area. The figures reveal that agricultural, agro-industrial, and urban expansion are the primary factors contributing to landscape modification, accounting for 83.52% of the current land use. Additionally, aside from the various identified land use and occupation classes, there are two wastewater treatment plants (WWTP1 and WWTP2) of waste stabilization pond type. These plants directly impact the surface springs that supply both WTPs discussed in this study. Table 1 shows the classes of land use and occupation identified in the area.

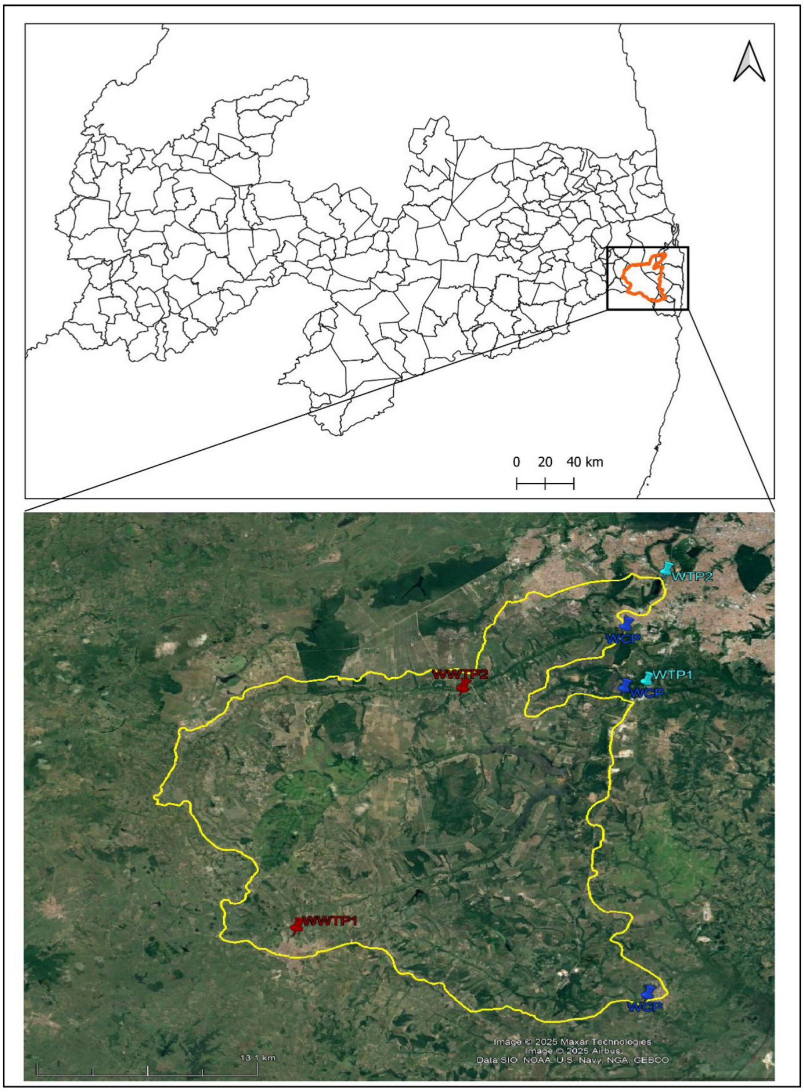

Figure 1. Delimitation of the study area includes the entire area directly influencing the surface springs responsible for water production in WTP1 and WTP2. *WTP: Water Treatment Plant; WWTP: Wastewater Treatment Plant; WCP: Water Catchment Point

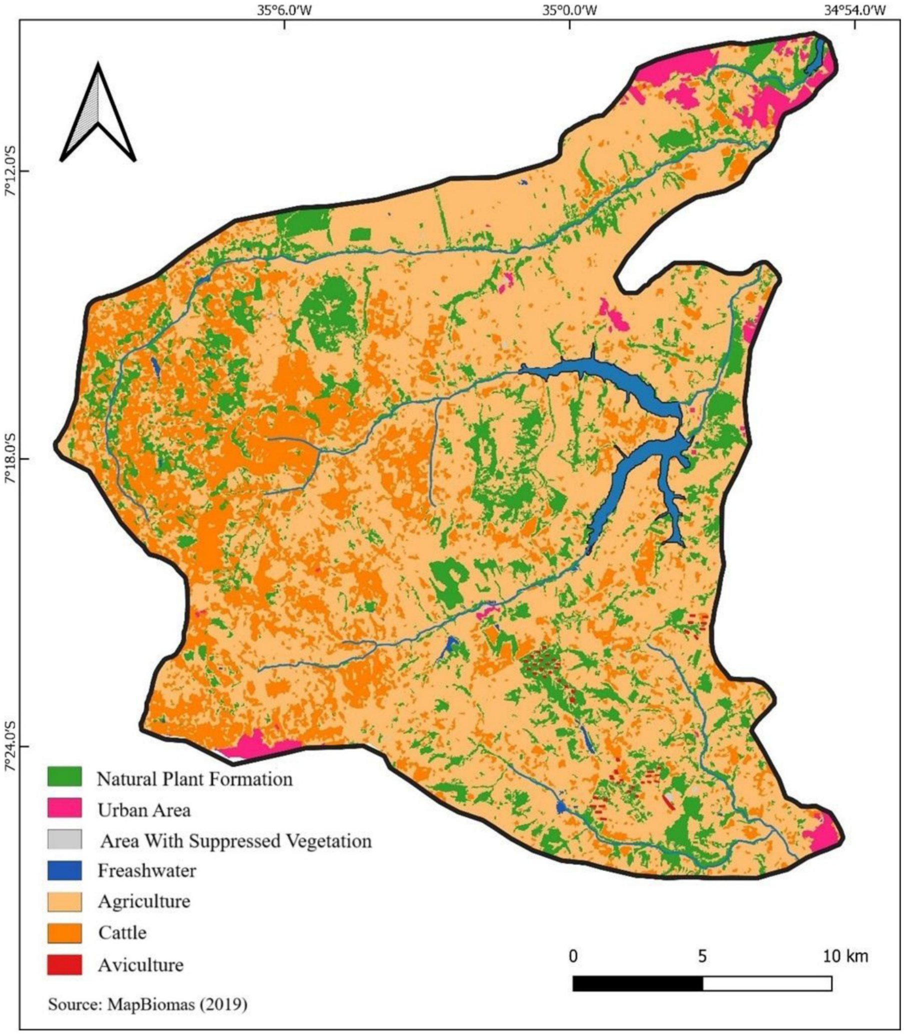

Figure 2. Graphical representation of land use and occupation in the study area for 2020. The total area is 595 km^2.

Table 1. Land use and occupation in the study area (reference year 2020).

Classes	Area (km^2)	**Area (%)**
Agriculture	369.5	62.10
Cattle	115.2	19.36
Natural Plant Formation	89.6	15.06
Urban area	12.2	2.05
Freshwater	8.0	1.34
Area with suppressed vegetation	0.5	0.08
Aviculture	0.1	0.01
Total	595	100

Sampling

The local water company granted access to the WTP, allowing collection at both inlet and outlet devices (after disinfection). Thus, four collection points were used: WTP1 – inlet, WTP1 – outlet, WTP2 – inlet, WTP2 – outlet. Three separate sampling campaigns were conducted at each collection point, in July and October 2021 and in November 2022. The contaminants analyzed were the pesticides atrazine, 2,4-D and carbendazim. The description of the methodology is presented in the following sections.

Solid Phase Extraction (SPE)

The SPE system used was similar to the one reported by Donato et al. (2015) and Silva (2015). The raw water samples were filtered using qualitative filter paper with a diameter of 12.5 cm, followed by filtration through cellulose acetate membranes with a porosity of 0.45 µm. The treated water samples were not filtered. Raimundo (2011), in tests carried out with samples of water treated with and without filtration, obtained better recovery results in samples that had not undergone filtration. The water samples were extracted using a manifold coupled to a Prismatec vacuum pump, with an average flow rate of approximately 5 ml min^{-1}. The solid-phase extraction cartridge used was the Oasis HLB® (200 mg, 3 ml) from Waters Corporation (Milford, MA, EUA).

After filtering the samples, the cartridges were conditioned with 3 ml of HPLC (Dynamic) grade methanol, 3 ml of ultrapure water, and a solution of 3 ml of ultrapure water previously adjusted to pH 2.5 with phosphoric acid. The pH of the samples was also adjusted to pH 2.5 with phosphoric acid.

Afterwards, the samples were passed through the SPE cartridge using a vacuum pump. The cartridges were then dried with a gentle flow of nitrogen for about 10 minutes to ensure they were free of moisture. Following extraction, the cartridges were covered with PVC film, labeled, and stored in a refrigerator (<4 ºC) until the chromatographic analyses were performed. This was done because the elution and reconstitution were carried out after the analytical methods were defined and the calibration curves were prepared.

The compounds were eluted by adding 3 ml of HPLC-grade acetonitrile (Dynamic) and 3 ml of methanol to each extraction cartridge. Each eluate was collected in a test tube with a PTFE cap. The volume of each extract was reduced under gentle nitrogen flow until complete drying. In preparation for chromatography, the samples were reconstituted with 1 ml of methanol.

Chromatographic conditions

The analytes were separated using a Thermo Scientific High Performance Liquid Chromatography (HPLC/UV) detector. The equipment is equipped with a 600 bar quaternary pump and a column (Eclipse Plus C18) with a 3 µm particle diameter, 100 mm length, and 4.6 mm internal diameter.

Some variables, such as wavelength, mobile phase composition, flow, column temperature, and running time, must be defined to define the chromatographic method. For the definition of the wavelengths, stock solutions of each compound were prepared in ultrapure water from the exact measurement of the mass of the standards. The readings were performed in a UV-Vis/Mini 1240 spectrophotometer (Shimadzu), at wavelengths from 190 nm to 300 nm.

In addition to this process, the stock solutions prepared with the standards of each compound were injected directly into the HPLC/UV to ascertain the best composition of the mobile phase, the retention time of the analytes, the flow, and the temperature of the column.

After studying several chromatographic conditions, two chromatographic methods were used: method 1 (M1) and method 2 (M2). In M1, isocratic elution was used with a mobile phase of ultrapure water acidified at pH 3.0 and acetonitrile (60:40, v/v), with a running time of 10 minutes and column temperature of 35 ºC. The contaminants analyzed by this method were 2,4-D and atrazine. The wavelength monitored for this method was 225 nm. In method M2, the mobile phase consisted of ultrapure water acidified to pH 3.0 and methanol in a 70:30 ratio (v/v). The method had a running time of 20 minutes and a column temperature of 25°C. Carbendazim was the analyte quantified by this method, and the wavelength monitored was 275 nm.

According to the ANVISA's Guide for Validation of Analytical Methods, achieving the required level of selectivity may necessitate the use of two or more analytical identification methods. Table 2 provides a summary of the two methods utilized.

Table 2. Summary of analytical methods used.

Method	Mobile Phase Composition (v/v)	Running Time (min)	Wavelength (nm)	Flux (ml/min)	Column Temperature (ºC)	Sample volume injected (µL)
M1	Water:Acetonitrile (60:40)	10	225	1	35	20
M2	Water:Methanol (70:30)	20	275	1	25	20

After defining the methods, the compounds were quantified by creating analytical curves. Individual curves for each contaminant were created using stock solutions prepared in HPLC grade methanol from accurately measured standard masses. These solutions were stored in 100 ml amber vials and kept in a refrigerator. Working solutions, obtained through the dilution of stock solutions, were prepared in HPLC-grade methanol, stored in 10 mL amber bottles, and kept in a refrigerator. For the analytical curve, 5 points were obtained with concentrations ranging from 0.1 μg.L^{-1} to 100 μg.L^{-1}.

Method Validation

The chromatographic analysis carried out in this study was validated using the parameters of linearity, Limit of Detection (LD), Limit of Quantification (LQ), accuracy (recovery) (Ribani et al. 2004).

Removal of emerging contaminants in WTPs

The removal of contaminants by the WTP was calculated according to Equation 1.

$$Removal(\%) = \left(\frac{CI - CE}{CI}\right) * 100 \quad (1)$$

Where:
CI: concentration of the analyte in the influent of the WTP (natural surface water);
CE: concentration of the analyte in the effluent of the WTP (drinking water).

RESULTS AND DISCUSSION

Method Validation

Table 3 shows the equations of the analytical curves for each contaminant analyzed, along with the corresponding correlation coefficient values (r^2), and the LD and LQ values obtained from the methods. These values are adjusted for the concentration factor of 2,100 times, which accounts for the conversion from 2.1 L of sample to 1 ml of the extract.

Table 3. Equation of the line, correlation coefficient, LD and LQ of the three contaminants analyzed.

Pesticide	Analytical Curve	Correlation Coefficient	LD (ng L^{-1})	LQ (ng L^{-1})
Atrazine	Area = 0.0017 Conc. + 0.0018	r^2 = 0.9901	1.6790	5.0420
2,4-D	Area = 0.0023 Conc + 0.0258	r^2 = 0.9936	17.7876	53.4161
Carbendazim	Area = 0.0006 Conc + 0.0016	r^2 = 0.9911	4.2286	12.6984

Conc.: Concentration

The recovery percentages for atrazine, 2,4-D, and carbendazim were 95.10%, 93.79%, and 99.47%, respectively. The final concentrations of the analytes were adjusted based on these percentages.

Determination of Emerging Contaminants in Water Samples

It is important to mention that in both the influent and effluent samples at the WTP2, none of the three pesticides were detected. These results may be associated with the land use and occupation predominantly serving WTP2, that receives water from an area with more urbanization and less agricultural activities in comparison with WTP1.

This demonstrates the good quality, in terms of pesticide-type emerging pollutants, of the water supply from this system.

Table 4 shows the results of the analysis of the three pesticides identified and quantified in the raw and treated water of the WTP1.

Table 4. Concentration of contaminants in natural surface and drinking water at WTP1 (ng L^{-1})

Sampling point	1st sampling campaign			2nd sampling campaign			3rd sampling campaign		
	ATZ	2,4-D	CBZ	ATZ	2,4-D	CBZ	ATZ	2,4-D	CBZ
WTP1 influent	n.d.	105.19	38.10	39.10	171.94	730.88	86.00	n.d.	n.d.
WTP1 effluent	n.d.	<LQ	n.d.	15.70	<LQ	31.95	n.d.	n.d	n.d.

ATZ: atrazine; CBZ: carbendazim; n.d.: not detected; <LQ: lower than the LQ.

For atrazine compound, results shown at Table 4 are lower than those presented in literature (Sposito et al., 2018; Santos, 2013; Moura, 2013; Moreira et al., 2012; Raimundo, 2011) for river water at Brazilian context. With regard to the carbendazim, Sposito et al. (2018), also for river water at Brazilian context, reported similar concentration (96 ng L^{-1}) to those presented at Table 4. These results may be associated with the land use and occupation predominantly serving each WTP. WTP1 predominantly receives water from an area in which agricultural activities are more intense, as compared to that of WTP2.

According to Montagner & Jardim (2011), the degree of contamination of water bodies reflects local land use and occupation, thus being directly related to the levels of sewerage coverage, in addition to factors such as population density and the type of economy of the different Brazilian states.

In the study of land use and occupation of the area in consideration, it was found that 62.11% of the area is dedicated to agriculture, with sugarcane being the predominant crop. According to Laini et al. (2012) the intensive use of herbicides from sugarcane activity, poor soil management, adverse land slope, and unfavorable soil type, among others, promotes the accumulation of herbicides in nearby water bodies. In a study conducted by Belluck et al. (1991), it was found that the herbicide atrazine was present in residential wells in the United States of America in amounts that exceeded the permitted levels set by the country's Ministry of Health.

Still regarding atrazine, the levels in untreated water varied from 39.10 to 86.00 ng L^{-1}, while in treated water it was found only once, at the concentration of 15.70 ng L^{-1}. In spite of being relatively stable in the environment, the presence of this herbicide in water bodies is linked to leaching from agricultural soils. As a result, there may be an increase in concentration not only during rainy periods, but also, primarily, at the time of application. This is when the highest concentrations of atrazine are expected to be detected in the environment (Correia, 2018). In the Brazilian context, concentrations of atrazine ranging from 3 to 687 ng L^{-1} have been reported in drinking water (Machado, 2015, Machado et al., 2016; Caldas et al., 2013; Raimundo, 2011).

Concerning the herbicide 2,4-D, the concentrations in raw water ranged from 105.19 to 171.94 ng L^{-1}. The results for treated water were below the LQ of 2,4-D, which was 53.41 ng L^{-1}.

Concentrations of carbendazim in raw water ranged from 38.10 to 730.88 ng L^{-1}, and it was only detected once in treated water at a concentration of 31.95 ng L^{-1}. It is important to note that among the three pesticides detected in the water, carbendazim presented the highest concentrations.

Moura (2013) found an average concentration of 178.00 ng L^{-1} of carbendazim in the Piquiri River, located in the state of Paraná. Sposito et al. (2018) also reported the detection of carbendazim in the Dourados River at a concentration of 96.00 ng L^{-1}. Both studies refer to Brazilian territory.

In Brazil, ANVISA authorizes carbendazim for agricultural purposes. ANVISA defines a limit of 0.02 mg per kg^{-1} of body weight as the acceptable daily intake for humans (Agência Nacional de Vigilância Sanitária, 2024). On the other hand, its use is prohibited in the United States of America due to its association with an increased risk of liver tumors in animals (Kupper et al., 2012).

In 2012, carbendazim was found in orange juices manufactured in Brazil. While the concentrations were within the limit set by Brazilian law, this raised concerns among Brazilian producers. The United States of America, which accounts for 15% of the product's imports, refused to accept juices contaminated with the fungicide (Kupper et al., 2012).

Table 5 shows the limits for atrazine, carbendazim, and 2,4-D in drinking water and raw surface water according to Ordinance 888/2021 of the Ministry of Health and CONAMA Resolution 357/2005 (Brasil, 2005), respectively. The highest concentration found in this study is also shown. The results for drinking water are also compared with European legislation (European Union, 2020).

Table 5. Maximum concentrations of pesticides detected in raw and treated water, compared with the Brazilian Maximum Permitted Values (MPVs) and European Legislation.

Pesticide	Concentration found in raw surface water (ng L^{-1})	MPV CONAMA 357/2005 (ng L^{-1})	Concentration found in drinking water (ng L^{-1})	MPV Ordinance 888/2021 (ng L^{-1})	MPV European legislation (ng L^{-1})
Atrazine	86.0	2,000$^{\alpha}$	15.7	2,000	100.0
2,4-D	171.9	4,000$^{\beta/}$30,000$^{\chi}$	<53.4	30,000	100.0
Carbendazim	730.9	-	31.9	120,000	100.0

[a] Surface water Classes 1, 2 and 3; [b] Surface water Classes 1 and 2; [c] Surface water Class 3.

It is noteworthy that the quality of both raw and treated water with regard to the pesticides atrazine, 2,4-D, and carbendazim complies with the standards set by Brazilian legislation CONAMA 357/2005 (Brasil, 2005) for raw water entering the water treatment plant, and by Ordinance 888/2021(Brasil, 2021) for public water supply at the outlet of the WTP, as well as with European drinking water legislation (European Union, 2020). The concentrations of all three pesticides were found to be lower than the permitted levels.

Removal efficiency of emerging contaminants in the WTP1

WTP1 consists of the following processes: coagulation-flocculation, clarification, sand and anthracite bed filtration, and chlorine disinfection. Similar to WTP2, WTP1 follows a conventional design and utilizes liquid aluminum sulfate, lime, and chlorine as chemical products. Table 6 displays the results of the removal of the three ECs detected in WTP1.

Table 6. Removal efficiency of ECs identified in the WTP1

WTP	1st sampling campaign			2nd sampling campaign			3rd sampling campaign		
	ATZ	2,4-D	CBZ	ATZ	2,4-D	CBZ	ATZ	2,4-D	CBZ
WTP1	-	>49.00%	>99.90%	59.85%	>68.00%	95.62%	>99.90%	-	-

ATZ: atrazine; CBZ: carbendazim; n.d.: not detected; <LQ: lower than the LQ.

The analysis of Table 6 shows that the overall removal efficiency of pesticides in WPT1 is high. Although the first collection did not provide specific data for atrazine because it was not detected in those samples, the second collection showed a removal efficiency of 59.85% for this contaminant, while the third collection achieved complete removal (>99.90%). For 2,4-D, an efficiency of more than 49.00% was observed in the first collection and more than 68.00% in the second collection. Carbendazim, on the other hand, was completely removed (>99.90%) in the first collection and presented a removal efficiency of 95.62% in the second collection.

These results are consistent with those reported by Tao et al. (2024), who found overall efficiency of 78.3% of the total pesticides content in three full-cycle WTP. Results are also similar to those presented by Voltan (2014), who reported removal efficiency of the pesticides diuron and hexazinone of 94.8 and 73.8%, respectively, in a WTP employing adsorption process using powdered activated carbon.

Adsorption onto natural substances present in the water and onto suspended particles and coagulation flocs surfaces in the coagulation-sedimentation stage may be an important removal mechanism of pesticides in conventional full-cycle WTP, as emphasized by Thuy et al. (2008) and Benner et al. (2013).

This indicates that WTP1 plays an important complementary role in removing emerging contaminants from the environment. Together with the low concentrations of pesticides in the raw waters, this contributes positively to the quality of the treated water.

The values demonstrate that the full-cycle WTPs are effective in reducing the concentrations of emerging contaminants of the pesticide-type. This contributes to the production of drinking water with significantly lower levels of unwanted chemicals. The consistent results reinforce confidence in the treatment process ability to meet established water quality standards.

LIMITATIONS OF THE STUDY

This study offers important contributions by addressing the occurrence of pesticides in water treatment plants located in a metropolitan region of Northeast Brazil, a region with limited data on the topic. However, some limitations should be considered.

The first refers to the reduced number of sampling campaigns (three in total), distributed over more than a year. While these campaigns allowed for some observation of temporal variability, a denser sampling frequency over a full hydrological cycle, especially covering periods of intensive pesticide application or heavy rainfall, could provide a more comprehensive understanding of the behavior of these contaminants.

Furthermore, a separate analysis of the areas serving each of the WTP was avoided, since there are transfers between the river water within the area. This approach also limits the findings of this study.

Another limitation concerns the geographic scope of the study, which was restricted to two WTPs with similar characteristics located in a single region. Although this allowed for a deeper understanding of the local context, the results obtained cannot be automatically generalized to other regions of Brazil or to WTPs with different operational configurations. Future studies in different geographic contexts and with higher temporal resolution are recommended to validate and expand the findings presented here.

CONCLUSIONS

No pesticide residues were found in the tributary waters entering WTP2, nor in its treated water, indicating that, in this public water supply production system, the water quality is good in terms of pesticide residues. At WTP1, although three pesticides were identified and measured, their concentrations were far below the maximum limits established by Brazilian legislation for both raw and drinking water. Additionally, when considering the parameters recommended by European drinking water legislation, it was also observed that the concentrations of the three pesticides were lower than the allowed limits.

In WTP1, atrazine was removed by 59.85 to >99.90%, while carbendazim was removed by 95.62 to >99.90%. For 2,4-D, the removal efficiency was 49.00% in the 1st collection and 68.00% in the 2nd collection. These results indicate that the full-cycle WTPs, probably through adsorption process onto natural substances present in the water and onto suspended particles and coagulation flocs surfaces, can be effective in removing these compounds, which is crucial for ensuring the quality of the water supplied to the population in terms of pesticide residues.

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