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Presence of emerging and conventional contaminants in water sources in the city of Cuiabá (MT): potential sources and damages

Presença de contaminantes convencionais e emergentes em mananciais de água do município de Cuiabá (MT): potenciais fontes e riscos

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ABSTRACT

This study evaluated the water sources at the points of water collection for human supply, identifying conventional and emerging pollutants that could compromise the public supply of the municipality of Cuiabá-MT. Raw water was analyzed at three water pumping sites, using secondary (2014 to 2019) and primary (June and November 2019) data. The parameters described in current regulations were used to calculate the Index of Conformity with the Guidelines, which assesses the distance between planned quality and measured quality. Drugs were discussed based on ecotoxicological studies. There was a reduction in the quality of water sources in the urbanized area, with the disposal of *in natura* domestic sewage and surface runoff as the most important causes of this reduction. Measures are needed to expand and ensure adequate and efficient collection and treatment of effluents, preventing pollutants from reaching rivers.

Keywords: Environmental pollution; Water resources; Water security.

RESUMO

Este estudo avaliou os mananciais hídricos nos pontos de captação de água para abastecimento, identificando poluentes convencionais e emergentes que possam comprometer o abastecimento público do município de Cuiabá-MT. Foi analisada água bruta em três pontos de captação de água para abastecimento, por meio de dados secundários (2014 a 2019) e primários (junho e novembro de 2019). Os parâmetros descritos em normas vigentes foram usados para calcular o Índice de Conformidade ao Enquadramento, que avalia a distância entre a qualidade planejada e qualidade medida. Os fármacos foram discutidos com base em estudos ecotoxicológicos. Observou-se redução na qualidade dos mananciais na área urbanizada, sendo o lançamento de esgoto doméstico *in natura* e o escoamento superficial as causas mais importantes dessa redução. São necessárias medidas para ampliação e garantia da coleta e tratamento adequados e eficientes de efluentes, evitando que poluentes cheguem aos rios.

Palavras-chave: Poluição ambiental; Recursos hídricos; Segurança hídrica.

INTRODUCTION

The growing urbanization, sometimes disorganized, may not be accompanied by the required adaptation of the infrastructure and adequate sanitation, causing impacts on water quality (Goel et al., 2018; Vatanpour et al., 2020). The reduction in water quality in many regions has been attributed to contamination, intensive water uses without proper availability assessment, suppression of green areas and riparian vegetation, and increasing changes in land use and coverage (Nie et al., 2011; Meneses et al., 2015). Efficient management of a watershed integrated to land use and occupation is essential to mitigate the reduction of water quality (Pizella, 2015; Serrao-Neumann et al., 2017). Water supply in urban spaces may be compromised when the proper management of a watershed is not implemented.

Traditionally, water quality monitoring studies investigate pollutants with known health effects, such as bacteria, heavy metals and priority substances as pesticides or industrial chemicals. However, the development of extremely sensitive analytical techniques allowed the detection of new pollutants and the research of possible risks to environment and human health (Pal et al., 2014).

This group of pollutants, known as emerging organic pollutants or simply emerging contaminants, has been detected worldwide at concentrations at the ng L^{-1} levels, but there are no established threshold limits so far (Silva et al., 2011; Al-Rajab et al., 2015; Kodešová et al., 2016; Nantaba et al., 2020). The detection of these substances indicate that water quality monitoring programs should comprise distinct contaminants regularly in order to generate historical series data that are essential to water governance (Behmel et al., 2016).

The first published study reporting the occurrence of pharmaceuticals in raw sewage, treated wastewater and river water in Brazil was carried out in the Rio de Janeiro State, Southeastern region (Stumpf et al., 1999). After that several others in the most different regions of the country were published as for example: Souza et al., (2014) in São Paulo State, Machado et al. (2016) that participated of a nationwide survey of emerging contaminants that include pharmaceuticals in water collected around 22 Brazilian state capitals (Cuiabá among them) and Thomas et al. (2014) in the Amazon State. Most of the monitored pharmaceuticals were not the same in the several studies.

The monitoring and analysis of quality of drinking water sources is essential for the investigation of factors causing their degradation. The identification of pollution sources subsidizes the watershed management in order to guarantee the acceptable water quality and protection of human health. In this perspective, two lines of actions can be drawn: (i) to prevent the pollutants from reaching water sources; (ii) or to eliminate them during treatment processes.

Even if it is not possible to prevent pollutants from reaching water sources, it is possible, from their identification, to seek solutions to minimize their impacts. Another important aspect is that actions to preserve the quality of water sources used for human supply must also protect aquatic communities. This study contributes to the discussion regarding the main environmental risks to water resources in the Cuiabá River basin, as well as adding relevant and unpublished monitoring data to the discussion.

Thus, this study aimed to assess the water quality at pumping sites of water treatment plants, identifying conventional and emerging pollutants that can degrade water quality and compromise the public supply of the municipality of Cuiabá, state of Mato Grosso, discussing the potential origin of pollutants.

MATERIALS AND METHODS

Study area

The Cuiabá River basin encompasses the Cuiabá and Várzea Grande municipalities, the two largest urban agglomerates of the Mato Grosso, and has a high economic, social, cultural, and environmental importance. Besides the urban occupation, several agricultural activities occur in highlands surrounding the higher portion of the river, while extensive cattle raising is carried out in its lower portion, the Pantanal lowland (Lima et al., 2015). Among the main economic activities developed in this area, commerce, industry, and tourism, together with fishing and aquiculture are also significant. The areas of Pantanal (downstream of the studied area), the Guimarães Highlands as well as the municipality of Nobres (upstream of the studied area) have a strong national and international touristic appeal in this basin (Mato Grosso, 2018b).

The estimated population of the municipality of Cuiabá in 2019 was 612,547 inhabitants, with Municipal Human Development Index (HDI) of 0.785, based on the census of 2010. It occupies approximately an area of 3,226 km^2 with vegetation typical of the cerrado bioma. The per capita Gross Domestic Product (GDP) of Cuiabá in 2019 was R$ 40,199; the municipality is the largest contributor to the GDP of the state of Mato Grosso State (Instituto Brasileiro de Geografia e Estatística, 2022; Mato Grosso, 2019).

The local geology is formed by low-grade metamorphic rocks, known as Cuiabá Group, and consists predominantly of phyllites, mica schist, quartzites, metagraywacke, lime, and meta-agglomerate as well as golden quartz veins. The climate in Cuiabá, according to the Köppen classification, is tropical with average annual temperature around 26 ºC, altitudes ranging from 146 to 259 m, with a rainy season from October to April and a dry season from May to September (Cuiabá, 2019).

The city of Cuiabá has three main treatment water systems, the Ribeirão do Lipa that correspond to 51% of the total treated distributed water, Tijucal that represents 34% and the Coophema System corresponding to 7%. So, together, these three systems are responsible for water distribution to approximately 86% of the Cuiabá population (Cuiabá, 2019). The remaining 14% of the supply is distributed among other smaller water pumping stations within the urban perimeter and outside it. The water pumping stations for these three treatment plants are localized in two sources, in the Cuiabá River that withdraw water for the Ribeirão do Lipa and Coophema Systems and in the Coxipó River (an affluent of the Cuiabá River) that supply the Tijucal treatment plant (Figure 1). The catchment area considered for the study refers to the upper part of the Cuiabá River and corresponds to approximately 27,000 km^2.

Therefore, the raw water sampling points – P1 – Lipa, P2 – Tijucal and P3 – Coophema pumping stations – were chosen

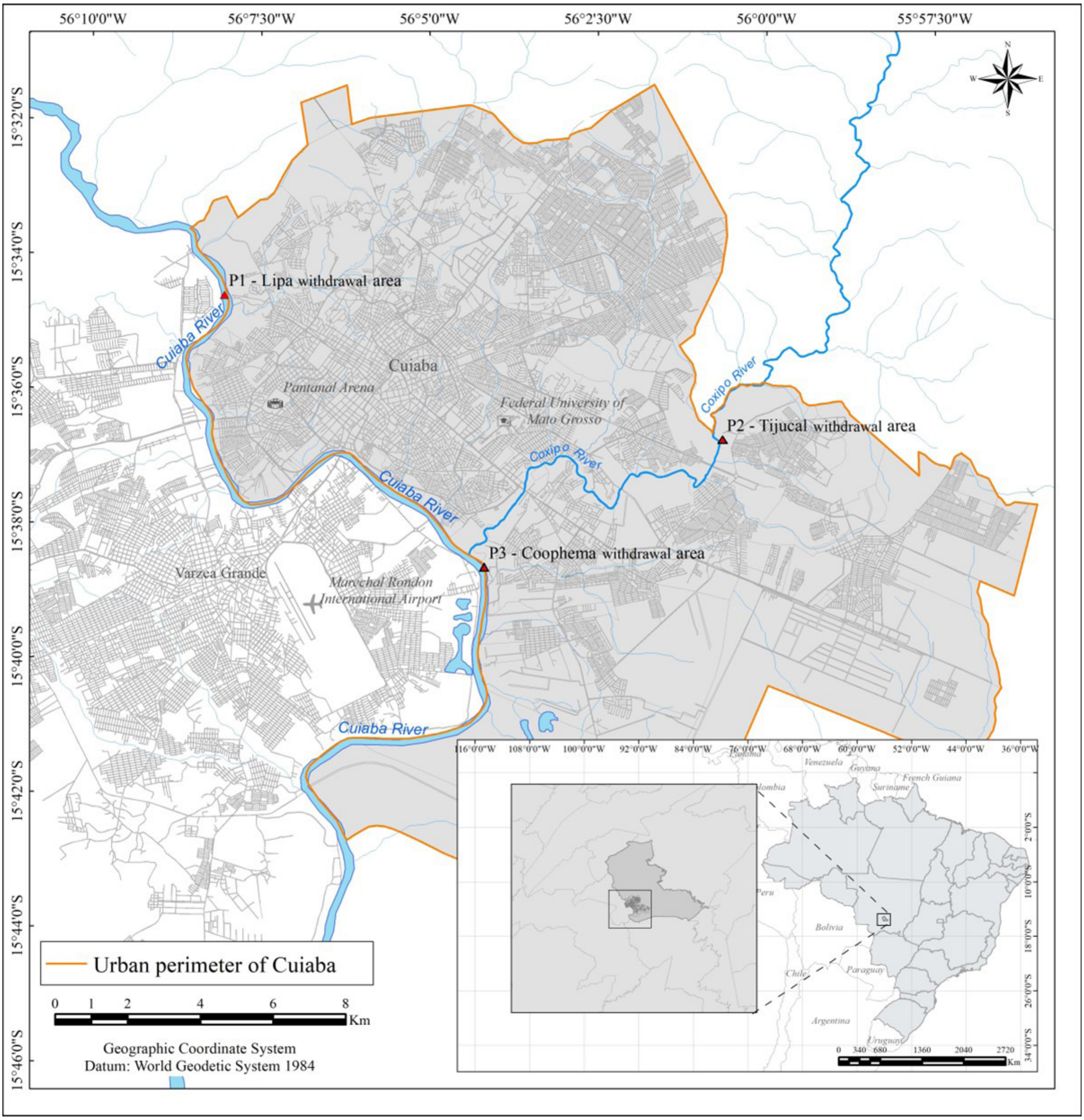

Figure 1. Localization of the water pumping stations and sampling points.
Source: the authors.

for this study so that the two main water sources used for drinking water supply of Cuiabá could be evaluated (Figure 1).

Parameters analyzed

The parameters used to evaluate quality of the water sources used for human supply in the municipality of Cuiabá comprehend the physical, chemical, and biological ones established in the Internal Normative of CONAMA (National Council of Environment) Resolution n. 357/2005 (Brasil, 2005). Overall, 112 parameters were determined, divided in five groups as described in Table 1. The analytical procedures used by the laboratories responsible for the analysis as well as the maximum allowed concentrations determined by the CONAMA n. 357/2005 are listed in the supplementary material.

Besides the conventional parameters described in the legislation, pharmaceutical substances were included in the present study since they have been described as contaminants from urban areas (Table 1). The analyzed pharmaceuticals were chosen based on

Table 1. Water quality parameters analyzed in the water sources used for public supply in the municipality of Cuiabá, MT, Brazil.

Groups	Parameters
Physical, Chemical, and organoleptic	boron; cyanide; color; total chloride; total residual chlorine; BOD (biological oxygen demand); COD (chemical oxygen demand); total phosphorus; fluoride; nitrate; nitrite; ammonia; DO (dissolved oxygen); pH; selenium; dissolved solids; sulfate; hydrogen sulfide; turbidity; odor
Microbiological and hydrobiological	cyanobacteria; chlorophyll-a; thermotolerant coliforms (*E. Colli*); total coliforms
Metals	Aluminum; Antimony; Arsenic; Barium; Beryllium; Cadmium; Cobalt; Copper; Lead; Chromium; Iron; Lithium; Manganese; Mercury; Nickel; Silver; Uranium; Vanadium; Zinc
Organic Chemicals	acrylamide; alachlor; aldrin+dieldrin; atrazine; benzene; benzidine; benzo(a)anthracene; benzene(a)pyrene; benzo(b)flouranthene; benzo(k)flouranthene; carbaryl; chlordane (cis+trans); 2-chlorophenol; crysene; 2,4-D; demeton (demeton-O + demeton-S); dibenzo(a,h)anthracene; dichloroethene; 1,2-dichloroethane; 1,1-dichloroethene; 2,4-dichlorophenol; dichloromethane; DDT; dodecachlor; endosulfan (α, β, sulfate); endrin; styrene; ethylbenzene; total phenols; glyphosate; guthion; heptachlor epoxide + heptachlor; hexachlorobenzene; indene(1,2,3-cd)pyrene; lindane (γ-HCH); malathion; metolachlor; metoxychlor; parathion; PCBs – polychlorinated biphenyls; pentachlorophenol; simazine; surfactant substances; 2,4,5-T; carbon tetrachloride; tetrachloroethene; toluene; toxaphene; 2,4,5-TP; tributyltin; trichlorobenzene (1,2,3-TCB + 1,2,4-TCB); trichloroethene; 2,4,6-trichlorophenol; trifluralin; xylene
Pharmaceuticals	atenolol; caffeine (psychostimulant); carbamazepine; diclofenac; estrone; ibuprofen; naproxen; paracetamol; propranolol; triclosan; 17α-ethinylestradiol; 17β-estradiol

Source: the authors.

other studies carried out in Brazil and South America (Souza et al., 2014; Barcellos et al., 2020; Thomas et al., 2014) also considering the ones that are included in the list of the main ones provided to the population by the public health system through the Popular Pharmacy Program of the Ministry of Health and the published validated method of Souza et al. (2014).

Caffeine is a psychostimulant that is present in the composition of several pharmaceuticals, such as analgesic, as well as in food and cosmetics. This substance was included among the pharmaceuticals to be monitored as it is considered an indicator of the occurrence and route of organic contaminants (Ide et al., 2005). The hormones estrone, 17α-ethinylestradiol and 17β-estradiol, were also analyzed due to their potential as endocrine modulators (Sodré et al., 2007).

Primary data survey

Sample collection and storage

Six sampling campaigns were carried out, monthly from June to November 2019. In the samples collected in June and July, the following parameters were determined: COD, BOD, total dissolved solids, pH, fluoride, iron, nitrate, ammonia, DO, turbidity, thermotolerant coliforms, cyanobacteria, cadmium, lead, mercury, copper, chromium, manganese, and zinc and all the substances listed in the organic chemicals group (Table 1). In August to November, only the pharmaceuticals and caffeine were determined.

Sampling for the determination of the physical, chemical, microbiological and hydrobiological parameters was carried out following the specific orientations for each parameter. All samples were kept in thermal boxes under ice and transported to the laboratory. The sample collection, storage and preservation followed the National Guide of Sample Collection and Preservation (Companhia Ambiental do Estadual de São Paulo, 2011).

Samples for analysis of pharmaceuticals were collected in 5 L opaque plastic flasks, previously rinsed with the sample, and covered with black plastic bags to prevent photodegradation. All samples were kept in thermal boxes under ice and sent to the laboratory.

Laboratory analysis

The collected samples (described above) were kept under refrigeration and sent to private accredited laboratories where the water quality parameters listed in Table 1 were determined. The analysis followed methods indicated in the Standard Methods for the Examination of Water and Wastewater (SMEWW) (American Public Health Association, 2017) and by the United States Environmental Protection Agency (USEPA). The specific method used for each parameter is listed in the supplementary material.

The pharmaceuticals were analyzed in the Laboratory of Environmental Biogeochemistry of the Federal University of São Carlos following the method described by Souza et al. (2014).

Secondary data survey

The secondary data were obtained from the water quality analysis monitoring program carried on semesterly by the water distribution company of the municipality of Cuiabá from 2014 to 2019. This semestral monitoring of raw water must be carried out by the water distribution companies as established in the Internal Normative on drinking water of the Ministry of Health (Consolidation Ordinance n. 888/2021) (Brasil, 2021) and include the parameters that have quality standards established in the CONAMA Resolution n. 357/2005 (Brasil, 2005). For cyanobacteria, besides the data from the monthly monitoring (2014 to 2019) done by the water distribution company defined in Consolidation Ordinance n. 888/2021, the results of the study carried out by Siqueira et al. (2017) (see supplementary material) were also included.

The analysis of the semiannual water sampling campaigns from 2014 to 2019 at the pumping stations of the Ribeirão do Lipa, Tijucal and Coophema treatment plants (Figure 1) were carried out in private accredited laboratories hired by the water distribution company of the Cuiabá municipality and were provided by this company for the present study.

Data analysis

The internal normative of the National Environmental Council (Resolution n. 357/2005) defines water classes depending upon the intended uses of the water source and the specific limits of contaminants for each class. Except for cyanobacteria, all results were compared to the limits established in this normative for Class 2 waters, which is the class for waters used for public supply after conventional treatment. Cyanobacteria was compared to the internal normative of the Ministry of Health (Consolidation Ordinance n. 888/2021) since the water is destined to treatment for human consumption (Brasil, 2021).

The results of 14 sampling campaigns were surveyed corresponding to the primary and secondary obtained data. For each sampling point, the frequency of results that do not comply with the Brazilian legislation, the range of detected concentrations and the median of detected values were determined. Median was calculated only for the variables which had at least five results above quantification limits.

In order to evaluate the situation of each sampling site considering the compliance with the Brazilian regulations, an Index of Conformity with Guidelines (ICG) was calculated for the period of 2014 to 2019. This index corresponds to the WQI (Water Quality Index) used in Canada (CCME, 2006). This index is calculated based on the comparison of the values of the water quality parameters with the guidelines, considering (i) number of variables with values in disagreement with the guidelines, (ii) frequency of occurrence of disagreement and (iii) amplitude of the difference between the obtained value and the established limit. Higher ICG values mean that the water quality is nearer to the established target considering the intended uses (Table 2). Details of the method of calculation of ICG is given in the supplementary material.

There are no limits established by the Brazilian legislation for pharmaceuticals that would allow to evaluate safety regarding the presence of these substances in water. To the best of our knowledge, in other countries there are also no specific legally enforcement limits for the analyzed pharmaceutical products determined by consensus regarding the potential risk for these substances in water neither to the environment or human health. However, there are some studies that evaluate the toxicity to aquatic organisms and determine EC50 (lethal concentration for 50% test animals) and LOEC (lowest observed effect concentration) or NOEC (non-observed effect concentration). These values were used to discuss possible impacts to aquatic life. Regarding human life, no parameters were found that allow a discussion on the effects to people. The results were discussed considering the possible risk to the aquatic environment. The determined concentrations were compared to published results from other regions of Brazil.

RESULTS AND DISCUSSION

Conventional pollutants

Evaluating the compliance of water quality with the Brazilian legislation (Brasil, 2005) (Table 3), it was observed that the water pumping station P2 (Tijucal) presented the higher number of parameters (13) in disagreement with the established limits followed by P1 (Lipa station) with 12 and P3 (Coophema) with 11 parameters that did not comply with the legislation (Table 3).

At least one parameter of each group of analysis shown in Table 2 presented results exceeding the guidelines.

Among the metals, total aluminum and manganese and dissolved copper and iron were the ones that presented higher number of samples with concentrations exceeding the Maximum Allowed Concentration (MAC), notably aluminum and iron, in all sampling points (Table 3).

The geological formation and soil type in a watershed have a high influence on water quality. Aluminum, copper, iron, and manganese concentrations is mostly associated to the soil types that compose the geology of the Cuiabá Group (Cuiabá, 2019) allowing to state that most of the observed high concentrations of these metals are a consequence of soil use and occupation intensifying erosive processes and run-off.

Table 2. Classification of index values (ICG).

Range	CLASS	Interpretation
100 - 95	Excellent	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels.
94 - 80	Good	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels.
79 - 65	Fair	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels
64 - 45	Marginal	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.
44 - 0	Poor	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels.

Source: CCME (2006).

Table 3. Parameters with results in disagreement with the normative CONAMA N. 357/2005 for class 2 waters and Ordinance n. 888/2021 of the Ministry of Health, for samples from Cuiabá River (Lipa and Coophema) and Coxipó River (Tijucal) collected from 2014 and 2019.

Parameter	Unity	Limit	P1 - Lipa Pumping Station						P2 - Tijucal Pumping Station						P3 - Coophema Pumping Station					
			N[a]	F[b]	Min[c]	-	Max[c]	Median[d]	N	F	Min	-	Max	Median	N	F	Min	-	Max	Median
Aluminum	mg L^{-1}	0.100	12	41.7	0.003	-	0.591	0.14	14	35.7	0.016	-	0.739	0.17	12	33.3	0.0058	-	0.454	0.18
Manganese	mg L^{-1}	0.100	14	0	0.006	-	0.09	0.04	14	7.1	0.00997	-	0.133	0.03	14	0.0	0.001	-	0.07	0.04
Dissolved iron	mg L^{-1}	0.300	12	50.0	0.00287	-	1.192	0.27	12	25.0	0.0105	-	1.51	0.21	12	50.0	0.01	-	1.009	0.26
Dissolved copper	mg L^{-1}	0.009	14	0	0.002	-	0.007	-	14	7.1	0.002	-	0.01	0,006	14	7.1	0.001	-	0.001	-
Free cyanide	mg CN^{-} L^{-1}	0.005	12	8.3	0.011	-	0.011	-	12	8.3	0.01	-	0.01	-	12	0	0.005	-	0.005	-
Residual chlorine	mg L^{-1}	0.010	9	44.4	0.05	-	1	0,06	8	37.5	0.03	-	0.58	0,06	9	33.3	0.05	-	1	0,14
True color	mg Pt L^{-1}	75	12	8.3	5	-	100	13.85	14	0	2.2	-	64	-	12	8.3	5.1	-	100	23.50
BOD[e]	mg L^{-1}	5	14	0	1.44	-	3.6	3,00	12	8.3	1.56	-	6.36	3,10	14	0	1.43	-	3.8	2,70
DO[f]	mg L^{-1}	5[i]	6	16.7	1	-	9	7.63	6	0	5.5	-	9.2	7.83	6	0	5	-	9.6	7.01
pH	-	6 _ 9[j]	12	8.3	5.64	-	8.96	7.40	14	14.3	5.38	-	7.7	7.10	12	8.3	2.52	-	8.68	7.15
Turbidity	NTU	100	14	7.1	2.9	-	143	10.16	14	14.3	1.96	-	171	11.00	14	14.3	2.05	-	105	14.50
Total phosphorus	mg L^{-1}	0.100[k]	12	33.3	0.02	-	0.251	0.06	12	25.0	0.02	-	0.339	0.07	12	41.7	0.03	-	0.277	0.09
TDS[g]	mg L^{-1}	500	14	0	19	-	83	55.00	14	7.1	13	-	563	54.50	14	0	7	-	252	70.50
Hydrogen sulfide	mg S^{2-} L^{-1}	0.002	12	8.3	0.015	-	0.015	-	12	8.3	0.006	-	0.006	-	12	8.3	0.005	-	0.005	-
E. Coli	NMP 100 mL^{-1}	1000	14	14.3	10	-	8,500	182.50	14	64.3	6	-	75,000	4,336.5	14	35.7	20	-	34,480	500.50
Cyanobacteria	cel mL^{-1}	10,000	92	16.3	3	-	92,600	798.50	68	0	3	-	1316	62.50	102	15.7	3	-	60,300	1257
Total phenols	mg phenol L^{-1}	0.003	14	0	n.d[h]	-	n.d.	-	14	0	n.d.	-	n.d.	-	14	7.1	0.005	-	0.005	-

Legend: (a) N: number of samples where the parameter was analyzed. (b) F: frequency calculated considering the number of results outside legislation limits. (c) Minimum and maximum detected values; when the parameter was detected only once, minimum and maximum values are equal. (d) Median: median of detected results, analyzed, parameter detected at least 3 times. (e) BOD – biological oxygen demand; (f) DO – dissolved oxygen; (g) TDS – total dissolved solids. (h) n.d.: not detected. (i) Minimum allowed concentration. (j) pH - range of values established in the legislation. (k) Phosphorus - limit established for lotic environments: 0.100 mg L^{-1}.

Our results of color and turbidity, some of them above the legal limits (Table 2) indicate similarly the presence of suspended particles and dissolved substances, probably from soil run-off and effluent discharge. The degradation of the riparian forest area in the basin is a contributing factor to this impact since the breakage and suspension of these particles is favored.

As stated by Kreischer et al. (2012); Andrietti et al. (2016) and Oliveira et al. (2018) the variability in the values of color and turbidity is associated to the run-off of particles to the river once the soil use and management influence greatly the potential for soil erosion increasing the concentration of particles in water (Souza & Gastaldini, 2014).

Among the organic contaminants, phenols were the only one that presented results above the MAC in the Coophema station (P3). Phenolic compounds exist naturally in the aquatic environment from decomposition of dead plants and animals (organic matter) in the water and are also synthesized by microorganisms and plants. Anthropogenic sources of water pollution by phenols are industrial (waste from several chemical industries), domestic (component of many household chemicals such as disinfectants, antiseptics and slimicide), agricultural (degradation of pesticides) and municipal (effluents from municipal waste treatment plants, and leachates from municipal solid waste landfill) activities (Michałowicz & Duda, 2007). The only point where phenols were detected above MAC was the Coophema pumping station, the most downstream point among the sampled sites, which receives the contribution of most of the urban area.

The violation of the guidelines for the parameters DO, pH, BOD and the anions cyanide and sulfide can be associated to effluents discharge. Queiroz et al. (2020) reported similar values of DO and BOD in water bodies used for human supply in highly urbanized areas and attributed it to the effects of urbanization, resulting mainly from sewage discharge. Likewise, the results above the MAC for free chlorine are probably related to domestic and industrial effluents since chlorine is used as disinfectant agent in treatment plants (Arraes et al., 2009).

Phosphorus is another parameter normally associated to sewage discharge. In our study, total phosphorus concentrations (Table 2) were of the same order of magnitude as other studies on surface waters (Medeiros et al., 2018; Queiroz et al., 2020) and below the maximum values detected in the monitoring program of the Environmental Secretary of Mato Grosso (SEMA) during the period 2015-2018 (Mato Grosso, 2018b). Phosphorus concentrations may be related to the discharge of effluents from pisciculture as well, as pointed out by Fantin-Cruz et al. (2019). These authors highlighted that intensive pisciculture generate effluents rich in phosphorus and with high densities of cyanobacteria.

In the fishponds, the formed organic matter produces an environment favorable to the development of high densities of cyanobacteria (Cyrino et al., 2010; Macedo & Sipaúba-Tavares, 2010). In points P1 and P3, our results were similar to those reported by Costa et al. (2017) who pointed out that the pisciculture contributes to the bloom of cyanobacteria. The municipality of Cuiabá is home to about a quarter of all aquiculture enterprises registered in Mato Grosso State with 1695 fish farms (Siqueira et al., 2017). According to the state Law n. 10,669 of January 16, 2018, small fish farms (up to 5 ha of water surface in excavated tanks or dams or up to 10,000 m^3 of water in fishnet tanks) are not obliged to have a license (Mato Grosso, 2018a). However, Fantin-Cruz et al. (2019) pointed out that the cumulative effects of fish farming in series along the river may impair the water quality and the multiple uses of water, so indicating the need to the aquaculture effluents discharge to be licensed.

In the microbiological group, thermotolerant coliforms (*E. coli*) were detected in all samples (Table 2), with 14.3% of results above the MAC in P1 (Lipa), 64.3% in P2 (Tijucal) and 35.7% in P3 (Coophema). The water quality of Cuiabá River in the metropolitan area of Cuiabá was studied by Marchetto et al. (2019) using the SEMA monitoring data from 2011 and 2016 and verified total coliforms and *E. Colli* in concentrations similar to the ones detected in our study. Those authors observed an increase in the coliforms concentration downstream as the river crosses the urban perimeter of Cuiabá and Várzea Grande, indicating a significant anthropic effect on water quality.

In the water pumping stations located in the Cuiabá River (P1 and P3), the density of cyanobacteria, determined monthly, presented results not complying with the Ordinance 5/2017 (Brasil, 2021) in 16% samples (Figure 2). No result above MAC was detected in the Coxipó River (P2).

The occurrence of several parameters in disagreement with the Brazilian legislation (Table 3) indicate that the water quality of the Cuiabá and Coxipó Rivers is undergoing a deterioration process. Several studies in the Cuiabá watershed, within the urban perimeter of Cuiabá have already pointed out that effluents *in natura* are being discharged in the urban creeks that are affluents of the Cuiabá River (Silva et al., 2008; Kreischer et al., 2012; Silva, 2015). In the Cuiabá River, Kreischer et al. (2012); Andrietti et al. (2016) and Oliveira et al. (2018) found similar values to the ones found in the present study.

The impairment of the Coxipó river water quality have also been detected in previous studies. Silva (2015) identified illegal sewage discharge points along Coxipó River which receives water from urban creeks which in turn also receives illegal discharge (Kreischer et al., 2012).

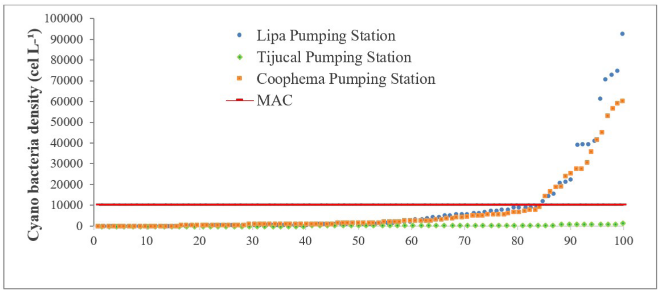

Figure 2. Frequency of occurrence *versus* cyanobacteria density in raw water samples collected in the pumping sites during the period from 2014 to 2019.

Source: prepared by the authors. Legend: MAC (maximum allowed value): 10,000 cel L^{-1} – limit established by Consolidation Ordinance n. 888/2021 (Brasil, 2021).

Index of Conformity with Guidelines (ICG)

ICG was calculated using all the quality data from the semiannual monitoring compared with CONAMA Resolution n. 357/2005 (Brasil, 2005) for each study year considering only the parameters whose results were above limit of detection. The ICG values obtained for points P1 – Lipa and P3 – Cuiabá allowed them to be classified as excellent for the years 2014 to 2018 with reduction to good in 2019 while for the point P2, the classification varied randomly between good and excellent (Table 4).

Another water quality index (WQI - Water Quality Index) that considers the parameters that indicate pollution by sewage discharge (9 parameters) is used by the Mato Grosso Environment Secretary (SEMA). SEMA calculated WQI using data from sampling points different from those used in the present study in the Cuiabá and Coxipó rivers with greater frequency of monitoring. SEMA reported that WQI results indicated a greater deterioration of the water quality of these rivers, considering the evaluation of specific parameters, indicating the presence of pollution by domestic sewage (Mato Grosso, 2018b).

It is noteworthy that the WQI results cannot be compared to the ICG. While WQI refers only to the pollution from domestic sewage, the ICG contribute to the discussion of several polluting sources since a higher number of parameters is used to calculate this index. So, the WQI determined by SEMA only give support to the discussion of the results in relation to the lack of sewage collection and treatment.

Therefore, the results non-compliant with the normative CONAMA n. 357/2005 for class 2 waters found in our study may be mainly associated to sewage discharge in the watershed and run-off. This pollution source impairs quality, health, and sustainability of hydric bodies with ecological, social, and economic damages. Besides the impacts over other water uses such as fishing and recreation (traditional uses of this watershed), the incorrect sewage discharge may also cause problems to the water treatment for human supply, increasing costs.

The Lipa and Tijucal pumping stations are located at the upper limits of the Cuiabá urban area and may be less impacted from effluent discharge than the Coophema site, however, some results show signs of pollution in this two upstream stations as well. Although not greatly impacted, a pollution control plan is urgent in the Cuiabá River basin in order to avoid further reductions in water quality. This pollution control plan should include actions that inhibit or reduce the entrance of pollutants to the water bodies. The treatment of effluent collection systems must be efficient, ensuring that residual waters returning to the environment will not impair water quality as well. So, investments on infrastructure and water management are required. The Municipal Basic Sanitation Plan of Cuiabá planned investments to guarantee 91% of sewage collection with 100% treatment by 2023, a significant increase against the current 79% coverage (Cuiabá, 2019). Regarding the impacts of economic activities, with special attention to aquaculture, it is necessary to carry out in-depth studies on their impacts in search for new policies that guarantee the adequate quality of effluents for the receiving water bodies.

Emerging pollutants

The Coophema pumping station (P3) was the sampling site where the highest number of emerging pollutants were identified (10 out of 12 analyzed) (Table 3), followed by the Lipa (P1) and Tijucal (P3) pumping stations with seven and five pollutants identified. Caffeine was the substance with highest detection frequency and concentrations occurring in 100% of the sampling campaigns in the three points at a maximum concentration of 743.2 ng L^{-1}. Carbamazepine and ibuprofen were detected at maximum levels of 780.7 and 102.1 ng L^{-1}, respectively, identified in 100% of the samples in the Coophema station and in at least 50% in Lipa and Tijucal stations.

Among the quantified pharmaceuticals, the higher amplitude of concentrations was observed for carbamazepine (5.8 to 780.7 ng L^{-1}) in the Lipa station and ibuprofen (2.9 to 102 ng L^{-1}) in Tijucal station (Table 3). Except for estrone which was detected in only one sample, all analyzed pharmaceuticals were quantified, at least once, in the Coophema station. Comparing Lipa (P1) and Tijucal (P2), a higher number of compounds were identified in P1 than in P2 but at lower concentrations in P1 than in P2 (except for carbamezapine).

The concentrations of pharmaceuticals in the Cuiabá and Coxipó rivers were of the same order of magnitude as those obtained for these same substances in surface waters of different regions of Brazil (Table 5).

The Coophema pumping station (P3), located in the Cuiabá River downstream of Coxipó River mouth, at the final third of the urban perimeter, receives effluent discharge from the central urban area and the Coxipó River (region without full collection of sewage and effluent treatment), explaining the highest number of pharmaceuticals and mostly at higher concentrations than the other two sampling sites.

Several studies report that rivers crossing or surrounding urban perimeters and receiving raw domestic effluents contain higher pharmaceuticals concentrations downstream than upstream (Souza et al., 2014; Campanha et al., 2015).

Vannini et al. (2011) evaluated ecotoxicological effects of a mixture of 13 drugs, including two pharmaceuticals at concentrations of the same order of magnitude as those detected in our study – carbamazepine (observed risk dose of 150 ng L^{-1}) and

Table 4. Results of ICG for samples from Cuiabá River (Lipa and Coophema) and Coxipó River (Tijucal) from 2014 and 2019.

	2014		2015		2016		2017		2018		2019	
	ICG	**Status[a]**	**ICG**	**Status**	**ICG**	**Status**	**ICG**	**Status**	**ICG**	**Status**	**ICG**	**Status**
P1	100	Excellent	95	Excellent	95	Excellent	96	Excellent	95	Excellent	94	Good
P2	98	Excellent	94	Good	95	Excellent	94	Good	94	Good	95	Excellent
P3	100	Excellent	95	Excellent	95	Excellent	95	Excellent	96	Excellent	94	Good

Legend: (a) Qualitative condition of the water pumping station.

Table 5. Frequency of detection and concentrations of pharmaceuticals in water samples collected from June to November 2019 at pumping stations for public water supply in the Cuiabá municipality and range of pharmaceuticals concentrations reported in surface water in Brazil.

Group	Compound (ng L^{-1})	LQ	P1 - Lipa Pumping Station				P2 - Tijucal Pumping Station				P3 - Coophema Pumping Station				Range of concentrations in Brazil reported in the literature[a]			
			F	Mín.	-	Max.	F	Mín.	-	Max.	F	Mín.	-	Max.	Mín.	-	Max.	Reference
Psychostimulant	Caffeine	5.7	100	11.8	-	47.1	100	18.4	-	137.8	100	155.1	-	743.2	<1	-	127.092	2-4, 6, 8, 9, 15, 25-27, 29
Anti-inflammatory	Ibrupofen	2.9	50	4.4	-	6.8	66.7	2.9	-	102.1	100	13.6	-	34.1	<0,1	-	4,155.5	1, 20, 21, 23-27
	Diclofenac	4.4	50	4.7	-	10.1	0	n.d.	-	n.d.	100	5.4	-	15	<0,04	-	6.000	1, 2, 6, 15, 20, 21, 23-27
	Naproxen	7.6	0	n.d.	-	n.d.	0	n.d.	-	n.d.	100	7.9	-	27.3	<0,1	-	390	1, 9, 17, 20, 21, 24-27
Analgesic, antipyretic	Paracetamol	1.2	16.7	4.9	-	4.9	83.3	3.4	-	10.5	100	10.4	-	43.7	0.84	-	30.421	9, 27
Anti-hypertensive	Atenolol	11.2	0	n.d.	-	n.d.	0	n.d.	-	n.d.	50	11.2	-	25.9	<0,04	-	8.199	2, 17, 25, 27
	Propranolol	5.2	33.3	8.6	-	19.5	50	6.6	-	14.8	66.7	5.8	-	15.2	<0,08	-	77.3	9, 17, 25-27
Anti-epileptic, antidepressant	Carbamazepine	3.7	83.3	5.8	-	780.7	83.3	6	-	172.1	100	3.7	-	130.8	<0,05	-	659.5	17, 25-27
Antiseptic	Triclosan	4.4	16.7	15	-	15	0	n.d.	-	n.d.	33.3	5	-	5.8	<0,70	-	323.5	25, 27
Hormones	Estrone	4.3	0	n.d.	-	n.d.	0	n.d.	-	n.d.	16.7	6	-	6	<0,10	-	78.1	6, 10, 13, 14, 18, 20, 21, 23-25, 27, 28
	17 - β - estradiol	6.5	0	n.d.	-	n.d.	0	n.d.	-	n.d.	0	n.d.	-	n.d.	0.038	-	6.806	5, 6, 7, 9, 10, 11, 13, 15, 28
	17 - α - ethinylestradiol	7.2	0	n.d.	-	n.d.	0	n.d.	-	n.d.	0	n.d.	-	n.d.	0.3	-	35	6, 9, 10, 11, 13, 15, 28

Source: the authors. Legend: LQ: limit of quantification; For substances detected just once, maximum and minimum values were the same; n.d.: not detected. Observation: (a) Adapted from Lima et al. (2017); Quadra et al. (2017) e Bisgonin et al. (2018). The minimum value corresponds to the lowest value of reported LQ (limit of quantification) among the listed references or to the lowest detected value, which is smaller. 1: Stumpf et al. (1999); 2: Almeida & Weber (2006); 3: Ferreira (2005); 4: Ide et al. (2005); 5: Ghiselli (2006); 6: Ghiselli (2006); 7: Moreira et al. (2011); 8: Raimundo (2007); 9: Bergamasco et al. (2011); 10: Montagner & Jardim (2011); 11: Moreira et al. (2011); 12: Gonçalves (2012); 13: Jardim et al. (2012); 14: López-Serna (2012); 15: Sanson (2012); 16: Souza et al. (2012); 17: Dias (2014); 18: Quaresma (2014); 19: Souza (2014); 20: Thomas et al. (2014); 21: Campanha et al. (2015); 22: Torres et al (2015); 23: Pereira et al.(2016).

ibuprofen (observed risk range of 92 to 920 ng L^{-1}) – and identified alterations in the photosynthetic process of algae. Pomati et al. (2006) studied risks to human health and pointed out possible interferences in the growth of kidney cells of human embryos exposed to a mixture of 13 pharmaceuticals, at concentrations from 10 to 1,000 ng L^{-1}. Therefore, the obtained results, even lower than the maximum values found by those authors, indicate a possible risk of impairment of productivity of aquatic ecosystems and the human health, due to the potential cumulative effect of a chronic exposure to a combination of different pharmaceuticals. Further investigations are required to study in details exposure risks of different mixtures present in environments and particularly in water used for human consumption.

The detection of estrone in one of the samplings indicate a possible contamination by hormones. The detection of such molecules in water bodies is complex due to the relatively high detection limits associated with the interaction to water particulate in water (Duong et al., 2009).

The improper discharge of pharmaceuticals may be the major source of contamination since, in general, the human excretion of unchanged molecules through urine is low (Holford, 2017). Moreover, these substances have a short half-life in the organism, indicating that identification of these molecules in environmental water may be related to other sources rather than excretions (Table 6).

The drugs detected: atenolol, carbamazepine, ibuprofen, naproxen and paracetamol are on the list of drugs distributed in the public network of SUS (National Brazilian Health System) in the state of Mato Grosso (Mato Grosso, 2020) and are widely used by the population. Likewise, they are mentioned by Barcellos et al. (2020) as priority drugs to be studied, since they are widely prescribed and used.

Table 6. Pharmacokinetic parameters for pharmaceuticals in adults.

Compound	Half-live[1] (h)	Urinay excretion of the unaltered pharmaceutical[2] (%)
Atenolol	6.1	94
Carbamazepine	15	1
Diclofenac	1.1	<1
Ibuprofen	2	<1
Naproxen	14	<1
Paracetamol	2	3
Propranolol	3.9	1

Source: Holford (2017). [1]Half-life: an estimate of the period of time necessary for the ingested amount in the body to be reduced by exactly a half. [2]The excretion of the unaltered pharmaceutical considers the depuration of creatinine of 100 mL min^{-1} for a body weight of 70 kg.

The study by Machado et al. (2016) evaluated the occurrence of emerging pollutants in surface waters and water supply systems in several Brazilian capitals. In Cuiabá, those authors collected treated water samples and determined caffeine at a concentration of 629 ng L^{-1}. In our study, the maximum concentration of caffeine was 743.2 ng L^{-1} at pumping site of Coophema (P3). Caffeine is not present only in medicine formulations, but its detection indicates the occurrence of other pharmaceuticals.

As studies regarding effects on human health and environment are scarce and legal limits are inexistent, it is not possible to state that there are immediate health risks. The European Union's Strategic Approach to Pharmaceuticals in the Environment produced a report updating the Progress and Implementation of studies that assess the presence and effects of pharmaceuticals in water. The report addresses the importance of studies that strengthen knowledge on the subject and allow safe environmental limits to be established in the future for the effects of these contaminants on aquatic organisms (European Union, 2020).

The free WikiPharma database contains publicly available ecotoxicity data for pharmaceutical substances, focusing on human pharmaceuticals available on the Swedish market, aiming to be a useful tool for researchers, risk assessors and regulators worldwide (WikiPharma, 2022). The results presented in this database, for the drugs analyzed in this study, are presented in Table 7. The results were collected according to the lowest ecotoxicological concentration with observed effect (LOEC).

None of the detected pharmaceuticals analyzed in this study (Table 5) presented concentrations above the LOEC listed in WikiPharma (2022). However, no study evaluated effects of a mixture of active ingredients as observed in the Cuiabá River sampling sites. Anyhow, it is important to emphasize that these substances do not occur naturally in the environment and their occurrence in water is a consequence of deficient urban sanitation system.

The detection of these substances may indicate a potential risk of chronic exposure and alert to the need for continuous studies on the subject and measures to prevent future problems. Understanding the occurrence, behavior and effects in different species is a fundamental step in order to establish safe limits and

Table 7. WikiPharma results for drugs analyzed at pumping station, species affected and critical effect according to LOEC.

Compound	LOEC[a,b] (ng L^{-1})	Species affected	Critical effect	Reference
Caffeine	3,000	*Carassius auratus* (goldfish)	SOD (superoxide dismutase) activity	1
	3,200		EROD (7-ethoxyresorufin O-deethylase) activity	
	16,000		GST (glutathione S-transferase) activity	
	40,000		AChE (acethylcholinesterase) activity	
Ibuprofen	2,000	*Dreissena polymorpha* (mussels)	Frecuency of micronucleated hemocytes; Neutral red retention time;	2
	8,000		Precentages of apoptotic hemocytes; Frequency of micronucleated hemocytes; growth inhibition	

Source: WikiPharma (2022). (a) LOEC: ecotoxicological lowest observed effect concentration.(b) Result not exceeded in this study. Reference: (1) Li et al. (2011); (2) Parolini et al. (2011); (3) Feito et al. (2012); (4) Bowman et al. (2009); (5) Ribeiro et al. (2015); (6) Oropesa et al. (2016); (7) Matozzo et al. (2012); (8) Zalęska-Radziwill et al. (2014); (9) Villain et al. (2016).

Table 7. Continued...

Compound	LOEC[a,b] (ng L^{-1})	Species affected	Critical effect	Reference
Diclofenac	3,000	*Polystichum setiferum* (plant)	Mitochondrial activity	3
Atenolol	100,000,000	Microorganisms	Microbial respiration	4
Propanolol	5,000	*Paracentrotus lividus* (Sea urchin)	Embryonic development	5
Carbamazepine	10,000	*Daphnia magna* (Crustacean)	Juvenoid activity	6
Triclosan	300	*Ruditapes philippinarum* (mussel)	Number of haemocytes; Effects on pinocytotic activity; Effects on haemocyte proliferation; Effects on lactate dehydrogenase activity	7
	600		DNA fragmentation in haemocytes	
	900		Haemocytes diameter; Haemocyte volume	
17-β-estradiol	4	*Oryzias latipes* (Japanese ricefish)	induced intersex (testis-ova)	8
17-α-ethinylestradiol	0. 03	*Oryzias latipes* (Japanese ricefish)	induced intersex (testis-ova)	9

Source: WikiPharma (2022). (a) LOEC: ecotoxicological lowest observed effect concentration.(b) Result not exceeded in this study. Reference: (1) Li et al. (2011); (2) Parolini et al. (2011); (3) Feito et al. (2012); (4) Bowman et al. (2009); (5) Ribeiro et al. (2015); (6) Oropesa et al. (2016); (7) Matozzo et al. (2012); (8) Zalęska-Radziwiłł et al. (2014); (9) Villain et al. (2016).

directions for water treatment systems. This is because, another fact that deserves attention is that conventional water treatment plants are not efficient in eliminating emerging pollutants due to the polar nature of many of them. Several studies point to the need for advanced treatment techniques to efficiently remove emerging pollutants (Lin et al., 2016; Fu et al., 2019; Cartaxo et al., 2020).

CONCLUSIONS

The evaluated physical, chemical, biological and organoleptic parameters indicate that a reduction in water quality in the pumping sites of water treatment plants in the Cuiabá River basin is occurring owing to the detection of several contaminants characteristic of urbanized areas. However, the ICG (Index of Conformity with Guidelines) values allowed the classification of these sites as excellent and good, once the parameters non-compliant with legislation presented values slightly higher than the legal limits. In any case, the observed alterations point to the need for measures to prevent water quality to be further reduced in the near future, impairing the several uses, since prevention is always better than remediation.

Sewage discharge was the main factor leading to water quality degradation in Cuiabá and Coxipó rivers. Therefore, it is urgent to increase collection and treatment of urban effluents combined with sanitation actions, such as proper disposal of solid residues. Moreover, it should be assured that economic activities carried out in the basin, particularly in urban centers, comply with environmental legislation to ensure the integrity of aquatic ecosystems and environmental conservation.

The concentrations of potentially toxic metals and pharmaceuticals indicate that water quality may be impaired in the near future to meet the most demanding uses. Our results reinforce the need for new studies to evaluate the potential impacts of the exposure to these substances. Only a thorough understanding of the occurring concentrations and potential impacts of these pollutants would allow the development of adequate and efficient water treatment to eliminate or reduce their levels.

Furthermore, once the improper disposal of the medicines is one of the main sources of pollution by pharmaceuticals, it is also necessary to sensitize and orient the population regarding the adequate disposal of these products.

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Supplementary material - A
Supplementary material - B
Supplementary material - C

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