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The Importance of the Management of Micropollutants in an Advanced Wastewater Treatment Plant in the Amazon

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Abstract

Objective: This study aims to determine the dynamics of the discharge of micropollutants in the Amazon River from an advanced wastewater treatment plant (WWTP) and discusses the importance of management in order to minimize impacts.
Methodology: A total of 13 micropollutants: ibuprofen (IBP), paracetamol (PCM), atenolol (ATL), loratadine (LTD), fexofenadine hydrochloride (FXF), amoxicillin (AMX), 17α-ethynyl estradiol (EE2), caffeine (CAF), sodium diclofenac (DCF), estrone (E1), estriol (E3), bisphenol A (BPA), and bis(2-ethylhexyl) phthalate (DEHP) were analyzed in effluent samples that came from different treatment stages of a WWTP with advanced treatment technology at different periods of the day. The presence of micropollutants and their quantification were obtained using LC-MS and GC-MS techniques.
Originality/Relevance: This is the first study carried out at a WWTP in Manaus, a city in Brazil that is located within one of the most extensive fluvial system in the world. The data obtained are important for understanding the dynamics of the discharge of micropollutants into the Amazon River and its implications.
Main results: After the treatment process, the micropollutants paracetamol, fexofenadine hydrochloride, caffeine, sodium diclofenac, and bis(2-ethylhexyl) phthalate were detected in the final effluent.
Contributions: The results obtained in this study indicate the need for integrated management, considering technical, governmental, organizational and community-based approaches to minimize the effects of the discharge of micropollutants into the environment.

Keywords: micropollutants; removal; wastewater; technologies; integrated management.

A importância da Gestão de Micropoluentes em uma Estação de Tratamento de Efluentes Avançada na Região Amazônica

Resumo

Objetivo do estudo: O estudo visa determinar a dinâmica de descarga de micropoluentes no rio Amazonas a partir de uma ETE avançada e discutir a importância da gestão na minimização dos impactos.

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Metodologia: Foram analisados 13 micropoluentes: ibuprofeno (IBP), paracetamol (PCM), atenolol (ATL), loratadina (LTD), cloridrato de fexofenadina (FXF), amoxicilina (AMX), 17α-ethynil estradiol (EE2), cafeína (CAF), diclofenaco de sódio (DCF), estrona (E1), estriol (E3), bisfenol A (BPA), and bis(2-etilexil) ftalato (DEHP) em amostras de efluente vindas de diferentes estágios de tratamento de uma ETE com tecnologias de tratamento avançado, em diferentes períodos do dia. A presença de micropoluentes e sua quantificação foram realizadas usando técnicas de CL-EM e CG-EM.
Originalidade/Relevância: Este é o primeiro estudo realizado em uma ETE de Manaus, cidade brasileira que está localizada em um dos mais extensos sistemas fluviais do mundo. Os dados obtidos são importantes para compreender o comportamento da descarga de micropoluentes no rio Amazonas e suas implicações.
Principais resultados: Depois do tratamento, os micropoluentes paracetamol, cloridrato de fexofenadina, cafeína, diclofenaco de sódio, e, bis (2-etilexil) ftalato foram detectados no efluente final.
Contribuições: Os resultados obtidos neste estudo indicam a necessidade de um gerenciamento integrado, considerando abordagens técnicas, governamentais, organizacionais e comunitárias para minimizar os efeitos da descarga de micropoluentes no meio ambiente.

Palavras-chave: micropoluentes; remoção; efluente; tecnologias; gerenciamento integrado.

Importancia del manejo de los Micropoluentes en un Sistema Avanzado de Tratamiento de Efluentes en la Región Amazónica

Resumen

Objetivo del estudio: Este estudio tiene como objetivo determinar la dinámica de la descarga de Micropoluentes en el Río Amazonas desde una Planta de Tratamiento de Aguas Residuales (PTAR), con tecnología avanzada, en y discutir la importancia de la gestión para minimizar los impactos.
Metodología: se analizaron 13 micropoluentes: ibuprofeno (IBP), paracetamol (PCM), atenolol (ATL), Loratadine (LTD), clorhidrato de fexofenadine (FXF), amoxicilina (AMX), 17α-etinilo estradiol (EE2), cafeína (CAF), diclofenaco de sodio (DCF), estrona (E1), estriol (E3), bisphenol A (BPA), y ftalato de bis(2-etilhexilo) (DEHP), en muestras de efluentes colectadas en diferentes períodos del día y en diferentes etapas de tratamiento de una PTAR, que incorpora tecnologías avanzadas en su proceso. La presencia de micropoluentes y la cuantificación de los mismos fueron realizadas con el uso de técnicas de LC-MS y GC-MS.
Originalidad/Relevancia: Este es el primer estudio realizado en una PTAR en Manaus, una importante ciudad de Brasil, que está localizada en uno de los sistemas fluviales más extensos del mundo. De este modo, los datos obtenidos son importantes para entender el comportamiento de la descarga de micropoluentes en el Río Amazonas e sus implicaciones.
Principales resultados: Después del proceso de tratamiento, los micropoluentes paracetamol, clorhidrato de fexofenadine, cafeína, diclofenaco de sodio y ftalato de bis(2-etilhexilo) fueron detectados en el efluente final.
Contribuciones: Los resultados obtenidos en este estudio indicaron la necesidad de un manejo integrado que considere enfoque técnico, gubernamental, organizacional y comunitario para minimizar los efectos de la descarga de micropoluentes en el medio ambiente.

Palabras clave: micropoluentes; remoción; agua residual; tecnologías; manejo integrado.

Introduction

The largest and most extensive fluvial system in the world is located in the Amazon and it has an important role in maintaining the global balance of hydrology and climate, while also hosting an enormous freshwater biodiversity (Fabregat-Safont et al., 2021; Fassoni-Andrade et al., 2021; Oberdorff et al., 2019). The construction of hydroelectric dams, mining, deforestation, biomass burning and agriculture expansion are the main anthropogenic impacts studied in the Amazon basin; however, urbanization also exerts significant pressure on this ecosystem, and the treatment of wastewater is a related issue (Fabregat-Safont et al., 2021; Latrubesse et al., 2017; Pasquini et al., 2014; Ruiz-Vásquez et al., 2020). Just 13.1% of the population of Brazilian Amazon have a public wastewater collection system and only 21.4% of this contingent benefits from wastewater treatment (SNIS, 2021). About two thirds of the people in the Amazon live in large cities such as Manaus, which is the most populous city of the Brazilian Amazon and has an estimated population of 2,255,903 people (IBGE, 2021). In addition to the pollution caused by the organic matter present in the untreated wastewater, other chemical compounds, such as micropollutants, are discharged into receiving water bodies.

Micropollutants are chemical substances that are detected in environmental samples at trace concentrations, in µg/L or lower (Isik et al., 2022). These substances, also known as emerging contaminants, consist of diverse anthropogenic and natural substances, including personal care products, endocrine disruptors, biocides, and polyfluoroalkyl substances (Ren et al., 2022). Over the last few decades, the occurrence of micropollutants in the aquatic environment has become an issue of increasing environmental concern. This has occurred because the effect of these substances in non-target organisms is not well known, but the results obtained in studies show these substances can be potentially harmful (Carles et al., 2021; Gallego et al., 2021; Li et al., 2016; Ngweme et al., 2021; Yang et al., 2017).

According to Ofrydopoulou et al. (2022), wastewater treatment plants (WWTPs) have been identified as the main origin of micropollutants that enter natural water bodies. Numerous studies have shown that conventional WWTPs are incapable of eliminating many organic compounds found in wastewater, including micropollutants (Bogunović et al., 2021; Guillossou et al., 2019; Pasquini et al., 2014). The effluents released from WWTPs can be discharged into the receiving water bodies, such as surface waters or seawaters, and the compounds found in wastewater and/or their metabolites and transformation products are detected in surface waters and, as a consequence, in water sources for human supply (Glassmeyer et al., 2017; Rogowska et al., 2020; Undeman et al., 2022). These results directly affect the intentions of achieving one of the Global Sustainable Development Goals (SDG) created by the United Nations, which is universal and equitable access to safe and affordable drinking water for all by 2030 (United Nations, 2015).

The Amazon River is one of the sources of data on micropollutants in the Amazon region. Rico et al. (2021) found more than 40 different chemical compounds in the Amazon River (antibiotics, anti-arrhythmics, anti-hypertensives, lipid regulators, anti-diabetics, gastrointestinal protectants, anti-inflammatories, analgesics, anti-depressants, anti-epileptics, anxiolytics and psychostimulants). In addition to pharmaceutical drugs, illegal drugs and other micropollutants such as cocaine, benzoylecgonine, sucralose, methylparaben, propylparaben and benzophenone-3 are found in the same receiving basin (Fabregat-Safont et al., 2021; Thomas et al., 2014).

In a recent review of the removal of micropollutants from wastewater, Ribas et al. (2021) discuss the studies that have been carried out in Brazil, and show that the studies are mostly concentrated in the southeastern region of the country and were conducted by public institutions. The studies are usually related to conventional treatments and only a few deal with advanced treatments (such as advanced oxidation processes). According to the authors, researchers in the Brazilian Amazon are not conducing any studies about the removal of micropollutants in WWTPs.

The first study about wastewater treatment in this region was published by Ribas et al. (2022), but it is restricted to *in vitro* assays. Considering the relevance of the Amazon basin and the lack of wastewater treatment in the region and the inefficiency of the removal of many micropollutants in conventional wastewater treatment plants, this research is considered innovative and aims to determine the dynamics of the discharge of micropollutants into the Amazon River from an advanced WWTP, while also discussing the importance of management in order to in minimize impacts.

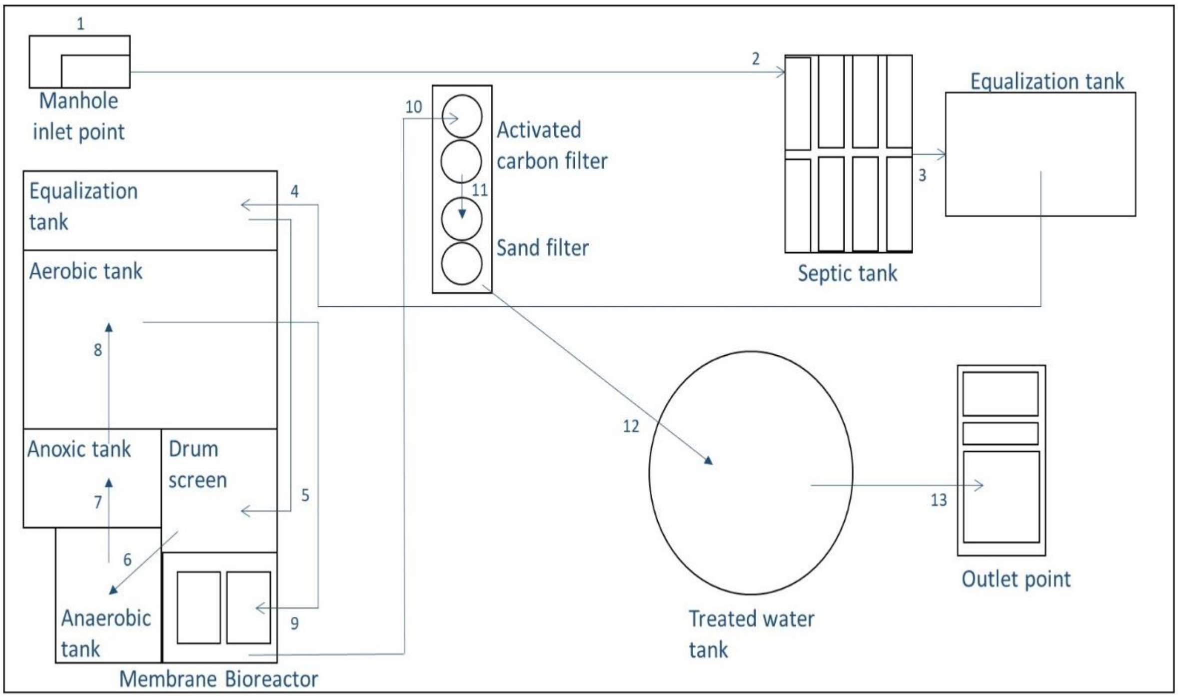
Material and Methods

Sampling

Samples were collected in five campaigns that were carried out between July and August 2021 at a WWTP for domestic wastewater located in the industrial district of Manaus, Amazonas state, Brazil. The WWTP has a wastewater processing capacity of 1,140 m^3/day and includes primary and secondary treatment with activated sludge technology and tertiary treatment with membrane bioreactor technology, an activated carbon filter and a sand filter. The schematics for the wastewater treatment are presented in Figure 1. The figure is for illustrative purposes only and it does not represent the actual scale of the WWTP.

Figure 1

Schematics of a Wastewater Treatment Plant (WWTP) located in the industrial district of Manaus, Amazonas state



The wastewater treated in this WWTP is composed of domestic wastewater, and Table 1 presents a characterization of the influent during the sampling period. Samples were collected in three different WWTP points: a) inlet (influent), b) after the membrane bioreactor treatment (MBR) and c) outlet (effluent) three times per day (9 a.m., 2 p.m. and 5 p.m.), totalizing 45 samples. Sampling was performed manually using an amber glass bottle (1,000 mL). In the laboratory, all samples had the pH adjusted to 5.0 and were kept refrigerated (4 °C) until preparation of the sample and posterior analysis.

Table 1

Wastewater characterization

Sampling campaign	I and II	III, IV and V
Parameter	13/07/2021 and 15/07/2021	09/08/2021, 11/08/2021 and 12/08/2021
TSS (mg/L)	2,78	1,382
pH	5.57	5.0
t (°C)	31.3	30.7
Total P (mg/L)	2.12	1.79
Total N-NH_3^+ (mg/L)	134.94	100.77
NO_3^- (mg/L)	27.32	24.78
Cl^- (mg/L)	126.32	94.28
Total SO_4^{2-} (mg/L)	83.14	79.41
COD (O_2 mg/L)	535.2	513.6
BOD (O_2 mg/L)	294.3	256.8

Source: Wastewater Treatment Laboratory. Abbreviations: TSS - total suspended solids; COD – chemical oxygen demand; BOD – biochemical oxygen demand.

Chemical information

A total of 13 micropollutants were chosen for the study, which included: i) pharmaceutical compounds: ibuprofen (IBP), paracetamol (PCM), atenolol (ATL), loratadine (LTD), fexofenadine hydrochloride (FXF), amoxicillin (AMX), 17α-ethynyl estradiol (EE2), caffeine (CAF), sodium diclofenac (DCF), and two natural hormones -estrone (E1) and estriol (E3); and, ii) industrial chemicals: bisphenol A (BPA), and bis (2-ethylhexyl) phthalate (DEHP). Table 2 presents more details about the micropollutants used in this study. The assays were performed using GC-MS and LC-MS analysis, covering as many techniques as possible for determining possible micropollutants in the samples.

Table 2

Chemical information about the micropollutants studied

Micropollutant	Empirical formula	Molecular weight (g/mol)	CAS number	Producer
IBP	$C_{13}H_{18}O_2$	206.28	15687-27-1	LGC Standards
PCM	$CH_3CONHC_6H_4OH$	151.16	103-90-2	European Pharmacopeia Standard
ATL	$C_{14}H_{22}N_2O_3$	266.34	29122-68-7	Sigma-Aldrich
LTD	$C_{22}H_{23}N_2O_2Cl$	382.88	79794-75-5	European Pharmacopeia Standard
FXF	$C_{32}H_{39}NO_{4.}HCl$	538.12	153439-40-8	European Pharmacopeia Standard
AMX	$C_{16}H_{19}N_3O_5S.3H_2O$	419.45	61336-70-7	European Pharmacopeia Standard
EE2	$C_{20}H_{24}O_2$	296.40	57-63-6	Sigma-Aldrich
CAF	$C_9H_{10}N_4O_2$	194.19	58-08-2	LGC Standards
DCF	$C_{14}H_{10}Cl_2NNaO_2$	318.13	15307-79-6	Sigma-Aldrich
E1	$C_{18}H_{22}0_2$	270.37	53-16-7	LGC Standards
E3	$C_{18}H_{24}O_3$	288.38	50-27-1	LGC Standards
BPA	$(CH_3)_2C(C_6H_4OH)_2$	228.29	80-05-7	Sigma-Aldrich
DEHP	$C_{24}H_{38}0_4$	390.56	117-81-7	Sigma-Aldrich

GC-MS analysis

All samples, whether influent, MBR effluent or final effluent, received the same treatment. First, 250 mL of each sample were filtered through a glass fiber microfilter (GF-3, particle retention < 0.6 µm, Macherey-Nagel, Germany) to prevent the clogging of the solid phase extraction (SPE) cartridge. Samples were acidified with HCl (pH = 2) and concentrated on a DSC-18 SPE cartridge (Supelco) in a vacuum manifold system (Supelco). Solid-phase extraction and derivatization procedures, as previously reported by Pessoa et al. (2012), were applied. After loading, the samples were eluted with a 4 mL of 50:50 solution (v/v) of acetone and methanol. For evaporation of the solvent, the eluate was maintained in an oven at 60 °C. All eluates were derivatized with 150 µL N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA – Sigma-Aldrich) at 60 °C for 30 minutes.

Samples were analyzed using gas chromatography with mass spectrometry, GC–MS (Shimadzu, QP 2020) and the parameters, according to the methodology presented by Ribas et al. (2022), are presented in the Table 3.

Table 3

Gas chromatography parameters

GC parameters	Description
GC Column	RXI-5 MS capillary column
Column dimensions	30 m × 0.25 mm Restek
Film thickness	0.25 µm
Carrier gas	Helium
Inlet temperature	290 °C
Inlet mode	Splitless
Oven initial temperature	100 °C
Íon source temperature	200 °C
Mass selective detector transfer line	290 °C
Solvent cut	10 min
Injection volume	1 µL
Constant flow	1.43 mL/min
Oven temperature ramp	100 °C (5 min) 20 °C/min at 150 °C (1 min) 20 °C/min at 250 °C (0 min) 20 °C/min at 290 °C (4 min) 10 °C/min at 320 °C (5 min)
Acquisition mode	SIM
Ionization method	IE

All the analytical parameters applied to the compounds that were able to be quantified with GC-MS are presented in Table 4.

Table 4

Analytical parameters applied to the quantification of micropollutants using GC-MS

Micropollutant	Retention Time (min)	Target ion (m/z)	Reference ion (m/z)	Calibration range (mg L^{-1})
Ibuprofen (IBP)	11.567	160	263	0.25-10
Paracetamol (PCM)	11.653	206	280	0.25-5
Caffeine (CAF)	13.242	194	109	0.25-10
Bisphenol A (BPA)	15.175	357	358	0.25-2.5
Sodium diclofenac (DCF)	15.683	214	242	0.25-10
Bis(2-ethylhexyl) phtalate (DEHP)	16.825	149	167	0.25-2.5
Estrone (E1)	17.733	342	257	0.25-10
17α-ethynyl estradiol (EE2)	18.950	425	285	0.25-20
Estriol (E3)	19.775	504	297	0.25-20
Loratadine (LTD)	22.200	382	266	0.25-10

LC-MS analysis

To perform the identification of micropollutants using LC-MS, 250 mL of each sample (influent, MBR treatment effluent and final effluent,) were filtered through a glass fiber microfilter (GF-3, particle retention < 0.6 µm, Macherey-Nagel, Germany). Initially, they were acidified with HCl (pH = 2) and concentrated in a sorbent cartridge (Oasis HLB 6cc 500 mg) in a Vacuum Manifold system (Supelco). The samples were eluted with 8 mL of 50:50 acetonitrile and methanol solution (v/v). The solvent was then removed under N_2, reconstituted in 1 mL of methanol and stored at 4°C until the UHPLC analysis.

The instrumental analysis was performed using an UHPLC system (Dionex Ultimate 3000 UHPLC, Dionex Corporation Sunnyvale, USA), coupled to a high resolution mass spectrometer, equipped with an automatic injector (LC TriPlus RSH, Thermo Scientific) using the parameters of the methodology of Ribas et al. (2022), which are presented in Table 5.

Table 5

Liquid chromatography parameters

LC parameters	Description
LC Column	Syncronis C18 column
Column dimensions	2,1 x 50 mm Thermo Fisher Scientific
Mobile phase A	Acidified water (0.1% of formic acid) and ammonium formate (5mM)
Mobile phase B	Acidified methanol (formic acid)
Gradient elution	1% of eluent B 100% of eluent B (7 min) 100% of eluent B (1 min) 5% of eluent B (1 min)
Mobile phase flow rate	0.4 mL/min
Injection volume	10 µL
Column temperature	40 °C
Electrospray ionization heater	380 °C
Ion mode	Positive
Mass range	150-600 amu

Table 6 shows all the analytical parameters applied to eight compounds quantified using LC-MS.

Table 6

Analytical parameters applied to the quantification micropollutants using LC-MS

Micropollutant	Retention Time (min)	Target ion (m/z)	Calibration range (µg L^{-1})
Atenolol (ATL)	0.35	152	5-1.500
Paracetamol (PCM)	1.90	195	5-1.500
Caffeine (CAF)	3.90	267,17	5-400
Fexofenadina hidrochloride (FXF)	6.02	502	5-2.000
Amoxicilin (AMX)	4.45	332	5-1.500
Sodium diclofenac (DCF)	7.43	366	15-2.000
Loratadine (LTD)	7.67	383	5-1.500
Bis(2-ethylhexyl) phthalate (DEHP)	9.86	391	5-1.500

Conventional treatment versus advanced treatment: the difference in removal of micropollutants

The secondary wastewater treatment, used to remove organic matter by biodegradation, is also known as conventional wastewater treatment. In Brazil, the most common treatment process applied in WWTPs are the anaerobic reactor combined with a facultative pond, UASB reactor and activated sludge (Von Sperling, 2016). However, these processes are often inefficient in the removal of micropollutants from wastewater. Studying different WWTPs, Lin et al. (2009) observed that many antibiotics (erythromycin-H_2O, ampicillin, metronidazole, and lincomycin, among others), vasodilators (pentoxifyleine) and lipid regulators (clofibic acid, genfibrozil, bezafibrate and pravastatin) were not removed by the activated sludge process. In addition, hormone removal was incomplete when UASB reactors were used for wastewater treatment. The results obtained by Vassalle et al. (2020) show that the removal of ethinylestradiol is around 25% and the removal efficiency of estradiol is 84.9% when using a UASB reactor. The difficulty in achieving the complete removal of hormones is also presented in Louros et al. (2021), who, when using a UASB in continuous operation, obtained a removal efficiency of 49% for estrone and 39% for ethinylestradiol.

Other related issues are found with the concentration of micropollutants in effluents released after treatment. Even with high removal efficiency in WWTPs, the final concentration of some micropollutants, such as triclosan and estrogens, might be higher than their predicted no effect concentration (PNEC), thus posing a risk to aquatic organisms when discharged (Komolafe et al., 2021). Furthermore, in some cases, the biological process could increase the concentration of micropollutants in the treated effluent in comparison with raw influent because of the deconjugation of biotransformation conjugates. Pessoa et al. (2014) showed that estrone concentrations in the influent were five times higher than those of β-estradiol. Estrone was more frequently detected in influents due to partial degradation of β-estradiol to estrone, and deconjugation of estrone conjugated compounds (estrone sulfonide or glucuronide) in wastewater treatment systems. The same behavior was found in wastewater treated for pharmaceutical products, such as carbamazepine (removal efficiency -76%, - 89%), nalidixic acid (removal efficiency -5%, -96%), nevirapine (removal efficiency -7%, -88%), in wastewater stabilization ponds (K'oreje et al., 2018).

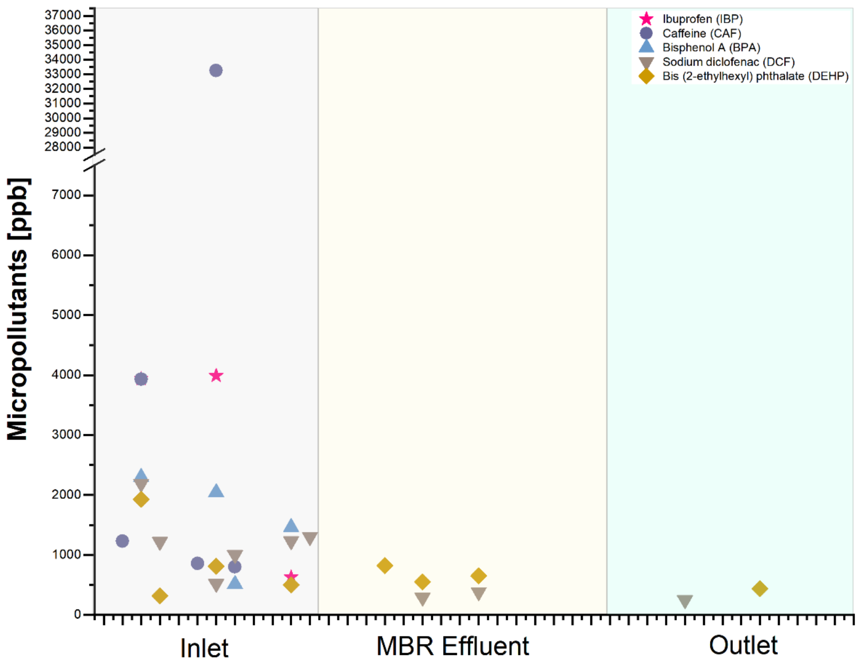
In Brazil, the environmental occurrence of micropollutants is rarely studied, and micropollutant compounds are not part of national water quality guidelines (Quadra et al., 2021). As expected, the urban and industrial wastewater treatment plants in Brazil do not plan for the removal of micropollutants in their projects and studies about the different technologies for removal are few. In a recent publication, Ribas et al. (2021) presented a list of studies that were carried out in Brazil regarding micropollutant removal technologies in the last 20 years. In this review, it was observed that although more advanced techniques (advanced oxidative processes, for example) are known, in Brazil, the studies aim to adapt the most used techniques in conventional treatment in order to verify their effectiveness in the removal of micropollutants. Biological treatment is the most often studied, with use of a UASB reactor or its use in combination with other processes, followed by photodegradation, activated sludge and also, treatment via macrophytes.

The WWTP analyzed in this study presents advanced techniques such as tertiary treatment, which is not common in the majority of urban WWTPs and could contribute to the removal of micropollutants. All the compounds studied had analytical parameters determined by GC-MS or, LC-MS or by both; however, not all compounds were quantified in the analyzed samples. The compounds ATL, LTD, EE2, E1 and E3 were not identified or quantified in any of the samples analyzed. CAF, DCF and DEHP were identified and quantified using both chromatographic techniques. IBP and BPA were identified and quantified via GC-MS and PCM, FXF and AMX by using LC-MS.

Considering the treatment process used at the WWTP, it was observed that the concentration of micropollutants is highest at the inlet point and reduces after treatment. The results are presented in the graphs created using Origin PRO 2021 (Figure 2 and Figure 3).

Figure 2

Determination of micropollutants in a wastewater treatment plant using GC-MS

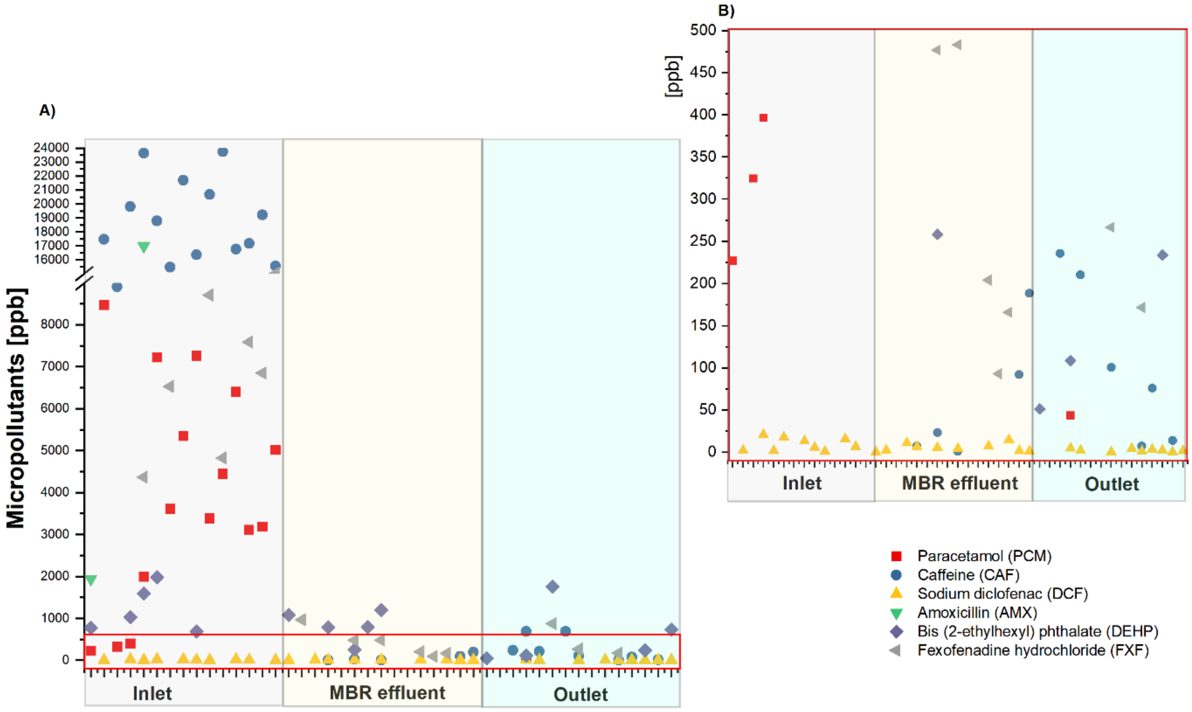


According to the GC-MS results (Figure 2), IBP, CAF and BPA were completely removed during the treatment process and the concentration of DCF and DEHP was reduced after MBR treatment (73% and 24%, respectively) until the outlet point (80% and 51%, respectively).

Using LC-MS, the same behavior was observed (Figure 3); however, as the sensibility of technique is higher, lower concentrations could be detected. The concentration of micropollutants reduces after treatment. Considering the detection limit, AMX was completely removed during the treatment process and the concentrations of PCM, CAF, DCF, DEHP and FXF reduced after MBR treatment until the outlet point (99%, 99%, 72%, 53% and 64%, respectively).

Figure 3

Determination of micropollutants in a wastewater treatment plant using LC-MS; (A) all compounds; (B) zoom of the compounds with lower concentrations



The membrane bioreactor (MBR) technique is a promising alternative to conventional treatment, and its usage is increasing in municipal wastewater treatment and reuse. However, great concerns have been raised regarding removal of some micropollutants found in aquatic environments in the last decade, notably the pharmaceuticals using microfiltration, ultrafiltration or nanofiltration techniques (Mert et al., 2018; Zaviska et al., 2013). Phan et al. (2015) observed a stable removal (> 90%) of micropollutants such as CAF and IBP in the MBR system. These compounds are hydrophilic and, thus, biodegradation is thought to be the main removal mechanism during biological treatment processes (Alvarino et al., 2017; Phan et al., 2015). The removal of paracetamol (acetaminophen) by MBR systems is based on their degradation/transformation since no presence was detected in sorption onto sludge or in final effluent when 100% removal was detected (Kim et al., 2014). The combination of activated sludge and MBR treatments is also efficient for removing more than 70% of AMX in wastewater (Le et al., 2018).

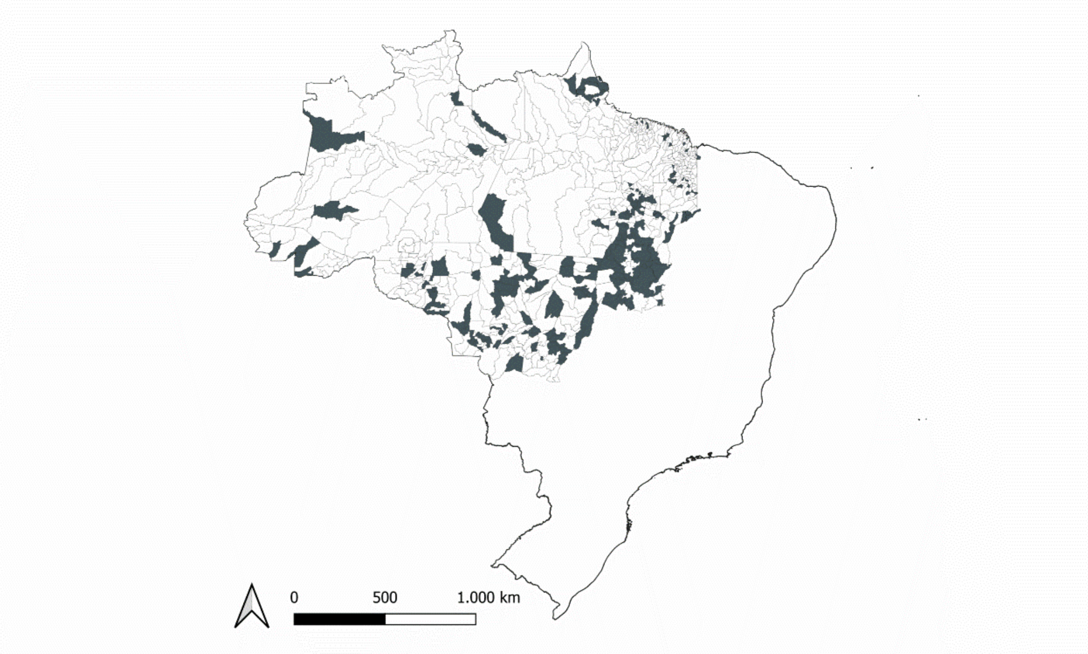
The effectiveness of the MBR system in removing BPA (over 94%) was also confirmed by Fudala-Ksiazek et al. (2018). DCF is a recalcitrant substance and this behavior justified the lower efficiency of its removal in MBR systems (Abegglen et al., 2009; Alvarino et al., 2017; Phan et al., 2015). DEHP has stable chemical properties and is difficult to degrade in the environment. According to Zhang et al. (2021), just 15% of the initial concentration of DEHP was removed in an MBR system. The removal of FXF is considered low in the MBR system studied. Similar results were reported by Henning et al. (2019), with 41% removal. According to the authors, this happens because the FXF is removed faster when in contact with carriers (biofilters) compared to the suspended sludge used in MBR systems.

The use of the MBR system to increase the removal of micropollutants in addition to conventional activated sludge is a feasible alternative and presents good results (Goswami et al., 2018). To increase the removal range, other technologies can be integrated in the WWTP, for example, an MBR system with an activated carbon filter, which generates better results for the parameters monitored during treatment (Alighardashi et al., 2017). Adsorption or biosorption could be one of the most effective methods for removing organic micropollutants from aqueous effluents (García-Mateos et al., 2015). The advantage of this method is the possibility of selectively adsorbing target substances from multicomponent mixtures, as well as achieving a high degree of purification, especially of wastewaters with low pollutant concentrations via a simple method and at a low cost (Sekulic et al., 2019; Tatarchuk et al., 2019).

As the WWTP studied serves a population of approximately 6,000 people, the results obtained may be similar to what we would find in at least 254 municipalities of the Brazilian Amazon that have less than 10,000 inhabitants (33%). Thus, we can expect that the same micropollutants are found in these municipal wastewater treatment plants and, therefore, our study can be applied as a model for the development of environmental policies, not only in the company where it was carried, out but also in municipalities with similar population sizes (Figure 4).

Figure 4

Municipalities of the Brazilian Amazon that have less than 10,000 inhabitants



Considering the situation of wastewater treatment in Brazil, the results presented in this study showed the importance of evaluating the contribution of a wastewater treatment plant in regards to the discharge of micropollutants into the Amazon River. As such, the analysis of the wastewater samples evidenced that, although advanced treatment technologies contribute by removing or reducing the concentration of micropollutants, in most cases, without a planned management strategy, the environment remains affected by these substances. Consequently, if we consider that the volume of effluent treated in Manaus and other cities in Brazil is very low and there few units of WWTP with the capability for advanced treatment, the environmental impact is most certainly considerable.

The importance of the management of micropollutants for reducing the impacts of discharges

As observed, in major cases, the WWTPs around the world are not able to remove micropollutants during the wastewater treatment and, when there is a treatment, even combinations of different (advanced) processes do not entirely remove the micropollutants and sometimes they only even remove a minor share of them (Kümmerer et al., 2019). Moreover, considering that many countries, such as Brazil, do not have public policies to regulate the discharge of micropollutants into aquatic environments, the presence of these substances in water is a concern for public health and the environment. Due to the large number of substances, sources and entry-paths into aquatic environments, it is a complex task to develop a pertinent response policy.

In this way, possible policy responses to aquatic micropollutants comprise three types: source-directed measures, end-of-pipe approaches, and control strategies (Barcellos et al., 2021; Metz et al., 2019). Source-directed solutions target the reduction of the entry of micropollutants into water bodies through education and training of producers in order to reduce the production of items using toxic substances and the education of consumers so as to change their behavior in relation to products containing these substances. End of-pipe solutions aim to remove micropollutants from wastewater, mainly by improving the technology of WWTPs. Control approaches are preliminary strategies and include the monitoring of the level of pollution for further policy intervention (Tosun et al., 2020).

Despite the lack of government management, some actions based on these policies can be applied, mainly induced by organizations and communities, like private enterprises and municipalities that intend to implement WWTPs, in order to minimize the impact of the discharge of micropollutants into aquatic environments (Barcellos et al., 2021). The simple fact of opting for the implementation of an MBR instead of conventional treatment is a step towards managing the discharge of micropollutants into the environment and the evolution of this treatment technique will increasingly enable sustainability in relation to the capital and operational costs, operational efficiency and stability, and resources saving and recovery (Xiao et al., 2019).

Barcellos et al. (2021) presented other strategies for the management of micropollutants that could be explored in developing countries, such as Brazil. These strategies cover the technical, governmental, organizational and community-based approaches, such as a reduction in the consumption of micropollutants, educational programs at all levels of education for the proper disposal and correct use of medicines, best organizational practices, evaluation studies on green technologies and the reconfiguration of WWTPs. Therefore, the implementation of integrated management systems is a way to transform the discharge of micropollutants into something less dependent on heavy investments in technological solutions incorporated by material bases and more dependent on social technologies, initiatives, and convergence of interests in networks formed by multiple stakeholders involved in the productive chain.

The government's role in micropollutant management and the Global Sustainable Development Goals

According to Aragão et al. (2020), there is no international standard on how to deal with the issue of the micropollutants, and each country adopts the public policy that best suits the location. Brazil, despite having some legislation that deals with the theme, still lacks effective public policies and stakeholder awareness. Considering the importance of wastewater treatment to reduce the environmental impact caused by micropollutants, a monitoring program could be the first step in defining public polices in countries without any regulations for the problem.

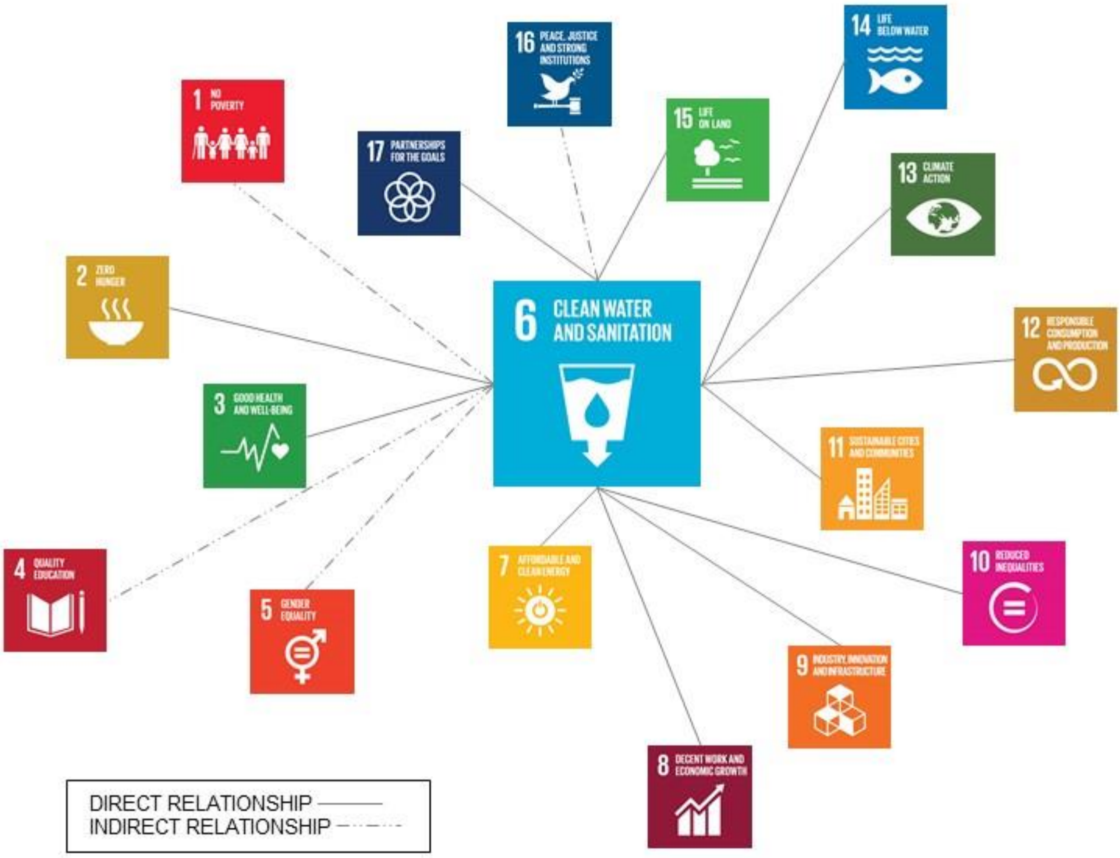
Our study shows that micropollutants are present in the domestic wastewater and that the advanced treatment process could be an alternative for reducing the impact of the discharge of micropollutants into the river basin. These data are important for defining public polices, but a wide monitoring may be needed to aid decision-making in the governmental process, as suggested by Wang et al. (2018).

After 10 years of a wide monitoring of micropollutants in the environment, Mutzner et al. (2022) showed that, through these strategies, it is possible to (i) identify the sources of micropollutants in urban areas (ii) assess their threat to the aquatic environment, (iii) quantify the loads of micropollutants discharged from urban areas at the catchment/city/river-basin scale, (iv) assess the performance of pollution control strategies, and (v) issue discharge permits by local authorities. Working from these points of view, government officials will be contributing to achieving the UN’s Sustainable Development Goals (United Nations, 2015).

By reducing the discharge of micropollutants, we can contribute to giving people access to safe drinking water and improve the sanitation processes used by municipalities and industries via advanced treatment technologies. Thus, we can consider SDG 6 as the main target in this process. However, in order to achieve the desired water quality, treatment performed on the wastewater directly and indirectly affects all the other SDGs (Figure 5). SDG 6 has been considered to be directly related to all the SDGs involving water consumption and, as being indirectly related to the SDGs that do not involve water consumption, though have some role in its acquisition process (such as quality education – SDG 4).

Figure 5

Relationship of SDG 6 with the other SDGs



Conclusion

This study tried to understand the dynamics of the discharge of micropollutants in the Amazon by evaluating the contribution of an advanced wastewater treatment plant located in the industrial district of Manaus, the most populous city of the Brazilian Amazon. This WWTP has a secondary treatment system, with MBR, an activated carbon filter and a sand filter. The concentrations of the 13 micropollutants tested at different stages of the wastewater treatment showed that, even in a WWTP with an advanced treatment system, many micropollutants can persist in the final effluent in very low concentrations. This fact demonstrates that the control of the discharge of micropollutants cannot depend only of the technical issues involved in the treatment. The integrated management involving technical, governmental, organizational and community-based approaches seems to be an important strategy for reducing the discharge of micropollutants through actions for monitoring, replacement and conscious use of micropollutants.

The study published here is only the first report on the presence of micropollutants in a

WWTP in the Amazon and it has technical limitations, such as its sampling and analysis methods, so it cannot be considered a complete monitoring of the presence of micropollutants in a WWTP. Thus, we suggest carrying out complementary studies with a longer monitoring period, river-basin monitoring and determination of the correlation between the concentration of micropollutants in the river and the WWTP. Thus, new studies may contribute to the development of public policies on the subject that helps in Brazil's compliance with SDG 6 and other related SDGs.

Since the Amazon River is the main source of water supply, food, transportation and income for riverine communities, guaranteeing the quality of its water is essential for maintaining biodiversity, human health and the environment in the region. Thus, considering this study as a first alert and by deepening knowledge with future studies, the decision makers will be able to intervene in the way that the wastewater is treated, and guarantee the removal of micropollutants to safe levels.

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