DOI: 10.1007/978-3-031-71758-1_19

Chapter 19
Direct Potable Reuse: A Prioritization of Emerging Contaminants for Monitoring Strategies and Pilot-Scale Advanced Treatment

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Abstract Direct potable reuse (DPR) has emerged as a promising and practical solution to address the challenges of water scarcity (*e.g.*, climate dependency, limited space availability, water waste, and financial constraints) by treating wastewater to meet stringent drinking water quality standards given its potential to reduce water age within the distribution network, enhance water quality, and yield energy savings. Despite the potential benefits, the presence of emerging contaminants in treated wastewater has raised concerns among researchers and policymakers due to their unknown long-term toxicological risks, necessitating continuous research and rigorous monitoring to ensure the safety and sustainability of DPR initiatives. In the present work, ten emerging contaminants were assessed at a pilot-scale treatment plant in the city of Campinas, Brazil, previously selected based on consumption and previous monitoring data. The pilot-scale plant allowed for the evaluation of various treatment configurations, ultimately selecting reverse osmosis + photoperoxidation (UV/H_2O_2) + activated carbon as the most effective scheme for DPR. The effluent from the pilot plant met the guidelines for potable water set by Brazilian regulations. Among the monitored emerging contaminants, albendazole, carbamazepine, hydrochlorothiazide, sulfamethoxazole, and sucralose were identified as marker compounds for monitoring purposes, as they were detectable in both the influent and effluent of the pilot plant. The findings of this research contribute to the development of robust strategies for monitoring and mitigating the risks associated with emerging contaminants in DPR, ensuring the production of safe and sustainable drinking water sources.

Keywords Marker compounds · Potable reuse · Prioritization of emerging contaminants · Water purification · Water scarcity

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S. Zandaryaa et al. (eds.), *Emerging Pollutants*, Advances in Water Security,
https://doi.org/10.1007/978-3-031-71758-1_19

19.1 Introduction

Direct potable reuse (DPR) has emerged as an innovative and promising water management strategy, offering a potential solution to the pressing global water scarcity crisis (Soller et al. 2018; Liu et al. 2020).[1] By treating wastewater to a level that meets or exceeds potable water standards and subsequently distributing it directly into the drinking water supply, DPR closes the water loop and maximizes the utilization of water resources, providing a reliable and sustainable water supply for communities (Reddy et al. 2023).

The World Health Organization (WHO) has categorized potable reuse into three types: (i) unplanned potable reuse, which involves discharging treated or untreated wastewater into rivers, followed by downstream communities using the same water body as a drinking water source, without prior planning; (ii) indirect potable reuse, where treated wastewater is deliberately mixed with environmental buffers such as rivers, lakes, reservoirs, or aquifers, under controlled conditions, before being utilized as a drinking water source; and (iii) DPR, which entails directly introducing treated wastewater into a drinking water supply system, without prior discharge to an environmental buffer (WHO 2017).

While DPR holds great promise, its implementation poses challenges and costs due to the complex composition of municipal wastewaters, which contain recalcitrant compounds and diverse microbial communities (WHO 2017). In recent years, there have been increasing efforts to develop safe, robust, and cost-effective processes for DPR (Liu et al. 2020).

The WHO's Guidance for Producing Safe Drinking Water underscores the importance of reliability, redundancy, robustness, and resilience (the 4Rs criteria) in DPR projects (WHO 2017). Achieving these criteria requires defining quality indicators, including emerging contaminants, and employing multi-barrier treatment approaches (WHO 2017).

The multi-barrier approach has become the preffered configuration used in potable reuse treatment systems worldwide (Jeffrey et al. 2022; WHO 2017). The most commonly used multi-barrier process combines membrane filtration, oxidation, and media filtration (Table 19.1). In addition to ensuring the effective removal of a range of contaminants, the combination of these processes gives greater reliability to treatment systems by allowing for adaptability, security, and time to address potential process failures.

However, as the practice of DPR evolves, concerns have arisen regarding the presence and fate of emerging contaminants in treated wastewater (Wallmann et al. 2021; Villarin and Merel 2020). Emerging contaminants are a diverse range of chemical and biological substances that are not typically monitored or regulated in the drinking water industry, but have the potential to pose risks to human health and the environment (Puri et al. 2023; Mukhopadhyay et al. 2022). The analysis of sewage samples has revealed a staggering array of emerging contaminants, presenting a complex

[1] Brazil's Health Authority known as, Agência Nacional de Vigilância Sanitária (ANVISA): Portaria GM/MS Nº 888, de 4 de maio de 2021.

Table 19.1 DPR installations worldwide

Project name and country	Start date and status	Capacity (m^3/day)	Unit process technology
Old Goreangab plant, Namibia	1969–2002/replaced	7,500	DAF, rapid sand filtration, GAC, Cl_2, blending (30–35%)
New Goreangab plant, Namibia	2002/operational	21,000	PAC, O_3, DAF, rapid sand filtration, O_3, BAC, GAC, UF and Cl_2
Beaufort West, South Africa	2011/built	1,000	Sand filtration, UF, RO, UV/H_2O_2, Cl_2
Big Spring, Texas, USA	2013/operational	7,000	MF, RO, UV/H_2O_2, DWTP
Wichita Falls, Texas, USA	2014–15/operational	26,000	MF, RO, UV, storage, DWTP
San Diego advanced water purification facility, California, USA	Under construction	68,000	MF, RO, UV/AOP
El Paso—advanced water purification facility, Texas, USA	Under design	38,000	MF, RO, UV/AOP, GAC, Cl_2
Morbylånga drinking water treatment plant, Sweden	2019/operational	4,000	Oxidation ($KMnO_4$), blending, UF, RO, UV, Cl_2

DAF: dissolved air flotation; GAC: granular activated carbon; Cl_2: chlorination; PAC: powder activated carbon; O_3: ozonation; BAC: biological activated carbon; UF: ultrafiltration; RO: reverse osmosis; UV/H_2O_2: photoperoxidation; DWTP: drinking water treatment plant; MF: microfiltration; AOP: advanced oxidation process
Source Authors

challenge for water resource management and treatment (Porto et al. 2019; Pivetta et al. 2020; Alves et al. 2021). The diverse range of emerging contaminants detected in sewage includes pharmaceuticals, hormones, microplastics, flame retardants, per- and polyfluoroalkyl substances, and a multitude of other chemical and biological compounds (Richardson and Kimura 2020). The detection of such a vast number of contaminants highlights the dynamic nature of our society and the constant introduction of new substances into the environment. This emphasizes the urgent need for continued research, monitoring, and proactive measures to mitigate the potential risks associated with these emerging contaminants and safeguard public health and the environment. Given the vast number of emerging contaminants, prioritization studies are urgently needed.

Prioritizing emerging contaminants in the context of DPR requires a multifaceted approach, considering human health risks, ecological impacts, and the technical feasibility of removal during treatment processes. The assessment of human health risks requires a thorough understanding of the toxicological properties of contaminants, their potential exposure pathways, and the potential for accumulation in the human body (Ritter et al. 2002). Additionally, the ecological risks associated with these contaminants must be evaluated to ensure the protection of sensitive ecosystems that may be impacted by the discharge of treated wastewater (Fawell and Ong 2012). Furthermore, the implementation of effective treatment technologies is crucial for the removal of emerging contaminants, necessitating consideration of their technical feasibility and cost-effectiveness (Diniz et al. 2023a, b), as well as the identification of appropriate marker compounds, in both raw and treated sewage, which can be quantified using current analytical methods. By integrating these various aspects, a comprehensive prioritization framework can guide decision-makers in identifying the most critical emerging contaminants that warrant attention and targeted mitigation strategies in the context of DPR, ultimately ensuring the production of safe and sustainable drinking water sources. Therefore, in the subsequent sections of this chapter, an in-depth discussion of the prioritization of emerging contaminants based on their recalcitrant properties is provided. This analysis facilitated the selection of specific contaminants for assessing the proper functioning of a pilot-scale DPR system.

The EPAR Capivari II wastewater treatment plant (WWTP), located in the city of Campinas (São Paulo state, Brazil), currently produces non-potable reuse water. This WWTP operates using one of the most advanced technologies in the world for sewage treatment, known as the membrane bioreactor system (MBR) and has installed a pilot-scale water treatment plant. Campinas is the third-largest city in São Paulo state, with 1,138,309 inhabitants. The region faced a significant water crisis in 2014 and 2015, resulting from a combination of political challenges, such as a lack of awareness of the root causes of the water crisis, which extends beyond the technical aspects, necessitating accounting for socio-ecological factors and the importance of prior planning, and an intense drought (Millington 2018). This water crisis prompted efforts to explore alternative water supply options that are not reliant on rainfall patterns. Since municipal wastewater systems are among the most reliable potential sources of water, even for drinking purposes (Liu et al. 2020), advances in wastewater treatment technologies have been made in the last few years. However, the presence of a wider variety of emerging contaminants in sewage can be a drawback for DPR. Therefore, special attention has been paid to the presence of emerging contaminants in Brazilian water matrices in the last few years (Marson et al. 2022).

In the last decade, our research group has worked with several emerging contaminant classes, including anesthetics, anthelmintics, antiacids, antiallergics, antidiabetics, antihypertensives, antilipidemics, antimicrobials, antipsychotics, artificial sweeteners, corticosteroids, cytotoxics, diuretics, steroidal anti-inflammatory drugs, and stimulants. Monitoring, degradation, leaching, and ecotoxicology studies were used to identify emerging contaminant markers suitable for monitoring purposes (Pivetta et al. 2020; Alves et al. 2021; Porto et al. 2019; Rodrigues-Silva et al. 2019; Caianelo et al. 2022; Diniz et al. 2020; Diniz et al. 2022; Diniz et al. 2021; Porto et al. 2021; Spina et al. 2021; Venancio et al. 2021; Caianelo et al. 2021; Diniz and Rath 2023; Diniz et al. 2023a, b). These studies have reported a wide array of emerging contaminants in WWTPs, with concentrations ranging from ng L^{-1} to μg L^{-1}. Bench-scale experiments have demonstrated that the majority of these emerging contaminants exhibit resistance to traditional treatment processes and pose toxicity risks to bacteria and algae. Therefore, the present work aimed to select emerging contaminants as potential marker compounds to assess the proper functioning of multi-barrier treatment in the pilot-scale treatment plant for DPR production installed at the EPAR Capivari II WWTP, which would facilitate further monitoring programs and speed up the decision-making process.

The pilot-scale water treatment plant allows the investigation of different treatment configurations consisting of reverse osmosis, photoperoxidation, and a fixed-bed column loaded with activated carbon. The emerging contaminants were quantified by bidimensional liquid chromatography coupled with tandem mass spectrometry (LC-UHPLC-MS/MS). As the primary outcome, the objective was to select emerging contaminants possessing the characteristics required for use as a marker compound.

19.2 EPAR Capivari II Wastewater Treatment Plant

The EPAR Capivari II WWTP in Campinas (−22.956785, −47.221532) can produce non-potable reuse water. This WWTP operates using an MBR system consisting of a bioreactor with three distinct anaerobic, anoxic, and aerated zones, together with a hollow fiber ultrafiltration membrane composed of polyvinylidene fluoride (LE-4040, DOW FILMTEC).

In the anaerobic zone, bacteria break down organic matter, such as wastewater biosolids and food wastes, in the absence of free and bound oxygen. In the anoxic zone, molecular or free oxygen (O_2) is also absent, but there may be the presence of nitrates (NO_3^-) or nitrites (NO_2^-). Denitrifying bacteria in this zone break down nitrogen products, releasing oxygen for their proliferation, while removing nitrogen compounds from the sewage. Subsequently, in the aerobic zone, a mechanical process introduces oxygen into the effluent. The oxygen is then exploited as a terminal electron acceptor for different reactions, such as the oxidation of organic material, which reduces the biochemical oxygen demand, oxidation of ammonia to nitrate, which reduces the ammonia concentration, and the uptake of phosphate, with the synthesis of polyphosphate, which reduces the effluent phosphate concentration. The hollow fiber ultrafiltration membrane, located at the end of the bioreactor, effectively removes protozoa, bacteria, and suspended solids from the treated water, resulting in values below the limit of detection of the methods.

Before entering the bioreactor and the membrane, the sewage undergoes a primary treatment process, which includes a mechanical medium bar screening system with a spacing of 15 mm, a rotary drum screen with 2 mm apertures, and a mechanical sand remover. This initial treatment helps to remove larger debris and solids from the sewage. As a result of these treatment processes, the final effluent of the EPAR Capivari II WWTP meets the most stringent criteria.

The treated effluent from the EPAR Capivari II WWTP has been successfully utilized for non-potable reuse purposes by the city of Campinas. This has led to significant savings in potable drinking water, reaching up to 80% for the Campinas fire department, while nearby industries have achieved savings of up to 88%. Additionally, the EPAR Capivari II WWTP features a pilot plant dedicated to further research and development in DPR schemes, demonstrating the exploration of DPR as a highly promising solution to address water scarcity challenges.

19.2.1 Pilot-Scale Treatment Plant

The pilot-scale treatment plant of the EPAR Capivari II WWTP was first designed by Hespanhol et al. (2019) and comprised different treatment units employing activated carbon, biological activated carbon, photoperoxidation, reverse osmosis, and ozonation. The current design of the plant (Diniz et al. 2023a, b) operates with a flow of 350 L h^{-1} and is composed of a multichannel system that allows the testing of different treatment configurations for the effluent of the MBR system: I—photoperoxidation; II—activated carbon; III—reverse osmosis; IV—reverse osmosis + photoperoxidation; V—reverse osmosis + activated carbon; and VI—reverse osmosis + photoperoxidation + activated carbon (Fig. 19.1).

The reverse osmosis unit is composed of a membrane (LE-4040, DOW FILMTEC) with a feed spacer thickness of 34 mil and an active area of 7.2 m^2. The photoperoxidation operates using an ultraviolet reactor (17.5 L) equipped with 12 UV-C lamps

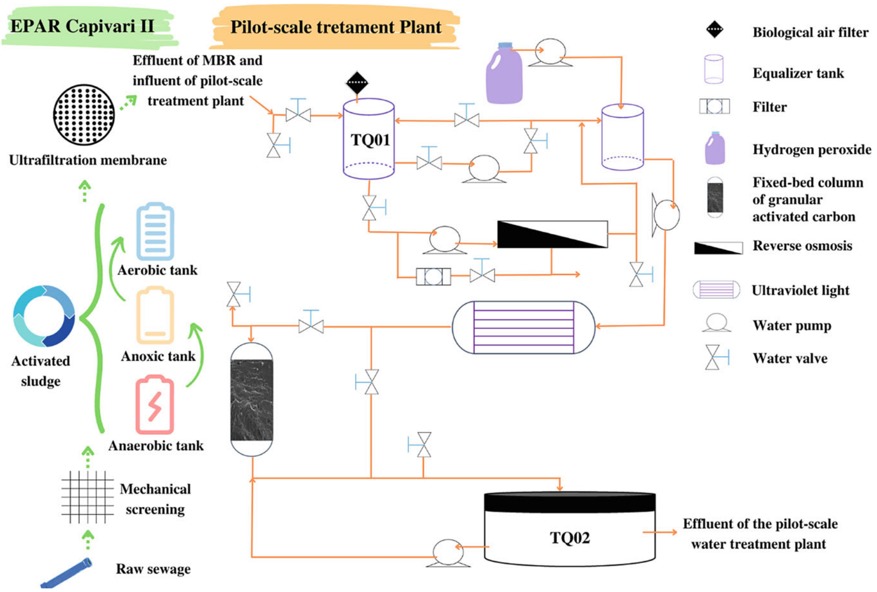

Fig. 19.1 Schematic description of the EPAR Capivari II wastewater treatment plant and the pilot-scale water treatment plant. TQ01 and TQ02 are equalizer tanks. *Source* Authors

(HNS 55W G13 HO, Osram). The total UV-C dose applied is 1590 mJ cm^{-2}. Before the ultraviolet reactor, there is an equalizer tank that receives a hydrogen peroxide dose of 6 mg L^{-1}. The adsorption unit consists of a fixed-bed column (2.2 m × 0.2 m and 0.5 m of freeboard) loaded with 27 kg of activated carbon (Charbon500, 12 × 24 mesh, Carbonado, Brazil). The activated carbon loaded in the fixed column was characterized in our previous study (Diniz et al. 2023a, b). Briefly, The activated carbon had an average pore diameter of 2.6 nm and a total pore volume of 0.36 cm^3 g^{-1}, of which 75% consisted of micropores (≤2 nm). The N_2 adsorption isotherm for the activated carbon (specific surface area of 536.5 m^2 g^{-1}) was type IV with H4 hysteresis, indicating cylindrical pore channels, which was confirmed by scanning electron microscopy. Thermogravimetric analysis showed a mass loss of up to 6% at 105 °C, with high thermal stability up to 500 °C.

The activated carbon consisted mainly of carbon (48.9%), oxygen (19.8%), and silicon (12.7%), with other elements present. Fourier transform infrared spectroscopy revealed various functional groups, including -OH, C–H, C=C, carbonyl C=O, and C–O of phenols and alcohols, as well as Si–O bonds of silicates. Boehm titration experiments indicated the presence of carboxylic, phenol, and lactone groups on the activated carbon surface and also the presence of basic groups on the surface of the activated carbon. Further point of zero charge (PZC) determinations confirmed the basic character of the activated carbon with a pH_{PZC} of 9.2. Raman and X-ray diffraction spectra confirmed the expected graphitic structure and the disordered nature of the activated carbon.

19.2.2 Prioritization of Emerging Contaminants to Be Monitored at the EPAR Capivari II WWTP and the Pilot-Scale Treatment Plant

Understanding the dynamics and occurrence of emerging contaminants in WWTPs is crucial for identifying compounds that can serve as chemical markers to assess treatment efficiency. In this study, particular focus was placed on selecting pharmaceutical active ingredients and artificial sweeteners as marker compounds to address the quality of water produced by the pilot-scale treatment plant installed at the EPAR Capivari II WWTP. Key characteristics of a marker compound are its presence in both raw and treated sewage, as well as its easy quantification using available analytical methods. This implies that the compound should be resistant to removal or be moderately removed during sewage treatment. Therefore, pharmaceutical active ingredients compounds that are widely consumed, minimally metabolized in the human body, and excreted as the parent compound were preferred for prioritization. However, predicting pharmaceutical active ingredients concentrations in Brazilian wastewater is challenging, due to the lack of official consumption data in governmental databases. Furthermore, it needs to be considered that the consumption of pharmaceutical active ingredients may vary according to region and country (Marson et al. 2022). For the prioritization of pharmaceutical active ingredients, sales information for the year 2018 (number of boxes and market size) was obtained from IQVIA Soluções de Tecnologia do Brasil Ltda., a non-governmental company, enabling estimation of the daily dose and the pharmaceutical active ingredients consumption (kg/year/inhab). Estimation of consumption was based on a worst-case scenario, considering the highest quantity of units per package and the highest pharmaceutical active ingredients amount (mg) in each unit. The predicted concentrations of the pharmaceutical active ingredients in the influents of the WWTP were calculated based on the European Medicine Agency guideline (EMEA 2006). The calculations assumed a linear distribution (Eqs. 19.1 and 19.2) of consumption during the year and throughout the local population (Pivetta et al. 2020). In this first prioritization work, 45 pharmaceutical active ingredients were initially selected: sulfamethoxazole, ciprofloxacin, azithromycin, cefepime, ampicillin, trimethoprim, penicillin, piperacillin, tetracycline, cloxacillin, levofloxacin, imipenem, amoxicillin, chloramphenicol, cefazolin, fluoxetine, bupropion, escitalopram, clonazepam, carbamazepine, nortriptyline, amitriptyline, sertraline, trazodone, alprazolam, diazepam, hydrochlorothiazide, albendazole, ricobendazole, prednisolone, lidocaine, diclofenac, ibuprofen, acetaminophen, piroxicam, capecitabine, simvastatin, metformin, atenolol, propranolol, captopril, fexofenadine, dexamethasone, ranitidine, and caffeine.

$$PhAI_{consumption} = \frac{Pck * N_{units} * Strength * 10^{-6}}{Inhab_{Brazil}} \tag{19.1}$$

where $PhAI_{consumption}$ is the annual sales in Brazil in 2018 (kg y^{-1} inhab^{-1}), Pck is the number of packages sold in one year, N_{units} is the maximum number of units in one package, Strength is the amount (mg) of the active substance in one unit of the package, and $Inhab_{Brazil}$ is the estimated population of Brazil in 2018 (210 million).

$$PEC_{WWTPin} = \frac{PhAI_{consumption} * F_{excretion} * 10^{12}}{365 * Inhab_{wwtp} * V_{wwtp}} \tag{19.2}$$

where PEC_{WWTPin} is the predicted concentration in the raw sewage (ng L^{-1}), $F_{excretion}$ is the fraction of the pharmaceutical active ingredients excreted, $inhab_{WWTP}$ is the number of inhabitants served by the WWTP, and V_{WWTP} is the volume of wastewater produced per inhabitant per day (L inhab^{-1} d^{-1}). The volume of wastewater produced per inhabitant can vary significantly depending on several factors, including the country, region, urbanization level, water usage patterns, and industrial activities. In this work, the volume of wastewater produced per inhabitant was estimated to be around 136 L per day, and it was considered that 182,000 inhabitants were served by this WWTP.

In addition, permitted artificial sweeteners in Brazil were also considered for testing, including aspartame, saccharin, sucralose, acesulfame, neotame, and cyclamate. Low-calorie sweeteners have gained considerable attention, due to their widespread consumption worldwide. It is estimated that around 28% of the global population consumes artificial sweeteners daily (Shankar et al. 2013). Most artificial sweeteners are minimally metabolized in vivo and are primarily excreted unchanged, except for aspartame, which is metabolized to phenylalanine, aspartic acid, and methanol (Li et al. 2020). Despite the high global consumption of artificial sweeteners (Luo et al. 2019; Li et al. 2021), these compounds are poorly removed by WWTPs (Alves et al. 2021) and specific data on Brazilian consumption are lacking.

For analysis of the emerging contaminants in raw and treated wastewater, analytical methods using LC-UHPLC-MS/MS were developed and validated. The strategy was to avoid laborious sample preparation procedures before quantitation. The samples received the addition of surrogates, followed by filtration and direct injection into the LC-UHPLC-MS/MS system. Table 19.2 shows an example of the results for 12 selected compounds measured in the raw and treated sewage, together with the calculated PEC values (Table 19.2).

The predicted concentrations (PEC_{WWTP}) of the selected compounds were compared with the measured concentrations (MEC_{WWTP}), to determine the accuracy of the prediction model. Some compounds are efficiently removed during wastewater treatment, such as acetaminophen, metformin, acesulfame, and cyclamate (Table 19.2) (Alves et al. 2021; Pivetta et al. 2020; Porto et al. 2019; Diniz et al. 2023a, b). Therefore, it would not be appropriate to use these compounds as markers to evaluate the processes in the pilot-scale treatment plant.

Considering these aspects, the following compounds were selected for further monitoring: albendazole and its metabolite ricobendazole, carbamazepine, diclofenac, hydrochlorothiazide, propranolol, sulfamethoxazole, sucralose, and saccharin. Although propranolol was not monitored in previous studies, subsequent campaigns demonstrated its suitability as a marker residue, so it was included for further monitoring. Caffeine was added as a target analyte since it has been widely used for this purpose (Buerge et al. 2003).

Monitoring these emerging contaminants during several campaigns led to the selection of ten out of the 51 (pharmaceutical active ingredients + artificial sweeteners) potential marker compounds initially considered: albendazole, caffeine, carbamazepine, diclofenac, hydrochlorothiazide, propranolol, ricobendazole, saccharin, sulfamethoxazole, and sucralose. These compounds were used to evaluate the treatment process in the pilot-scale treatment plant.

19.3 Emerging Contaminants in Raw and Treated Effluent of the EPAR Capivari II WWTP

In this study, the ten previouly selected emerging contaminants (see sect. 19.2) were monitored in the effluent of the MBR system (sampled at TQ-01, Fig. 19.1), during four different sampling campaigns conducted between 2021 and 2022. Diclofenac

Table 19.2 Data used to calculate the predicted concentrations of the 12 selected emerging contaminants in the raw sewage at the EPAR Capivari II WWTP and measured median concentrations of three campaigns

Pharmaceutical active ingredients (PhAI)	Annual sales consumption (kg/year)	$PhAI_{consumption}$ (kg/year/inhab)	Fraction excreted in urine (%)	Estimated annual discharge into the effluent (kg)	PEC_{WWTP} (raw) (ng/L)	MEC_{WWTP} (raw) (ng/L), n = 3	MEC_{WWTP} post-MBR (ng/L), n = 3	**Removal (%)**
Acetaminophen	2,494,949.7	0.011881	5	108.1	11,945	4900	< 500	> 90
Albendazole	4581.7	0.000022	1	0.040	4	250	250	ND
Carbamazepine	37,100	0.000177	3	1.0	107	517	585	−13.1
Diclofenac	116,101.4	0.000553	35	35.2	3891	800	<500	>63
Hydrochlorothiazide	83,774.6	0.000399	100	114.9	8022	1800	3900	−117
Propranolol	62,307.5	0.000297	25	13.5	1492	NE	NE	NE
Sulfamethoxazole	29,671.8	0.000141	54	13.9	1534	250	250	ND
Metformin	6,794,547.1	0.032355	90	5299.7	585,554	20,000	700	96.5
Sucralose	NA	NA	100	NA	NA	23,000	23,000	ND
Saccharin	NA	NA	>92	NA	NA	46,000	3000	94
Acesulfame	NA	NA	100	NA	NA	42,000	ND	100
Cyclamate	NA	NA	100	NA	NA	138,000	ND	100

NA: not available; NE: not evaluated; ND: not detected; PEC_{WWTP} is the predicted concentration in the raw sewage; MEC_{WWTP} is the measured concentration in the WWTP.
Source Authors

and ricobendazole were not detected in any of the campaigns, while sulfamethoxazole was absent in the third campaign (Table 19.3). On the other hand, sucralose consistently appeared at the highest concentration in all four campaigns, with values ranging from 21,607 to 98,402 ng L^{-1}. Hydrochlorothiazide was also observed at high concentrations in all the campaigns, with concentrations ranging from 5,554 to 19,958 ng L^{-1}. Sulfamethoxazole, in contrast, was quantified at the lowest concentrations, with values ranging from 103 to 707 ng L^{-1}. It is pertinent to highlight that the minimum and maximum concentrations presented in Table 19.3 pertain to individual samples within each respective campaign.

These findings highlight the effectiveness of the MBR system in reducing the concentrations of certain emerging contaminants, such as acetaminophen, acesulfame, and diclofenac, to below detection limits. However, the persistence of sucralose and hydrochlorothiazide at relatively high concentrations in the effluent shows the importance of continued monitoring programs and advanced treatment strategies to ensure the effective removal of emerging contaminants in DPR schemes. These findings emphasize the importance of ongoing research efforts to optimize treatment processes and ensure the safety and sustainability of DPR initiatives.

19.4 Studies in the Pilot-Scale Treatment Plant

The pilot-scale treatment plant of the EPAR Capivari II served as a valuable testing ground for the processes most widely implemented in DPR schemes, namely membrane filtration, oxidation, and media filtration. The goal of these studies at the pilot-scale plant was to validate the selected treatment process, optimize system performance, and ensure that the treated water meets the necessary regulatory standards for potable reuse. This is an essential step in the development and implementation of water reuse projects, providing valuable data and insights, before moving to larger-scale operations.

The studies were conducted with the real treated MBR effluent of the EPAR Capivari II WWTP. It became evident that none of the individual processes in the pilot-scale plant when applied, could achieve complete removal of all the target emerging contaminants to below the limit of quantification obtained for the analytical method (Fig. 19.2). Overall, the removal efficiency was in the following order: reverse osmosis > activated carbon > photoperoxidation. However, it was noteworthy that regardless of the process employed, sulfamethoxazole, a well-known antimicrobial agent known for inducing the development of antimicrobial resistance genes in bacteria (Larcher and Yargeau 2012), was consistently eliminated to concentrations below the limit of quantification. Hence, the removal of sulfamethoxazole, as well as other antimicrobials, appears as a critical prerequisite for all DPR processes.

To address the challenges encountered in the previous experiments, further investigations were conducted to assess the efficacy of combining reverse osmosis with either activated carbon or photoperoxidation. In both configurations, all the emerging

Table 19.3 Concentrations of emerging contaminants in the effluent of the MBR system during campaigns in 2021 and 2022 (n = 6 for each campaign)

Emerging contaminant	Campaign average (s) (ng L^{-1})				Minimum concentration (ng L^{-1})	Maximum concentration (ng L^{-1})	Frequency (%)
	1st	2nd	3rd	4th			
Albendazole$^{(1)}$	1,779 (203)	1,795 (268)	6,431 (1253)	1,757 (313)	1,217	8,014	100.0
Caffeine$^{(1)}$	2,153 (141)	2,008 (73)	774 (319)	1,569 (126)	324	2,311	100.0
Carbamazepine$^{(1)}$	2,361 (567)	3,083 (1,497)	2,900 (1,466)	1,969 (123)	1,788	5,437	100.0
Hydrochlorothiazide$^{(3)}$	9,241 (917)	8,720 (2,353)	1,1741 (5,395)	8,715 (316)	5,554	19,658	100.0
Propranolol$^{(2)}$	2,487 (2,668)	2,101 (1,012)	865 (354)	NA	510	6,012	75.0
Saccharin$^{(3)}$	3,126 (259)	2,929 (190)	3,172 (290)	2,685 (116)	2503	3,642	100.0
Sulfamethoxazole$^{(1)}$	464 (142)	318 (163)	<LOQ	601 (46)	130	707	75.0
Sucralose$^{(3)}$	42,186 (5,499)	46,999 (34,848)	27,438 (4,129)	30,133 (909)	21,607	98,402	100.0

Limit of quantification: $^{(1)}$100 ng L^{-1}; $^{(2)}$500 ng L^{-1}; $^{(3)}$1000 ng L^{-1}. NA: not available; s: standard deviation
Source Authors

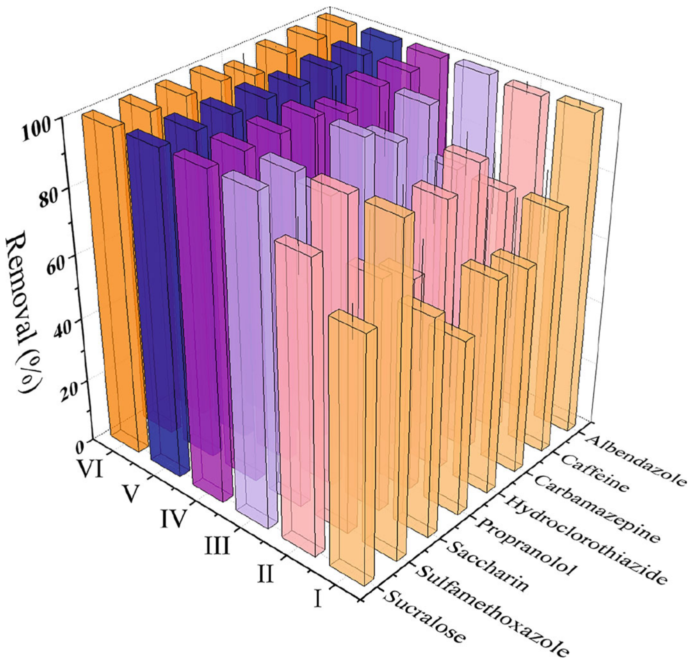

Fig. 19.2 Removal of the emerging contaminants by the different processes in the pilot-scale treatment plant: I—photoperoxidation (UV/H_2O_2); II—activated carbon; III—reverse osmosis (RO); IV—reverse osmosis + photoperoxidation; V—reverse osmosis + activated carbon; VI—reverse osmosis + photoperoxidation + activated carbon. *Source* Authors

contaminants, except hydrochlorothiazide, were successfully reduced to concentrations below the limit of quantification of the analytical method. However, despite achieving the desired removal of emerging contaminants, the implementation of a two-step treatment scheme raised concerns about compromising the four essential pillars of the treatment plant: reliability, resilience, robustness, and redundancy (the 4Rs). This concern arises from the possibility that if one of the treatment steps were to malfunction, the other might be unable to maintain the high quality of the effluent.

The utilization of photoperoxidation, an alternative to primary disinfection (Kruithof et al. 2007), may bring a new challenge related to the formation of undesirable byproducts (Spina et al. 2021; Venancio et al. 2021). Due to this issue, the introduction of activated carbon, capable of adsorbing and removing such undesirable byproducts, became essential. However, activated carbon alone lacks disinfection capabilities. Consequently, a novel configuration was tested, consisting of reverse osmosis, photoperoxidation, and activated carbon. This configuration not only allowed the reverse osmosis membrane to effectively remove particles larger than 7 Å and a portion of the emerging contaminants (Franke et al. 2021), but also enabled the residual amounts of the emerging contaminants to be oxidized by photoperoxidation, serving as a primary disinfection unit. In addition, the activated carbon acted as a robust barrier against undesirable byproducts that might arise from the oxidation process, while also removing residual hydrogen peroxide.

By strategically combining these treatment processes, the pilot-scale treatment plant of the EPAR Capivari II aimed to address the challenges of contaminant removal, disinfection, and byproduct mitigation, while preserving the 4Rs. The proposed configuration had the potential to deliver treated water of high quality for DPR, paving the way for the safe and sustainable management of water resources.

19.4.1 Direct Potable Reuse Scheme

In addition to monitoring the emerging contaminants, various parameters were also monitored, including apparent color, turbidity, conductivity, biological oxygen demand, chemical oxygen demand, total phosphorus, ammoniacal nitrogen, total Kjeldahl nitrogen, nitrate nitrogen, nitrite nitrogen, total solids, total dissolved solids, total suspended solids, and pH.

The selected pilot-scale plant process, comprising reverse osmosis + photoperoxidation + activated carbon (RO + UV/H_2O_2 + AC), was evaluated during different campaigns in the year 2022.

Initially, sampling of the influent and effluent at the pilot plant was conducted in a manner that allowed the plant to operate only during the sample collection period. During one of these campaigns (C1), it was observed that the biological oxygen demand and chemical oxygen demand values for the effluent from the pilot plant (using RO + UV/H_2O_2 + AC) were higher than the values for the raw sewage and the MBR effluent. Additionally, an exceptionally high conductivity value was measured for the sample collected at TQ02 (Fig. 19.3). This discrepancy indicated a malfunction in the RO membrane and the formation of a biofilm on the surface of the activated carbon. To address this issue, both units were replaced, with subsequent results returning to the expected values (as shown for the samples from C3 at TQ02).

Subsequently, the pilot-scale water treatment plant remained in continuous operation from March to December 2022. During this period, four sample collection campaigns (C2, C3, C4, and C5) were conducted. Figure 19.3 presents a comparison between the results of campaigns C1 and C3 for biological oxygen demand, chemical oxygen demand, and conductivity, obtained from samples collected at the WWTP inlet (raw sewage) and the TQ01 inlet (post-MBR) and TQ02 outlet (pilot plant effluent).

These results highlight the importance of regular monitoring and maintenance of the treatment plant to ensure optimal performance and the desired water quality. The replacement of malfunctioning units successfully resolved the issues observed in the first campaign, enabling the achievement of consistent and satisfactory results in the subsequent sampling campaigns.

It was also observed that the apparent color, total solids, nitrate nitrogen, and water hardness levels decreased significantly after treating the effluent using the RO + UV/

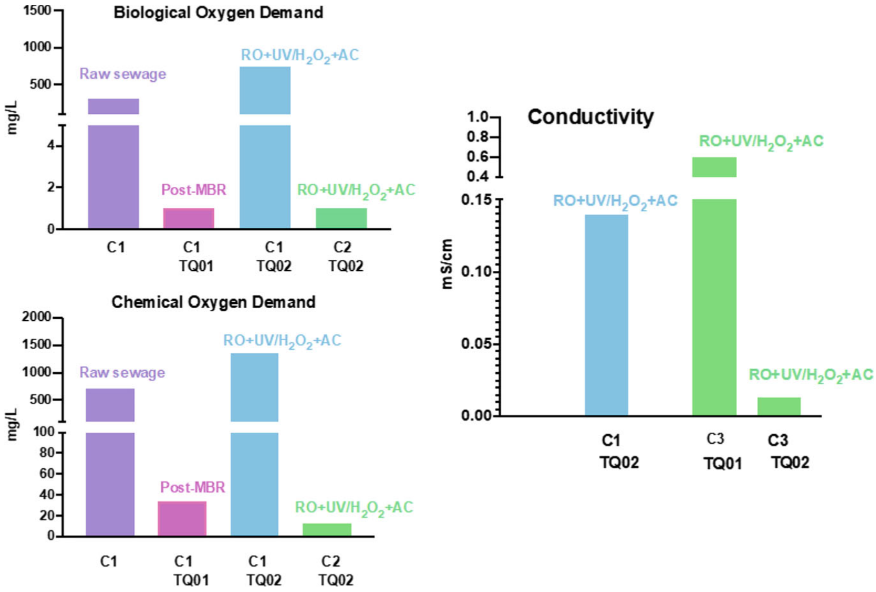

Fig. 19.3 Biological oxygen demand, chemical oxygen demand, and conductivity of the raw sewage and samples obtained post-MBR and after the RO + UV/H_2O_2 + AC treatment, in two campaigns (C1 and C3). *Source* Authors

H_2O_2 + AC process (Fig. 19.4). Furthermore, the treatment process contributed to decreases of sulfate, sodium, and phosphorus.

In all the campaigns, the selected emerging contaminants were quantified, with the results showing that the pilot-scale treatment plant successfully removed these contaminants to below the limit of quantification of the analytical method. The possibility of quantifying albendazole, carbamazepine, hydrochlorothiazide, and sucralose by the developed and validated analytical methods, coupled with the effective removal of the compounds using the reverse osmosis + photoperoxidation + activated carbon system (Fig. 19.5), established them as potential markers for monitoring removal efficiency and the quality of the treated effluent at the pilot plant.

The online LC-UHPLC-MS/MS technique was shown to be highly effective, as evidenced by the limits of quantification achieved for various compounds. The detection limit for sucralose was 1000 ng L^{-1}, while very low values of 10 ng L^{-1} were obtained for carbamazepine and albendazole. In turn, a detection limit of 100 ng L^{-1} was obtained for hydrochlorothiazide. It is noteworthy that sulfamethoxazole, despite being eliminated by all the tested processes, warrants inclusion in monitoring programs due to its easy quantification (quantification limit of 10 ng L^{-1}) and the potential risk it poses by stimulating resistance genes in bacteria.

A major advantage of employing this method is its streamlined process, which facilitates routine analysis, as samples only require filtration and the addition of surrogate deuterated internal standards, before injection into the instrument. The limits

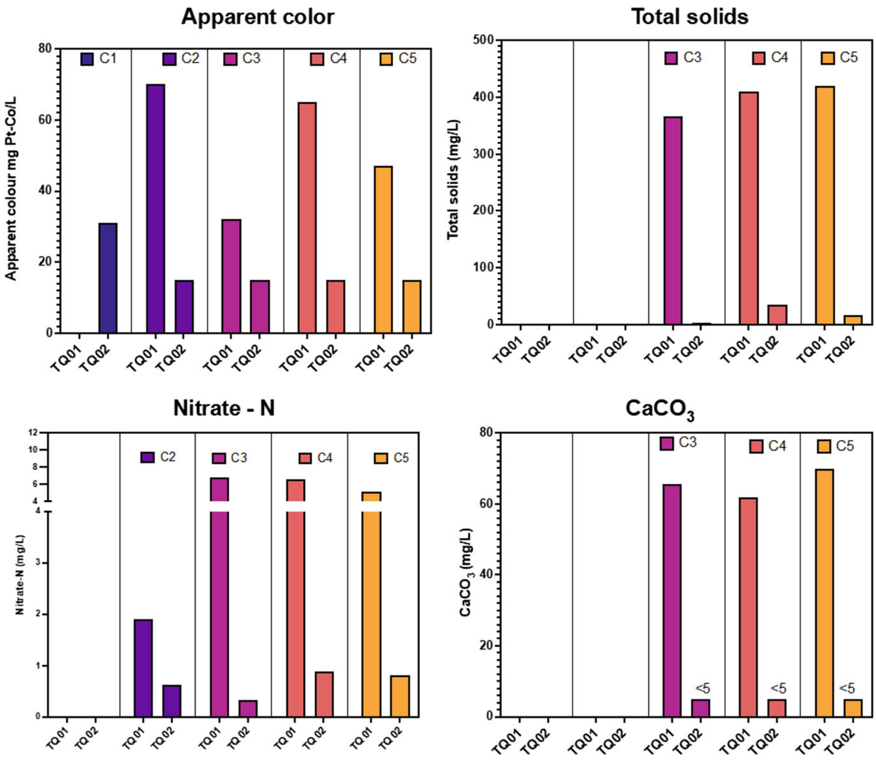

Fig. 19.4 Nitrate-N, total solids, apparent color, and $CaCO_3$ (water hardness) values for the samples collected at TQ01 (post-MBR) and TQ02 (effluent treated by RO + UV/H_2O_2 + AC). *Source* Authors

of quantification could be further improved by implementing a pre-concentration step utilizing a solid-phase extraction cartridge, which could achieve values approximately 100-fold lower. However, it is important to note that this enhanced procedure would demand more time and incur additional expenses. For monitoring purposes at the EPAR II Capivari II pilot-scale treatment plant, offline preconcentration steps to reduce the limits of quantification would not seem to be necessary. In this case, the simple addition of surrogate deuterated internal standards, followed by filtration and direct injection into the LC-UHPLC-MS/MS, provided lower cost and easier handling.

Furthermore, it is extremely important to emphasize that the effluent from the pilot-scale treatment plant fully complied with all the potability criteria stipulated by Brazilian legislation, which include consideration of organoleptic properties, inorganic and organic substances posing health risks (including pesticides and metabolites), protozoa, and bacteria. This accomplishment demonstrates the excellent potential of the MBR + reverse osmosis + photoperoxidation + activated carbon scheme for use in DPR. Nevertheless, confirmation of the safety of the treated effluent requires

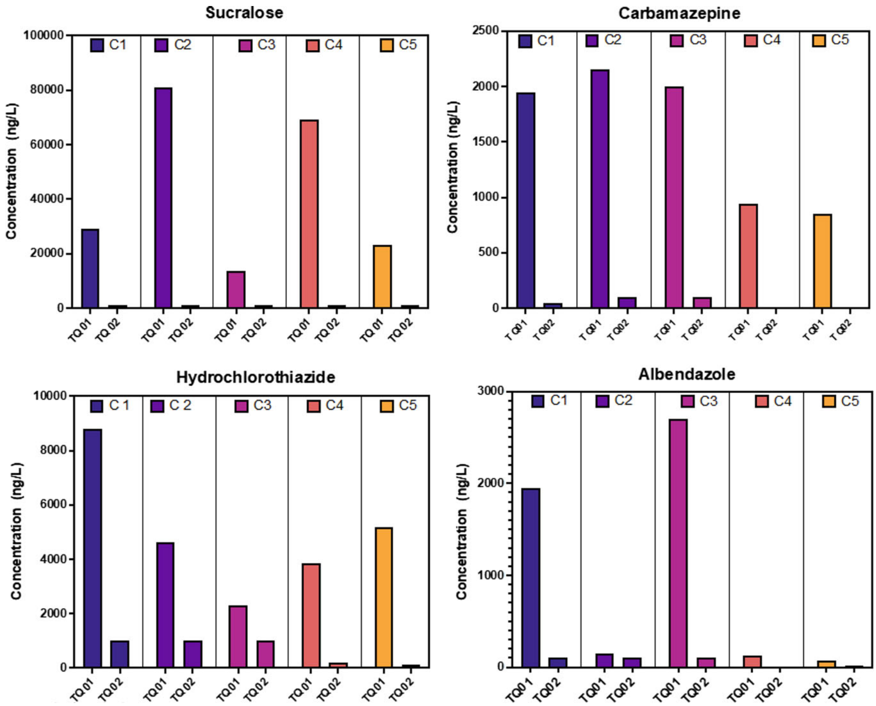

Fig. 19.5 Concentrations of the selected marker compounds in the samples collected at TQ01 (post-MBR) and TQ02 (effluent treated by RO + UV/H_2O_2 + AC). *Source* Authors

further comprehensive studies to investigate the ability of the system to deal with different viruses and bacteria.

19.5 Future Work

Although the findings of the present study highlighted the quality of the effluent of the pilot-scale treatment plant, it is essential to recognize that no disinfection/chlorination studies had been conducted. Disinfection units are mandatory for all Brazilian drinking water treatment plants and, depending on the process used, they may result in the formation of disinfection byproducts (Pandian et al. 2022). In addition, as future steps, it would be beneficial to consider the continuation of studies involving the evaluation of bacteria, protozoa, and viruses, as well as toxicity assays (Zhu et al. 2022). These additional investigations should provide a comprehensive understanding of the potential risks associated with the treated effluent. Assessment of microbial pathogens and toxicity levels is essential to ensure the safety of the water and its suitability for the intended reuse purposes, reinforcing the need for comprehensive and rigorous research to guarantee the efficacy and safety of DPR practices.

19.6 Conclusions

The findings obtained from the work at the pilot-scale treatment plant at the EPAR Capivari II WWTP demonstrated the viability of producing DPR water from MBR-treated sewage, using the integrated multibarrier process of RO + UV/H_2O_2 + AC. This combination proved to be effective in removing a wide range of emerging contaminants, ensuring the production of high-quality treated effluent that meets the potability criteria stipulated by Brazilian legislation.

Key indicators including conductivity, apparent color, water hardness, and chemical oxygen demand, together with specific emerging contaminants such as sucralose, hydrochlorothiazide, carbamazepine, sulfamethoxazole, and albendazole, were identified as crucial parameters for assessment of the proper functioning of the treatment at the pilot-scale plant. Monitoring these indicators over an extended period and across different seasons can provide a comprehensive understanding of the performance and efficiency of the treatment.

While the results are promising, it is essential to acknowledge the need for further studies and continuous monitoring to ensure the safety of the treated effluent and its suitability for direct potable reuse. Future investigations should include disinfection/chlorination studies to assess the potential formation of disinfection byproducts and evaluate the presence of microbial pathogens. Additionally, comprehensive toxicity assays will help to confirm the overall safety of the water for its intended reuse purposes. It is also important to recognize that the selection of markers for emerging contaminants may require adjustments over time, as it depends on the dynamic consumption patterns of the population. Therefore, ongoing research and monitoring are critical to stay abreast of emerging contaminants and continuously optimize the treatment process.

In conclusion, the successful operation of the pilot-scale treatment plant and the consistent removal of emerging contaminants using the RO + UV/H_2O_2 + AC scheme demonstrate the promising potential of DPR as a sustainable solution for water scarcity challenges. Nevertheless, the pursuit of safe and reliable DPR requires a multidisciplinary and proactive approach, encompassing continuous monitoring, advanced treatment strategies, and comprehensive risk assessment, to ensure the long-term sustainability and safety of water resources. The collaborative efforts of researchers, policymakers, and stakeholders are paramount to achieving the vision of a future where DPR plays a vital role in securing a reliable and sustainable water supply for communities worldwide.

Acknowledgements The authors are grateful for the financial support provided by the Brazilian public agencies São Paulo State Research Foundation (INCTAA, FAPESP #2014/50951-4, FAPESP #2021/03239-0) and CNPq (#465768/2014-8 and #301737/2017-7). Scholarships were awarded to

V.D. (FAPESP #2021/08123-0 and #2022/11350-1). The authors also would like to thank SANASA for their support during the development of this study.

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