Title: Occurrence of PPCPs in a Brazilian Water Reservoir and their Removal Efficiency by Ecological Filtration.
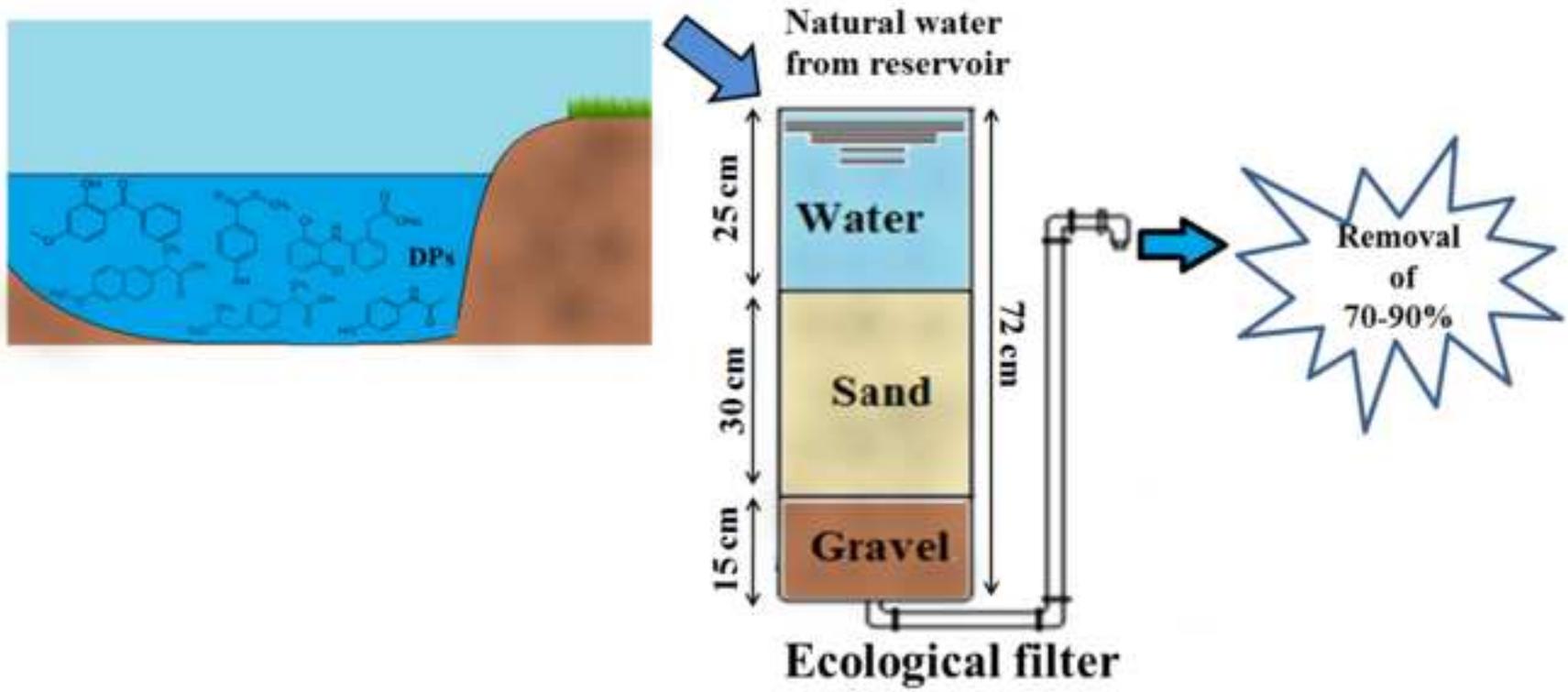
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Order of Authors: Caroline Moço Erba Pompei, Ph.D; Luiza C Campos, Ph.D; Bianca F Silva, Ph.D; José C Fogo, Ph.D; Eny M Vieira, Ph.D

Abstract: The presence of PPCPs (Pharmaceuticals and Personal Care Products) in water sources and drinking water has concerned researchers in recent times. This study was carried out to evaluate the occurrence of 6 PPCPs (namely paracetamol, diclofenac, naproxen, ibuprofen, benzophenone-3 and methylparaben) in the Lobo reservoir, their degradation products, and how efficienctly they were removed by 22 ecological filters, considering individual and mixtures of compounds. There were 3 spiking events of PPCPs (2 µg L-1) in the ecological filter influents conducted with a lag period of 15 days between spikes. Water sample were collected from the influent and effluent of the filters at 3, 6 and 24 hours after each spiking event. All target PPCPs were identified in the Lobo reservoir water in the range of µg L-1. The personal care products were detected with 100 % frequency in the samples, and in higher concentrations compared to the pharmaceuticals. Degradation products of diclofenac and benzophenone-3 were identified in the water samples. Results of this investigation show that an ecological filter was an effective process (70 - 99 %) to remove 2 µg L-1 of the selected PPCPs, and demonstrated that the filters were resilient to individual compounds and to their mixtures.

Graphical Abstract

Natural water from reservoir

DPs

25 cm

30 cm

15 cm

72 cm

Water

Sand

Gravel

Ecological filter

Removal of 70-90%
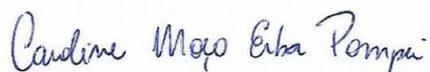
Chemosphere

14 November 2018

Dear Editors,

I am writing to put forward the manuscript entitled "Occurrence of PPCPs in a Brazilian Water Reservoir and their Removal by Ecological Filtration.", authored by Caroline Moço Erba Pompei; Luiza C. Campos; Bianca Ferreira da Silva; José Carlos Fogo; Eny Maria Vieira.

The authors strongly believe that this work relates to the aims and scope of the Chemosphere. The paper describes a unique experimental work carried out to investigate the occurrence of six selected PPCPs in a Brazilian water reservoir and their removal by an ecological filtration system consisted of 22 filters receiving the reservoir water. The research investigated the efficiency of the filters to remove individual target PPCPs and their mixture, being each filter and water samples in triplicates.

This paper is of interest to researchers and practitioners working with biological filtration, low cost techniques to drinking water and with interest in understanding the contamination of freshwater by PPCPs and their removal by ecological filtration.

The authors state that the paper is not being submitted elsewhere and their contents have not been previously published. The authors also state that there are no competing interests and the authors' contributions to the manuscript are: Caroline Moço Erba Pompei carried out the research and led the paper preparation; Luiza C. Campos supported manuscript preparation and submission, Bianca Ferreira da Silva supervised the LC/MSMS analysis and reviewed the paper;; José Carlos Fogo supported the statistical analyzes and reviewed the paper; and Eny Maria Vieira supervised the research and reviewed the paper. In addition to myself, we would like to include Dr Luiza C. Campos as co-corresponding author, given her significant contribution during the preparation and corrections of the manuscript.

Yours faithfully,

Dr. Caroline Moço Erba Pompei

Occurrence of PPCPs in a Brazilian Water Reservoir and their Removal Efficiency by Ecological Filtration.

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Highlights

- Six PPCPs were found in the reservoir water, and personal care products had 100% of frequency;
- Two DPs were found in the reservoir water and ecological filter effluents;
- Performance of the ecological filters was not affected by PPCP contamination;
- 2 μg L^{-1} of PPCPs were effectively removed by all ecological filters (70-99%);
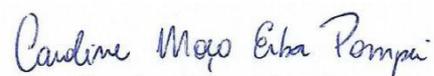- Results show that filters are resilient to individual PPCP and their mixture.

*Response to reviewers/editor in question & answer format (word file)

12 March 2019.

Dear Editors,

Thank you very much for giving us the chance of correcting and improving our manuscript further.

We inform that the manuscript and all associated files have been reviewed by a native English speaker.

Considering our initial request in the cover letter submitted with our first manuscript submission, we would like to inform that we have added Dr Luiza C. Campos as a co-corresponding author in this corrected version. Dr Campos will support dealing with queries after the paper publication.

Yours faithfully,

Caroline Moço Erba Pompei
Dr. Caroline Moço Erba Pompei

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Abstract

The presence of PPCPs (Pharmaceuticals and Personal Care Products) in water sources and drinking water has concerned researchers in recent times. This study was carried out to evaluate the occurrence of 6 PPCPs (namely paracetamol, diclofenac, naproxen, ibuprofen, benzophenone-3 and methylparaben) in <u>the</u> Lobo reservoir, their degradation products, and <u>how</u>~~their~~ efficienc<u>tly they were</u>~~y~~ remov<u>ed</u>~~als~~ by 22 ecological filters, considering individual and ~~a~~ mixture<u>s</u> of compounds. There were ~~conducted~~ 3 spiking events of PPCPs (2 μg L^{-1}) in the ecological filter influents <u>conducted</u> with a lag period of 15 days between spikes. Water ~~samplings~~ <u>sample</u> were collected from the influent and effluent of the filters at 3, 6 and 24 hours after each spiking event~~s~~. All target PPCPs were identified in the Lobo reservoir water in the range of μg L^{-1}. The personal care products were detected with 100 % ~~of~~ frequency in the samples<u>,</u> and in higher concentrations compared to the pharmaceuticals. Degradation products of diclofenac and benzophenone-3 were identified in the water samples. Results of this investigation show that <u>an</u> ecological filter was an effective process (70 - 99 %) to remove 2 μg L^{-1} of the selected PPCPs<u>,</u> and demonstrate<u>d</u> that the filters were resilient to individual compounds and to their mixture<u>s</u>.

Keywords: Ecological filtration; drinking water treatment; removal of PPCPs; degradation products.

1. Introduction

Pharmaceuticals and Personal Care Products (PPCPs) are of scientific and public concern as newly recognized classes of environmental pollutants; described as emerging water contaminants with potential psychoactive properties and unknown effects to the aquatic environment (Evgenidou et al., 2015). The term "PPCPs" refers to any chemical product with healthcare or medical purposes for humans and/or animals (Schumock et al. 2014).

The most consumed non-steroidal anti-inflammatory drugs frequently found in aquatic environments are aspirin, acetaminophen, ibuprofen, naproxen and diclofenac (Fent et al., 2006). These PPCPs and others have been detected worldwide in surface water, groundwater, sewage and even drinking water in the order of ng-µg L^{-1} (Heberer, 2002; Petrović et al., 2003; Fent et al., 2006; Ellis, 2006; Sui et al., 2015). AdditionallyAlso, degradation products (DPs) of these PPCPs have been found in water bodies and water samples after treatment, as a result of a multiplicity of biotic and abiotic processes (e.g. hydrolysis, photolysis, oxidation, and microbiological metabolism) acting on the original compounds or their metabolites (Mompelat et al., 2009; Dévier et al., 2011; Andrés-Costa et al., 2014; Van Doorslaer et al., 2014; Postigo and Richardson, 2014).

PPCP removal has been observed in wastewater treatment plants (WWTPs) (e.g. Ternes et al., 1998; Thomas and Foster, 2004, Camacho-Munoz et al., 2012). However, in general, most of WWTPs are not designed to treat this type of substance, and consequently a significantlysignificant portion of these compounds are not degraded/removed during treatment. Therefore, the pure compound and/or their metabolites may enter the aquatic environment via sewage effuents (Daughton and Ternes, 1999; Heberer, 2002; Petrović et al., 2003; Jones et al., 2005; Fent et al., 2006;

Matamoros et al., 2009). FurthermoreAlso, conventional drinking water treatment processes have been reported as ineffective for the removal of most pharmaceuticals, with efficiency ranging from < 5 to 40 % (Vieno et al., 2007; Pojana et al., 2011).

Recently, numerous many investigations have been carried out using advanced oxidation processes (AOPs) such as ozonation, UV oxidation, fenton and fenton-like processes, and photocatalytic degradation to remove PPCPs from water and wastewater (Tayo et al., 2018; Goel and Das, 2018; Xu et al., 2017). However, the relatively high cost of these processes currently stand as the major barrier for their large-scale implementation (Xu et al., 2017), especially in developing countries such as Brazil. ConverselyOn the other hand, there are is evidence of PPCP removal by sandfiltration, in which biodegradation has been suggested as one of the removal mechanisms (Westerhoff, 2003; Fujii and Kikuchi, 2005; Hallé, 2010; Onesios et al., 2009; Camacho-Munoz et al. 2012; Chen et al., 2015; Chen et al., 2016). For example, Qiao et al. (2011) investigating investigated the occurrence of 15 PPCPs in two full-scale conventional treatment plants,; they found that the type and concentration of PPCP decreased gradually along the treatment train, especially after sand filtration. Beretelkamp et al. (2014), simulating simulated the removal of 14 organic compounds by river bank filtration at a laboratory scale,; they obtained a statistically significant relationship between the biological degradation rates and the compound functional groups. In addition, removal of PPCPs has been observed in slow sand filtration (SSF) and granular activated carbon (GAC) sandwich SSF (Erba et al., 2014; Escolà Casas and Bester, 2015; Pompei et al., 2017; Li et al., 2018). Therefore, biosandfiltration seems an attractive option due to its demonstrated potential of removing PPCPs from water and its low operational cost for not requiring chemical coagulation. Slow sand filtration has been recently referred to as ecological filtration due to the presence of a biofilm that

4

forms on top of the sand filter and is believed to be essential to water purification (Nakamoto, 2008).

The aim of this work was to evaluate the occurrence of selected PPCPs and DPs in a Brazilian water reservoir, and their removal by ecological filters installed under natural environmental conditions, receiving water from the Lobo reservoir in Itirapina, São Paulo state. To the best of the authors' knowekedgeknowledge, this is the first study investigating the removal of individual target compounds, their mixture, and their degradation products by ecological filtration at a pilot scale.

2. Material and methods

2.1. Chemicals and Reagents

Acetonitrile (CH_3CN) and methanol (CH_3OH) were of HPLC grade from J.T. Baker (Xalostoc, México);), , formie Formic acid; , 4-Acetaminophen (ACT), Diclofenac sodium salt (DCF), Naproxen (NAP), Ibuprofen (IBU), Metyl 4-hydroxybenzoate (MEP) and 2-Hydroxy-4-methoxybenzophenone (BP-3) (all 99 % purity or more) were purchased from Sigma-Aldrich. The deuterated compounds were used as internal standards, namely paracetamol-*d4*, diclofenac-*d4*, naproxen-*d3*, ibuprofen-*d3*; all obtained from CDN Isotopes (Quebec, Canada). Additional information about each compound is shown in Table S1. Stock solutions were prepared in methanol for each compound and stored in a refrigerator at 4 °C. For all reagent solutions, water was previously distilled and further deionized using a Milli-Q system Millipore (Millipore, Bedford, MA, USA).

2.2. Filter construction

Twenty-two ecological filters (Nakamoto, 2008) were constructed with PVC columns (Figure S1). Each ecological filter had ~~25 cm of~~ an internal diameter of 25 cm and height of 72 cm. The support layer in each filter was formed by a 15 cm gravel layer, with 3 sub-layers of 12.50 mm to 1.41 mm. The sand layer had 30 cm height with grain sizes varying from 1.00 to 0.08 mm. The sand uniformity ~~coeficient~~coefficient was between 2 and 3, and the effective grain size was 0.25 mm (Bellamy et al., 1985; Di Bernardo, 1993). The water layer on the top of the sand bed varied from 25 to 27 cm. The influent water to the 22 ecological filters was pumped from the Lobo reservoir (22°10'18.09"S 47°54'5.00"W), located at Itirapina city, São Paulo, Brazil, to a constant level tank before being supplied continuously to the filters.

2.3. Water Sampling

The operation of filters was continuous and the average water filtration flow rate was $3m^3/d.m^2$. There was triplicate of ~~six~~ 6 filters ~~with receiving~~ each individually receiving a ~~each~~ PPCP compound (18 filters), triplicate of ~~one~~ 1 filter receiving a mixture of the 6 PPCP compounds (3 filters), and ~~one~~ 1 control filter receiving only water from the Lobo reservoir (Table S2).

After maturation of the filters, three spiking events of the target PPCPs were conducted with a lag period of 15 days between spikes. The spikes were created ~~made~~ to certify that a known concentration would enter the ecological filters, as the main concentration of PPCPs on the reservoir water may vary and may not be detected every day. The spike solution (1L) was added to the raw water inlet via a dosing pump. Samples of the reservoir water were collected at the same time as the filter effluent water (3, 6, and 24 hours after spikes) to determine the background concentration of the target PPCPs. The point of water sample collection in the reservoir was always the

6

147 same, ~~which is the place where is located~~at the location of the hydraulic pump used to

148 supply the 22 filters (22°10'18.09"S 47°54'5.00"W).

149   For PPCP detection, water samples (500 mL ~~each~~) were collected in each

150 contaminated filter after ~~each~~ every contamination event (total per filter = 3 samples

151 (triplicate) x 3 spike events = 9 samples; total = 189 samples), while in the control filter

152 only 9 samples were collected in total. To evaluate the removal efficiency of each filter,

153 the total initial concentration of each target PPCP compound was considered ~~to be~~as the

154 sum of the background concentration found in the reservoir water. plus the spiked PPCP

155 concentration of 2 μg L^{-1}. For physico-chemical and bacteriological analyses, samples

156 of 500 mL ~~each~~ were collected weekly from the influent and effluent of each filter

157 during the first month of operation; ~~and~~ they were also collected from 9th October in

158 2013, when the filters were considered matured, water samples were collected 3 times

159 per week (samples in each filter = 30; total samples = 660 samples).

160

161   **2.3.1. Water quality parameters**

162   Parameters concerning the treated water quality by the ecological filters were

163 measured from September to December 2013. Turbidity and apparent colour were

164 determined by a HACH DR 2000 espectrofotometer, selecting UV_{455nm} for colour and

165 UV_{750nm} for turbidity. The true colour was measured after filtering the water samples

166 through a 0.45 μm membrane (Millipore, cellulose ester, 90 mm diameter). and

167 determined using the espectrofotometer at $UV_{455nm.}$ The pH was determined by pHmeter

168 B374 – Micronal; temperature, conductivity and total dissolved solids (TDS) of water

169 samples were measured by Orion multiparameter - model 145. Total coliforms and *E.*

170 *coli* were measured using the Colilert® kit method once a week before contamination,

171 and during the contamination period, samplings were done before and 24 hours after

172 spiking the PPCPs into the ecological filters.

173

174 **2.4. PPCPs and DPs detection**

175 The PPCPs were extracted from the water samples using solid phase extraction

176 (SPE) with Strata-X (Phenomenex) Polymeric Reversed Phase 200 mg/6 mL (8B-S100–

177 FCH). Each cartridge was pre-conditioned with 6 mL of methanol (2 times), 6 mL of

178 purified water (Milli-Q), and 6 mL of purified water (Milli-Q) acidified with HCl for

179 pH 3 per gravity. After, 300 mL of water (pH 3.0) was passed through the cartridge

180 sorbent at a flow rate of 5 mL min $^{-1}$. The PPCPs were eluted passing 4 mL of methanol

181 twice, and the volume was reduced with a gentle stream of nitrogen gas and

182 reconstituted to 300 μL with MeOH + Milli-Q water (1:1 v/v). ~~Then, the~~The samples

183 were then analyzed by LC-MS/MS. Additional information about the LC-MS/MS

184 equipment, method used and how analyses were conducted for the identification of DPs

185 are described in the Supporting Information. Quality assurance and quality control

186 (QA/QC) were implemented for the accuracy of the quantification of the target PPCPs.

187 More details are also presented in the Supporting Information and Tables S3 and S4.

188

189 **2.5. Statistical analysis**

190 The results derived from the quantification of PPCPs were subjected to statistical

191 analysis profiles for repeated measures, performed with PRCO GLM software from

192 SAS. This analysis was carried out to study the effect of different type of treatments, the

193 different times of collection, and interactions between types of treatment and times of

194 collection. The multivariate character of analyses was previously verified by Mauchly's

sphericity test. MANOVA analysis considered the following tests: Wilks' Lambda, Pillai's Trace, Hotelling-Lawley Trace and Roy's Greatest Root.

To determine the variability of the water quality parameters between the 22 ecological filters, the standard deviation (SD) and coefficient of variation (CV) were determined. CV was considered with high variation for values between 20 to 30 % (Isensee, 1976). In addition, t-tests were done to examine the relationships between influent and effluent water from ecological filters; values were significant at $p < 0.05$. The averages, SDs, CVs and t-tests of data were calculated using Microsoft Excel 2010.

3. Results and discussion

3.1. LC-MS/MS

The adjustment of parameters for each compound and deuterates of the mass spectrometer to the individual samples of all compounds are shown in Table S5. The transition ions, or ion fragments selected in this study are in agreement with fragment ions for the same compounds described elsewhere (Miao et al., 2002; Löffler and Ternes, 2003; Rodil and Moeder, 2008; Magi et al., 2013) (Figure S2).

3.2. Water quality parameters

The mean values of each water quality parameters are shown in Figure S3 and Table S6. The ecological filters met the quality parameters, except that for coliform counts, set by the Ordinance No. 2914/2011 which defines the standards of water potability in Brazil (Brasil, 2011). However, the filters had a high percentage of removal of coliforms (Figure S4) as the raw water was diluted 500 times to be count, and in the effluent of filters no dilutions were made. The filters were considered mature from 9th

October (± 1 month of maturation). In addition, total coliforms and *E. coli* were observed to have low variability among the 22 ecological filters, as SD and CV were lower than 20-30 % (Isensee, 1976) in each water sample collected during the sampling period (Table S7),); this demonstrating demonstrated the stability and robustness of the ecological filtration system. Thus, the removal of bacteria was not affected by the presence of PPCPs.

3.3. Oceurence Occurrence of PPCPs in the Lobo reservoir water

The 6 target PPCPs were identified and quantified in the Lobo reservoir water, which supplied the 22 ecological filters from September to December of 2013. The concentration of each compound detected in the filter influent water are shown in Table 1. It shows that all pharmaceuticals (i.e. ACT, DCF, NAP, IBU and IBU) were not found, at least in one sampling day, in the Lobo reservoir water. In contrast, personal care products (i.e. MEP and BP-3) were found with 100 % of frequency, and in high concentrations compared to the pharmaceutical compounds. These results are discussed below.

Table 1: Concentrations of the compounds detected by SPE-LC-MS/MS in water samples from the Lobo reservoir.

	Raw water			
PPCPs	Min. Conc. ($\mu g\ L^{-1}$)	Max. Conc. ($\mu g\ L^{-1}$)	Mean Conc. ($\mu g\ L^{-1}$)	Frequency detected (%)
ACT	n.d.	0.13	0.03	85.70
DCF	n.d.	0.05	0.02	71.40
NAP	n.d.	0.10	0.01	85.70
IBU	n.d.	0.13	0.01	42.80

10

MEP	0.10	1192.39	170.87	100.00
BP-3	0.32	2.10	1.14	100.00

n.d.: not detected.

In the first water sampling event the concentrations of MEP and BP-3 were the highest detected throughout the study period (1192.39 µg L^{-1} and 1.48 µg L^{-1}, respectively). Similarly, investigation work done in the state of São Paulo, Brazil, found MEP at several points of the river Mogi Guaçu at which the water had on average concentrations of 8 µg L^{-1}, where 27.50 µg L^{-1} was the highest concentration (Galinaro et al., 2015). In our study, the average concentration of MEP detected in the Lobo reservoir water was 170.87 µg L^{-1}, which is much higher than the spiked concentration of 2 µg L^{-1}.

If neglecting atypical days, the average concentration detected of MEP was 0.62 µg L^{-1}, which is similar to concentrations found from 0.005 to 79.60 µg L^{-1} in several water bodies worldwide e.g. India, USA, UK, China and several European countries (Benijts et al., 2004; Loraine and Pettigrove, 2006; Peng et al., 2008; Blanco et al., 2009; Pedrouzo et al., 2009; Jonkers et al., 2010; Ramaswamy et al., 2011; Renz et al., 2013; Haman et al., 2015). However, the average concentration of BP-3 in the Lobo reservoir water was 1.14 µg L^{-1}, higher than the other published work. For example, in lakes in Switzerland the concentration of BP-3 was found to range from < 2 to 125 ng L^{-1} (Poiger et al., 2004). In Brazil, Silva et al. (2013) reported < 2 ng L^{-1} in Araraquara city, São Paulo. It has also been found in several countries such as Japan, Spain, South Korea, United Kingdom etc. at concentrations from < 0.30 to 103 ng L^{-1} (Kim and Choi, 2014).

ACT was found in concentrations ranging from 0.01 µg L^{-1} to 0.13 µg L^{-1} over the study period, with an average concentration of 0.04 µg L^{-1}. In other studies

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conducted in Brazil, Almeida and Weber, (2009) reported ACT concentrations in Billings dam between 0.30 and 10.30 ng L^{-1}. Montagner and Jardim, (2011) found 13.44 ng L^{-1} in water samples from the basin of Atibaia, and Oliveira, (2014) reported the concentration 11-531 ng L^{-1} in the Guarapiranga dam. In other countries, ACT was found with a mean concentration of 0.05 µg L^{-1} (Bound and Voulvolis, 2006; Gros et al., 2006). ACT is one of the most frequently found drugs in surface water, wastewater and drinking water (Parolini et al., 2009). Henschel et al. (1997) classified this compound as harmful to aquatic organisms, based on some ecotoxicological tests with different biological models such as bacteria, algae, cladocerans and fish.

DCF is among the 10 compounds most often found in aquatic ecosystems (Sotelo et al., 2014). In our work its average detected concentration was 0.02 µg L^{-1}, and it was not found or was below the detection limit in 3 of the 9 samples taken. In Brazil, DCF was also found in the Billings dam in concentrations from 8.10 to 394.50 ng L^{-1} (Almeida and Weber, 2009), the concentration in the Guarapiranga dam was between 6 to 36 ng L^{-1} (Oliveira, 2014), and in Rio de Janeiro it was found at a concentration of 60 ng L^{-1} (Stumpf et al., 1999). In Germany, the concentration reached 600 ng L^{-1} (Heberer, 2002). In addition, NAP and IBU, are also amongst the most frequent drugs found in water bodies, and were found with an average concentration of 0.03 µg L^{-1} and 0.06 µg L^{-1}, respectively. However, the results agree with other Brazilian studies that found these compounds in the Billings dam (10 to 78.20 ng L^{-1}) (Almeida and Weber, 2009), and Rio de Janeiro (< 0.01 µg L^{-1}) (Stumpf et al., 1999). In our study, NAP was not found in one of the sampling days, and was below the limit of quantification in 3 three of the sampling days. Also, IBU was not found in 4 four of the sampling days, and was below the limit of quantification in one of them.

According to meteorological data collected at the climatological station of the Centre for Water Resources and Environmental Studies (CRHEA in Portuguese), which follows the rules of the World Meteorological Organization, on the day of the first collection it rained an average of 55.40 mm. However, the reservoir has several houses in its surroundings and high recreational and tourist activities, a fact that has been described previously (Calijuri and Tundisi, 1990) to have resulted in environmental changes by human activities such as deforestation, dumping of domestic sewage and fertilizers used in some agriculture areas. The first water sampling took place on 11.04.2013 (Monday), and interestingly, on the previous weekend there was a national bank holiday. Therefore, there was a likely increase in the use of the reservoir for bathing, and its surroundings for recreational activities. This combined with the potential wastewater discharge by the ranches that border the reservoir might have contributed to the increase in the concentration of the target compounds such as DCF (0.05 µg L^{-1}), NAP (0.10 µg L^{-1}), IBU (0.13 µg L^{-1}), and especially MEP (1192.39 µg L^{-1}).

3.4. Degradation Products

The DP extractions were performed for each mass found for all DPs of each PPCP compound, and those that were detected in the samples were selected for fragmentation analysis. The selected masses were: m/z 292 and m/z 278 (DP of DCF), m/z 201 (DP of MEP), m/z 282 (DP of DCF), m/z 185 (DP of MEP), m/z 245 and m/z 215 (DP of BP-3), m/z 231 (DP of BP-3), based on the literature described in Section 1.1 of the Supporting Information. The ion scanning experiments for the samples were carried out, and through analysing the spectra, it was observed that the same compounds detected in the reservoir water samples, at all times and days

of sampling, were the same found in the filter effluent samples. This suggests the same compounds, which were expected to be identified as DPs generated by the treatment during ecological filtration, were already present in the incoming water (Lobo reservoir). This is confirmed by the presence of the background concentration of each target compound in the reservoir water (Table 1).

The selected masses m/z 292 and 245, DPs of DCF and BP-3, respectively, were found in all samples and ~~were~~ further analysed. The DP 291 (m/z 292) showed fragments ion 274 ($C_{14}H_9NO_3Cl$), 218 ($C_{12}H_9NOCl$) and 150 ($C_{11}H_4N$) (Figure 1a). The DP 244 (m/z 245) was presented as the principal fragments 217 ($C_{13}H_{13}O3$), 199 ($C_{13}H_{11}O_2$), 189 ($C_{12}H_{13}O_2$) and 157 ($C_{11}H_9O$) (Figure 1b). Both compounds are consistent with the literature (e.g. Wiesenberg-Boettcher et al, 1991; Agüera et al., 2005; Gong et al., 2015), and have been detected in water bodies. It is worth noting that the DPs were only identified but not quantified by the method, as there was no sufficient sensitivity at trace levels. Therefore, further research on quantification of the DP compounds in the water reservoir and the effluent of the ecological filters is recommended.
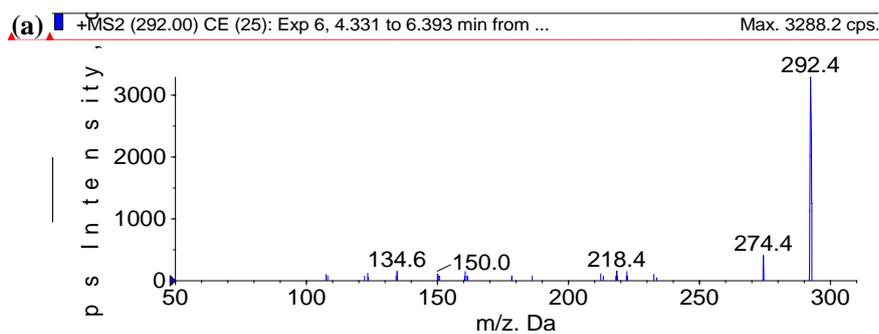
(a) +MS2 (292.00) CE (25): Exp 6, 4.331 to 6.393 min from ...   Max. 3288.2 cps.

335

b)

+MS2 (245.00) CE (25): Exp 12, 4.640 to 5.550 min fro...   Max. 3742.4 cps.

m/z 292 — $-H_2O$ → m/z 274 — $-CO$ → m/z 246

$-CO$ → m/z 218

$-HCl$ $-CH_2$ $-H_2O$ → m/z 150

336

Intensity, cps

3742

245.3

107.2   157.3   189.1   199.3   217.5

0

60 80 100 120 140 160 180 200 220 240 260

m/z, Da

337

15
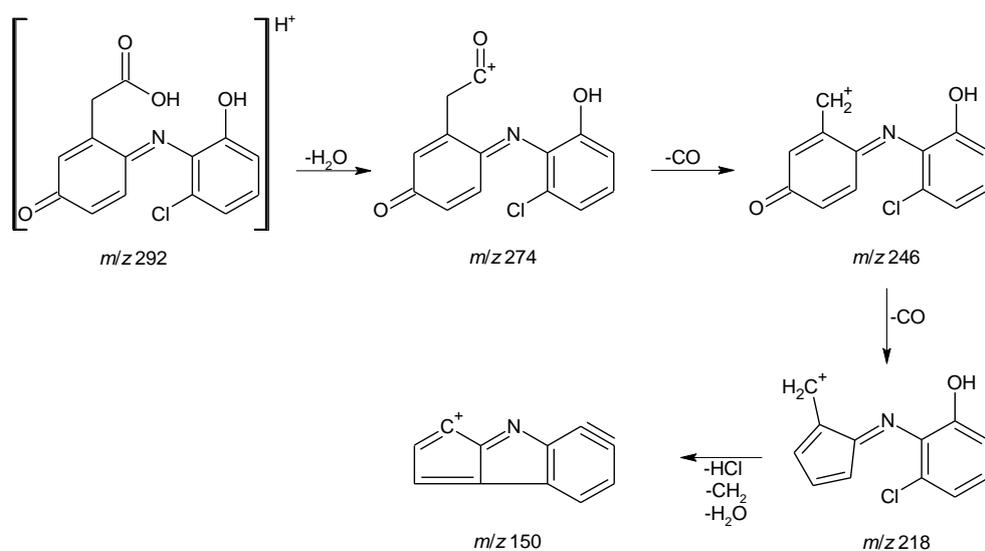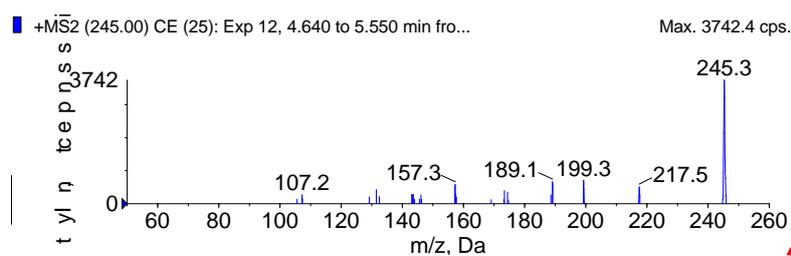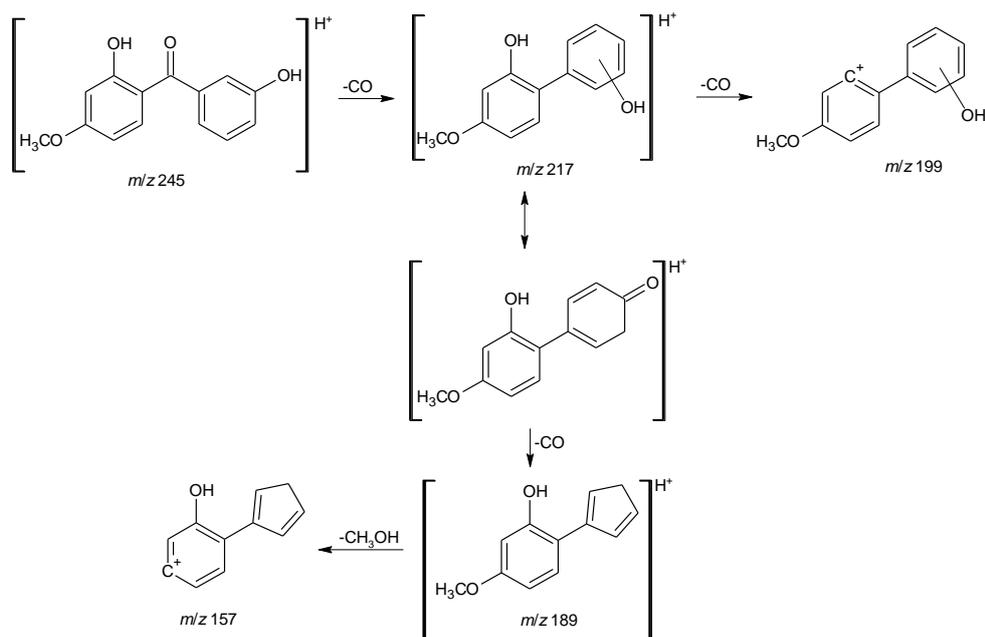
Figure 1: Identified fFragment ions spectra of the degradation products (DPs) identified, and proposal proposed fragmentation mechanism for both water reservoir and effluent of the ecological filters: a) DP of DCF; b) DP of BP-3.

3.5. Removal of PPCPs by the ecological filters

The mean removal efficiencies of the selected PPCPs are discussed below by class of compounds i.e. pharmaceuticals (Figures 2 and 3) and personal care products (Figure 4). AlsoAdditionally, the results are presented by the types of filter i.e. filters receiving individual compound (FEco), control filter (Control) and three filters receiving the mix solution (Mix).

3.5.1. Removal of pharmaceuticals

Analgesic (ACT)

The efficiency of ecological filters to remove ACT in this study was on average 81 % (Figure 2) and this agrees well with other research using a similar filtration

16

system. For example, Erba et al. (2012) reported 80 % removal of 2 μg L^{-1} of ACT by an ecological filter. On the other hand, Li et al. (2018) reported removals above 78-67 % of 25 μg L^{-1} of ACT using GAC-sandwich SSF, while Pompei et al. (2017) found 65 % removal of 2 μg L^{-1} ACT using household SSF. Our higher removal values might have been due to the fact that the filters were located outdoors and not in laboratory as per Pompei et al. (2017) and Li et al. (2018). Although laboratory tests attempt to simulate natural conditions, these tests do not consider environmental changes such as microbial community diversity, quantity, and climatic conditions, which evolve over time and space in nature (Ranjard et al., 2013). Therefore, biological degradation processes in environmental conditions are influenced by other variables that are present in natural environments (Francois et al., 2016). Because of the variability between laboratory and environmental conditions, it is suggested to carry out research in natural conditions to produce more authentic real application results.

Other Another reason for the difference in results could be the sand uniformity coefficient used in each filter. Erba et al. (2012) worked with a filter sand of similar uniformity coefficient (effective size = 0.25 mm, uniformity coefficient = 2-3) to our swork, while Pompei et al. (2017) (effective size = 0.210 mm, uniformity coefficient = 1.4) and Li et al. (2018) (effective size of 0.6 mm, uniformity coefficient = 1.4) had smaller values for the uniformity coefficient. These confirm the findings by Di Bernardo and Rivera (1996) who found that the biological layer (i.e. *schmutzdecke*) was larger in filters containing sand with a larger uniformity coefficient. Therefore, it is possible that the biological layer in our work was larger than the ones in Pompei et al. (2017) and Li et al. (2018), leading to a larger removal of the target PPCPs. Campos et al. (2002) suggested that the *schmutzdecke* is responsible for significant inputs of carbon substrates to the underlying sand layer supporting interstitial microbial growth. These

results confirm that biodegradation is a major mechanism for ACT removal (Onesios et al., 2009; Lin et al., 2010).

Comparing with other water treatment processesThe ecological filters were less efficient than , such as AOP systemss such as ; fenton, UV and ozone oxidations which were shown to remove , reached 100 % removal of ACT when using synthetic water (Tayo et al., 2018). However, the high cost of these technologies and the use of chemicals during the treatment makes them not very unattractive when compared to ecological filters which have presented very good levels of ACT removals. Finally, the statistical analysis MANOVA showed no significant difference ($p > 0.05$) between the type of filter (Control, FEco or Mix) and collection times (3, 6 and 24 hours), although the Control filter had a lower percentage of removal compared to the FEco and Mix filters (Figure 2). The error bars were higher in the Control filter, because there were no triplicates of this filter, but only for FEco and Mix filters (Figure 2).
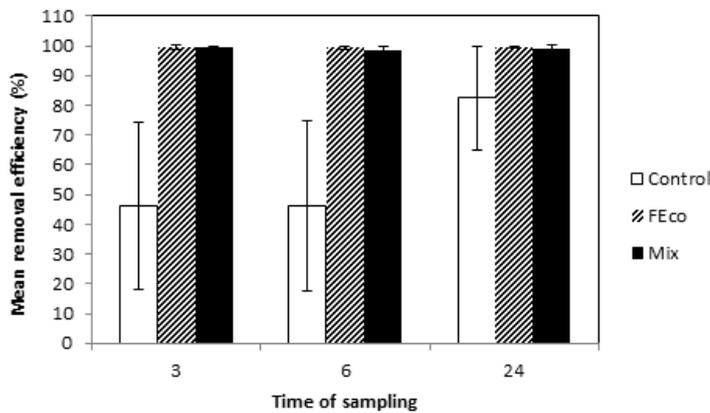
Figure 2: Mean removal (%) of ACT by ecological filtration, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27).

Anti-inflamatoryinflammatory (DCF, IBU, NAP)

18

The removal of DCF by ecological filters was on average 91 %, confirming previous findings of 94 % DCF removal by ecological filters elsewhere (Erba et al., 2012). On the other hand, Rigobello et al. (2013) found that there was no removal of DCF by conventional SSF, however, their experiment was conducted using synthetic water. Therefore, it is possible that there was no ideal formation of the biofilm which is easily formed using natural water from lakes and/or rivers, where there is already an aquatic biota that can colonize the top of the filter sand. Also, DCF removal by WWTPs showed large differences in removal, e.g. 17 % (Heberer, 2002), 69 % (Ternes, 1998), and 100 % (Thomas and Foster, 2004), this may be due to differences in temperature and climate (Delpla et al., 2009). When comparing this to advanced treatment, the ecological filters provided similar DCF removal (91 %) to AOPs applying ozonation and UV oxidation (100 %), and fenton oxidation (> 85 %) (Tayo et al., 2018). The results again demonstrate the benefit of using ecological filtration without the need of chemicals, and confirm that biodegradation is an important mechanism for DCF removal (Onesios et al., 2009).

For IBU the ecological filters removed on average 99 % of it. This is in agreement with Erba et al. (2012) who found IBU removal of 76 % by ecological filters, and Winkler et al. (2001) who evaluated the biodegradation of IBU by biofilm from surface waters and observed a rapid degradation up to 90 %. Yet for NAP the ecological filters removed on average 97 % of it; this result also agrees with Erba et al. (2012) who found NAP removal of 87 % using ecological filters. In comparison with advanced processes, our results show that the ecological filter is capable of also removing IBU and NAP with similar efficiencies to AOPs using ozonation (> 99 %), UV oxidation (100 %) and fenton oxidation (> 50 %) (Tayo et al., 2018).

19

429

Figure 3: Mean removal of: a) DCF; b) IBU; c) NAP, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27). The * corresponds to the situations when, in one or more samples of the raw water, the compounds were not detected, thereby disabling the calculation of the standard deviation and consequently the error.

Assessing the types of filter, MANOVA test shows that there were no differences between the filters (Control, FEco and Mix filters) for DCF, but indicates there was one effluent concentration significantly different to the others ($p = 0.04$) between collection times. However, the specific analysis of contrasts (Table S8) did not show the difference indicated by the general test. In this case, it was considered the difference between the mean concentrations in at the times 6 and 24 hours, since they were, respectively, the highest and the lowest sample means (3 hours: 0.04 µg L^{-1}, 6 hours: 0.06 µg L^{-1}, 24 hours: 0.02 µg L^{-1}). For IBU, MANOVA shows no significant difference ($p > 0.05$) between the types of filters (Control, FEco and Mix filters),

20

between the sampling times (3, 6 and 24 hours), and between the types of filter and sampling time (Figure 3b). For NAP, MANOVA shows that there were also no diferencesdifferences between the types of filters (Control, FEco or Mix filters). However, the tests indicate there was at least one concentration different in relation to the others at times 3, 6 and 24 hours ($p = 0.01$). The specific analysis of contrasts identified that the difference was between 3 and 24 hours (Table S7). At the sampling time of 24 hours the effluent concentration of NAP was lower than in the two previous sampling times, with the values of the sample means being as 0.02 μg L^{-1} in the time of 3 hours; 0.01 μg L^{-1} at 6 hours; and 0.001 μg L^{-1} at 24 hours after the contamination of the filters.

3.5.2. Removal of personal care products

The removal of personal care products by ecological filters was lower than the removal of pharmaceutical compounds. And; this may have been due to the fact MEP and BP-3 were found with high concentrations in the Lobo reservoir water as discussed above. However, MEP and BP-3 had similar removals, being of on average 70 % and 71 %, respectively (Figure 4). On the other hand, Pompei et al. (2017) reported 100 % removal of 2 μg L^{-1} of MEP and BP-3 by household SSF. However, these compounds were not found in the water of Regent's Park as identified in the Lobo reservoir water. Verlicchi et al. (2014) performed a literature review on the removal of personal care products by wetlands in Europe, North America and Asia, showing that removal was influenced mainly by redox potential, temperature, hydraulic retention time and affluent concentration of the compound. And thisThis may explain the difference between the findings by Pompei et al. (2017) and ours. Furthermore, when comparing compared with other treatment processes, the removals of MEP and BP-3 were was not as high as

those achieved by AOPs (Tayo et al., 2018). However, it ~~is hightlighted~~should be noted that Gomes et al. (2017) reported the generation of toxic by-products of paraben which are not completely mineralized when photocatalytic ozonation using TiO_2 was used.

Finally, despite the differences in removal~~s~~ of MEP in the Control filter in relation to the other filters (Figure 4b), MANOVA tests show that there were no difference between the treatments (Control, FEco or Mix filters) ($p > 0.05$), between sampling times of 3, 6 and 24 hours ($p = 0.35$), and between types of filter and sampling time ($p > 0.05$). For ~~the~~ BP-3, the MANOVA tests show there were no ~~diference~~difference between the treatments (Control, FEco or Mix filters) ($p > 0.05$), but there was a difference between sampling time ($p = 0.02$). The specific analysis of contrasts identified that the difference was between 3 hours (0.99 µg L^{-1}) and 24 hours (0.35 µg L^{-1}) (Table S7).

Figure 4: Mean removals of personal care products for a) BP-3 and b) MEP, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27).

4. Conclusions

The results of water quality parameters indicated that the water treated by the ecological filters was within the standard of potability from Brazil. It is noted that filtered water needs to be disinfected for human consumption to totally remove coliforms.

The target PPCPs were identified in the Lobo reservoir water in the range of μg L^{-1}. The personal care products were detected with 100 % frequency in samples, and in high concentrations compared to the pharmaceutical compounds. These results were attributed to recreational use of the reservoir and wastewater effluent discharges.

Two DPs (DCF and BP-3) were identified in the reservoir and effluent filter water samples. The fragment ions were identified, and a degradation path for both compounds were proposed. To evaluate their removal by ecological filters a further investigation on quantification of the DP compounds is recommended.

Ecological filters removed more of the pharmaceutical compounds (81 to 99 %) than the personal care products (70 to 71 %). The statistical tests by MANOVA did not show significant differences for any of the compounds in relation to the type of filter (Control, FEco or Mix filters), showing the robustness of the ecological filtration system. Results showed that the filters are resilient to an individual compound as to their mixture. Some compounds (DCF, NAP, and BP-3) showed differences between some of the sampling times, but this was probably due to the variation of background contamination in the reservoir water and the spiked contamination of 2 μg L^{-1}.

In comparison with other advanced technologies (e.g. ozone, fenton, UV irradiation) that may remove 100 % of our target PPCPs, the authors believe that with optimised operational conditions, ecological filtration offers a low cost and chemical free treatment option for the effective PPCP removal in decentralized systems.

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Occurrence of PPCPs in a Brazilian Water Reservoir and their Removal Efficiency

by Ecological Filtration.

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Abstract

The presence of PPCPs (Pharmaceuticals and Personal Care Products) in water sources and drinking water has concerned researchers in recent times. This study was carried out to evaluate the occurrence of 6 PPCPs (namely paracetamol, diclofenac, naproxen, ibuprofen, benzophenone-3 and methylparaben) in the Lobo reservoir, their degradation products, and how efficienctly they were removed by 22 ecological filters, considering individual and mixtures of compounds. There were 3 spiking events of PPCPs (2 μg L^{-1}) in the ecological filter influents conducted with a lag period of 15 days between spikes. Water sample were collected from the influent and effluent of the filters at 3, 6 and 24 hours after each spiking event. All target PPCPs were identified in the Lobo reservoir water in the range of μg L^{-1}. The personal care products were detected with 100 % frequency in the samples, and in higher concentrations compared to the pharmaceuticals. Degradation products of diclofenac and benzophenone-3 were identified in the water samples. Results of this investigation show that an ecological filter was an effective process (70 - 99 %) to remove 2 μg L^{-1} of the selected PPCPs, and demonstrated that the filters were resilient to individual compounds and to their mixtures.

Keywords: Ecological filtration; drinking water treatment; removal of PPCPs; degradation products.

1. Introduction

Pharmaceuticals and Personal Care Products (PPCPs) are of scientific and public concern as newly recognized classes of environmental pollutants; described as emerging water contaminants with potential psychoactive properties and unknown effects to the aquatic environment (Evgenidou et al., 2015). The term "PPCPs" refers to any chemical product with healthcare or medical purposes for humans and/or animals (Schumock et al. 2014).

The most consumed non-steroidal anti-inflammatory drugs frequently found in aquatic environments are aspirin, acetaminophen, ibuprofen, naproxen and diclofenac (Fent et al., 2006). These PPCPs and others have been detected worldwide in surface water, groundwater, sewage and even drinking water in the order of ng-µg L^{-1} (Heberer, 2002; Petrović et al., 2003; Fent et al., 2006; Ellis, 2006; Sui et al., 2015). Additionally, degradation products (DPs) of these PPCPs have been found in water bodies and water samples after treatment as a result of a multiplicity of biotic and abiotic processes (e.g. hydrolysis, photolysis, oxidation, and microbiological metabolism) acting on the original compounds or their metabolites (Mompelat et al., 2009; Dévier et al., 2011; Andrés-Costa et al., 2014; Van Doorslaer et al., 2014; Postigo and Richardson, 2014).

PPCP removal has been observed in wastewater treatment plants (WWTPs) (e.g. Ternes et al., 1998; Thomas and Foster, 2004, Camacho-Munoz et al., 2012). However, in general, most of WWTPs are not designed to treat this type of substance, and consequently a significant portion of these compounds are not degraded/removed during treatment. Therefore, the pure compound and/or their metabolites may enter the aquatic environment via sewage effuents (Daughton and Ternes, 1999; Heberer, 2002; Petrović et al., 2003; Jones et al., 2005; Fent et al., 2006; Matamoros et al., 2009). Furthermore, conventional drinking water treatment processes have been reported as ineffective for

the removal of most pharmaceuticals, with efficiency ranging from < 5 to 40 % (Vieno et al., 2007; Pojana et al., 2011).

Recently, numerous investigations have been carried out using advanced oxidation processes (AOPs) such as ozonation, UV oxidation, fenton and fenton-like processes, and photocatalytic degradation to remove PPCPs from water and wastewater (Tayo et al., 2018; Goel and Das, 2018; Xu et al., 2017). However, the relatively high cost of these processes currently stand as the major barrier for their large-scale implementation (Xu et al., 2017), especially in developing countries such as Brazil. Conversely, there is evidence of PPCP removal by sandfiltration, in which biodegradation has been suggested as one of the removal mechanisms (Westerhoff, 2003; Fujii and Kikuchi, 2005; Hallé, 2010; Onesios et al., 2009; Camacho-Munoz et al. 2012; Chen et al., 2015; Chen et al., 2016). For example, Qiao et al. (2011) investigated the occurrence of 15 PPCPs in two full-scale conventional treatment plants; they found that the type and concentration of PPCP decreased gradually along the treatment train, especially after sand filtration. Beretelkamp et al. (2014), simulated the removal of 14 organic compounds by river bank filtration at a laboratory scale; they obtained a statistically significant relationship between the biological degradation rates and the compound functional groups. In addition, removal of PPCPs has been observed in slow sand filtration (SSF) and granular activated carbon (GAC) sandwich SSF (Erba et al., 2014; Escolà Casas and Bester, 2015; Pompei et al., 2017; Li et al., 2018). Therefore, biosandfiltration seems an attractive option due to its demonstrated potential of removing PPCPs from water and its low operational cost for not requiring chemical coagulation. Slow sand filtration has been recently referred to as ecological filtration due to the presence of a biofilm that forms on top of the sand filter and is believed to be essential to water purification (Nakamoto, 2008).

98   The aim of this work was to evaluate the occurrence of selected PPCPs and DPs

99   in a Brazilian water reservoir, and their removal by ecological filters installed under

100   natural environmental conditions, receiving water from the Lobo reservoir in Itirapina,

101   São Paulo state. To the best of the authors' knowledge, this is the first study

102   investigating the removal of individual target compounds, their mixture, and their

103   degradation products by ecological filtration at a pilot scale.

104

105   **2.   Material and methods**

106   **2.1. Chemicals and Reagents**

107   Acetonitrile (CH$_3$CN) and methanol (CH$_3$OH) were of HPLC grade from J.T.

108   Baker (Xalostoc, México), Formic acid, 4-Acetaminophen (ACT), Diclofenac sodium

109   salt (DCF), Naproxen (NAP), Ibuprofen (IBU), Metyl 4-hydroxybenzoate (MEP) and 2-

110   Hydroxy-4-methoxybenzophenone (BP-3) (all 99 % purity or more) were purchased

111   from Sigma-Aldrich. The deuterated compounds were used as internal standards,

112   namely paracetamol-*d4*, diclofenac-*d4*, naproxen-*d3*, ibuprofen-*d3*; all obtained from

113   CDN Isotopes (Quebec, Canada). Additional information about each compound is

114   shown in Table S1. Stock solutions were prepared in methanol for each compound and

115   stored in a refrigerator at 4 °C. For all reagent solutions, water was previously distilled

116   and further deionized using a Milli-Q system Millipore (Millipore, Bedford, MA, USA).

117

118   **2.2. Filter construction**

119   Twenty-two ecological filters (Nakamoto, 2008) were constructed with PVC

120   columns (Figure S1). Each ecological filter had an internal diameter of 25 cm and

121   height of 72 cm. The support layer in each filter was formed by a 15 cm gravel layer,

122   with 3 sub-layers of 12.50 mm to 1.41 mm. The sand layer had 30 cm height with grain

123   sizes varying from 1.00 to 0.08 mm. The sand uniformity coefficient was between 2 and

124   3, and the effective grain size was 0.25 mm (Bellamy et al., 1985; Di Bernardo, 1993).

125   The water layer on the top of the sand bed varied from 25 to 27 cm. The influent water

126   to the 22 ecological filters was pumped from the Lobo reservoir (22°10'18.09"S

127   47°54'5.00"W), located at Itirapina city, São Paulo, Brazil, to a constant level tank

128   before being supplied continuously to the filters.

129

130   **2.3.Water Sampling**

131   The operation of filters was continuous and the average water filtration flow rate

132   was $3m^3/d.m^2$. There was triplicate of 6 filters with each individually receiving a PPCP

133   compound (18 filters), triplicate of 1 filter receiving a mixture of the 6 PPCP

134   compounds (3 filters), and 1 control filter receiving only water from the Lobo reservoir

135   (Table S2).

136   After maturation of the filters, three spiking events of the target PPCPs were

137   conducted with a lag period of 15 days between spikes. The spikes were created to

138   certify that a known concentration would enter the ecological filters, as the main

139   concentration of PPCPs on the reservoir water may vary and may not be detected every

140   day. The spike solution (1L) was added to the raw water inlet via a dosing pump.

141   Samples of the reservoir water were collected at the same time as the filter effluent

142   water (3, 6, and 24 hours after spikes) to determine the background concentration of the

143   target PPCPs. The point of water sample collection in the reservoir was always the

144   same, at the location of the hydraulic pump used to supply the 22 filters (22°10'18.09"S

145   47°54'5.00"W).

146   For PPCP detection, water samples (500 mL) were collected in each

147   contaminated filter after every contamination event (total per filter = 3 samples

148   (triplicate) x 3 spike events = 9 samples; total = 189 samples), while in the control filter

149   only 9 samples were collected in total. To evaluate the removal efficiency of each filter,

150   the total initial concentration of each target PPCP compound was considered as the sum

151   of the background concentration found in the reservoir water, plus the spiked PPCP

152   concentration of 2 $\mu g\ L^{-1}$. For physico-chemical and bacteriological analyses, samples

153   of 500 mL were collected weekly from the influent and effluent of each filter during the

154   first month of operation; they were also collected from 9th October in 2013, when the

155   filters were considered matured, water samples were collected 3 times per week

156   (samples in each filter = 30; total samples = 660 samples).

157

158   ### 2.3.1. Water quality parameters

159   Parameters concerning the treated water quality by the ecological filters were

160   measured from September to December 2013. Turbidity and apparent colour were

161   determined by a HACH DR 2000 espectrofotometer, selecting UV_{455nm} for colour and

162   UV_{750nm} for turbidity. The true colour was measured after filtering the water samples

163   through a 0.45 µm membrane (Millipore, cellulose ester, 90 mm diameter), and

164   determined using the espectrofotometer at $UV_{455nm.}$ The pH was determined by pHmeter

165   B374 – Micronal; temperature, conductivity and total dissolved solids (TDS) of water

166   samples were measured by Orion multiparameter - model 145. Total coliforms and *E.*

167   c*oli* were measured using the Colilert® kit method once a week before contamination,

168   and during the contamination period samplings were done before and 24 hours after

169   spiking the PPCPs into the ecological filters.

170

171   ### 2.4. PPCPs and DPs detection

172   The PPCPs were extracted from the water samples using solid phase extraction

173   (SPE) with Strata-X (Phenomenex) Polymeric Reversed Phase 200 mg/6 mL (8B-S100–

174   FCH). Each cartridge was pre-conditioned with 6 mL of methanol (2 times), 6 mL of

175   purified water (Milli-Q), and 6 mL of purified water (Milli-Q) acidified with HCl for

176   pH 3 per gravity. After, 300 mL of water (pH 3.0) was passed through the cartridge

177   sorbent at a flow rate of 5 mL min $^{-1}$. The PPCPs were eluted passing 4 mL of methanol

178   twice, and the volume was reduced with a gentle stream of nitrogen gas and

179   reconstituted to 300 µL with MeOH + Milli-Q water (1:1 v/v). The samples were then

180   analyzed by LC-MS/MS. Additional information about the LC-MS/MS equipment,

181   method used and how analyses were conducted for the identification of DPs are

182   described in the Supporting Information. Quality assurance and quality control

183   (QA/QC) were implemented for the accuracy of the quantification of the target PPCPs.

184   More details are also presented in the Supporting Information and Tables S3 and S4.

185

186   **2.5. Statistical analysis**

187   The results derived from the quantification of PPCPs were subjected to statistical

188   analysis profiles for repeated measures, performed with PRCO GLM software from

189   SAS. This analysis was carried out to study the effect of different type of treatments, the

190   different times of collection, and interactions between types of treatment and times of

191   collection. The multivariate character of analyses was previously verified by Mauchly's

192   sphericity test. MANOVA analysis considered the following tests: Wilks' Lambda,

193   Pillai's Trace, Hotelling-Lawley Trace and Roy's Greatest Root.

194   To determine the variability of the water quality parameters between the 22

195   ecological filters, the standard deviation (SD) and coefficient of variation (CV) were

196   determined. CV was considered with high variation for values between 20 to 30 %

197   (Isensee, 1976). In addition, t-tests were done to examine the relationships between

198   influent and effluent water from ecological filters; values were significant at $p < 0.05$.

199   The averages, SDs, CVs and t-tests of data were calculated using Microsoft Excel

200   2010.

201

202   **3. Results and discussion**

203   **3.1. LC-MS/MS**

204   The adjustment of parameters for each compound and deuterates of the mass

205   spectrometer to the individual samples of all compounds are shown in Table S5. The

206   transition ions, or ion fragments selected in this study are in agreement with fragment

207   ions for the same compounds described elsewhere (Miao et al., 2002; Löffler and

208   Ternes, 2003; Rodil and Moeder, 2008; Magi et al., 2013) (Figure S2).

209

210   **3.2. Water quality parameters**

211   The mean values of each water quality parameters are shown in Figure S3 and

212   Table S6. The ecological filters met the quality parameters except that for coliform

213   counts, set by the Ordinance No. 2914/2011 which defines the standards of water

214   potability in Brazil (Brasil, 2011). However, the filters had a high percentage of removal

215   of coliforms (Figure S4) as the raw water was diluted 500 times to be count, and in the

216   effluent of filters no dilutions were made. The filters were considered mature from 9th

217   October (± 1 month of maturation). In addition, total coliforms and *E. coli* were

218   observed to have low variability among the 22 ecological filters, as SD and CV were

219   lower than 20-30 % (Isensee, 1976) in each water sample collected during the sampling

220   period (Table S7); this demonstrated the stability and robustness of the ecological

221 filtration system. Thus, the removal of bacteria was not affected by the presence of

222 PPCPs.

223

224   **3.3. Occurrence of PPCPs in the Lobo reservoir water**

225   The 6 target PPCPs were identified and quantified in the Lobo reservoir water,

226 which supplied the 22 ecological filters from September to December of 2013. The

227 concentration of each compound detected in the filter influent water are shown in Table

228 1. It shows that all pharmaceuticals (i.e. ACT, DCF, NAP, and IBU) were not found, at

229 least in one sampling day in the Lobo reservoir water. In contrast, personal care

230 products (i.e. MEP and BP-3) were found with 100 % frequency, and in high

231 concentrations compared to the pharmaceutical compounds.

232

233 **Table 1:** Concentrations of the compounds detected by SPE-LC-MS/MS in water samples from

234 the Lobo reservoir.

PPCPs	Raw water			
	Min. Conc. (μg L^{-1})	Max. Conc. (μg L^{-1})	Mean Conc. (μg L^{-1})	Frequency detected (%)
ACT	n.d.	0.13	0.03	85.70
DCF	n.d.	0.05	0.02	71.40
NAP	n.d.	0.10	0.01	85.70
IBU	n.d.	0.13	0.01	42.80
MEP	0.10	1192.39	170.87	100.00
BP-3	0.32	2.10	1.14	100.00

235   n.d.: not detected.

236

237   In the first water sampling event the concentrations of MEP and BP-3 were the

238 highest detected throughout the study period (1192.39 μg L^{-1} and 1.48 μg L^{-1},

239   respectively). Similarly, investigation work done in the state of São Paulo, Brazil, found

240   MEP at several points of the river Mogi Guaçu at which the water had on average

241   concentrations of 8 µg L^{-1}, where 27.50 µg L^{-1} was the highest concentration (Galinaro

242   et al., 2015). In our study, the average concentration of MEP detected in the Lobo

243   reservoir water was 170.87 µg L^{-1}, which is much higher than the spiked concentration

244   of 2 µg L^{-1}.

245   If neglecting atypical days, the average concentration detected of MEP was 0.62

246   µg L^{-1}, which is similar to concentrations found from 0.005 to 79.60 µg L^{-1} in several

247   water bodies worldwide e.g. India, USA, UK, China and several European countries

248   (Benijts et al., 2004; Loraine and Pettigrove, 2006; Peng et al., 2008; Blanco et al.,

249   2009; Pedrouzo et al., 2009; Jonkers et al., 2010; Ramaswamy et al., 2011; Renz et al.,

250   2013; Haman et al., 2015). However, the average concentration of BP-3 in the Lobo

251   reservoir water was 1.14 µg L^{-1}, higher than the other published work. For example, in

252   lakes in Switzerland the concentration of BP-3 was found to range from < 2 to 125 ng L^{-1}

253   (Poiger et al., 2004). In Brazil, Silva et al. (2013) reported < 2 ng L^{-1} in Araraquara

254   city, São Paulo. It has also been found in several countries such as Japan, Spain, South

255   Korea, United Kingdom etc. at concentrations from < 0.30 to 103 ng L^{-1} (Kim and Choi,

256   2014).

257   ACT was found in concentrations ranging from 0.01 µg L^{-1} to 0.13 µg L^{-1} over

258   the study period, with an average concentration of 0.04 µg L^{-1}. In other studies

259   conducted in Brazil, Almeida and Weber (2009) reported ACT concentrations in

260   Billings dam between 0.30 and 10.30 ng L^{-1}. Montagner and Jardim (2011) found 13.44

261   ng L^{-1} in water samples from the basin of Atibaia, and Oliveira (2014) reported the

262   concentration 11-531 ng L^{-1} in the Guarapiranga dam. In other countries ACT was

263   found with a mean concentration of 0.05 µg L^{-1} (Bound and Voulvolis, 2006; Gros et

al., 2006). ACT is one of the most frequently found drugs in surface water, wastewater and drinking water (Parolini et al., 2009). Henschel et al. (1997) classified this compound as harmful to aquatic organisms, based on some ecotoxicological tests with different biological models such as bacteria, algae, cladocerans and fish.

DCF is among the 10 compounds most often found in aquatic ecosystems (Sotelo et al., 2014). In our work its average detected concentration was 0.02 µg L^{-1}, and it was not found or was below the detection limit in 3 of the 9 samples taken. In Brazil, DCF was also found in the Billings dam in concentrations from 8.10 to 394.50 ng L^{-1} (Almeida and Weber, 2009), the concentration in the Guarapiranga dam was between 6 to 36 ng L^{-1} (Oliveira, 2014), and in Rio de Janeiro it was found at a concentration of 60 ng L^{-1} (Stumpf et al., 1999). In Germany, the concentration reached 600 ng L^{-1} (Heberer, 2002). In addition, NAP and IBU, are also amongst the most frequent drugs found in water bodies, and were found with an average concentration of 0.03 µg L^{-1} and 0.06 µg L^{-1}, respectively. However, the results agree with other Brazilian studies that found these compounds in the Billings dam (10 to 78.20 ng L^{-1}) (Almeida and Weber, 2009), and Rio de Janeiro (< 0.01 µg L^{-1}) (Stumpf et al., 1999). In our study NAP was not found in one of the sampling days, and was below the limit of quantification in three of the sampling days. Also, IBU was not found in four of the sampling days, and was below the limit of quantification in one of them.

According to meteorological data collected at the climatological station of the Centre for Water Resources and Environmental Studies (CRHEA in Portuguese), which follows the rules of the World Meteorological Organization, on the day of the first collection it rained an average of 55.40 mm. However, the reservoir has several houses in its surroundings and high recreational and tourist activities, a fact that has been described previously (Calijuri and Tundisi, 1990) to have resulted in environmental

289   changes by human activities such as deforestation, dumping of domestic sewage and

290   fertilizers used in some agriculture areas. The first water sampling took place on

291   11.04.2013 (Monday), and interestingly, on the previous weekend there was a national

292   bank holiday. Therefore, there was a likely increase in the use of the reservoir for

293   bathing, and its surroundings for recreational activities. This combined with the

294   potential wastewater discharge by the ranches that border the reservoir might have

295   contributed to the increase in the concentration of the target compounds such as DCF

296   (0.05 µg L^{-1}), NAP (0.10 µg L^{-1}), IBU (0.13 µg L^{-1}), and especially MEP (1192.39 µg

297   L^{-1}).

298

299   **3.4. Degradation Products**

300   The DP extractions were performed for each mass found for all DPs of each

301   PPCP compound, and those that were detected in the samples were selected for

302   fragmentation analysis. The selected masses were: m/z 292 and m/z 278 (DP of DCF),

303   m/z 201 (DP of MEP), m/z 282 (DP of DCF), m/z 185 (DP of MEP), m/z 245 and m/z

304   215 (DP of BP-3), m/z 231 (DP of BP-3), based on the literature described in Section

305   1.1 of the Supporting Information. The ion scanning experiments for the samples were

306   carried out, and through analysing the spectra it was observed that the same compounds

307   detected in the reservoir water samples, at all times and days of sampling, were the

308   same found in the filter effluent samples. This suggests the same compounds, which

309   were expected to be identified as DPs generated by the treatment during ecological

310   filtration, were already present in the incoming water (Lobo reservoir). This is

311   confirmed by the presence of the background concentration of each target compound in

312   the reservoir water (Table 1).

313   The selected masses *m/z* 292 and 245, DPs of DCF and BP-3, respectively, were

314 found in all samples and further analysed. The DP 291 (*m/z* 292) showed fragments ion

315 274 ($C_{14}H_9NO_3Cl$), 218 ($C_{12}H_9NOCl$) and 150 ($C_{11}H_4N$) (Figure 1a). The DP 244 (*m/z*

316 245) was presented as the principal fragments 217 ($C_{13}H_{13}O3$), 199 ($C_{13}H_{11}O_2$), 189

317 ($C_{12}H_{13}O_2$) and 157 ($C_{11}H_9O$) (Figure 1b). Both compounds are consistent with the

318 literature (e.g. Wiesenberg-Boettcher et al, 1991; Agüera et al., 2005; Gong et al.,

319 2015), and have been detected in water bodies. It is worth noting that the DPs were only

320 identified but not quantified by the method, as there was no sufficient sensitivity at trace

321 levels. Therefore, further research on quantification of the DP compounds in the water

322 reservoir and the effluent of the ecological filters is recommended.

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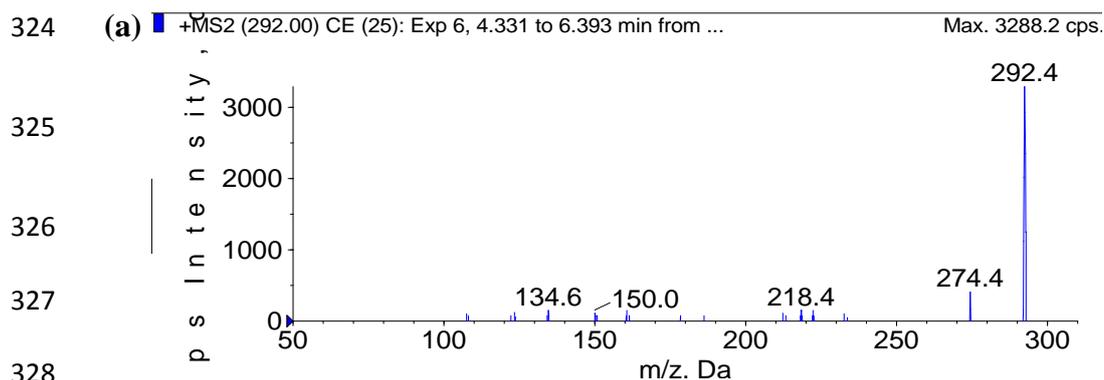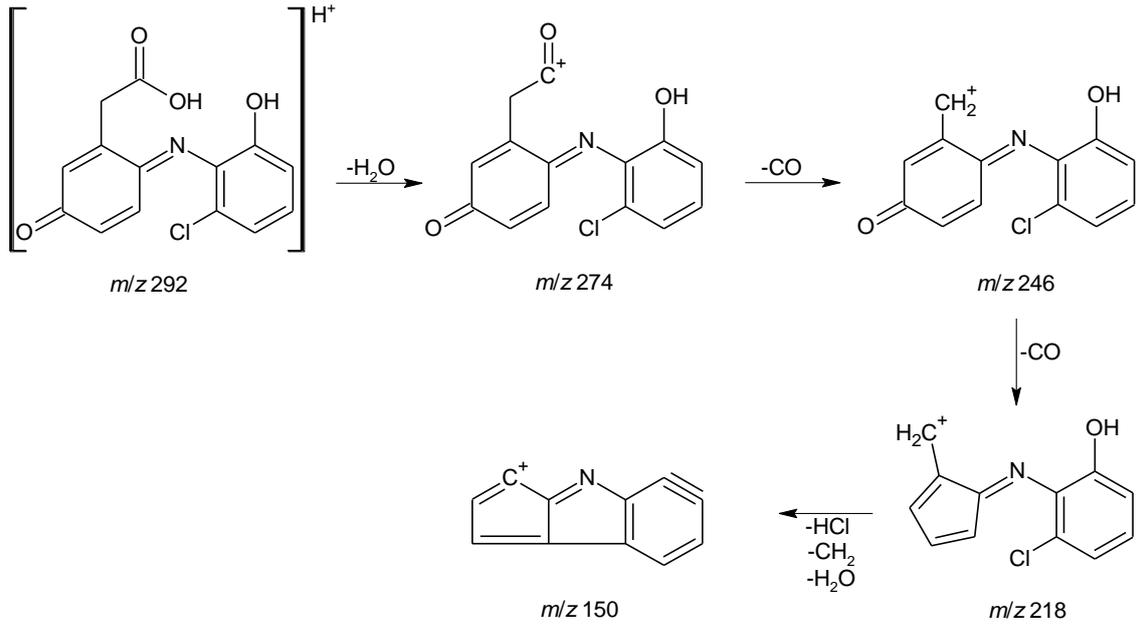
324 **(a)**
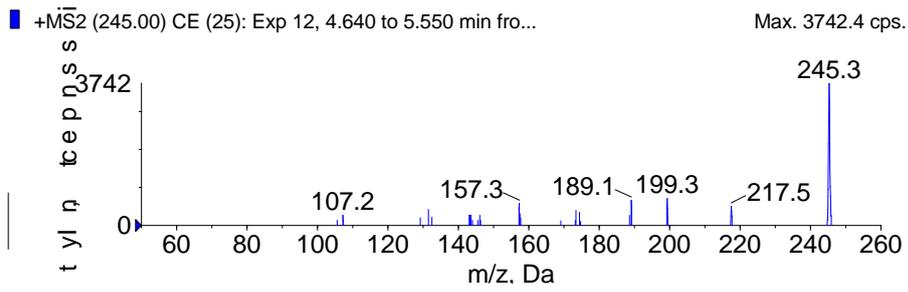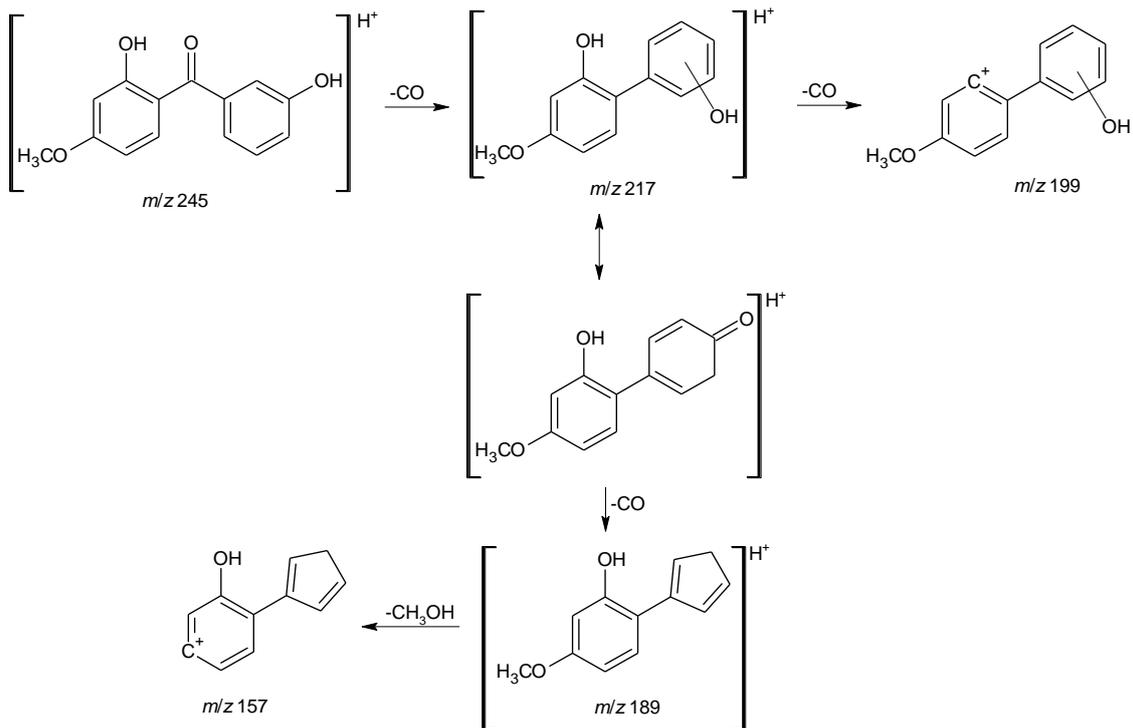
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330

331 **b)**

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333

Figure 1: Identified fragment ions spectra of the degradation products (DPs), and proposed

fragmentation mechanism for both water reservoir and effluent of the ecological filters: a) DP of

DCF; b) DP of BP-3.

337

3.5. Removal of PPCPs by the ecological filters

The mean removal efficiencies of the selected PPCPs are discussed below by

class of compounds i.e. pharmaceuticals (Figures 2 and 3) and personal care products

(Figure 4). Additionally, the results are presented by the types of filter i.e. filters

receiving individual compound (FEco), control filter (Control) and three filters

receiving the mix solution (Mix).

344

3.5.1. Removal of pharmaceuticals

Analgesic (ACT)

The efficiency of ecological filters to remove ACT in this study was on average

81 % (Figure 2) and this agrees well with other research using a similar filtration

349　system. For example, Erba et al. (2012) reported 80 % removal of 2 μg L^{-1} of ACT by

350　an ecological filter. On the other hand, Li et al. (2018) reported removals above 78-67

351　% of 25 μg L^{-1} of ACT using GAC-sandwich SSF, while Pompei et al. (2017) found 65

352　% removal of 2 μg L^{-1} ACT using household SSF. Our higher removal value might have

353　been due to the fact that the filters were located outdoors and not in laboratory as per

354　Pompei et al. (2017) and Li et al. (2018). Although laboratory tests attempt to simulate

355　natural conditions, these tests do not consider environmental changes such as microbial

356　community diversity, quantity, and climatic conditions, which evolve over time and

357　space in nature (Ranjard et al., 2013). Therefore, biological degradation processes in

358　environmental conditions are influenced by other variables that are present in natural

359　environments (Francois et al., 2016). Because of the variability between laboratory and

360　environmental conditions, it is suggested to carry out research in natural conditions to

361　produce more authentic application results.

362　　　　Another reason for the difference in results could be the sand uniformity

363　coefficient used in each filter. Erba et al. (2012) worked with a filter sand of similar

364　uniformity coefficient (effective size = 0.25 mm, uniformity coefficient = 2-3) to ours,

365　while Pompei et al. (2017) (effective size = 0.210 mm, uniformity coefficient = 1.4) and

366　Li et al. (2018) (effective size of 0.6 mm, uniformity coefficient = 1.4) had smaller

367　values for the uniformity coefficient. These confirm the findings by Di Bernardo and

368　Rivera (1996) who found that the biological layer (i.e. *schmutzdecke*) was larger in

369　filters containing sand with a larger uniformity coefficient. Therefore, it is possible that

370　the biological layer in our work was larger than the ones in Pompei et al. (2017) and Li

371　et al. (2018), leading to a larger removal of the target PPCPs. Campos et al. (2002)

372　suggested that the *schmutzdecke* is responsible for significant inputs of carbon substrates

373　to the underlying sand layer supporting interstitial microbial growth. These results

374 confirm that biodegradation is a major mechanism for ACT removal (Onesios et al.,

375 2009; Lin et al., 2010).

376   The ecological filters were less efficient than AOP systems such as fenton, UV

377 and ozone oxidations which were shown to remove 100 % of ACT when using synthetic

378 water (Tayo et al., 2018). However, the high cost of these technologies and the use of

379 chemicals during the treatment make them unattractive when compared to ecological

380 filters which have presented very good levels of ACT removal. Finally, the statistical

381 analysis MANOVA showed no significant difference ($p > 0.05$) between the type of

382 filter (Control, FEco or Mix) and collection times (3, 6 and 24 hours), although the

383 Control filter had a lower percentage of removal compared to the FEco and Mix filters

384 (Figure 2). The error bars were higher in the Control filter, because there were no

385 triplicates of this filter, but only for FEco and Mix filters (Figure 2).

386

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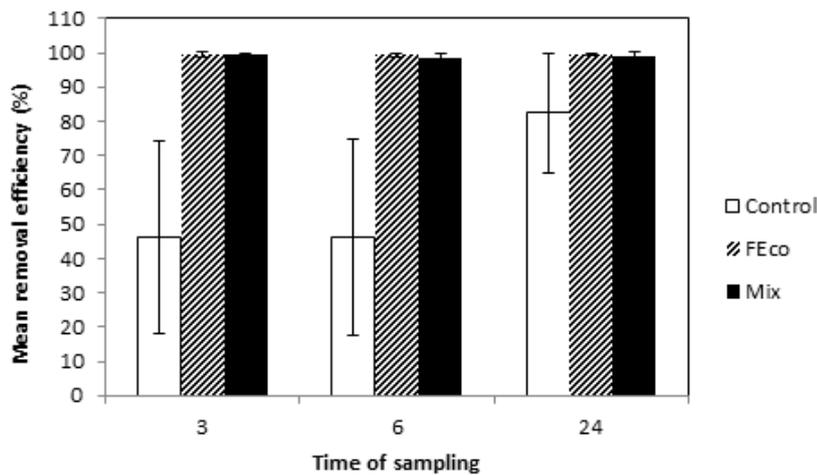
394 **Figure 2:** Mean removal (%) of ACT by ecological filtration, in Control filter (n = 9),

395 FEco (n = 27) and Mix (n = 27).

396

397 **Anti-inflammatory (DCF, IBU, NAP)**

398   The removal of DCF by ecological filters was on average 91 %, confirming

399   previous findings of 94 % DCF removal by ecological filters elsewhere (Erba et al.,

400   2012). On the other hand, Rigobello et al. (2013) found that there was no removal of

401   DCF by conventional SSF, however, their experiment was conducted using synthetic

402   water. Therefore, it is possible that there was no ideal formation of the biofilm which is

403   easily formed using natural water from lakes and/or rivers, where there is already an

404   aquatic biota that can colonize the top of the filter sand. Also, DCF removal by WWTPs

405   showed large differences in removal, e.g. 17 % (Heberer, 2002), 69 % (Ternes, 1998),

406   and 100 % (Thomas and Foster, 2004), this may be due to differences in temperature

407   and climate (Delpla et al., 2009). When comparing this to advanced treatment, the

408   ecological filters provided similar DCF removal (91 %) to AOPs applying ozonation

409   and UV oxidation (100 %), and fenton oxidation (> 85 %) (Tayo et al., 2018). The

410   results again demonstrate the benefit of using ecological filtration without the need of

411   chemicals, and confirm that biodegradation is an important mechanism for DCF

412   removal (Onesios et al., 2009).

413   For IBU the ecological filters removed on average 99 % of it. This is in

414   agreement with Erba et al. (2012) who found IBU removal of 76 % by ecological filters,

415   and Winkler et al. (2001) who evaluated the biodegradation of IBU by biofilm from

416   surface waters and observed a rapid degradation up to 90 %. Yet for NAP the ecological

417   filters removed on average 97 % of it; this result also agrees with Erba et al. (2012) who

418   found NAP removal of 87 % using ecological filters. In comparison with advanced

419   processes, our results show that the ecological filter is capable of also removing IBU

420   and NAP with similar efficiencies to AOPs using ozonation (> 99 %), UV oxidation

421   (100 %) and fenton oxidation (> 50 %) (Tayo et al., 2018).

422

Figure 3: Mean removal of: a) DCF; b) IBU; c) NAP, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27). The * corresponds to the situations when, in one or more samples of the raw water, the compounds were not detected, thereby disabling the calculation of the standard deviation and consequently the error.

Assessing the types of filter MANOVA test shows that there were no differences between the filters (Control, FEco and Mix filters) for DCF, but indicates there was one effluent concentration significantly different to the others ($p = 0.04$) between collection times. However, the specific analysis of contrasts (Table S8) did not show the difference indicated by the general test. In this case it was considered the difference between the mean concentrations at the times 6 and 24 hours, since they were, respectively, the highest and the lowest sample means (3 hours: 0.04 µg L^{-1}, 6 hours: 0.06 µg L^{-1}, 24 hours: 0.02 µg L^{-1}). For IBU, MANOVA shows no significant difference ($p > 0.05$) between the types of filters (Control, FEco and Mix filters), between the sampling times (3, 6 and 24 hours), and between the types of filter and

20

446   sampling time (Figure 3b). For NAP, MANOVA shows that there were also no

447   differences between the types of filters (Control, FEco or Mix filters). However, the

448   tests indicate there was at least one concentration different in relation to the others at

449   times 3, 6 and 24 hours ($p = 0.01$). The specific analysis of contrasts identified that the

450   difference was between 3 and 24 hours (Table S7). At the sampling time of 24 hours the

451   effluent concentration of NAP was lower than in the two previous sampling times, with

452   the values of the sample means as 0.02 µg L^{-1} in the time of 3 hours; 0.01 µg L^{-1} at 6

453   hours; and 0.001 µg L^{-1} at 24 hours after the contamination of the filters.

454

455   ### 3.5.2. Removal of personal care products

456   The removal of personal care products by ecological filters was lower than the

457   removal of pharmaceutical compounds; this may have been due to the fact MEP and

458   BP-3 were found with high concentrations in the Lobo reservoir water as discussed

459   above. However, MEP and BP-3 had similar removals of on average 70 % and 71 %,

460   respectively (Figure 4). On the other hand, Pompei et al. (2017) reported 100 % removal

461   of 2 µg L^{-1} of MEP and BP-3 by household SSF. However, these compounds were not

462   found in the water of Regent's Park as identified in the Lobo reservoir water. Verlicchi

463   et al. (2014) performed a literature review on the removal of personal care products by

464   wetlands in Europe, North America and Asia, showing that removal was influenced

465   mainly by redox potential, temperature, hydraulic retention time and affluent

466   concentration of the compound. This may explain the difference between the findings

467   by Pompei et al. (2017) and ours. Furthermore, when compared with other treatment

468   processes the removal of MEP and BP-3 was not as high as those achieved by AOPs

469   (Tayo et al., 2018). However, it should be noted that Gomes et al. (2017) reported the

470   generation of toxic by-products of paraben which are not completely mineralized when

471   photocatalytic ozonation using TiO_2 was used.

472   Finally, despite the differences in removal of MEP in the Control filter in

473   relation to the other filters (Figure 4b), MANOVA tests show that there were no

474   difference between the treatments (Control, FEco or Mix filters) ($p > 0.05$), between

475   sampling times of 3, 6 and 24 hours ($p = 0.35$), and between types of filter and sampling

476   time ($p > 0.05$). For BP-3, the MANOVA tests show there were no difference between

477   the treatments (Control, FEco or Mix filters) ($p > 0.05$), but there was a difference

478   between sampling time ($p = 0.02$). The specific analysis of contrasts identified that the

479   difference was between 3 hours (0.99 µg L^{-1}) and 24 hours (0.35 µg L^{-1}) (Table S7).

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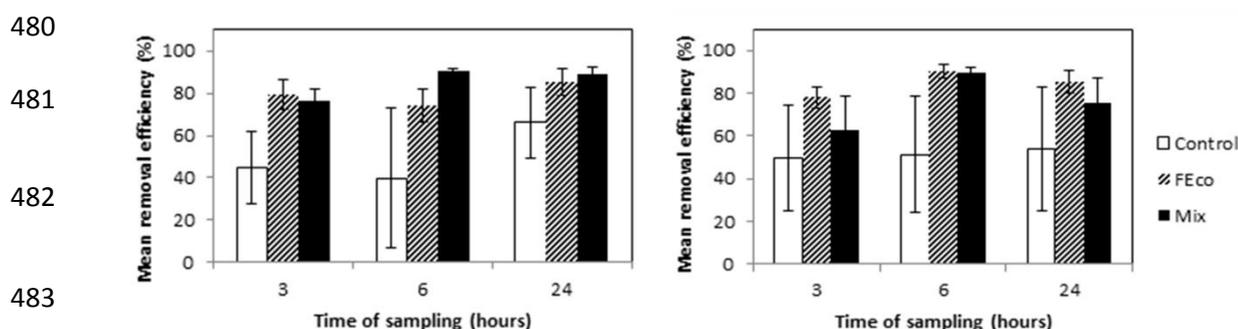
484   **Figure 4:** Mean removals of personal care products for a) BP-3 and b) MEP, in Control

485   filter (n = 9), FEco (n = 27) and Mix (n = 27).

486

487   **4. Conclusions**

488   The results of water quality parameters indicated that the water treated by the

489   ecological filters was within the standard of potability from Brazil. It is noted that

490   filtered water needs to be disinfected for human consumption to totally remove

491   coliforms.

492   The target PPCPs were identified in the Lobo reservoir water in the range of µg

493   L^{-1}. The personal care products were detected with 100 % frequency in samples, and in

494 high concentrations compared to the pharmaceutical compounds. These results were

495 attributed to recreational use of the reservoir and wastewater effluent discharges.

496   Two DPs (DCF and BP-3) were identified in the reservoir and effluent filter

497 water samples. The fragment ions were identified, and a degradation path for both

498 compounds were proposed. To evaluate their removal by ecological filters a further

499 investigation on quantification of the DP compounds is recommended.

500   Ecological filters removed more of the pharmaceutical compounds (81 to 99 %) than

501 the personal care products (70 to 71 %). The statistical tests by MANOVA did not show

502 significant differences for any of the compounds in relation to the type of filter (Control,

503 FEco or Mix filters), showing the robustness of the ecological filtration system. Results

504 showed that the filters are resilient to an individual compound as to their mixture. Some

505 compounds (DCF, NAP, and BP-3) showed differences between some of the sampling

506 times, but this was probably due to the variation of background contamination in the

507 reservoir water and the spiked contamination of 2 $\mu g\ L^{-1}$.

508   In comparison with other advanced technologies (e.g. ozone, fenton, UV irradiation)

509 that may remove 100 % of our target PPCPs, the authors believe that with optimised

510 operational conditions, ecological filtration offers a low cost and chemical free

511 treatment option for the effective PPCP removal in decentralized systems.

512

518

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Figure 1a. +MS2 (292.00) CE (25): Exp 6, 4.331 to 6.393 min from ... Max. 3288.2 cps.

Fragmentation pathway: m/z 292 → (−H₂O) → m/z 274 → (−CO) → m/z 246 → (−CO) → m/z 218 → (−HCl, −CH₂, −H₂O) → m/z 150

Figure 1b — +MS2 (245.00) CE (25): Exp 12, 4.640 to 5.550 min fro... Max. 3742.4 cps.
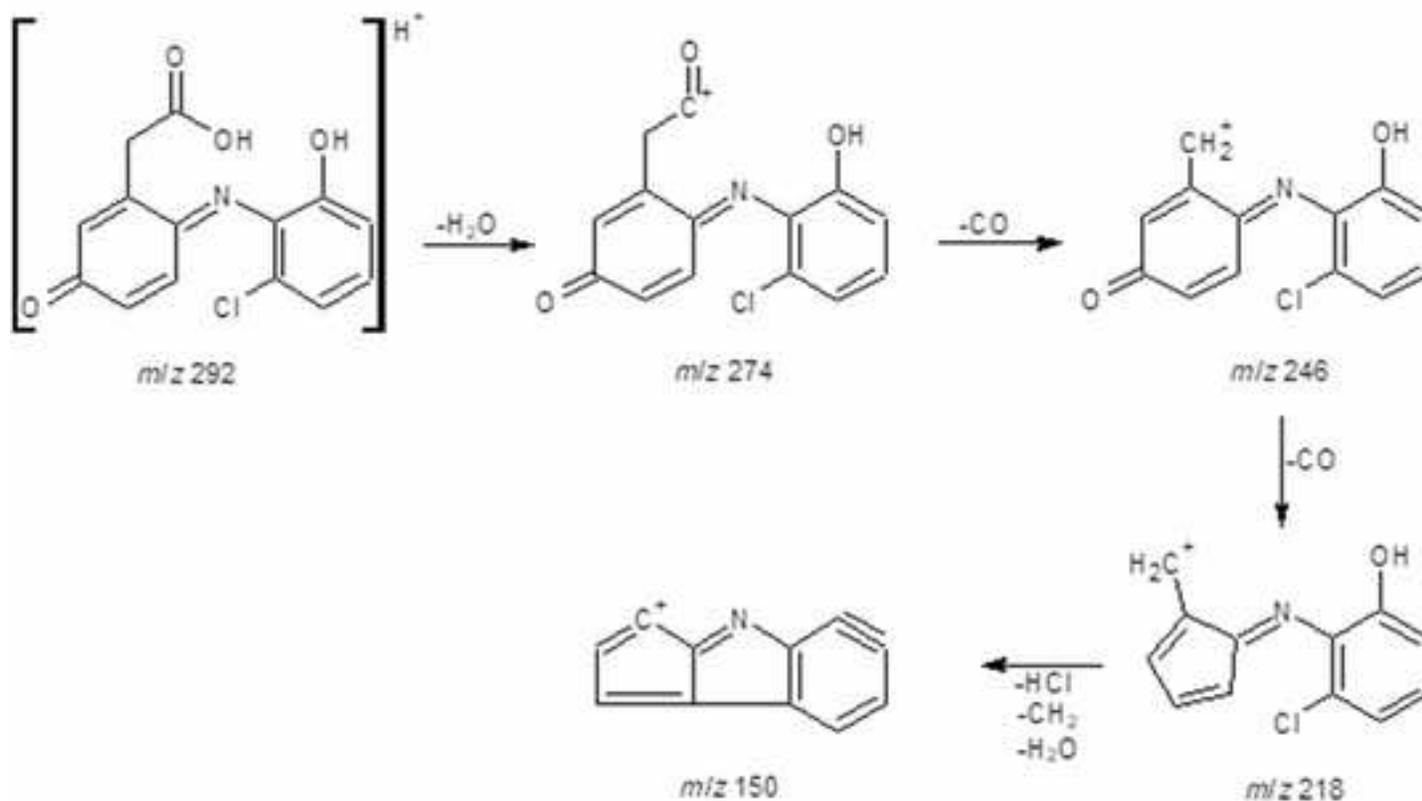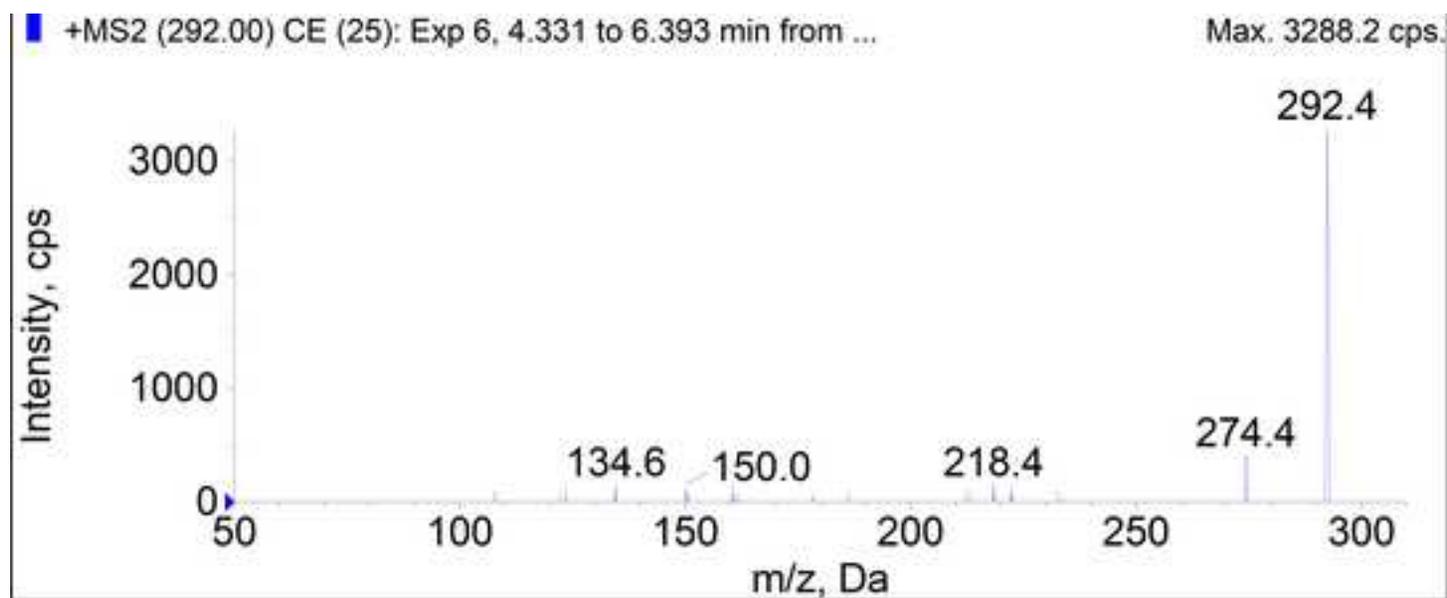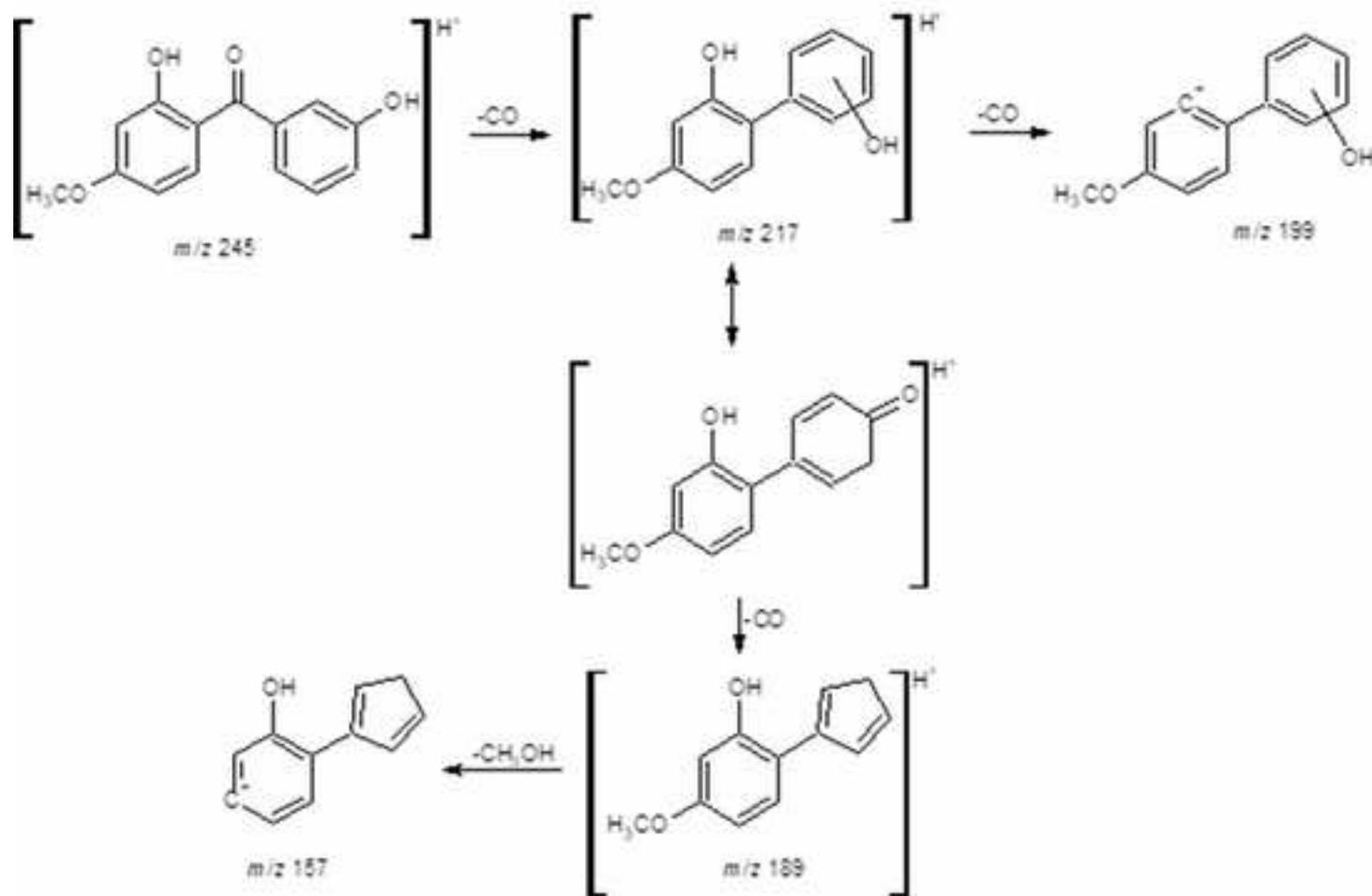
Figure 2
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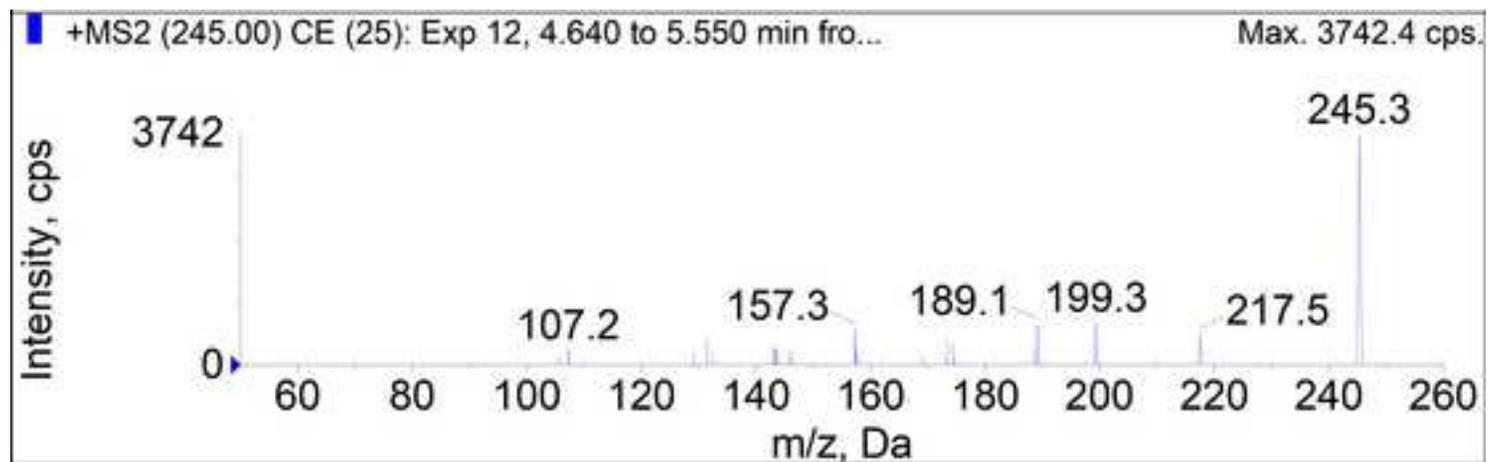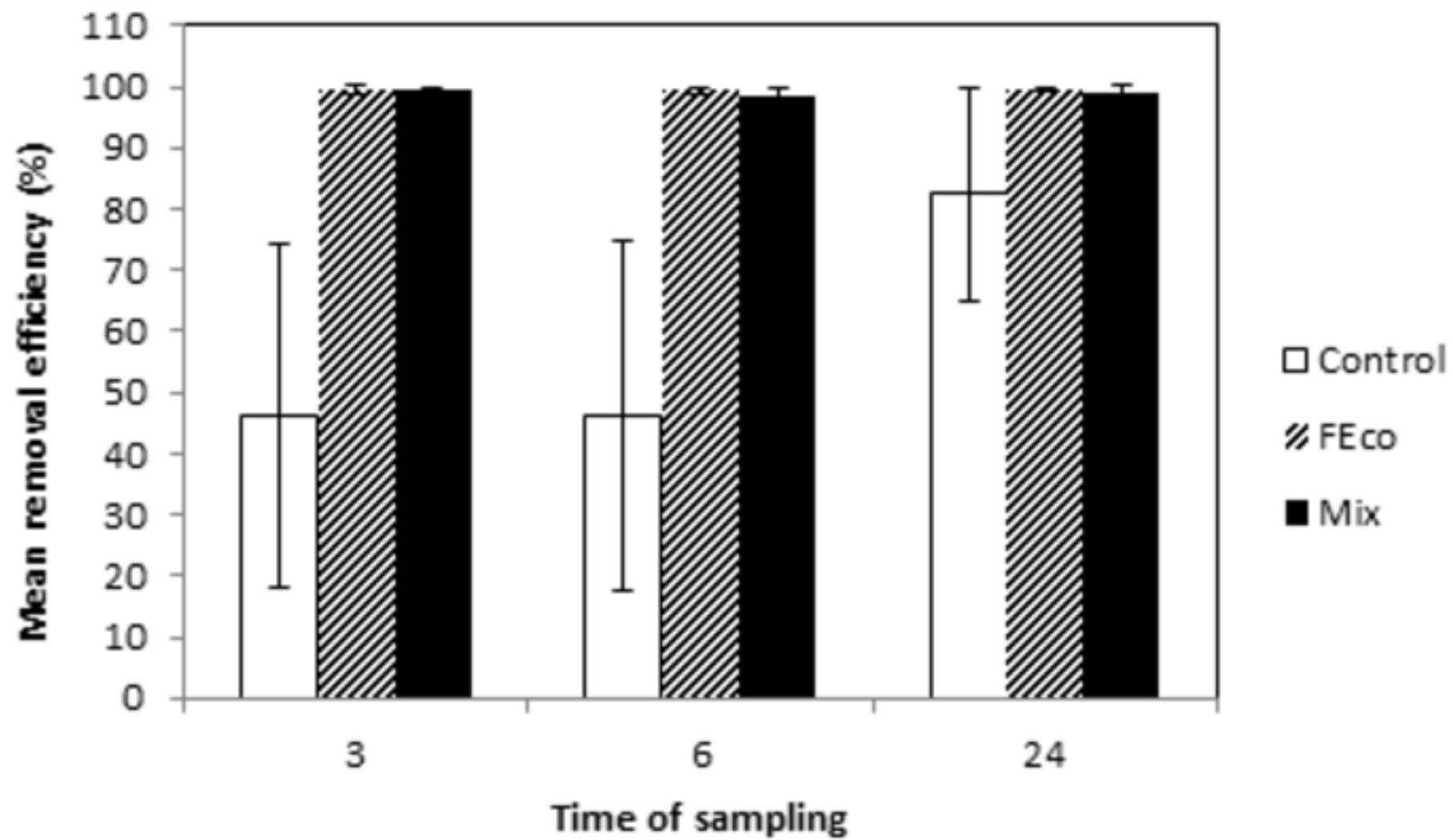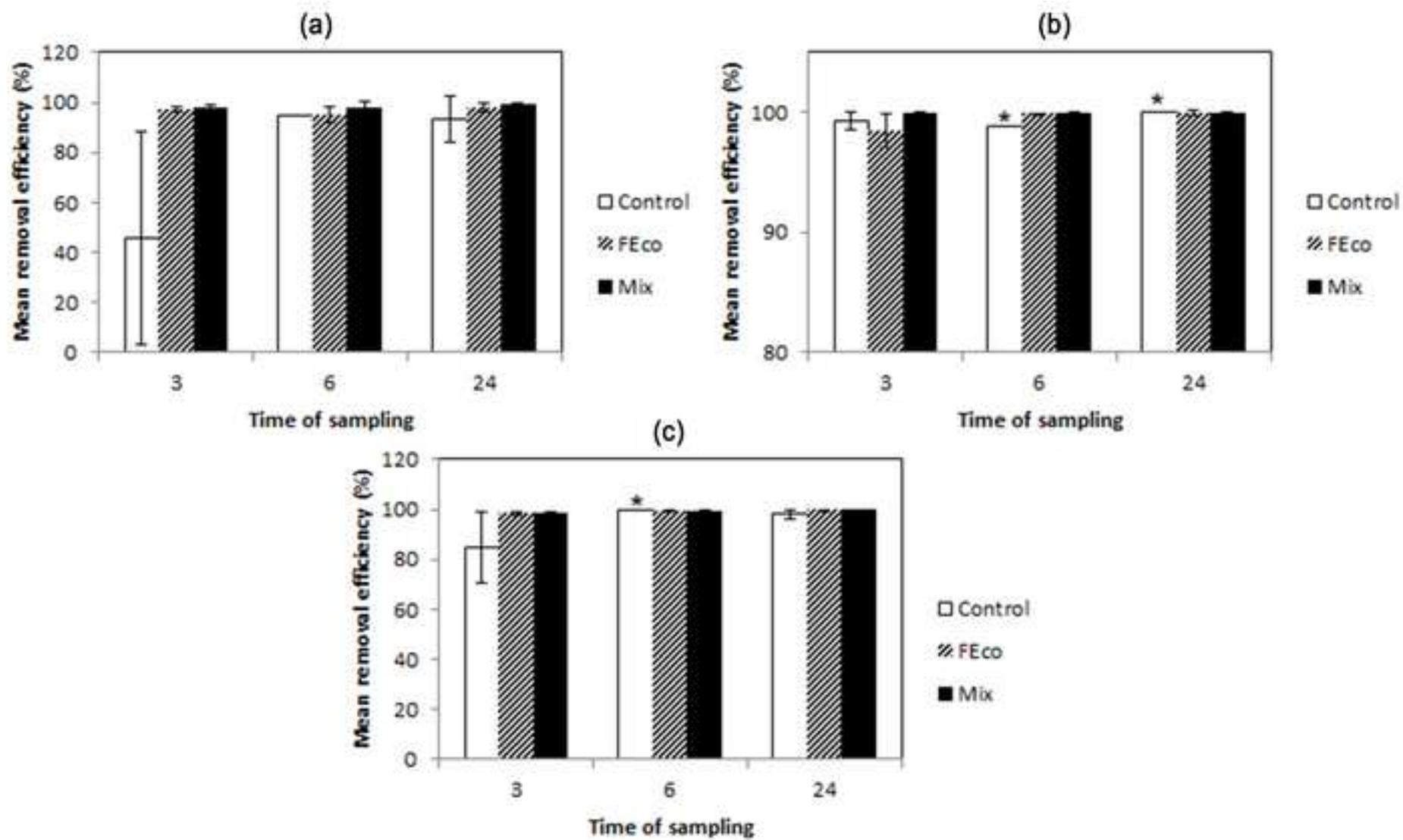**Figure 4**
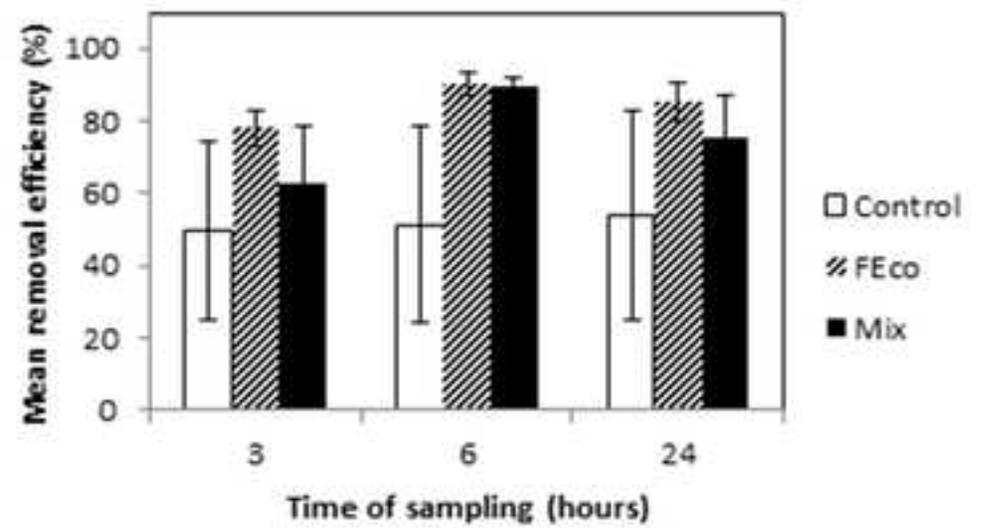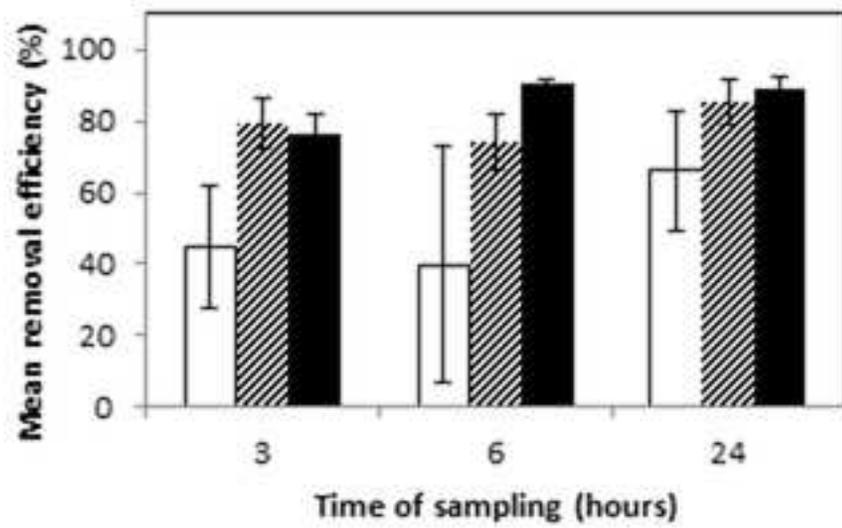**Click here to download high resolution image**

Table and Figure Captions

Table 1: Concentrations of the compounds detected by SPE-LC-MS/MS in water samples from the Lobo reservoir.

Figure 1: Identified fragment ions spectra of the degradation products (DPs), and proposed fragmentation mechanism for both water reservoir and effluent of the ecological filters: a) DP of DCF; b) DP of BP-3.

Figure 2: Mean removal (%) of ACT by ecological filtration, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27).

Figure 3: Mean removal of: a) DCF; b) IBU; c) NAP, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27). The * corresponds to the situations when, in one or more samples of the raw water, the compounds were not detected, disabling the calculation of the standard deviation and consequently the error.

Figure 4: Mean removals of personal care products for a) BP-3 and b) MEP, in Control filter (n = 9), FEco (n = 27) and Mix (n = 27).

Table 1: Concentrations of the compounds detected by SPE-LC-MS/MS in water samples from the Lobo reservoir.

PPCPs	Raw water			
	Min. Conc. ($\mu g\ L^{-1}$)	Max. Conc. ($\mu g\ L^{-1}$)	Mean Conc. ($\mu g\ L^{-1}$)	Frequency detected (%)
ACT	n.d.	0.13	0.03	85.70
DCF	n.d.	0.05	0.02	71.40
NAP	n.d.	0.10	0.01	85.70
IBU	n.d.	0.13	0.01	42.80
MEP	0.10	1192.39	170.87	100.00
BP-3	0.32	2.10	1.14	100.00

n.d.: not detected; <LOQ: less than the limit of quantitation.

Supplementary Material with no marked changes