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Modeling emerging contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing components of dissolved organic matter

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Surface water
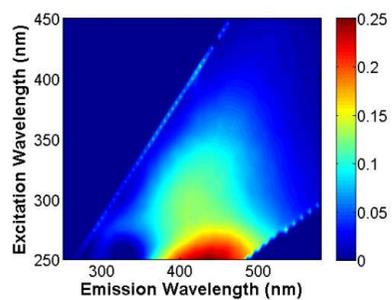
Synthetic water
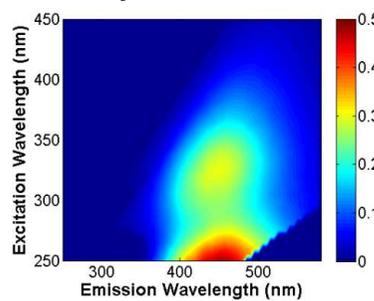
Wastewater
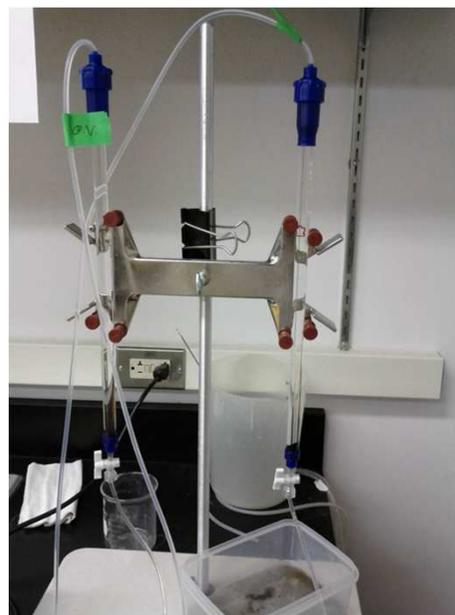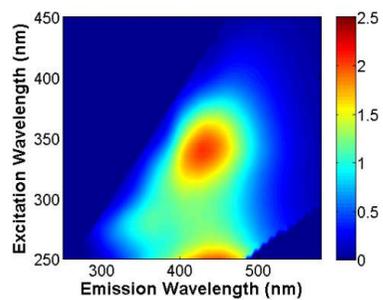
RSSCT for GAC adsorption

Carbamazepine

Fluorescence breakthrough (%)

Carbamazepine

UV Absorbance breakthrough (%)
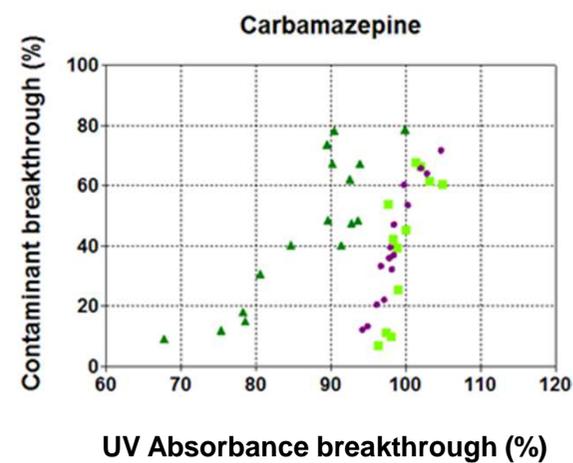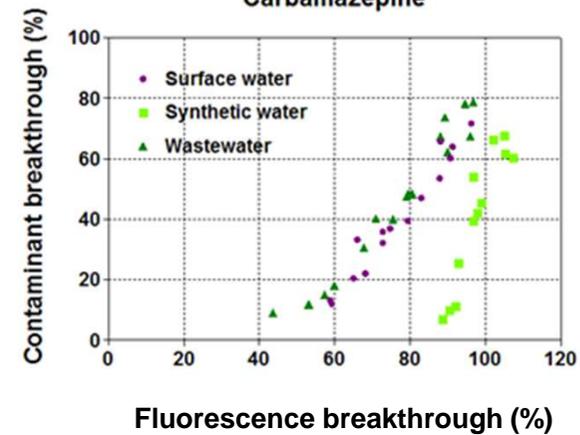
1 **Modeling emerging contaminants breakthrough in packed bed ad-**

2 **sorption columns by UV absorbance and fluorescing components of**

3 **dissolved organic matter**

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15 **ABSTRACT**

16 This study investigated, using rapid small-scale column testing, the breakthrough of dissolved

17 organic matter (DOM) and eleven emerging organic contaminants (EOCs) during granular acti-

18 vated carbon (GAC) filtration of different water qualities, including wastewater, surface water

19 and synthetic water (riverine organic matter dissolved in deionized water). Fluorescing organic

20   matter was better adsorbed than UV absorbance at 254 nm (UV_{254}) and dissolved organic carbon

21   (DOC) in all tested water. Furthermore, highest adsorption of DOM (in terms of DOC, UV_{254}

22   and fluorescence) was observed during wastewater filtration. UV absorbing DOM had fast and

23   similar breakthrough in surface water and synthetic water, whereas fluorescence breakthrough

24   was very rapid only in synthetic water. PARAFAC modeling showed that different fluorescing

25   components were differently adsorbed during GAC process. Particularly, fluorescing compo-

26   nents with maxima intensity at higher excitation wavelengths, which are corresponding to hu-

27   mic-like fluorescence substances, were better removed than other components in all waters. As

28   opposed to DOM, EOCs were better adsorbed during synthetic water filtration, whereas the fast-

29   est EOCs breakthrough was observed during filtration of wastewater, which was the water that

30   determined the highest carbon fouling. Exception was represented by long-chained perfluoroal-

31   kylated substances (i.e., PFOA, PFDA and PFOS). Indeed, adsorption of these compounds re-

32   sulted independent of water quality. In this study was also investigated the applicability of UV_{254}

33   and fluorescing PARAFAC components to act as surrogates in predicting EOCs removal by

34   GAC in different water matrices. Empirical linear correlation for the investigated EOCs were de-

35   termined with UV_{254} and fluorescing components in all water qualities. However, fluorescence

36   measurements resulted more sensitive than UV_{254} to predict EOC breakthrough during GAC ad-

37   sorption. When the data from all water qualities was combined, good correlations between the

38   microbial humic-like PARAFAC component and EOC removals were still observed and they re-

39   sulted independent of water quality if considering only real water matrices (wastewater and sur-

40   face water). On the contrary, correlations between EOC removals and UV_{254} removals were in-

41   dependent of water quality when combining data of surface waters and synthetic water, but a dif-

42   ferent correlation model was needed to predict EOCs breakthrough in wastewater.

1. Introduction

46 The occurrence of pharmaceuticals, steroid hormones, pesticides and personal care products, col-

47 lectively termed as emerging organic contaminants (EOCs) or contaminants of emerging concern

48 (CECs), have been consistently reported for over a decade in different water matrices, including

49 wastewater, surface water and drinking water (Benotti and Brownawell, 2007; Dickenson et al.,

50 2011; Focazio et al., 2008). Wastewater treatment plants (WWTPs) have been recognized as sig-

51 nificant hotspots for the transfer of EOCs into the environment (Michael et al., 2013; Vieno et

52 al., 2005), and with the increased focus on implementing potable water reuse schemes around the

53 world, there is a greater possibility of these wastewater derived contaminants entering drinking

54 water sources (Al-Rifai et al., 2007; Dickenson et al., 2011; Focazio et al., 2008). While effects

55 of many EOCs on public health remain largely unknown, studies have shown that some of these

56 contaminants can have drastic effects on aquatic organisms at concentrations typical for

57 wastewater discharges (Bevans et al., 1979). Other studies have demonstrated that a combination

58 of EOCs can have synergistic effects on some organisms (Carlsson et al., 2006; Daughton and

59 Ternes, 2009).

60 Advanced treatment technologies have been implemented in water reuse systems and drinking

61 water treatment plants as effective means to attenuate EOCs (Roccaro, 2018; Wert et al., 2009;

62 Wols et al., 2013). Advanced oxidation processes (AOPs) like ozone and UV with addition of

63 hydrogen peroxide, or high pressure membrane filtration have proven to remove many EOCs

64 from water (Kim et al., 2007; Wert et al., 2009; Wols et al., 2013), but with some drawbacks. For

3

65   example, studies have shown that AOPs produce transformation products of generally unknown

66   toxicity (Jia et al., 2015; Rizzo, 2011), whereas membrane processes generate concentrated brine

67   streams and entail relevant treatment costs (Roccaro et al., 2013). In contrast, adsorption pro-

68   cesses like granular activated carbon (GAC) are economically sustainable, do not result in trans-

69   formation products and are capable of removing a wide range of EOCs (Kim et al., 2007;

70   Roccaro et al., 2013; Snyder et al., 2007).

71   The analysis of EOCs at trace levels in water is laborious, time-consuming and expensive. In ad-

72   dition, it requires sophisticated analytical equipment and highly trained technicians. Hence, the

73   use of surrogate parameters that can accurately predict the removal of EOCs in a simple, fast,

74   and cost-effective manner is highly desirable. Spectroscopic parameters like UV absorbance and

75   fluorescence have been shown to be useful monitoring tools for both conventional and emerging

76   water contaminants in different natural and engineered water systems (Carstea et al., 2016;

77   Korshin et al., 2018; Sgroi et al., 2018, 2017a, 2017b). Particularly, extensive recent research in

78   this area has shown the possibility to accurately predict EOCs removal during various advanced

79   treatments (e.g., ozonation, UV/H_2O_2, adsorption) by surrogate parameters based on spectroscop-

80   ic measurements (Chys et al., 2018, 2017; Gerrity et al., 2012; Korshin et al., 2018; Merel et al.,

81   2015; H. W. Yu et al., 2015; Zietzschmann et al., 2016a).

82   Studies focused on adsorption processes have discussed the performance of UV absorbance at

83   254 nm (UV_{254}) and total fluorescence (Φ_{tot}) indicators to predict EOCs removal by activated

84   carbons in both powered activated carbon (PAC) processes (Altmann et al., 2016; Zietzschmann

85   et al., 2014a; Ziska et al., 2016) and granular activated carbon (GAC) filter (Anumol et al.,

86   2015). The developed models provided excellent predictions of EOCs removal in different sec-

87   ondary or tertiary wastewater effluents and these models resulted independent of the wastewater

88 quality (Altmann et al., 2016; Anumol et al., 2015; Zietzschmann et al., 2016a; Ziska et al.,

89 2016).

90 During adsorption processes, the most crucial factor impacting EOCs removal is the competition

91 caused by the presence of organic matter (OM) in water. OM is different in concentration and

92 composition between different waters (e.g., surface water and wastewater), and aspect of OM

93 character such as molecular weight distribution, degree of hydrophobicity, and charge distribu-

94 tion affect its adsorbability as well as the extent to which it decreases micro-pollutant adsorption

95 through direct competition and pore blockage, collectively termed fouling (Shimabuku et al.,

96 2017; Velten et al., 2011; Zietzschmann et al., 2014b). A recent study observed significant dif-

97 ferences between EOCs breakthrough curves in drinking water and wastewater effluent and these

98 differences were attributed to the concentrations of the low molecular weight (LMW) acid and

99 neutral organics of the waters (Zietzschmann et al., 2016b). Presenting the relative EOC concen-

100 trations over the specific throughput of the LMW organics, the EOC breakthrough curves in

101 drinking water and WWTP effluent superimposed each other (Zietzschmann et al., 2016b). In a

102 further study, the adsorption of organic micro-pollutants onto PAC was compared between re-

103 gionally different waters within two groups, namely five drinking waters and seven wastewater

104 effluents. Correlations between EOC removals and UV_{254} removals were independent of the wa-

105 ter quality within the respective group, but different regression parameters were obtained for

106 drinking waters and wastewaters (Zietzschmann et al., 2016a). To date, similar studies have not

107 been accomplished using fluorescence measurements and during GAC filtration.

108 Fluorescence spectroscopy is a rapid, cost-effective, reagentless technique that requires little or

109 no sample preparation prior to analysis. The acquisition of 3-dimensional excitation-emission

110 matrices (EEMs) provides a 'map' of contributions of different component classes comprising

111   dissolved organic matter (DOM) (Carstea et al., 2016; Henderson et al., 2009). EEM of natural

112   waters and wastewater tend to have distinct features with maxima located at characteristic com-

113   binations of excitation and emission wavelengths. Thus, an important advantage of fluorescence

114   versus UV–vis absorbance is the potential for discriminating between different sources of chro-

115   mophoric DOM that absorb at similar wavelengths. A further advantage of fluorescence is that

116   sensitivity is typically 10–1000x that of UV absorption spectroscopy (Carstea et al., 2016;

117   Henderson et al., 2009; Korshin et al., 2018).

118   EEMs offer varied possibilities of data interpretation, from simple peak-picking and Fluores-

119   cence Regional Integration to the more complex Parallel Factor Analysis (PARAFAC) and Self-

120   Organizing Maps (Carstea et al., 2016; Chen et al., 2003; Murphy et al., 2013). Among these

121   methods, PARAFAC is becoming the most popular in the research community due to its ability

122   to mathematically decompose the complex fluorescence spectra into a finite number of potential-

123   ly overlapping independent components characterized by their distinct spectroscopic features.

124   Such deconvolution helps discriminate and ascertain contributions of different DOM types and

125   sources, and provides an useful tool for DOM characterization in water (Murphy et al., 2013,

126   2011).

127   Accordingly, objectives of this study were: (i) to explore breakthrough curves of different DOM

128   components identified by PARAFAC analysis in different water matrices, including wastewater

129   and surface water during GAC filtration; (ii) to evaluate and compare the ability of different

130   spectroscopic indexes based on fluorescence and UV absorbance measurements to predict EOCs

131   breakthrough using surface water and wastewater. In this study, GAC processes have been simu-

132   lated using rapid small scale column testing (RSSCT), which are bench scale tools able to accu-

133   rately predict GAC performance in a short period of time (Anumol et al., 2015; Crittenden et al.,

134   1991). In addition, two different surface waters have been utilized, a real surface water and a

135   synthetic surface water obtained dissolving concentrate riverine organic matter in deionized (DI)

136   water. In this latter case, no salts were added in water, and thus, the impact of ionic strength in

137   the adsorption process is missing.

2. Materials and methods

2.1. Materials and tested waters

140   All purchased solvents, standards, and reagents were of high purity. The details concerning these

141   materials are reported in the Supplementary material section (Text S1).

142   Waters tested in this study included a non-chlorinated secondary wastewater effluents from the

143   city of Tucson (Arizona, USA), a surface water collected from the Central Arizona Project

144   (CAP), which is a diversion canal that convey water from the Colorado River to Central and

145   Southern Arizona, and a synthetic water obtained dissolving Suwannee River Natural Organic

146   Matter (NOM) (International Humic Substances Society, St. Paul, MN, USA) in DI water. All

147   water were filtered using a 0.45 μm cartridge filter (GE Healthcare, USA) prior to testing. Water

148   quality parameters after filtration are provided in Table 1.

2.2. Selection of EOCs

150   Eleven EOCs including pharmaceutical, personal care products, and perfluorinated compounds

151   (Table 2) were selected based on their octanol-water partition coefficients (log K_{ow}), charge, oc-

152   currence in water, and availability of authenticated standards. Compounds were selected in order

153   to have in water micropollutants with very different adsorption characteristics. To account for

154   ionic effects on the log K_{ow}, a pH corrected log D_{ow} term was calculated for the pH of each water

155 (Martínez-Hernández et al., 2014). In surface water and synthetic water, compounds were spiked

156 using a highly concentrated stock (100-250 µg/mL) in 50:50 (v/v) HPLC-water:methanol solu-

157 tion. In wastewater, EOCs were present at naturally occurring concentration. Due to the small

158 amount of spiked compounds solution (100 µL), the change in dissolved organic carbon (DOC)

159 was negligible. Relevant chemical properties and concentrations of EOCs (after spiking) in water

160 are reported in Table 2. In surface water spiked compounds were summed to naturally occurring

161 concentrations.

162 ### *2.3. Analytical methods*

163 All EOCs were analyzed using an automated liquid chromatography online SPE system coupled

164 to an Agilent 6460 triple-quadrupole mass spectrometer (Agilent Technologies, Santa Clara,

165 CA). The method required only 1.5 ml of sample thus allowing minimal sample collection during

166 the experiment. Resulting reporting limits ranged from 1 to 20 ng/L. Further details of the analyt-

167 ical method are available in previously published literature (Anumol and Snyder, 2015) and are

168 also briefly described in Supplementary material section (Text S2; Table S1 – S2). For dissolved

169 organic carbon (DOC) analysis, samples were filtered through 0.45 mm hydrophilic polypropyl-

170 ene filter (GHP Membrane Acrodisc, Pall Life Sciences) and acidified to pH < 3 with hydrochlo-

171 ric acid. A Shimadzu TOC-L$_{CSH}$ (Kyoto, Japan) total carbon analyzer was used for quantifica-

172 tion.

173 Ultraviolet light absorbance was analyzed using Varian Cary 50 UV/Vis spectrophotometer. Flu-

174 orescence data were collected using Varian Cary Eclipse fluorescence spectrophotometer with

175 the scanning range from excitation wavelength 200 nm to 450 nm at an interval of 5 nm and

176 emission wavelength from 250 nm to 580 nm at the interval of 1 nm. Excitation and emission slit

177 widths were both set at 5 nm. The Raman scatter effect was minimized by subtracting EEMs of

178 pure DI water from the sample EEMs; any negative intensity values produced by this subtraction

179 were converted to zero values. Then, the emission intensity data were normalized to the Raman

180 peak area of an emission wavelengths scan of DI water samples collected at the interval of 1 nm

181 and related to an excitation wavelength of 350 nm to produce fluorescence intensities in Raman

182 unit (RU) (Murphy et al., 2010). All the EEMs were subjected to inner filter effect correction ac-

183 cording to the methodology proposed by MacDonald et al. (MacDonald et al., 1997). Non-

184 trilinear data related to the Rayleigh scattering were eliminated and interpolated from either side

185 of the scatter band following the tutorial published by Murphy et al. (Murphy et al., 2013). Re-

186 gional integration was conducted according to previously published literature (Chen et al., 2003;

187 Sgroi et al., 2016) to calculate the total fluorescence intensities for each sample.

188 The point of zero charge (p_{zc}), defined as the pH at which the number of negatively and positive-

189 ly charged sites on the surface of the carbon are equal (net charge on surface = 0) was experi-

190 mentally determined by calculating the slurry pH (Redding et al., 2009).

2.4. PARAFAC modeling

192 PARAFAC analysis was carried out using the drEEM toolbox (Murphy et al., 2013). PARAFAC

193 modeling was performed independently for each tested water to avoid that source diversity un-

194 dermined the accuracy of the model (H. Yu et al., 2015). Fluorescence data set of wastewater in-

195 cluded 74 EEMs, data set of surface water and synthetic water included 25 EEMs each. Non-

196 negative constraints were applied for excitation and emission loadings. In order to examine the

197 soundness of the PARAFAC modeling and to identify the number of fluorescence components, a

198 series of criteria was applied to each EEM dataset: (1) the examination of the core consistency,

199 (2) the evaluation of the shape of the spectral loading, (3) the leverage analysis regarding the in-

200 fluence of a specific sample or certain excitation and emission wavelengths, (4) the residuals

201 analysis and (5) the split half analysis. No outlying samples emerged during the PARAFAC

202 modeling but it was needed to exclude part of the EEMs with excitation wavelength < 250 nm

203 that exerted disproportionate leverage on the model and impeded a correct model validation. A

204 PARAFAC model with 4 components was validated for the wastewater; a PARAFAC model

205 with 2 components was validated for the surface water, whereas a PARAFAC model with 3

206 components was validated for the synthetic water. The fluorescence intensity at the maximum for

207 each PARAFAC component was used as fluorescing index to monitor breakthrough curves dur-

208 ing GAC adsorption.

209 ### *2.5. RSSCT procedure*

210 All RSSCTs were designed according to the constant diffusivity (CD) model based on previous

211 studies (Anumol et al., 2015; Redding et al., 2009). All the RSSCTs were performed using the

212 same GAC (NORIT DARCO 12x40) with a simulated full-scale empty bed contact time (EBCT)

213 corresponding to 5.2 min. General characteristics of the used carbon are reported in Table S3.

214 Before the experiment, fresh carbon was crushed with a mortar and pestle and sieved using the

215 U.S standard sieves. The fraction between mesh size #100 and #140 (d_p = 0.125mm) was collect-

216 ed. The carbon was washed thoroughly with ultrapure water and stored in a sterile environment

217 until use. The crushed carbon slurry was placed in a 10 mm inner diameter glass column with

218 polypropylene caps and fittings (Kimble Chase, New Jersey). Care was taken in selecting the

219 column so that the aspect ratio was >10 to avoid wall effects and channeling (Knappe et al.,

220 1997). The flowrate of the water was adjusted using a peristaltic pump to achieve the desired

221 EBCT. Once the experiment was started, GAC effluent samples were collected periodically for

222   EOCs, DOC, UV and fluorescence analysis while influent control samples were collected daily

223   to determine if there was any degradation of EOCs in the feed water. Details of the RSSCT de-

224   sign with comparison to a full-scale system operating with the same EBCT are presented in Ta-

225   ble S4.

3. Results and discussion

3.1. GAC adsorption of organic matter

228   DOM concentration in water is typically measured by bulk parameters such as DOC, UV ab-

229   sorbance and fluorescence. Particularly, this latter method is growing in popularity to character-

230   ize DOM, as it is simple and provides a large amount of information. As previously discussed,

231   PARAFAC analysis is a useful tool for EEMs interpretation. Indeed, this method enables the de-

232   convolution of complex EEMs into independent components that represent groups of similarly

233   behaving fluorophores (Murphy et al., 2011; Sgroi et al., 2017b). In this study, the three devel-

234   oped PARAFAC models identified a total number of five independently varying fluorescing

235   components. Within these five components, four fluorescing components were identified in

236   wastewater, two components in surface water and three components in synthetic water. Figure 1

237   shows the spectral fingerprint of the identified fluorescing components, denoted henceforth as

238   C1–C5. Wavelengths corresponding to the positions of the excitation and emission maxima are

239   reported in Table S5 – S7, whereas the excitation and emission loadings are shown in Figure S1

240   – S3. Based on the position of the excitation and emission peaks ($\lambda_{ex}/\lambda_{em}$), components C1

241   ($\lambda_{ex}/\lambda_{em}$ = <250/355-400 and 285-305/355-400), C2 ($\lambda_{ex}/\lambda_{em}$ = <250-265/470-495 and 365-

242   395/470-495), C4 ($\lambda_{ex}/\lambda_{em}$ = <250/435 and 345/435), and C5 ($\lambda_{ex}/\lambda_{em}$ = <250-250/450 and

243   325/450) were identified as humic and fulvic-like fluorescence (Ishii and Boyer, 2012; Murphy

11

244   et al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015). Specifically, component C1 represents the

245   contribution of a microbial humic-like fluorescence, whereas component C2 that of a terrestrial

246   humic-like component. These two components have been previously observed in both surface

247   water and wastewater (Murphy et al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015). In this study,

248   component C1 was common to all the investigated waters, component C2 was found in

249   wastewater and synthetic water. Component C4 corresponds to a group of humic-like fluorescing

250   species found in prior studies in high nutrient and wastewater impacted environments (Murphy et

251   al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015; Yu et al., 2010). In this study, component C4

252   was found only in wastewater. Component C5 is commonly abundant in DOM dominated by ter-

253   restrial precursor material and it is generally absent from wastewater (He and Hur, 2015; Ishii

254   and Boyer, 2012). Accordingly, in this study component C5 was detected only in surface and

255   synthetic waters. Component 4 and 5 have both two fluorescence peaks situated at similar wave-

256   length positions. However, component C4 shows its maxima intensity at an excitation wave-

257   length of 435 nm, whereas component C5 has its maxima intensity at excitation wavelengths <

258   250 nm. Finally, protein and tryptophan-like fluorescing compounds, observed in prior studies as

259   typical fluorescence component of wastewater matrices, are associated with component C3

260   ($\lambda_{ex}/\lambda_{em}$= 275/330) (Murphy et al., 2011; Sgroi et al., 2017a; H. Yu et al., 2015).

261   The Fluorescence EEMs provide a qualitative estimate of treatment process efficacy and are

262   shown in Figure 2. As seen for all waters, initially there is a decolorizing effect in the EEMs as

263   the GAC is effective in removing fluorescent organic matter in all regions of the EEM compared

264   to the influent to the column. However, this decolorizing effect was very evident in wastewater

265   and in a less extent in surface water. In the synthetic water the decolorizing effect was limited.

266   With time, the active sites on the GAC are exhausted and gradually increased breakthrough of

267   fluorescent matter is seen in the three waters. The amount of breakthrough varies based on water

268   quality and bed volume when the carbon and EBCT are constant. These observations suggest

269   that DOM was removed in a different way from the three waters. It can be better observed in

270   Figure 3, which shows the breakthrough curves of the identified PARAFAC components. In

271   wastewater, breakthrough of components C1, C2, C4 was negligible at bed volumes (BVs) < 5,

272   except component C3 that when the experiment started showed immediately a breakthrough of

273   16%. Surface water had an immediate breakthrough of around 20% for component C1 and C5,

274   whereas organic matter in synthetic water was scarcely adsorbed and components C1, C2 and C5

275   showed an immediate breakthrough higher than 50%. It is interesting to observe that PARAFAC

276   components with maxima fluorescence intensity at higher excitation wavelengths, which are cor-

277   responding to humic-like fluorescence substances, were better removed than other components in

278   all waters. Component C4 was the component most adsorbed during the GAC process, followed

279   by the microbial humic-like component C1 (Figure 3).

280   Various DOM characteristics affect its adsorption in GAC filters and these include aromaticity,

281   degree of hydrophobicity, molecular size, charge distribution and ability to form hydrogen bonds

282   with the GAC surface (Shimabuku et al., 2017; Velten et al., 2011; Zietzschmann et al., 2015,

283   2014b). Particularly, recent studies showed that DOM adsorbability decreases when aromaticity

284   increase (Shimabuku et al., 2017). Accordingly, in this study component C3, which is typical of

285   aromatic protein and tryptophan-like substances, was the less adsorbed fluorescing component of

286   wastewater (Figure 3). In addition, it was shown that fluorescence components differ also for

287   molecular size (Wu et al., 2003), and that small sized DOM contains better adsorbable com-

288   pounds, which largely affects micro-pollutants fouling (Zietzschmann et al., 2014b). Further-

289   more, the charge of DOM and ionic strength of waters may have had a significant role in the ad-

290 sorption process, particularly determining the low adsorbability of DOM of synthetic water. The

291 pH_{zc} for the Norit DARCO 12 x 40 was found to be 6.4, which meant that at pH of tested waters,

292 its surface was negatively charged in surface water (pH 8.4) and wastewater (pH 7.5), and slight-

293 ly negatively charged in synthetic water (pH 6.7). Because of the presence of carboxylic acid and

294 phenolic groups in the DOM structure, DOM carries a negative charge at these pH values

295 (Perdue and Lytle, 1983). In these circumstances, surface-DOM electrostatic interaction should

296 oppose adsorption, because both DOM and carbon surface are negatively charged. However, it

297 has been demonstrated that if salts are present in water the ionic strength of water can increase

298 adsorption and salts effectively screen electrostatic repulsion (Bjelopavlic et al., 1999). In syn-

299 thetic water the absence of salts along with effects related to manipulation of Suwannee River

300 NOM during extraction and concentration processes may have reduced the adsorption capability

301 of this DOM. However, more research is needed to understand this phenomenon.

302 The rate of breakthrough of the different bulk parameters of water considered in this study was in

303 the order: DOC > UV_{254} > fluorescence indexes ($Ø_{tot}$ and PARAFAC components). It is in

304 agreement with previous studies, where it has been hypothesized fluorescence DOM to be lower

305 in molecular weight than UV-absorbing DOM or DOC measured compounds to explain its pref-

306 erential adsorption (Anumol et al., 2015; Shimabuku et al., 2017; Velten et al., 2011). In Figure 4

307 is reported a comparison for breakthrough curves of DOC, UV_{254}, $Ø_{tot}$ and PARAFAC compo-

308 nents in the three tested waters. Wastewater showed the slowest breakthrough for all these pa-

309 rameters except component C1, which was better adsorbed in surface water. On the other hand,

310 the fastest breakthrough for all the bulk parameters was always observed in synthetic water. The

311 breakthrough of UV_{254} was very fast and very similar in surface water and synthetic water, sug-

312 gesting that typical UV-absorbing DOM of surface water is scarcely adsorbed and probably non-

313   affected by ionic strength of water and/or other electrostatic interactions. On the contrary, fluo-

314   rescence DOM was better adsorbed in surface water than in synthetic water. $\emptyset_{tot}$ had a similar

315   breakthrough in surface water and wastewater. However, differences can be observed in the ad-

316   sorption process if considering specific fluorescing PARAFAC components. For example, the

317   adsorption rate of component C1 was similar in surface water and wastewater until 60% break-

318   through. Then, C1 breakthrough was faster in wastewater, probably due to the higher carbon

319   fouling of this water. Thus, these data show that DOM adsorption in GAC filter is a very com-

320   plex process, which is strongly influenced by DOM composition and charge distribution. In addi-

321   tion, different bulk parameters of water, such as DOC, UV absorbance and various fluorescence

322   components, are measurements of different components of DOM, which are differently adsorbed

323   in GAC processes.

324   **_3.2. Breakthrough curves of EOCs_**

325   The breakthrough curves of four representative EOCs in GAC reactors are shown in Figure 5.

326   The complete set of breakthrough profiles for the eleven investigated EOCs in all water qualities

327   are shown in Figure S4. The fastest breakthrough (i.e., the lowest adsorption) for all the com-

328   pounds was always observed in wastewater. On the contrary, the slowest breakthrough and high-

329   est adsorption of EOCs was observed in synthetic water. Thus, adsorption dynamics of EOCs

330   were opposed to those of DOM. Indeed, in waters where a higher DOM adsorption and carbon

331   fouling was observed, EOCs have always shown lower adsorbability. These evidences suggest

332   that competition effect with DOM was the main reason of differences in EOCs adsorption ob-

333   served between the tested water qualities. Only exception was represented by the perfluoalkylat-

334   ed substances (PFAS), which had a similar breakthrough in all water qualities and seemed to not

335   be influenced by the rate of DOM adsorption and carbon fouling. PFOA, PFDA and PFOS are

336 long-chained PFAS that due to the presence of a long hydrophobic chain are able to form molec-

337 ular aggregates which can be retained on the active surface (McCleaf et al., 2017; Zaggia et al.,

338 2016). Thus, adsorption of these compounds seems to be mainly related to hydrophobic interac-

339 tion, and the number of available active sites on activated carbon does not represent the main

340 limiting factor. This rationale may explain the similar breakthrough curves observed for long-

341 chained PFAS in waters with different content and quality of DOM. However, authors encourage

342 further research on this topic.

343 By an accurate analysis of breakthrough curves in Figure 5 and Figure S4, it can be observed

344 that, excluding PFAS compounds, breakthrough curves of EOCs in wastewater and surface water

345 almost overlapped each other during the initial phase of the GAC process, later breakthrough

346 was faster in wastewater due to the higher carbon fouling. Breakthrough curves for these two wa-

347 ters overlapped until ~20% of breakthrough for carbamazepine, trimethoprim and primidone, un-

348 til ~40% for gemfibrozil and until ~60% for sulfamethoxazole. This trend was also observed for

349 the breakthrough of PARAFAC component C1, as discussed previously. On the other hand,

350 breakthrough of EOCs in surface water was faster than in synthetic water during the initial phase

351 of the GAC process, whereas EOCs breakthrough curves tended to have similar values after 40%

352 – 80% breakthrough. Exceptions was ibuprofen, which had a very similar breakthrough in these

353 two waters, and sulfamethoxazole, where overlap of breakthrough curves was not observed. Fi-

354 nally, overlap of EOCs breakthrough curves was not observed when comparing GAC filtration of

355 wastewater and synthetic water.

356 ***3.3. Development of correlation models***

16

357 In this study, a regression analysis was carried to establish relationships between spectroscopic

358 indexes and EOCs removal during GAC filtration of wastewater, surface water and synthetic wa-

359 ter. Data was plotted as % breakthrough of surrogate parameter (x-axis) vs. % breakthrough of

360 EOC (y-axis). Only samples with breakthroughs between 5 and 95% were chosen for the correla-

361 tion models. This was done because the primary goal of this study is to develop a model which

362 can be used for tracking the breakthrough of EOCs, and to prevent clustering of data points at the

363 high and low end which would skew the R^2. The regression data for an individual water quality

364 indicate very good linear correlation when comparing UV_{254}, Φ_{tot} and PARAFAC fluorescing

365 components breakthrough with EOCs breakthrough. This suggests that all these spectroscopic

366 indexes can be used as surrogates to estimate EOCs breakthrough in a GAC process for a par-

367 ticular water quality. The regression parameters of the elaborated regression models for each wa-

368 ter quality and surrogate parameter are reported in Table S8 – S14. DOC breakthrough, on the

369 other hand, did not correlate well with EOCs breakthrough (Table S15) as observed in our previ-

370 ous study (Anumol et al., 2015). Thus, DOC was not considered for further elaborations. It is

371 noteworthy to observe that the slopes of the lines relating to breakthrough of EOCs and surrogate

372 parameters were much greater for UV_{254} compared to fluorescence indexes (Table S8 – S14) in-

373 dicating more EOCs removal per unit % change in UV_{254}, which showed a very limited range of

374 % breakthrough variation, particularly during surface waters filtration (>80 – 100%) (Figure 6).

375 It points to the potential greater sensitivity of fluorescence compared to UV_{254} when looking at

376 small changes in removal. Hence, fluorescence could be used as a better surrogate to predict

377 EOC attenuation in a GAC process compared to UV_{254}.

378 In Figure 6 and Figure S5 – S9 the data-points from all waters were combined to try to find a

379 unique empirical prediction model of EOCs breakthrough valuable for all water qualities and for

380 a particular carbon and EBCT. Plots of combined data were accomplished for all the developed

381 spectroscopic indexes. However, particular attention was given to spectroscopic parameters that

382 were concurrently available for all the investigated water qualities (i.e., UV_{254}, Φ_{tot} and PARA-

383 FAC component C1). From the plots in Figure 6 and Figure S9, it is possible to observe that Φ_{tot}

384 data-points from different waters were not well aligned, and, thus, this parameter does not seem

385 effective to predict EOCs breakthrough regardless of water quality. However, as reported in our

386 previous study (Anumol et al., 2015), this parameter is useful to predict EOCs removal during

387 adsorption process by an unique empirical correlation model when using different wastewater ef-

388 fluents. Correlations between EOC removals and UV_{254} removals were independent of the water

389 quality when considering only surface waters, but a different correlation model was needed to

390 predict EOCs breakthrough in wastewater (Figure 6 and Figure S8). This result is in agreement

391 with recent observation in PAC processes (Zietzschmann et al., 2016a). On the other hand, data

392 related to the microbial humic-like fluorescence PARAFAC component C1 were perfectly

393 aligned when using real water matrices, including wastewater and surface water. Hence, PARA-

394 FAC component C1 seem to be the surrogate parameter effective to predict EOCs breakthrough

395 independently of water qualities (Figure 6 and Figure S5). However, a different correlation mod-

396 el was needed to predict EOCs removal from the synthetic water using this fluorescing compo-

397 nent. This exception has to be ascribed to the unnatural fast breakthrough of DOM observed dur-

398 ing GAC filtration of this water. Regression parameters for correlation model developed using

399 combined data for the PARAFAC component C1 and UV_{254} absorbance are reported in Table 3.

400 Correlation models of combined data with the highest R^2 have been obtained for the PARAFAC

401 component C1. Excluding primidone ($R^2 = 0.777$), R^2 values were always > 0.85. Combined data

402 of surface and synthetic water have produced linear correlation for the UV_{254} parameter with R^2

403 > 0.7. Exception was sulfamethoxazole. Indeed, for this contaminant, correlation with UV_{254} data

404 had a low R^2 (0.302).

4. Conclusions

406 This study investigated the adsorption of DOM during GAC filtration from different water quali-

407 ties (i.e., wastewater, surface water and synthetic water) through the use of different bulk param-

408 eters of water, including DOC, UV_{254} and PARAFAC fluorescing components. Hence, the ability

409 of these parameters to predict EOCs breakthrough using different waters was evaluated. Based

410 on the results of the study, the following conclusions can be obtained:

411 • The different bulk parameters of water DOC, UV absorbance and fluorescence are meas-

412 urements of different components of DOM, which are differently adsorbed during GAC

413 processes. Particularly, the order of adsorption rate was fluorescence > UV_{254} > DOC in

414 all tested waters;

415 • Different fluorescing PARAFAC components were differently adsorbed during GAC fil-

416 tration. PARAFAC components with maxima fluorescence intensity at higher excitation

417 wavelengths, which are corresponding to humic-like fluorescence substances, were better

418 removed than other components in all waters;

419 • EOCs were better adsorbed when filtering synthetic water, whereas the fastest break-

420 through of EOCs was observed during wastewater filtration. These experimental differ-

421 ences can be ascribed to the different rate of DOM adsorption and carbon fouling that

422 took place during the filtration of different waters;

423 • Correlation models were developed to monitor breakthrough of EOCs during GAC filtra-

424 tion using fluorescence indexes and UV_{254}. Particularly, fluorescence indexes resulted

19

425   more sensitive surrogate than UV_{254} to predict EOC breakthrough during GAC adsorp-

426   tion;

427   • The need of different correlation models to predict EOCs breakthrough in different water

428   qualities was related to the surrogate parameter used for the prediction (i.e., UV absorb-

429   ance or fluorescence) and its adsorption during GAC processes. Particularly, correlations

430   between EOC removals and the microbial humic-like PARAFAC component C1 remov-

431   als were independent of water quality when considering real water matrices (i.e., surface

432   water and wastewater). On the contrary, two different correlation models were needed to

433   predict EOCs breakthrough in surface waters and wastewater when using UV_{254} as surro-

434   gate.

Supplementary data

436   Text S1 – S2, Table S1 – S15 and Figures S1 – S9. This material is available free of charge.

Acknowledgements

441

442

Tables

Table 1. Water qualities parameters of tested waters.

Water Matrix	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/m/mg)	$Ø_{tot}$ (RU)	pH
Synthetic water	4.3	0.096	2.3	1130	6.7
Surface water	5.4	0.184	3.4	858	8.4
Wastewater	7.0	0.162	2.3	10822	7.5

Table 2. Relevant chemical properties and concentration (ng/L) of EOCs in the three water qualities.

Compound	pK_a	Log D_{ow} (pH:6.7)	Log D_{ow} (pH:7.5)	Log D_{ow} (pH:8.4)	Charge	Synthetic water	Surface water	Wastewater
Atrazine	14.48	2.2	2.2	2.2	Neu	165	360	A
Carbamazepine	15.96	2.77	2.77	2.77	Neu	157	194	370
Gemfibrozil	4.42	2.13	1.44	0.99	Neg	195	226	214
Ibuprofen	4.85	2	1.25	0.61	Neg	78	295	A
Primidone	11.5	1.12	1.12	1.12	Neu	A	284	349
Perfluorodecanoic acid (PFDA)	-	2.98	2.98	2.98	Neg	282	238	A
Perfluorooctanoic acid (PFOA)	-	1.58	1.58	1.58	Neg	138	269	174
Perfluorooctane sulfonate (PFOS)	-	3.05	3.05	3.05	Neg	153	246	556
Sucralose	11.91	-0.47	-0.47	-0.47	Neu	210	961	A
Sulfamethoxazole	6.16	0.29	-0.03	-0.14	Neu/Neg	130	214	1294
Trimethoprim	7.16	0.74	1.13	1.26	Pos/Neu	A	362	100

A = compound non available; Neg = negative; Pos = positive; Neu = neutral. Chemical properties determined using ChemAxon software.

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Table 3. Summary of regression parameters for UV_{254} absorbance and PARAFAC component C1 models for combined datasets.

Compound	C1 model (surface water and wastewater)				UV_{254} model (surface water and synthetic water)			
	Slope	y-intercept	R^2	n	Slope	y-intercept	R^2	n
Atrazine	A	A	A	A	6.25	-578	0.742	27
Carbamazepine	1.470	-69.00	0.931	31	6.23	-577	0.719	27
Gemfibrozil	1.345	-41.47	0.959	32	6.09	-541	0.786	30
Ibuprofen	A	A	A	A	5.46	-473	0.854	31
PFDA	A	A	A	A	3.15	-238	0.749	33
PFOA	1.11	2.63	0.861	28	4.87	-392	0.924	26
PFOS	1.06	-8.89	0.852	24	4.95	-416	0.904	29
Primidone	1.27	-33.30	0.777	25	A	A	A	A
Sucralose	A	A	A	A	5.91	-509	0.713	27
Sulfamethoxazole	1.78	-47.40	0.966	20	3.99	-332	0.302	26
Trimethoprim	1.58	-88.20	0.912	29	A	A	A	A

A = correlation model non available; n = number of data points
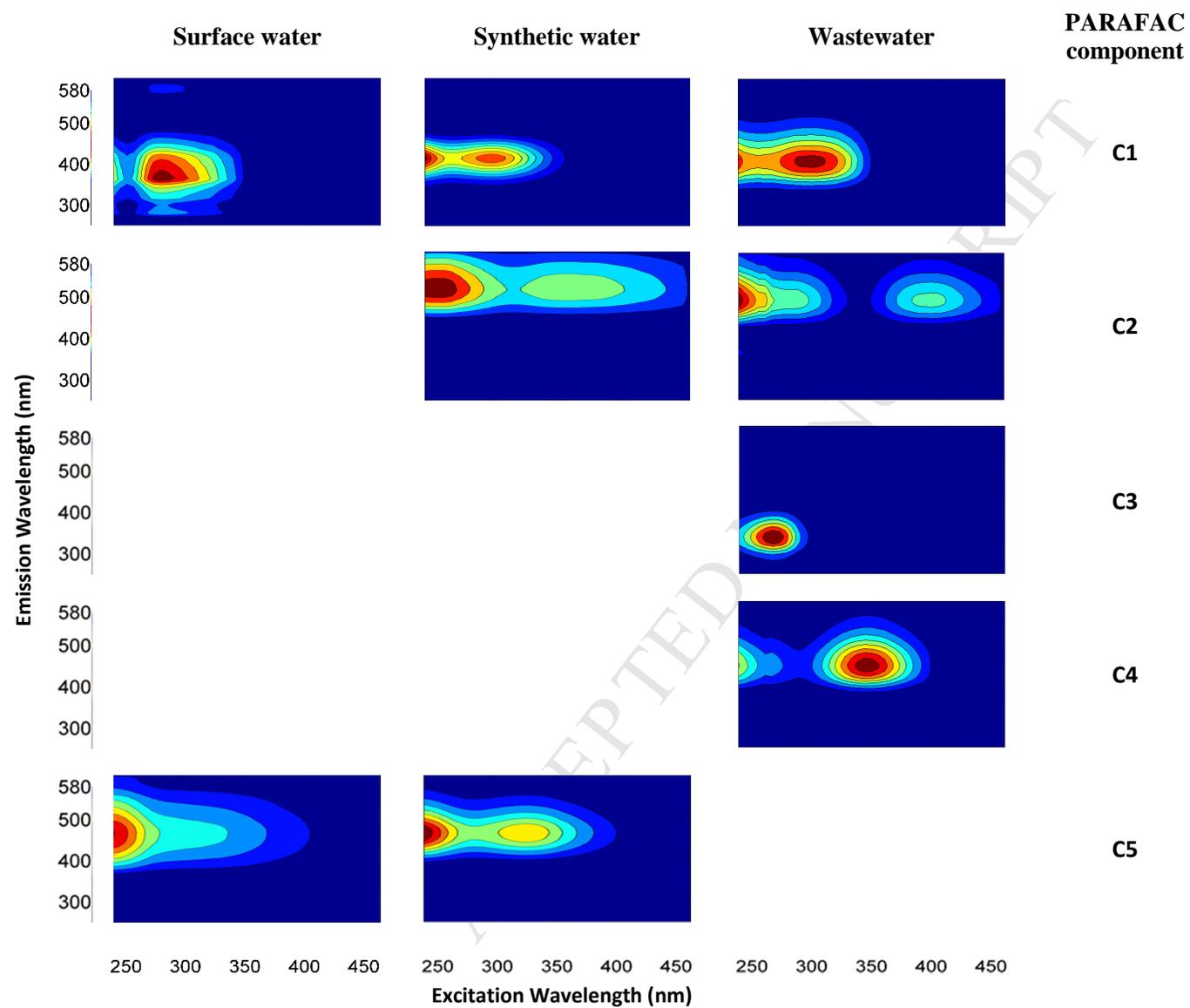
Figure 1. Spectral fingerprints of the identified fluorescing components in the three water qualities.
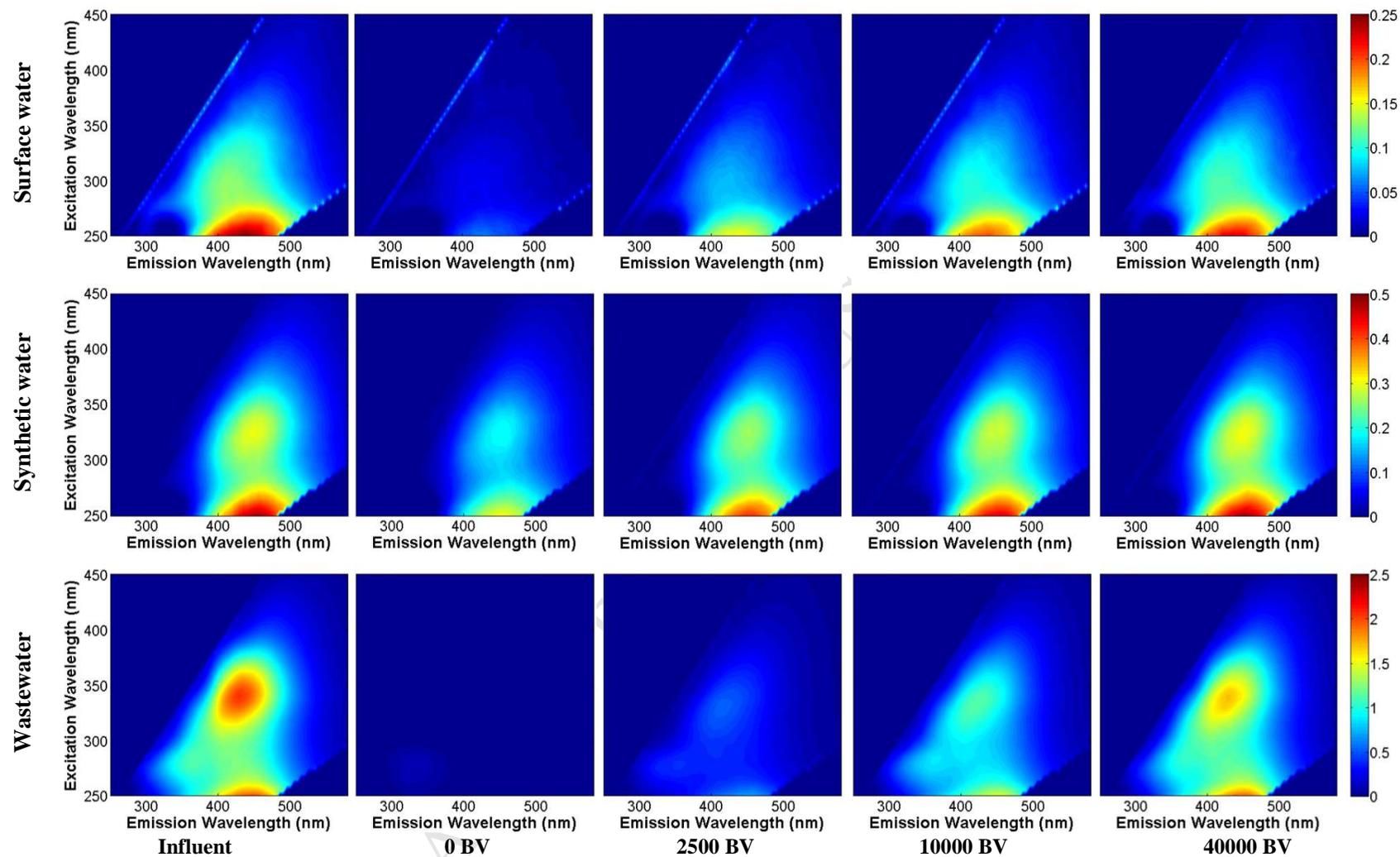
**Figure 2. EEMs at different bed volumes (BV) for the investigated water qualities.**
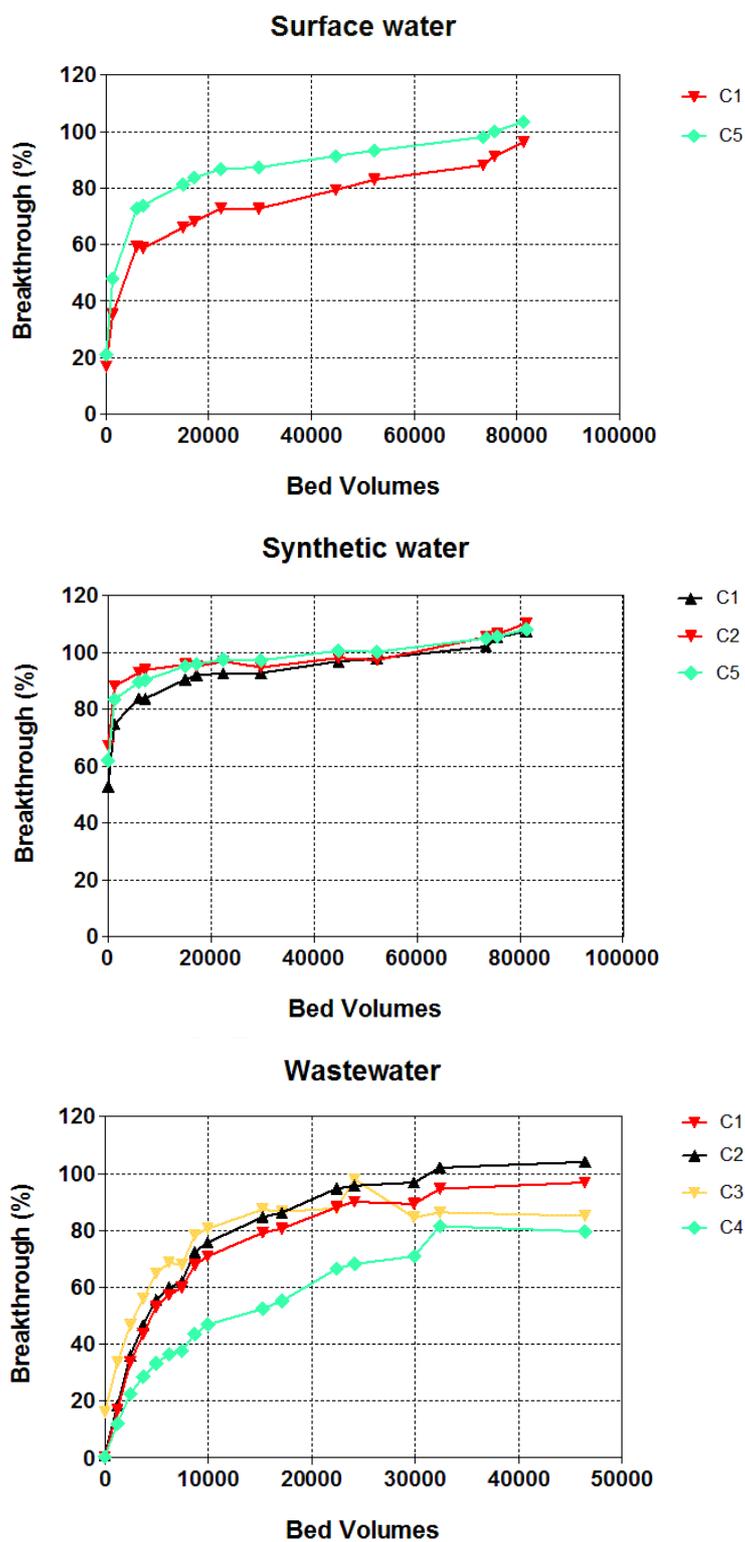
Figure 3. Breakthrough curves for PARAFAC components C1-C5 in the tested water qualities.

25
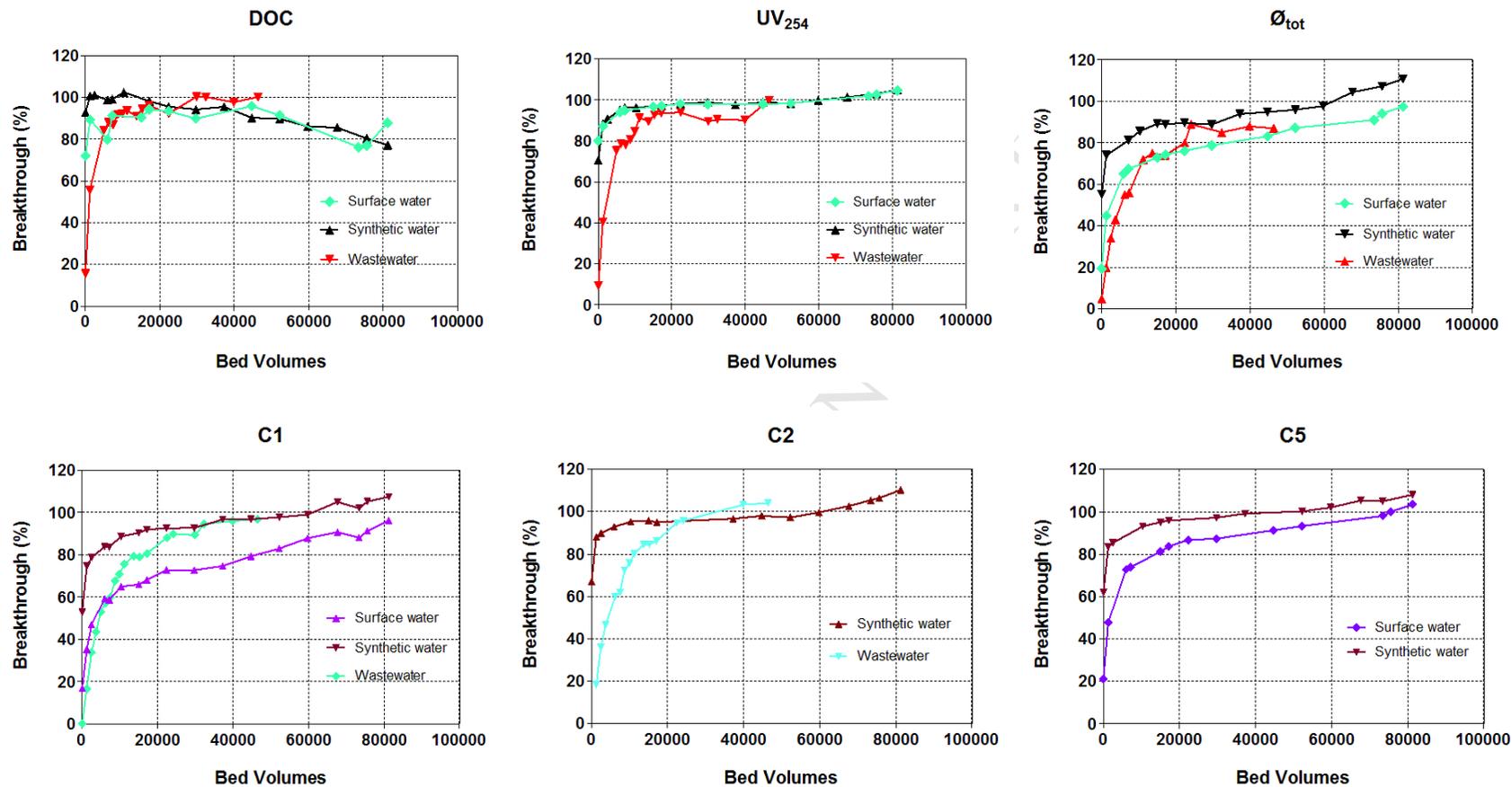
Figure 4. Breakthrough curves for DOC, UV$_{254}$, total fluorescence (Ø$_{tot}$) and PARAFAC components C1, C2 and C5 in all tested waters.
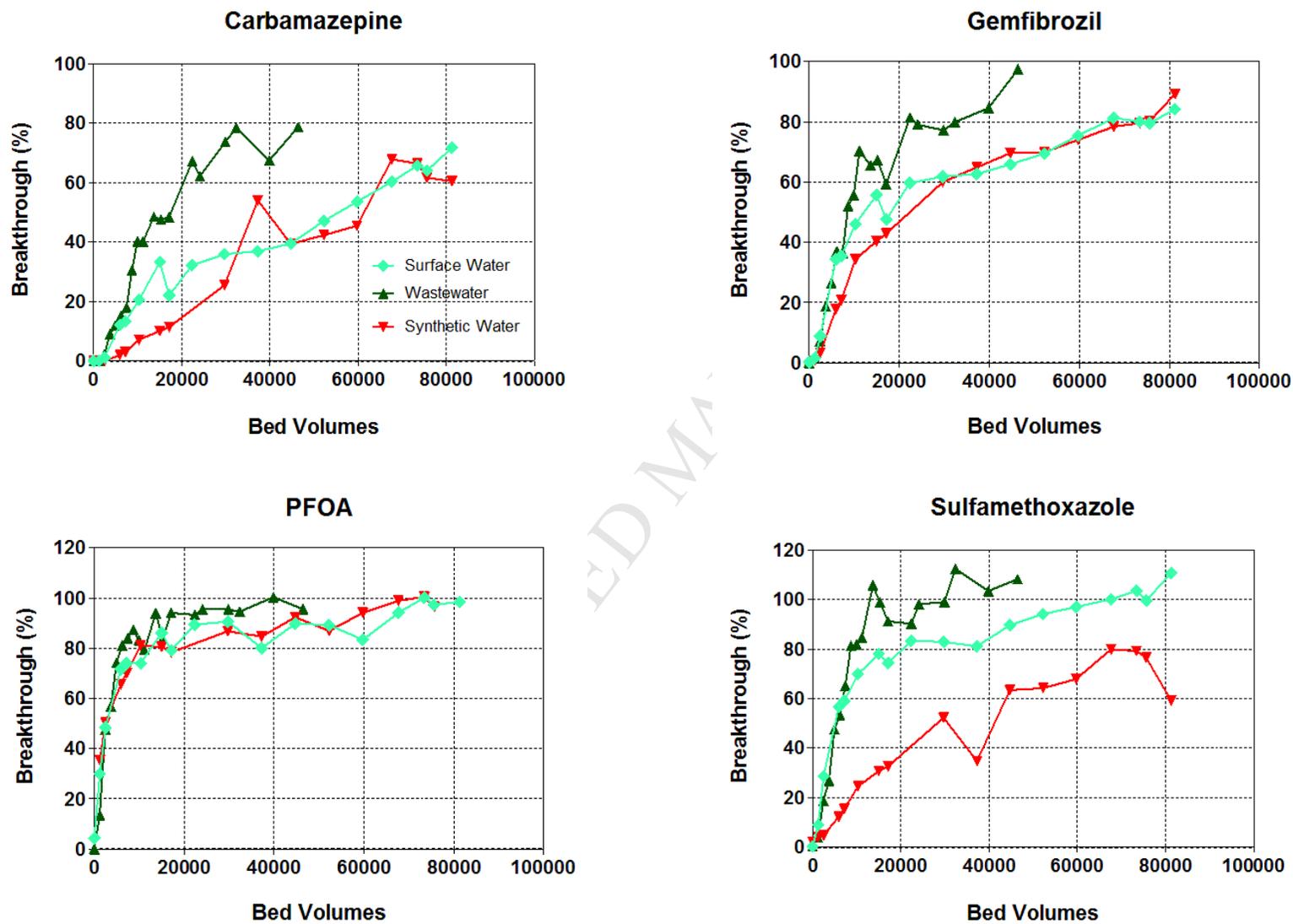
Figure 5. Examples of breakthrough curves for EOCs in tested water qualities.
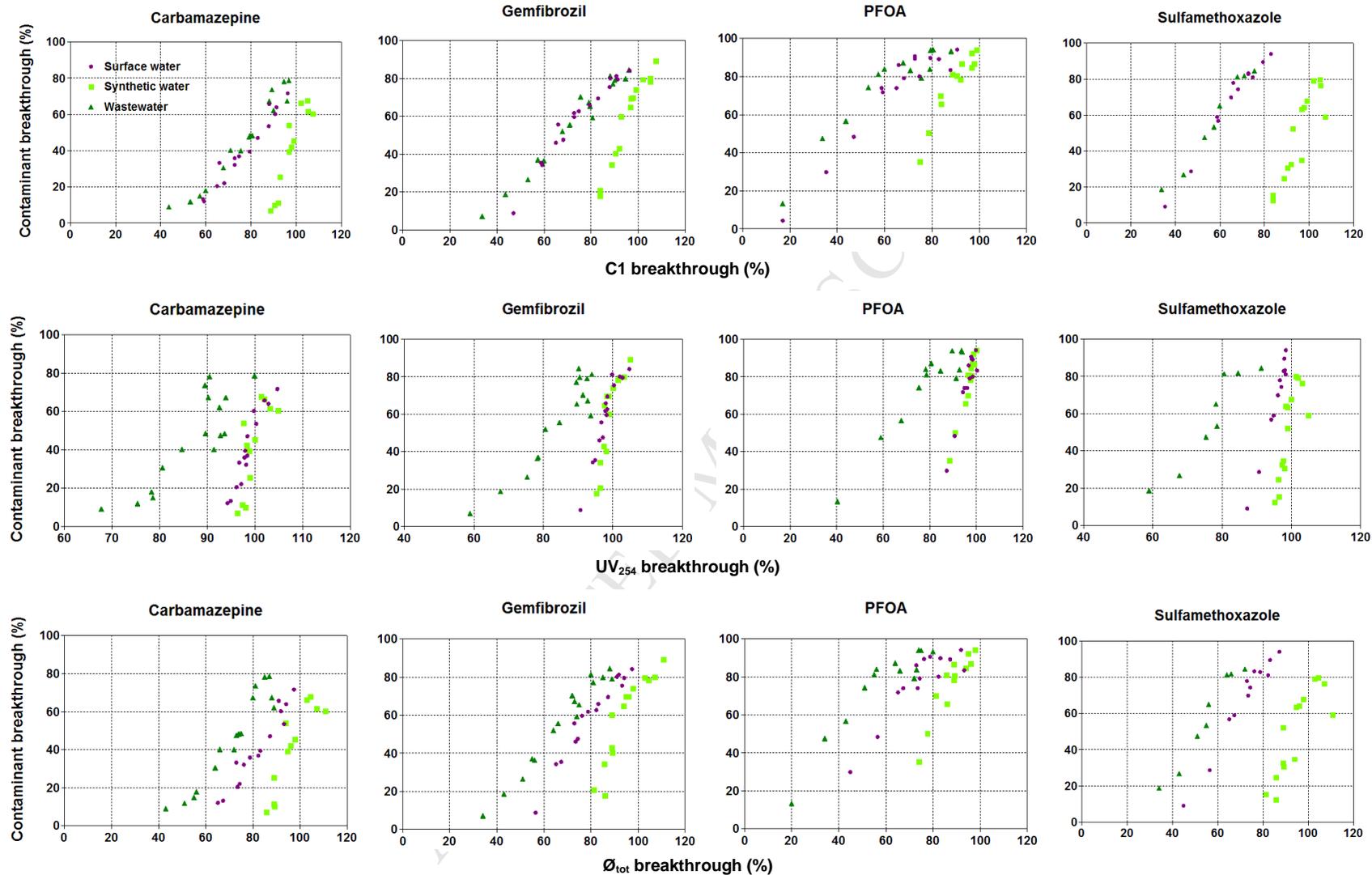
Figure 6. Correlations between PARAFAC component C1, UV$_{254}$ absorbance and total fluorescence (Ø$_{tot}$) breakthrough and EOCs breakthrough.

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Highlights

- Different DOM components are differently adsorbed in GAC filters

- Wastewater DOM was better adsorbed than surface water DOM

- Wastewater DOM determined the lowest adsorption of EOCs during GAC filtration

- Different correlation models were needed to monitor EOCs when using UV absorbance

- EOCs prediction by PARAFAC component was independent of water quality for real water