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1 Study of a large scale powdered activated carbon pilot: removals of a wide range of  
2 emerging and priority micropollutants from wastewater treatment plant effluents

3  
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17  
18 **HIGHLIGHTS**

- 19 • Pharmaceuticals and hormones (PhPHs) are well removed (> 60%) by powdered activated carbon (PAC)
- 20 • 50-95% removals are also achieved for parabens, bisphenol A and pesticides by PAC
- 21 • Treatment degradation leads to substantially lower PhPHs removals by PAC
- 22 • The fresh PAC dose is strongly correlated to the process efficacy
- 23 • Molecular charge, hydrophobicity and molecular weight have a great influence on the micropollutant fate
- 24
- 25

26 ABSTRACT

27 The efficacy of a fluidized powdered activated carbon (PAC) pilot (CarboPlus®) was studied in both nominal (total  
28 nitrification + post denitrification) and degraded (partial nitrification + no denitrification) configuration of the Seine  
29 Centre WWTP (Colombes, France). In addition to conventional wastewater parameters 54 pharmaceuticals and  
30 hormones (PhPHs) and 59 other emerging pollutants were monitored in influents and effluents of the pilot. Thus, the  
31 impacts of the WWTP configuration, the process operation and the physico-chemical properties of the studied  
32 compounds were assessed in this article.

33

34 Among the 26 PhPHs quantified in nominal WWTP configuration influents, 8 have high dissolved concentrations (>100  
35 ng/L), 11 have an intermediary concentration (10-100 ng/L) and 7 are quantified below 10 ng/L. Sulfamethoxazole is  
36 predominant (about 30% of the sum of the PhPHs). Overall, 6 PhPHs are poorly to moderately removed (<60%), such  
37 as ibuprofen, paracetamol or estrone, while 9 are very well removed (>80%), i.e. beta blockers, carbamazepine or  
38 trimethoprim, and 11 are well eliminated (60-80%), i.e. diclofenac, naproxen or sulfamethoxazole.

39 In degraded WWTP configuration, higher levels of organic matter and higher concentrations of most pollutants are  
40 observed. Consequently, most PhPHs are substantially less removed in percentages but the removed flux is higher.  
41 Thus, the PAC dose required to achieve a given removal percentage is higher in degraded WWTP configuration. For the  
42 other micropollutants (34 quantified), artificial sweeteners and phthalates are found at particularly high concentrations  
43 in degraded WWTP configuration influents, up to µg/L range. Only pesticides, bisphenol A and parabens are largely  
44 eliminated (50-95%), while perfluorinated acids, PAHs, triclosan and sweeteners are not or weakly removed (<50%).  
45 The remaining compounds exhibit a very variable fate from campaign to campaign.

46

47 The fresh PAC dose was identified as the most influencing operation parameter and is strongly correlated to  
48 performances. Charge and hydrophobicity of compounds have been recognized as crucial for the micropollutant  
49 adsorption on PAC, as well as the molecular weight. Finally, a PAC dose of 10 mg/L allows an average removal of 72-  
50 80% of the sum of the PhPHs in nominal WWTP configuration. The comparison of the results with those from the  
51 scarce other studies tends to indicate that an extrapolation of them to different PAC processes and to other WWTPs  
52 could be possible and relevant, taking into account the differences of water quality from WWTP to WWTP.

53

54 KEYWORDS

55 Pharmaceuticals; emerging pollutants; adsorption; powdered activated carbon; wastewater treatment

56

## 57 INTRODUCTION

58

59 In addition to priority pollutants (EC 2013), many other emerging micropollutants such as pharmaceuticals and  
60 hormones (PhPHs), personal care products (PCPs), pesticides, phthalates, artificial sweeteners, etc. are found in the  
61 aquatic environment (Jones et al. 2001, Lange et al. 2012, Luo et al. 2014). As bioactive and toxic substances, their  
62 environmental effects have been proven (Bolong et al. 2009, Daughton and Ternes 1999). For some of these compounds  
63 such as PhPHs and PCPs, wastewater treatment plant (WWTP) discharges have been identified as an important source  
64 in the aquatic environment (Halling-Sørensen et al. 1998, Heberer 2002).

65

66 Several studies have shown that conventional WWTPs (with primary and biological treatments) substantially remove  
67 hydrophobic, volatile and biodegradable micropollutants even if they are not designed and/or optimized for that purpose  
68 (Clara et al. 2007, Mailler et al. 2013, Ruel et al. 2012). However, hydrophilic or refractory organic compounds are still  
69 present in the treated wastewater at ng/L to µg/L level (Loos et al. 2013). Besides, emerging micropollutants,  
70 particularly pharmaceuticals such as diclofenac, may be included in future modifications of existing European (EC  
71 2013) or national regulations. Among the solutions to reduce the emerging contaminant discharges into the  
72 environment, the implementation of a tertiary treatment in conventional WWTPs is more and more considered by  
73 WWTP managers and decision makers. These technologies, such as membrane filtration, advanced oxidation and  
74 adsorption processes, are principally adapted from drinking water industry. They have been employed for a long time,  
75 but the generalization of their applications to wastewater treatment has been seriously considered recently. However,  
76 very few studies have shown the potential of such technologies to remove organic pollutants from treated wastewater  
77 (Boehler et al. 2012, Margot et al. 2013) and their economic feasibility (Abegglen and Siegrist 2012).

78

79 In this context, a large scale powdered activated carbon (PAC) pilot has been set up at the Seine Centre WWTP, treating  
80 wastewater from Paris conurbation and supervised by the Parisian public sanitation service (SIAAP). An extended  
81 sampling strategy, both in number of campaigns (n=14) and compounds (N=113), has been built.

82

83 Thus, this paper aims at displaying and comparing the performances of such a process for micropollutant removal in  
84 both nominal and degraded WWTP configurations, and to assess the influence of both operation parameters and  
85 physico-chemical properties of the pollutants. First, the influent dissolved concentrations for both micropollutants and

86 conventional wastewater parameters are discussed and compared to the literature. Then, the removals of the molecules  
87 are examined, as well as the effluent dissolved concentrations and the water quality. The difference between a normal  
88 and a degraded configuration of the WWTP is particularly analyzed. Finally, the influence of operation parameters  
89 (fresh PAC dose, total mass of carbon in the reactor, hydraulic velocity) and physico-chemical properties of the  
90 compounds (charge, hydrophobicity, size, functional groups, etc.) are also examined. Such results are of high interest  
91 and very relevant considering the poverty of the literature regarding the removal of micropollutants from wastewater by  
92 PAC.

93

94

## 95 MATERIALS AND METHODS

96

### 97 1. Site and process description

98

99 In nominal configuration, the Seine Centre WWTP treats 240 000 m<sup>3</sup> per day of domestic wastewater from Paris city,  
100 corresponding to 900 000 population equivalents. In these conditions (total nitrification + post denitrification), the  
101 treatment process is composed by three major steps: pre, primary and biological treatments. After the pretreatment  
102 (screening, grit and oil removal units), a physicochemical lamellar settling unit (Densadeg<sup>®</sup>) removes a great part of the  
103 particulate and colloidal pollution thanks to coagulant (ferric chloride) and flocculant (anionic polymer) addition.  
104 Finally, a three stage biofiltration system achieves the biological treatment. In nominal configuration, the first stage  
105 (Biofor<sup>®</sup> filters - biolite medium), allows the treatment of carbonaceous pollution in aerobic conditions, and the second  
106 (Biostyr<sup>®</sup> filters - biostyrene medium) and third (Biofor<sup>®</sup> filters) stages remove the nitrogenous pollution respectively in  
107 aerobic (total nitrification) and anoxic (denitrification) conditions (Rocher et al. 2012). This WWTP is able to switch to  
108 a degraded configuration to treat 405 000 m<sup>3</sup> of water per day but a partial nitrification and no denitrification are  
109 performed. A detailed layout of the WWTP in both configurations is given in supporting material - Figure S1.

110

111 The tertiary treatment process studied (CarboPlus<sup>®</sup> - Figure 1) is fed by Seine Centre treated effluents and treats  
112 between 700 and 1 200 m<sup>3</sup>/day. This pilot consists in a 5 m high reactor with a surface area of 4 m<sup>2</sup>, where water flows  
113 upstream through a fluidized bed of PAC. Depending on the mass of PAC inside the reactor and the hydraulic velocity,  
114 the bed depth varies between 1 and 3 m. A dose of fresh PAC is continuously injected. At steady state, a comparable  
115 amount of PAC is regularly removed from the reactor to obtain a solid retention time (SRT) of 5 to 7 days, and an

116 overall concentration of 5 to 10 g/L of PAC is maintained inside the bed. In addition, coagulant (ferric chloride) and  
117 flocculant (anionic polymer) are injected continuously with the fresh PAC to stabilize the bed expansion and to prevent  
118 the leakage of PAC with treated water. The hydraulic velocity can technically vary from 6 to 12 m/h and the hydraulic  
119 retention time considering the reactor size is comprised between 25 and 50 min. The observed contact time between the  
120 PAC bed and the water varies between 10 and 20 min considering the bed depth and the hydraulic velocity.

## 121 FIGURE 1

### 122 2. Study and sampling strategy

123  
124  
125 The study has been initially built to assess the process efficacy in different operation configuration (Table 1) during 14  
126 campaigns (from July to December 2013). However, the Seine Centre WWTP operated in degraded configuration  
127 during the 5 lasts campaigns (unplanned), because it received additional water from another WWTP that was in  
128 maintenance. Taking this into account, the campaigns performed have been organized in two phases in the results and  
129 discussion sections of the article. The first 9 campaigns, corresponding to phase 1, were performed during nominal  
130 WWTP configuration. The last 5 campaigns were carried out under degraded WWTP configuration, corresponding to  
131 phase 2.

132 In addition, different process configurations were tested during the first phase (Table 1) by varying the fresh PAC dose  
133 in the ranges operationally feasible within the process. Thus, three moderate PAC doses (5-10-20 mg/L) and one high  
134 PAC dose (70 mg/L), as well as four hydraulic velocities (6-7-8-10 m/h) were tested, allowing determining their  
135 influences on performances. The 70 mg/L of PAC campaign was performed to determine whether some compounds  
136 could still be recalcitrant to adsorption at high dose. Information about operation parameters during this phase are given  
137 in Table 1. In contrary, a stable and intermediate configuration (10 mg/L of PAC and 7 m/h), considered as the  
138 recommended configuration of the process, was maintained during the second phase.

139 Thus, this experimental design allows assessing the influences of both the process operation parameters and the  
140 configuration of the WWTP.

## 141 TABLE 1

142  
143 The same sampling procedure was applied for the 14 campaigns. Analyzes were performed on the dissolved phase. 24-h  
144 composite samples of 20 L were collected using automatic refrigerated samplers (4°C) equipped with glass bottles,  
145 properly cleaned, and Teflon<sup>®</sup> pipes to avoid any contamination or loss. When sampling was completed, glass bottles  
146 were collected, very carefully homogenized and sub-samples were distributed for analyses. Each sample was filtered

147 using 0.7  $\mu\text{m}$  GF/F filters (Whatman®). All samples were analyzed within 48-h after sampling, due to transport time to  
148 the laboratories involved, except for sweeteners. As recommended by the laboratory performing the artificial  
149 sweeteners analyses (internal tests), these samples were acidified (1% volumetric HCl) and stored in fridge (4°C) until  
150 analyses.

151

### 152 3. Activated carbon characterization

153

154 Activated carbon characteristics are very important in the adsorption mechanisms and can strongly influence the  
155 micropollutant fate (Çeçen and Aktas 2012). Apart from BET (Brunauer, Emmett and Teller) specific surface and  
156 particle size, the mesoporous structure is the best suited for micropollutants adsorption (Çeçen and Aktas 2012, Ebie et  
157 al. 2001), as it reduces the impact of organic matter competition with micropollutants. Thus, a mesoporous PAC  
158 (DaCarb PB-170) was tested in the pilot, after preliminary lab tests comparing different PACs. The characteristics of  
159 this PAC are given in supporting material - Table 1. Globally, the selected PAC is featured by a high BET surface of  
160  $957 \pm 28 \text{ g/m}^2$ , which is close to BET specific surfaces found in the literature, often comprised between 700 and 1 500  
161  $\text{m}^2/\text{g}$  (Çeçen and Aktas 2012, de Ridder et al. 2013, Margot et al. 2013). In addition, its granulometry is large but its  
162 median particle diameter is rather low ( $<20 \mu\text{m}$ ), which theoretically enhance the adsorption kinetics. PAC observations  
163 by scanning electron microscopy are provided in supporting material - Figure S2.

164

### 165 4. Pollutants and analytical procedures

166

167 In all samples, conventional wastewater parameters were analyzed by SIAAP French accredited laboratory (COFRAC,  
168 supporting material - Table S2) to characterize the general quality of water. These parameters include: dissolved organic  
169 carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD<sub>5</sub>), UV absorption at 254 nm (UV-  
170 254), total Kjeldahl nitrogen (TKN),  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , total phosphorous (TP) and total suspended solids (TSS).  
171 All analyses were performed according to standards (supporting material - Table S2).

172

173 113 micropollutants were monitored in the dissolved phase (Table 2). First, pharmaceuticals (N=44, N for the number  
174 of compounds) and hormones (N=10) were analyzed for all campaigns, as they are the compounds targeted by the  
175 process. In addition to these molecules, complementary analyses were performed for other micropollutants (N=59)  
176 during phase 2. Thus, chlorinated solvents (N=3), perfluorinated acids (N=2), pesticides (N=23), bisphenol A,

177 alkylphenols (N=2) and phthalates (N=4) were analyzed in all campaigns of phase 2, while PAHs (N=13 - the 16 US-  
178 EPA PAHs excluding naphthalene, acenaphthene and acenaphthylene) and PCPs (N=7) were monitored in 3 campaigns  
179 and artificial sweeteners (N=4) in 4 campaigns. The full list of molecules is given in supporting material - Table S3, as  
180 well as their respective limits of quantification (LQ).

181

182 Micropollutant analyses were performed by 4 laboratories: the Institute of Analytical Sciences (ISA - Villeurbanne,  
183 France) from CNRS, in charge of the PhPHs, chlorinated solvents, perfluorinated acids, pesticides and bisphenol A, the  
184 Water Environment and Urban Systems laboratory (LEESU - Créteil, France), in charge of PAHs and PCPs, the Central  
185 laboratory of the Police Prefecture (LCPP - Paris, France), in charge of phthalates and alkylphenols, and the Water  
186 Technology Center (TZW - Karlsruhe, Germany), in charge of artificial sweeteners.

187

#### TABLE 2

188 Information about the analytical procedures (Table 2) are available in the literature for PhPHs (Vulliet et al. 2011),  
189 pesticides and chlorinated solvents (Barrek et al. 2009), PAHs (Bressy et al. 2012), alkylphenols and phthalates (Bergé  
190 et al. 2014), sweeteners (Scheurer et al. 2009), and for PCPs (Gasperi et al. 2014).

191

#### 192 5. Data processing

193

194 The statistical calculations were performed separately for the nominal (n=9) and the degraded (n=5) WWTP  
195 configurations, for comparison purposes. When the number of values available was higher than six, box plots were  
196 plotted with minimum, 1<sup>st</sup> quartile (Q1), 3<sup>rd</sup> quartile (Q3) and maximum values of the series. In contrary ( $\leq 6$  values),  
197 individual values were plotted. Finally, the results given in text, concentrations as well as removals, are average results  
198  $\pm$  standard deviations ( $>6$  values) or minimum – maximum values ( $\leq 6$  values).

199

200 As no direct assessment of the uncertainties was performed, and to have an idea of the robustness of the data, limit  
201 values of 5 times the LQ were defined for each compound. The uncertainty was assumed moderate for concentrations  
202 measured above these limit values ( $<30\%$ ), while the uncertainty was considered high for concentrations below them  
203 ( $>30\%$ ). Such an approach has already been adopted by (Ruel et al. 2011), which stated that the uncertainty on the  
204 micropollutant concentration in wastewater is generally comprised between 30 and 100% when the value measured is  
205 lower than 2.5 to 10 times the LQ, depending on the compound, and lower than 30% when higher than this value.  
206 Considering that, the removal of micropollutants was estimated only in several situations to limit the propagation of



207 uncertainties and provide more reliable results. When the compound was quantified above 5 times the LQ in influents  
208 and above the LQ in effluents, the removal was conventionally calculated. In addition, when the compound was  
209 quantified above the LQ in influents ( $>LQ$  or  $>5 \times LQ$ ) and below the LQ in effluents, the removal was estimated using  
210  $LQ/2$  instead of the effluent concentration. The removals were not calculated when concentrations of both influents and  
211 effluents were measured between the LQ and 5 times the LQ.

212

213 Finally, 4 classes of behaviors were defined regarding the obtained removals: very good ( $>80\%$ ), good (60-80%),  
214 moderate (30-60%) and poor ( $<30\%$ ).

215

216

## 217 RESULTS AND DISCUSSION

218

### 219 1. Quality of influents in nominal and degraded WWTP configuration

220

#### 221 *1.1. Conventional wastewater parameters in influents*

222

223 As displayed in Table 3, the pilot influents are characterized by relatively low values of the conventional wastewater  
224 parameters in nominal WWTP configuration, particularly DOC ( $5.6 \pm 0.9$  mgC/L), UV-254 ( $0.110 \pm 0.013$  cm<sup>-1</sup>), COD  
225 and BOD<sub>5</sub> ( $26 \pm 11$  and  $4.8 \pm 3.5$  mgO<sub>2</sub>/L), TKN ( $1.5 \pm 0.2$  mgN/L), NH<sub>4</sub><sup>+</sup> ( $< 0.3$  mgN/L), TSS ( $3 \pm 1$  mg/L) and TP  
226 ( $< 0.3$  mgP/L). Indeed, this WWTP achieves very high removals of TSS (98%), COD (92%), TN (76%) and TP (95%)  
227 in nominal configuration (Mailler et al. 2013). In addition, a substantial fraction of the DOC ( $\approx 20\%$ ) is due to residual  
228 methanol from the post denitrification step (SIAAP source), in contrary to DOC from the degraded WWTP  
229 configuration (no denitrification).

230 In this study, the WWTP effluents are rather less concentrated (DOC, UV-254, etc.) than effluents from other studies  
231 focusing on PAC adsorption from wastewater. Besides, effluents with average DOC values of 9.6 - 14.4 mgC/L and  
232 UV-254 of 0.239 - 0.397 cm<sup>-1</sup> were recently studied by (Altmann et al. 2014), while DOC concentration of the water  
233 studied by (Löwenberg et al. 2014) was  $8.8 \pm 1.2$  mgC/L. Similarly, (Margot et al. 2013) performed PAC adsorption on  
234 biological treatment effluents with DOC of  $7.3 \pm 1.9$  mgC/L. Only the study of (Boehler et al. 2012) provides  
235 micropollutant removal by PAC data with lower DOC concentration water, between 5.6 and 8.9 mgC/L.

236

237 The degraded configuration, with partial nitrification and no denitrification, induces a notable increase of  
238 concentrations, particularly DOC ( $7.5 \pm 0.5$  mgC/L) and the UV-254 ( $0.139 \pm 0.011$  cm<sup>-1</sup>). In addition, as no  
239 denitrification is performed in this WWTP configuration, the composition of the DOC is different without residue of  
240 methanol. The difference of DOC concentration is then even higher between the two WWTP configurations.

241 The concentration of NH<sub>4</sub><sup>+</sup> in influents highlights the degradation of the nitrification step, with concentrations up to  $4.4$   
242  $\pm 0.7$  mgN/L. Similarly, the highest concentration of NO<sub>3</sub><sup>-</sup> in influents from degraded configuration ( $23.7 \pm 2.1$  mgN/L)  
243 reflects the lack of denitrification. Finally, the TSS concentration is doubled when WWTP configuration is degraded  
244 (Table 3). Overall, the obtained quality of influents in this WWTP configuration is degraded and quite comparable to  
245 the one from (Margot et al. 2013).

246 The higher quantity of organic matter and most of pollutants in degraded WWTP configuration should be unfavorable  
247 to micropollutant adsorption. Indeed, it has been demonstrated that a higher DOC concentration induces a stronger  
248 competition effect (Delgado et al. 2012, Margot et al. 2013).

249

250

#### 251 *1.2. Micropollutant concentrations in influents from nominal WWTP configuration*

252

253 Among the 54 PhPHs monitored, a total of 26 compounds were quantified at least during the nominal WWTP  
254 configuration. During this WWTP configuration, 14 were systematically quantified in influents, 12 in several samples  
255 but 28 were never quantified (supporting material - Table S4). The dissolved concentrations of the 26 compounds, in  
256 both nominal and degraded configuration of the WWTP, are presented in Table 2, with their occurrences.

257

258 8 compounds were measured in influents at average dissolved concentrations higher than 100 ng/L: sulfamethoxazole  
259 ( $993 \pm 817$  ng/L), ofloxacin ( $412 \pm 315$  ng/L), carbamazepine ( $215 \pm 85$  ng/L), atenolol ( $185 \pm 51$  ng/L), diclofenac  
260 ( $184 \pm 91$  ng/L), oxazepam ( $139 \pm 128$  ng/L) and erythromycin ( $124 \pm 32$  ng/L). 7 compounds were measured at  
261 concentrations lower than 10 ng/L, especially estrone ( $9 \pm 3$  ng/L) and ibuprofen ( $9 \pm 5$  ng/L). The 11 remaining  
262 compounds have average concentrations between 10 and 100 ng/L, i.e. naproxen ( $33 \pm 28$  ng/L), trimethoprim ( $64 \pm 79$   
263 ng/L) or propranolol ( $97 \pm 27$  ng/L).

264 These concentrations are rather in accordance with data available in the literature for WWTP effluents (Deblonde et al.  
265 2011, Loos et al. 2013, Luo et al. 2014, Miège et al. 2009), although they are overall in the lower part of the range (i.e.  
266 analgesics). This could be due to i) the dilution of the Parisian wastewater (combined sewer) by parasite waters (Gasperi

267 et al. 2008) and ii) intense biological treatment including a total nitrification step, known to enhance the biodegradation  
268 of micropollutants (Clara et al. 2005, McAdam et al. 2010). Sulfamethoxazole contributes about 30% of the total PhPHs  
269 concentration, and its concentration lies in the upper part of the range found in the literature. No data were found for  
270 testosterone, sulfadimerazine, sulfameter, and very scarce information are available for sulfadiazine, sulfathiazole,  
271 fenofibrate and lorazepam. A short review as regard concentrations found in WWTP effluents for these compounds (23  
272 references) is given in supporting material - Table S5.

273 In addition, most compounds are measured above 5 times their LQ (Table 3), leading to a moderate uncertainty on the  
274 concentration. Sulfadimerazine, sulfadiazine, sulfameter, sulfathiazole, fenofibrate and testosterone are rather measured  
275 between LQ and 5 times LQ, corresponding to high uncertainties, and the corresponding removals were consequently  
276 not calculated.

277

278

### 279 *1.3. Micropollutant concentrations in influents from degraded WWTP configuration*

280

281 In the degraded configuration, 21 PhPHs were quantified. A similar pattern is observed but most of the PhPHs are  
282 measured at higher average dissolved concentrations than in nominal WWTP configuration (Table 2), particularly  
283 paracetamol (x200 based on average concentrations), ibuprofen (x100), ketoprofen (x10) and bezafibrate (x10). This is  
284 mainly explained by both seasonal variations (phase 1 June-October, phase 2 November-December) and the lack of  
285 nitrification since this step has been identified as crucial for micropollutant biodegradation in biological treatments,  
286 especially for easily biodegradable molecules by biological treatments (Joss et al. 2005, Margot et al. 2013, Radjenović  
287 et al. 2009). The degree of nitrification is then correlated to some PhPHs biodegradation (Margot et al. 2013), and a  
288 total nitrification, as in nominal WWTP configuration, is known to be more efficient than a partial nitrification (Joss et  
289 al. 2008), as in degraded WWTP configuration. This results in lower concentrations in discharges from nominal WWTP  
290 configuration. Finally, the total concentration of the PhPHs doubles from  $2\,729 \pm 1\,057$  ng/L in nominal WWTP  
291 configuration to  $4\,956 \pm 3\,628$  ng/L in degraded WWTP configuration, mainly due to the increase of paracetamol and  
292 ibuprofen concentrations. In contrary, four compounds are measured at notably lower concentrations: sulfamethoxazole,  
293 carbamazepine, ofloxacin and ciprofloxacin, probably because of seasonal variability.

294

295 A total of 59 other emerging micropollutants were also monitored during phase 2 in order to improve and enlarge the  
296 performance overview of the PAC treatment. Concentrations are presented in Table 3. Among them, monitored during

297 degraded WWTP configuration, 34 were measured above the LQ. Only 3 pesticides (atrazine, diuron and isoproturon)  
298 out the 23 pesticides investigated were quantified due to both a low occurrence in treated wastewater and high LQ.  
299 Most of the compounds were always found in influents, especially PFOS, PFOA, bisphenol A, nonylphenols (NP),  
300 para-tert-octylphenol (t-OP), bis(2-ethylhexyl) phthalate (DEHP), artificial sweeteners, triclosan and parabens.

301

302 A wide variety of dissolved concentrations is observed, from a few ng/L to more than 1 000 ng/L. Phthalate levels are  
303 rather high, ranging from 300 to 3 000 ng/L. Similarly, acesulfame and sucralose exhibit the highest concentrations by  
304 far, respectively  $8\,725 \pm 602$  and  $7\,150 \pm 745$  ng/L, due to very poor removals by conventional WWTPs (Lange et al.  
305 2012). Artificial sweeteners have been recently recognized as a new class of emerging environmental contaminants  
306 (Lange et al. 2012), highly persistent, and their toxicity in the environment is still not well known. Bisphenol A, NP,  
307 cyclamate and saccharin are found at lower concentrations (100-1 000 ng/L), as well as diuron, isoproturon, PFOS,  
308 PFOA and parabens (10-100 ng/L). Then, all the PAHs present dissolved concentrations lower than 20 ng/L in the  
309 effluents. Finally, as the concentrations presented for these micropollutants were acquired in degraded WWTP  
310 configuration, it can be assumed that they should be lower or equal in nominal WWTP configuration. Levels found are  
311 very similar to other studies for pesticides, perfluorinated acids, bisphenol A, triclosan and phthalates (Bergé et al.  
312 2013, Deblonde et al. 2011, Loos et al. 2013, Luo et al. 2014, Zareitalabad et al. 2013). In contrary, substantially higher  
313 levels of sweeteners (Berset and Ochsenbein 2012, Ordóñez et al. 2012) and PAHs (Fatone et al. 2011, Qiao et al. 2014,  
314 Sánchez-Avila et al. 2011) were found in WWTP effluents in the literature. Similarly, levels of parabens found are  
315 rather high compared to the literature (Chen et al. 2012, Yu et al. 2012b). In particular, concentrations are slightly  
316 higher than those reported by (Geara-Matta 2012) for the same WWTP discharges, highlighting the impact of the  
317 degraded configuration. More information about data available in the literature is given in supporting material - Table  
318 S5.

319 Like PhPHs, most of these other emerging micropollutants feature concentrations higher than 5 times their LQ, except  
320 three PAHs (anthracene, benzo[a]anthracene and dibenzo[ah]anthracene) and some campaigns for NP, benzylbutyl  
321 phthalate (BBP), cyclamate and two parabens (benzyl and butyl paraben).

322

323

## 324 2. Efficacy of PAC in nominal and degraded WWTP configurations

325

### 326 2.1. Conventional wastewater parameter removal in nominal and degraded WWTP configurations

327

328 An overall improvement of the water quality is observed after the PAC treatment. In nominal WWTP configuration,  
329 concentration removals of DOC ( $35 \pm 24\%$ ), UV-254 ( $32 \pm 14\%$ ), COD ( $13 \pm 14\%$ ) and BOD<sub>5</sub> ( $39 \pm 19\%$ ) are  
330 observed (n=9, average PAC dose of 14 mg/L). These results are rather similar or lower than those of (Margot et al.  
331 2013), despite the same average PAC dose. Actually, this difference could be due to the filtration unit after the PAC  
332 contact tank in their study, which was recognized as the main cause of the general water quality improvements because  
333 it was biologically active. Furthermore, they evaluated between 20 and 35% the DOC removal due to the PAC against  
334  $35 \pm 24\%$  and  $23 \pm 4\%$  in nominal and degraded configurations respectively. Similarly, (Boehler et al. 2012) observed  
335 a DOC removal between 15 and 48%, consistent with previously cited results.

336

337 In degraded WWTP configuration, the influent quality (Table 3) is degraded (Figure 4). Indeed, DOC is rather better  
338 removed both in percentage and concentration in nominal WWTP configuration, despite higher influent concentrations.  
339 In contrary, UV-254, COD, BOD<sub>5</sub> and TKN are similarly removed in both WWTP configurations. In addition, the  
340 presence of NH<sub>4</sub><sup>+</sup> in degraded WWTP effluents (Table 3) allows highlighting that a nitrification process occurs in the  
341 pilot, with a removal of about  $20 \pm 7\%$ . This confirms the findings of (Margot et al. 2013) even if authors quote a  
342 higher NH<sub>4</sub><sup>+</sup> removal ( $85 \pm 20\%$ ) because of the biologically active filtration unit after the PAC contact tank. The  
343 formation of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> confirms the nitrification process.

344

345

## 346 *2.2. Micropollutant removal in nominal WWTP configuration*

347

348 The overall performances of the pilot in both nominal and degraded WWTP configuration are presented in Figure 2. For  
349 each compound, the results from nominal configuration are given on the left hand and the results from degraded  
350 configuration on the right hand. A short literature review about the micropollutant removals by PAC is also provided in  
351 supporting material - Table S5.

352

353 In nominal WWTP configuration with a fresh PAC dose at 10 mg/L (n=3), paracetamol and ibuprofen are poorly  
354 removed, and 4 compounds are moderately removed by the pilot, including estrone (32-61%, min-max). In contrary, 9  
355 substances are very well removed, including propranolol (96-98%), atenolol (86-92%), trimethoprim (84-98%),  
356 carbamazepine (86-97%), oxazepam (82-91%), bezafibrate (75-99%) and ciprofloxacin (76-91%). Finally, the 11

357 remaining compounds are well removed, i.e. ofloxacin (63-89%), naproxen (46-99%), sulfamethoxazole (53-72%) and  
358 diclofenac (72-85%).

359

360 To the best of our knowledge, papers dealing with the removal of micropollutants from wastewater by PAC are very  
361 scarce, especially at large scale. Among the 26 PhPHs quantified, only 16 have been already studied in a comparable  
362 context - adsorption from treated wastewater by PAC. Despite rather large standard deviations in our study, removals  
363 are similar to those of these studies (Altmann et al. 2014, Boehler et al. 2012, Löwenberg et al. 2014, Margot et al.  
364 2013) for these 16 common PhPHs, as shown by supporting materials - Table S3 and Figure S3. Only ibuprofen and  
365 estrone removals are notably lower in our study, probably because of their lower influent concentrations. In contrary,  
366 ciprofloxacin is better removed than in the literature. As the average fresh PAC doses are comparable for these studies  
367 (14-15 mg/L), this suggests that micropollutant adsorption on PAC is likely to be a very stable phenomenon and that  
368 these results could be extrapolated to other PAC treatments. A generalization of these results to other WWTPs and PAC  
369 processes could be then possible and relevant, even if efficacy in waters with slightly higher DOC concentrations  
370 should be slightly lower. In addition, some papers have already observed comparable performances over PhPHs with  
371 advanced oxidation processes such as ozonation (Altmann et al. 2014, Margot et al. 2013). For several compounds,  
372 scarce data are available displaying their removal by grain activated carbon filter and/or PAC batch experiments with  
373 surface water (paracetamol, roxithromycin, erythromycin and testosterone), while no reference was found for  
374 sulfadimerazine, sulfameter, sulfadiazine, sulfathiazole, lorazepam and fenofibrate (supporting material - Table S5).  
375 Overall, observed removals are similar to those from former studies (Altmann et al. 2014, Boehler et al. 2012,  
376 Löwenberg et al. 2014, Margot et al. 2013, Ruel et al. 2012, Snyder et al. 2007, Westerhoff et al. 2005).

377

378 The removals vary due to variations of the fresh PAC doses (supporting material - Table S1) and of the influent  
379 concentrations. Despite this, the variations of removal percentages are relatively moderate for most of the compounds,  
380 around 5-15% between Q1 and Q3, except for paracetamol, sulfamethoxazole and bezafibrate, which have higher  
381 variations of 20-30%. Moreover, the observed variations are lower for well and very well removed compounds (i.e. beta  
382 blockers or trimethoprim), i.e. below 10%.

383

384

385 *2.3. Micropollutant removal in degraded WWTP configuration*

386

387 In degraded WWTP configuration, different impacts can be observed on PhPHs removal percentages, depending on the  
388 compound (Figure 4). First, paracetamol and ibuprofen are better removed in percentage in degraded configuration,  
389 most likely due to their higher influent concentrations. Several compounds are rather similarly removed in both  
390 configurations, i.e. both beta blockers, trimethoprim, sulfadiazine and ofloxacin, despite variations of influent  
391 concentrations. Then, lower removals in percentage are observed for a majority of compounds, during degraded WWTP  
392 configuration (Figure 4), despite higher influent concentrations. Nevertheless, the removed pollutant load is higher in  
393 degraded than in nominal WWTP configuration (ketoprofen, naproxen, diclofenac, trimethoprim, roxithromycin,  
394 metronidazole, atenolol, propranolol, oxazepam, lorazepam, bezafibrate and estrone). In contrary, carbamazepine,  
395 ciprofloxacin and sulfamethoxazole have lower removal in degraded configuration due to lower influent concentrations.  
396 This decrease of the micropollutant removals can be explained by both the variations of influent concentrations and the  
397 water quality change. As demonstrated by higher DOC and UV-254, the influents in degraded WWTP exhibit higher  
398 organic matter levels, inducing a stronger competition with micropollutants for adsorption on the PAC by direct site  
399 competition and pore blocking (de Ridder et al. 2011, Delgado et al. 2012). In particular, the negative relation between  
400 DOC concentration and micropollutant removals has already been highlighted in the literature (Altmann et al. 2014,  
401 Margot et al. 2013).

402 Finally, the sum of PhPHs is similarly removed in nominal and degraded WWTP configurations (72-80% vs 70-81%).  
403 This is mainly explained by higher removals of the high concentrated pollutants such as paracetamol and ibuprofen and  
404 slightly lower removals of the other compounds.

405  
406 Regarding the other emerging micropollutants monitored (Figure 3), atrazine (51-64%, min-max), isoproturon (51-83%)  
407 and to a greater extent diuron (82-96%) have a good affinity for PAC, confirming the suitability of the process for  
408 pesticide removal. This confirms other studies observations (Margot et al. 2013, Ruel et al. 2012, Snyder et al. 2007),  
409 even if atrazine is slightly less removed in our case (lower PAC dose). In addition, parabens (>70%), particularly ethyl  
410 paraben (88-94%) and propyl paraben (91-96%), are also well or very well removed. As far as authors know, this is the  
411 first study displaying their fates within PAC in wastewater, as well as for phthalates and PAHs. In contrary, acesulfame  
412 (9-19%), sucralose (6-26%), triclosan (18-29%) and PFOS (6-52%) are poorly removed by adsorption. For PFOA, no  
413 clear conclusion can be drawn, since a systematic negative removal was observed, with concentrations always higher in  
414 effluents than in influents. No sampling blanks were performed for the study, but this potential contamination may  
415 result from Teflon® pipes or elements of the automatic samplers.

416

417 The 9 remaining compounds have variable removals but are rather moderately removed, such as saccharin (33-54%),  
418 DEHP (49-63%), bisphenol A (49-78%) or NP (3-97%). The removal of these substances from wastewater by  
419 adsorption was poorly studied, but (Ruel et al. 2012) reported that within a granulated activated carbon treatment,  
420 DEHP and NP are respectively moderately (30-70%) and poorly (<30%) removed. (Yu et al. 2008) also observed poor  
421 removal for NP by activated carbon. Similarly, (Scheurer et al. 2010) observed that moderate to good removals can be  
422 achieved by PAC adsorption for saccharin and sucralose, what is consistent with results obtained in our study. Finally,  
423 bisphenol A was found to be slightly better removed from wastewater by PAC in (Margot et al. 2013). Regarding  
424 PAHs, the variation of removal is high but these compounds are overall not eliminated by the process or poorly  
425 removed (10-40% for pyrene, fluoranthene, indeno[123]pyrene and benzo[ghi]perylene).

426

427 Even if the number of samples for these substances is limited, the variations of pesticide, sweetener and paraben  
428 removals from campaign to campaign are lower than 30%. Contrariwise, phthalates (except DEHP), PAHs,  
429 alkylphenols and perfluorinated acids have large variations of removals.

430

431

#### 432 *2.4. Water quality after the PAC treatment*

433

434 The tertiary PAC treatment doesn't radically change the micropollutant pattern between influent and effluent (Table 3),  
435 but it substantially decreases their dissolved concentrations. As the generalization of tertiary treatments to all WWTPs  
436 would depend strongly on regulations, having an idea of the levels that could be required for these compounds is  
437 crucial. Instead of an overall removal (average removal of 80%), such as required in Switzerland, environmental quality  
438 criteria (EQC) for freshwaters, comparable to environmental quality standards (EQS) for priority pollutants from (EC  
439 2013), could be used as references. Such EQC have been proposed in Switzerland by the Ecotoxicity Centre of  
440 EAWAG (supporting material - Table S6) (Götz et al. 2010, Kase et al. 2011). A comparison of the concentrations  
441 measured in effluents from the PAC treatment with these EQC or EQS enables to state if this process efficacy is  
442 sufficient to reach references. However, these EQC/EQS apply for freshwaters and not effluents from WWTP, so a  
443 dilution factor should be considered when evaluating the quality of the treatment and the compliance with regulations.

444

445 For PhPHs, naproxen, trimethoprim and atenolol concentrations are already measured below these proposed values  
446 before treatment. Ibuprofen, sulfamethoxazole, ciprofloxacin, propranolol, carbamazepine and bezafibrate are always



447 measured below levels proposed after the treatment, while a fresh PAC dose of 20 mg/L allows decreasing diclofenac,  
448 erythromycin and estrone concentrations below the EQC proposed in Switzerland. For diclofenac, this is particularly  
449 interesting as this compound is now listed on the first watch list of the (EC 2013).  
450 Among the other emerging micropollutants measured, some are listed as priority pollutants (EC 2013). Maximum  
451 admissible concentration (MAC-EQS) and annual average environmental quality standards (AA-EQS) have been set up  
452 for them in surface waters (supporting material - Table S5). All the compounds with MAC-EQS defined were always  
453 quantified below these values in the dissolved phase. For AA-EQS, different cases were encountered: pesticides, t-OP  
454 and DEHP were always found below, NP was measured below only after treatment; PFOS and benzo[*a*]pyrene were  
455 still found above after treatment. Bisphenol A and triclosan are not included in (EC 2013), but have EQC proposed by  
456 the Swiss Ecotoxicity Centre of EAWAG. Regarding it, bisphenol A was always measured below this criterion, even in  
457 influents and before dilution, while triclosan was still measured above its limit value after treatment. However, for these  
458 compounds, the campaigns have been performed when the WWTP operated in degraded configuration, what should  
459 lead to higher concentrations (Geara-Matta 2012). In addition, the WWTP discharges are diluted in the Seine River.

460

461

### 462 3. Influence of operation parameters and physico-chemical properties of the compounds

463

464 Different types of parameters can influence the adsorption processes (de Ridder et al. 2011, Delgado et al. 2012):  
465 structures and properties of the adsorbent, physico-chemical properties of the targeted compounds, water quality and  
466 composition and the operation parameters (dose of adsorbent, contact time, etc.). As explained previously, emerging  
467 micropollutant removals are lower when the WWTP operates in degraded configuration, because of stronger  
468 competition from effluent organic matter and higher concentrations. Results of this study also allow characterizing the  
469 relationship between fresh PAC dose and performances, as well as investigating the relations between physico-chemical  
470 properties of the compounds and their behaviors with PAC.

471

#### 472 3.1. Operation parameters

473

##### 474 *The fresh PAC dose*

475 To assess the influence of the fresh PAC dose, 4 doses (5-10-20-70 mg/L) were tested during nominal WWTP  
476 configuration and the results of the 12 PhPHs quantified in every campaigns of the phase 1 (Figure 4) were considered.

477 Based on our results, the fresh PAC dose appears to be the leading operation parameter as regards its influence on  
478 performances. In particular, a significant positive correlation is found between the removal of the 26 PhPHs and the  
479 dose of PAC ( $r_{\text{spearman}} = 0.962$ ; p-value < 0.001;  $\alpha = 0.05$ ) considering the results in nominal WWTP configuration.  
480 Similarly, significant correlations are found between their individual removals and the PAC dose, as well as for DOC  
481 removal (supporting material - Table S6). In particular, diclofenac, sulfamethoxazole, metronidazole, sulfadiazine,  
482 atenolol, propranolol and carbamazepine have all spearman coefficient of correlation higher than 0.8 with p-value lower  
483 than 0.05.

484 As previously reported (Boehler et al. 2012, Snyder et al. 2007), the higher the PAC dose, the higher the removals.  
485 Overall, the point of inflexion is reached around 10 mg/L for most of the compounds, explaining why the gain of  
486 removal is relatively moderate between 10 and 20 mg/L and between 20 and 70 mg/L of PAC, despite the strong  
487 correlation. In addition, while 9 compounds are very well removed at 10 mg/L of PAC, they are 14 at 20 mg/L and 3 at  
488 5 mg/L (Figure 4). Similarly, the number of well or very well removed compounds increases from 12 at 5 mg/L of  
489 PAC, to 20 at 10 mg/L and 26 at 20 mg/L. Finally, applying a high dose of fresh PAC (70 mg/L) enables to achieve a  
490 very high elimination of micropollutants, with removals higher than 90% for all compounds. In particular, diclofenac  
491 which is on the first watch list of the (EC 2013), is moderately removed at 5 mg/L of fresh PAC, well removed at 10  
492 mg/L and very well removed at 20 mg/L. Similarly, sulfamethoxazole is very impacted by the PAC dose. Finally, the  
493 removal of the total PhPHs concentration is around 76% at 10 mg/L of PAC, 45% at 5 mg/L and 83% at 20 mg/L.

494

#### 495 *Total mass of the PAC in the bed*

496 In normal operation of the pilot, the total mass of the PAC bed is close to 40 kg. Despite substantial variations of the  
497 total mass of PAC in the bed (supporting material - Table S1), no significant impact is observed on the performances,  
498 highlighting that this parameter is minor. However, the presence of a high mass of PAC in the bed should slightly  
499 enhance the performances compared to operating with only the fresh PAC dose, as it was observed with laboratory scale  
500 experiments (not presented). This confirms that the observed removals on the pilot are mainly achieved by the fresh  
501 PAC dose whereas the quantity of preloaded one in the bed allows a limited enhancement of the overall performances.  
502 This observation has to be confirmed by laboratory scale tests in order to clearly identify the role of injected or  
503 preloaded PAC.

504

#### 505 *Other operation parameters*

506 The hydraulic velocity has theoretically an influence on contact time. Moreover, contact time has been identified as  
507 significantly impacting the adsorption process in the literature (Snyder et al. 2007). However, the hydraulic velocity/the  
508 water flow has not a significant impact on the observed contact time in the CarboPlus® process because the variation of  
509 the hydraulic velocity is coupled with a modification of the bed depth. Indeed, a higher velocity means a higher bed  
510 depth by natural expansion, which balances the decrease of contact time. In addition, the experimental design doesn't  
511 allow deeply assessing this point, contrary to the PAC dose. Nevertheless, although a slight impact is observed on  
512 efficacy for some compounds (supporting material - Figure S4) such as atenolol, diclofenac or oxazepam, it seems that  
513 hydraulic velocity would not be a driving parameter of the process efficacy.

514

515 Finally, the solid retention time (SRT) of PAC and the presence of coagulant and flocculant were not studied in this  
516 paper. (Margot et al. 2013) have nevertheless observed a slight increase of micropollutant removal by PAC adsorption  
517 in presence of coagulant.

518

519

### 520 *3.2. Influence of the physico-chemical properties of the compounds on their removals*

521

522 The fate of many pollutants within PAC can be explained by their physico-chemical properties. First of all, the charge  
523 of the compound is a crucial parameter in their removal. Indeed, all positively charged compounds (atenolol,  
524 propranolol, trimethoprim, ciprofloxacin, norfloxacin) are well removed (>80%), regardless their other properties. This  
525 has already been underlined in the literature (de Ridder et al. 2011, Margot et al. 2013). In fact, depending on the point  
526 of zero charge (PZC) of the adsorbent, its surface can be neutral or slightly charged (positively or negatively) at influent  
527 pH (7-8). In addition, sorption of effluent organic matter, generally negatively charged in wastewater, on activated  
528 carbon surface can switch (if initially neutral or positive) or increase (if already negative) the charge, resulting overall in  
529 a surface negatively charged (Margot et al. 2013, Yu et al. 2012a). Therefore, this indicates that in this case the PAC  
530 surface has negative charges inducing strong electrostatic attraction of positive compounds. In spite of their positive  
531 charges, erythromycin and roxithromycin are less removed (50-60%), probably as a results of their high molecular  
532 masses (733.5 and 837.0 g/mol respectively; supporting material - Table S4), inducing a higher sensibility to  
533 competition with organic matter and other compounds (Ji et al. 2010), and a size exclusion (Moreno-Castilla et al.  
534 2003). For these compounds, a slight positive relation with hydrophobicity ( $\log D_{ow}$ ) is moreover observed, i.e.  
535 atenolol (80% -  $\log D_{ow} = -1.99$ ) vs. propranolol (94% -  $\log D_{ow} = 0.98$ ). The number of H-bond sites and the

536 compound structure do not seem to have any substantial influence for these compounds. Moreover, considering only  
537 compounds with similar log D<sub>OW</sub> and molecular mass, negatively charged compounds are less removed than positively  
538 charged ones (i.e. trimethoprim, propranolol, naproxen, diclofenac, sulfamethoxazole).

539

540 For neutral and negatively charged compounds (Figure 2 and supporting material - Table S3), the hydrophobicity and  
541 the structure of the compound seem to play a major role in removal. The influence of hydrophobicity, polarizability or  
542 structure of the compound (functional groups allowing H-bond or  $\pi$ - $\pi$  binding) has already been reported (de Ridder et  
543 al. 2010, Delgado et al. 2012). Indeed, the adsorption of the neutral compounds seems to be influenced by their  
544 hydrophobicity, as reflected by a significant positive correlation ( $r_{\text{spearman}} = 0.587$ ; p-value < 0.05;  $\alpha = 0.05$ ) found  
545 between log D<sub>OW</sub> and removals of PhPHs. (Westerhoff et al. 2005) observed a similar trend. In addition to the  
546 hydrophobicity, specific interactions between PhPHs functional groups and PAC should be involved. Indeed, (de Ridder  
547 et al. 2010) have reported that H-binding and  $\pi$ - $\pi$  interactions become very important at low hydrophobicity, inducing  
548 possible substantial differences in the fate of compounds with similar hydrophobicity.

549

550 No significant or specific relations were found for negative compounds between removal and properties.  
551 Hydrophobicity was not identified as enhancing their adsorption, in contrary to what (Margot et al. 2013) observed.  
552 Absence of direct relationship between adsorption and hydrophobicity was also observed for some antibiotics by (Ji et  
553 al. 2010). These compounds are more likely influenced by their structures and their fates should be driven by a balance  
554 between electrostatic repulsion and specific interactions with PAC surface. (Moreno-Castilla et al. 2003) concluded that  
555 aromatic compounds are mainly physisorbed on activated carbon, confirming the prevalence of these weak interactions.  
556 Some functional groups may enhance adsorption such as aromaticity and N-heterocycles (Delgado et al. 2012),  
557 explaining the high removal of ofloxacin although this compound is negatively charged. For instance, ofloxacin and  
558 diclofenac have three heterocycles, known to enhance adsorption on activated carbon (Delgado et al. 2012), while  
559 sulfamethoxazole and sulfadiazine have only one heterocycle.

560

561

## 562 CONCLUSIONS

563

564 Among the solutions to reduce the emerging contaminant discharges into the environment, the implementation of a  
565 tertiary treatment in actual WWTP is more and more considered. Besides, emerging micropollutants, particularly

566 pharmaceuticals, may be included in modifications of existing regulations. For instance, diclofenac, 17- $\alpha$ - and 17- $\beta$ -  
567 estradiols are now on the first watch list of the (EC 2013), and the Swiss Centre for applied ecotoxicology has proposed  
568 environmental quality criteria for several emerging micropollutants.

569

570 In this context, the fate of 113 micropollutants within a large scale PAC adsorption pilot (CarboPlus<sup>®</sup>) has been studied.  
571 54 pharmaceuticals and hormones (PhPHs) and 59 other micropollutants, such as pesticides, personal care products,  
572 phthalates, PAHs or artificial sweeteners, were then monitored. The 14 campaigns performed allowed assessing the  
573 overall performances of the process for these compounds, and the influence of the WWTP configuration, the operation  
574 parameters and the physico-chemical properties of the micropollutants on the process efficacy.

575

576 26 PhPHs were quantified in influents from nominal WWTP configuration including 8 substances with concentrations  
577 higher than 100 ng/L. Sulfamethoxazole is predominant with the highest average concentration, accounting for about  
578 30% in average of the sum of the 26 PhPHs. In contrary, the remaining molecules were measured whether at low (<10  
579 ng/L), like estrone or lorazepam, or at intermediate concentrations (10-100 ng/L), like naproxen or trimethoprim. 6 of  
580 them are poorly or moderately removed by the process (<60%), i.e. paracetamol, ibuprofen or sulfamethoxazole, and 11  
581 are rather well removed (60-80%), especially diclofenac, naproxen or oxazepam. The 9 remaining substances are very  
582 well eliminated (>80%), i.e. beta blockers, carbamazepine or trimethoprim

583 The change of the WWTP configuration has a substantial impact on the influents quality (DOC, UV-254, BOD<sub>5</sub>,  
584 nitrogen species, TSS) and most of the PhPHs have higher concentrations in this configuration, highlighting both the  
585 seasonal variations and the removal performed due to denitrification step in nominal configuration. Paracetamol and  
586 ibuprofen concentrations are multiplied by 100. PhPHs are overall slightly less removed in percentage in this WWTP  
587 configuration but a higher flux is eliminated. This is consistent considering the higher concentrations and the  
588 degradation of the influents quality which probably enhances the competition effects.

589 Concentrations of the other micropollutants during degraded WWTP configuration are variable but phthalates and  
590 artificial sweeteners are present at very high concentrations, up to 1 000-10 000 ng/L, bisphenol A and NP between 100  
591 and 1 000 ng/L, and pesticides, perfluorinated acids, PAHs and parabens below 100 ng/L. Except parabens and  
592 pesticides, which are largely removed (50-95%), most of the other micropollutants are poorly to moderately removed.  
593 However, similarly to PhPHs, it can be assumed that performances would be higher in nominal WWTP configuration  
594 for these compounds.

595 The fresh PAC dose has been identified as the main operation parameter which significantly influences the

596 performances for micropollutant removals. The total mass of PAC in the bed was not identified as influencing the  
597 performances in the studied range of mass. Overall, in nominal WWTP configuration, the CarboPlus<sup>®</sup> process reduces  
598 in average the sum of the PhPHs of about 53% at a dose of PAC of 5 mg/L, 76% at 10 mg/L and more than 83% at 20  
599 mg/L. Finally, a high dose of PAC allows to achieve very high removals (>90%) of all the PhPHs, but at higher costs.  
600 The molecular charge seems to be the most important property influencing the fate of micropollutants. However, the  
601 size of the molecule can be a limiting factor because high molecular weight compounds are more sensitive to organic  
602 matter competition. A higher dose is then needed for heavy compounds compared to others, at comparable other  
603 molecular properties. For neutral or negative compounds, hydrophobicity and structure of the molecule, particularly the  
604 presence of specific functional groups, become very important in their fates.

605

606 This pilot is still operating in 2014, and a new type of activated carbon is tested. This micro-grain activated carbon  
607 ( $\mu$ GAC) has an intermediary size between PAC (<50  $\mu$ m) and grain (>1 mm), that facilitates the bed handling (no need  
608 of chemical addition) together with good performances for micropollutants elimination. Moreover,  $\mu$ GAC selected is  
609 produced from regenerated activated carbon and is regenerated several times, ensuring a reduction of cost and a higher  
610 sustainability of the process.

611

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613

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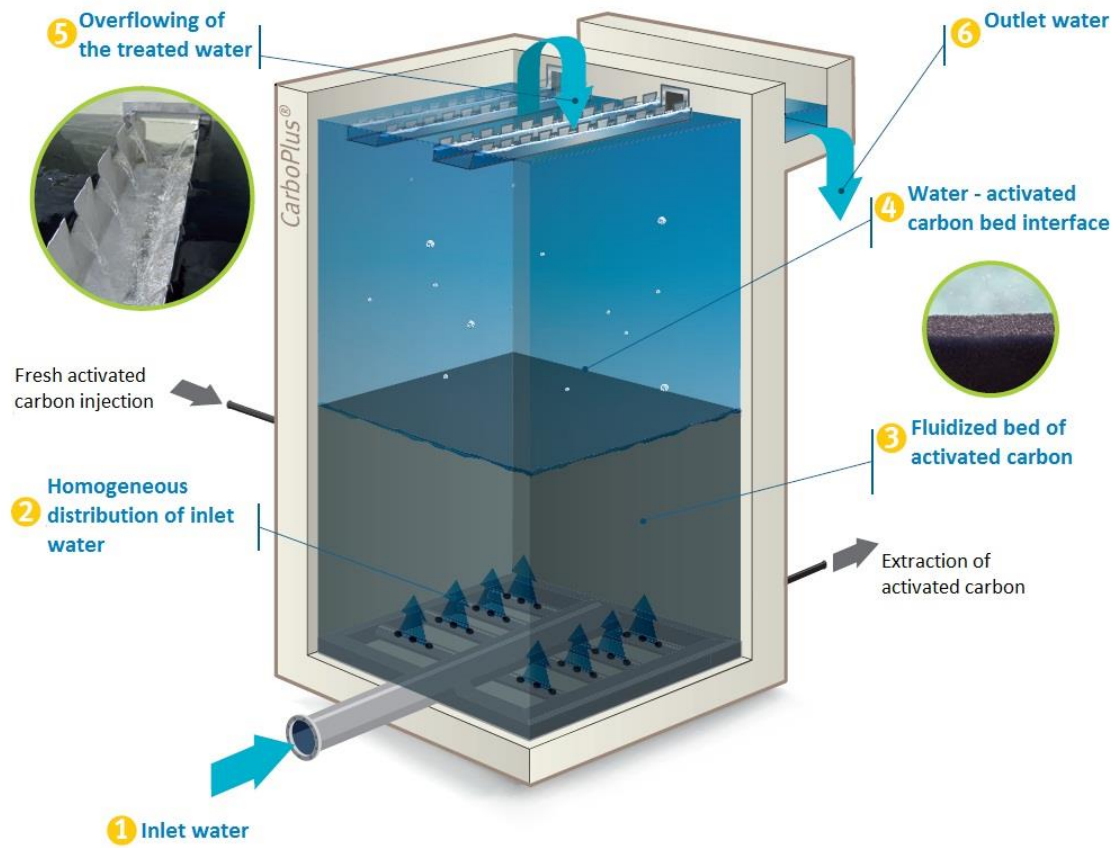


Figure 1 - Layout of the 20 m<sup>3</sup> (5 m x 4 m<sup>2</sup>) CarboPlus® pilot (SAUR source)

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**Table 1 - Operation parameters for the 14 campaigns performed**

	Date	WWTP configuration	PAC dose	Hydraulic velocity	Total PAC mass (kg)	
C1*	02/07/13	Nominal	70	8	-	
C2	09/07/13		20			
C3	16/07/13		5			
C4	23/07/13		20	10		
C5	30/07/13		10	6		
C6	06/08/13		5	8		
C7	20/08/13		10	7		
C8	27/08/13					62
C9	04/11/13					
C10	19/11/13	Degraded	10	7	46	
C11	27/11/13				52	
C12	03/12/13				53	
C13	10/12/13				45	
C14	17/12/13				58	

\*C for campaign.

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**Table 2 - Pollutants studied and their analytical methods**

Groups	N <sup>a</sup>	n <sup>b</sup>	Reference	Extraction <sup>c</sup>	Analysis <sup>d</sup>	LQ <sup>e</sup>
Antibiotics	31	14				0.2 - 110
Analgesic	5	14		SPE		0.04 - 1.0
Beta blockers	2	14		Autotrace®		0.02
Anxiolytics	4	14	(Vulliet et al. 2011)	StrataX® or Oasis HLB®	LC-MSMS	1.0 - 2.0
Hypolipemiant	2	14		cartridges		0.7 - 2.4
Hormones	10	14				1.0
Chlorinated solvents	3	5	(Barrek et al. 2009)		GC-MS	0.2 - 23
Perfluorinated acids	2	5	(Vulliet et al. 2011)	SPE	LC-MSMS	1.0
Pesticides / herbicides / insecticides	23	5	(Barrek et al. 2009)	Autotrace®	GC-MS	6 - 177
Bisphenol A	1	5	(Vulliet et al. 2011)	StrataX® cartridges	LC-MSMS	0.2
PAHs <sup>f</sup>	13	3	(Bressy et al. 2012)		LC-MSMS	10
Alkylphenols	2	5	(Bergé et al. 2014)	SPE	GC-MS	0.2
Phthalates	4	5	(Bergé et al. 2014)	Manual		0.6 - 100
PCPs <sup>f</sup>	7	3	(Gasperi et al. 2014)	Oasis HLB® cartridges	LC-MSMS	100
				SPE		
Sweeteners	4	4	(Scheurer et al. 2009)	Autotrace®	LC-MSMS	50 - 250
				Bakerbond SDB1 cartridges		
<i>Total micropollutants</i>	<i>113</i>					

<sup>a</sup> N = number of substances.

<sup>b</sup> n = number of campaigns performed.

<sup>c</sup> SPE = solid phase extraction.

<sup>d</sup> Analytical methods: LC = liquid chromatography, GC = gas chromatography, GC-MS = GC with mass spectrometry, LC-MSMS = LC with tandem mass spectrometry.

<sup>e</sup> LQ = limit of quantification.

<sup>f</sup> PAHs = polycyclic aromatic hydrocarbons; PCPs = personal care products.

**Table 3 - Micropollutant and conventional wastewater parameter concentrations in influents and effluents during nominal and degraded WWTP configuration**

	LQ (ng/L)	Nominal WWTP configuration (n=9)				Degraded WWTP configuration (n=5)			
		Influent		Effluent		Influent		Effluent	
		N	Concentration (ng/L) Av. $\pm$ SD (min - max)	N	Concentration (ng/L) Av. $\pm$ SD (min - max)	N	Concentration (ng/L) Av. $\pm$ SD (min - max)	N	Concentration (ng/L) Av. $\pm$ SD (min - max)
<i>Conventional wastewater parameters</i>									
UV 254 nm (cm <sup>-1</sup> )	0.01	9/9	0.110 $\pm$ 0.013 (0.087 - 0.120)	9/9	0.075 $\pm$ 0.020 (0.047 - 0.106)	5/5	0.139 $\pm$ 0.011 (0.126 - 0.152)	5/5	0.109 $\pm$ 0.008 (0.099 - 0.120)
DOC (mgC/L)	0.5	9/9	5.6 $\pm$ 0.9 (4.4 - 7.0)	9/9	3.5 $\pm$ 1.2 (1.2 - 5.2)	5/5	7.5 $\pm$ 0.5 (7.1 - 8.3)	5/5	5.8 $\pm$ 0.4 (5.4 - 6.4)
COD (mgO <sub>2</sub> /L)	4	9/9	26 $\pm$ 11 (17 - 47)	9/9	34 $\pm$ 22 (13 - 74)	5/5	26 $\pm$ 2 (23 - 28)	5/5	21 $\pm$ 2 (19 - 25)
BOD <sub>5</sub> (mgO <sub>2</sub> /L)	0.5	9/9	4.8 $\pm$ 3.3 (2.8 - 11.0)	9/9	3.5 $\pm$ 1.9 (1.3 - 7.0)	5/5	5.8 $\pm$ 0.9 (4.9 - 7.0)	5/5	3.0 $\pm$ 0.5 (2.4 - 3.7)
NH <sub>4</sub> <sup>+</sup> (mgN/L)	0.3	0/9	<LQ	0/9	<LQ	5/5	4.4 $\pm$ 0.7 (3.2 - 5.0)	5/5	3.5 $\pm$ 0.5 (2.9 - 4.0)
NO <sub>2</sub> <sup>-</sup> (mgN/L)	0.02	9/9	0.21 $\pm$ 0.17 (0.06 - 0.23)	8/9	0.15 $\pm$ 0.16 (<LQ - 0.30)	5/5	0.7 $\pm$ 0.02 (0.05 - 0.09)	5/5	0.29 $\pm$ 0.16 (0.03 - 0.46)
NO <sub>3</sub> <sup>-</sup> (mgN/L)	0.4	9/9	9.1 $\pm$ 2.9 (5.6 - 11.7)	9/9	8.5 $\pm$ 2.8 (4.9 - 13.7)	5/5	23.7 $\pm$ 2.1 (20.6 - 25.4)	5/5	24.4 $\pm$ 2.5 (20.7 - 26.6)
TKN (mgN/L)	0.5	9/9	1.5 $\pm$ 0.2 (1.1 - 1.8)	9/9	1.2 $\pm$ 0.1 (0.9 - 1.3)	5/5	4.9 $\pm$ 0.5 (4.1 - 5.5)	5/5	3.9 $\pm$ 0.4 (3.4 - 4.4)
PO <sub>4</sub> <sup>3-</sup> (mgP/L)	0.1	0/5	<LQ	0/5	<LQ	0/5	<LQ	0/5	<LQ
TP (mgP/L)	0.3	0/5	<LQ	0/5	<LQ	0/5	<LQ	0/5	<LQ
TSS (mg/L)	2.0	9/9	3 $\pm$ 1 (2 - 5)	9/9	9 $\pm$ 7 (2 - 21)	5/5	6 $\pm$ 2 (4 - 9)	5/5	5 $\pm$ 2 (2 - 6)
<i>Pharmaceuticals and hormones</i>									
Ketoprofen	0.3	9/9	34 $\pm$ 18 (13 - 61)	6/9	11 $\pm$ 10 (<LQ - 30)	5/5	367 $\pm$ 90 (273 - 501)	5/5	145 $\pm$ 28 (109 - 182)
Naproxen	0.7	8/8	33 $\pm$ 28 (8 - 83)	5/8	12 $\pm$ 13 (<LQ - 34)	5/5	154 $\pm$ 39 (122 - 220)	5/5	52 $\pm$ 9 (43 - 64)
Paracetamol	0.04	6/9	33 $\pm$ 22 (<LQ - 70)	6/9	32 $\pm$ 18 (<LQ - 56)	5/5	5 870 $\pm$ 2 597 (3 610 - 10 350)	5/5	1 030 $\pm$ 923 (349 - 2 650)
Ibuprofen	1.0	2/9	9 (<LQ - 13)	5/9	9 $\pm$ 5 (<LQ - 14)	5/5	951 $\pm$ 360 (590 - 1 439)	5/5	432 $\pm$ 200 (220 - 699)
Diclofenac	0.3	9/9	184 $\pm$ 91 (95 - 309)	9/9	52 $\pm$ 51 (3 - 166)	5/5	384 $\pm$ 76 (301 - 508)	5/5	171 $\pm$ 19 (147 - 196)
Sulfamethoxazole	1.0	9/9	993 $\pm$ 817 (175 - 3 010)	9/9	419 $\pm$ 318 (37 - 798)	5/5	233 $\pm$ 179 (70 - 470)	3/5	130 (<LQ - 235)
Ofloxacin	10	9/9	412 $\pm$ 314 (14 - 911)	8/9	70 $\pm$ 74 (<LQ - 218)	5/5	39 $\pm$ 7 (34 - 51)	3/5	18 (<LQ - 24)
Ciprofloxacin	1.0	8/9	175 $\pm$ 93 (64 - 312)	6/9	22 $\pm$ 17 (<LQ - 51)	5/5	13 $\pm$ 3 (11 - 17)	3/5	5 (<LQ - 8)
Trimethoprim	0.3	9/9	64 $\pm$ 79 (8 - 222)	8/9	4 $\pm$ 2 (<LQ - 8)	5/5	43 $\pm$ 28 (9 - 74)	4/5	6 $\pm$ 3 (<LQ - 9)
Metronidazole	0.2	9/9	19 $\pm$ 3 (15 - 24)	8/9	8 $\pm$ 3 (<LQ - 12)	5/5	30 $\pm$ 4 (23 - 33)	5/5	25 $\pm$ 4 (18 - 29)
Roxithromycin	1.0	4/4	99 $\pm$ 53 (57 - 173)	4/4	35 $\pm$ 33 (5 - 76)	5/5	175 $\pm$ 59 (126 - 271)	4/5	99 $\pm$ 42 (<LQ - 155)
Norfloxacin	1.0	5/9	80 $\pm$ 36 (<LQ - 118)	3/9	17 (<LQ - 29)	0/5	<LQ	0/5	<LQ
Erythromycin	1.0	4/4	124 $\pm$ 32 (97 - 170)	4/4	50 $\pm$ 38 (23 - 106)	0/5	<LQ	0/5	<LQ
Sulfadimerazine	1.0	2/9	4 (<LQ - 7)	1/9	(<LQ - 4)	0/5	<LQ	0/5	<LQ
Sulfadiazine	1.0	9/9	10 $\pm$ 6 (1 - 21)	7/9	4 $\pm$ 3 (<LQ - 8)	5/5	4 $\pm$ 1 (2 - 5)	4/5	1 $\pm$ 1 (<LQ - 2)
Sulfameter	1.0	1/9	(<LQ - 4)	0/9	<LQ	0/5	<LQ	0/5	<LQ
Sulfathiazole	1.0	3/9	1	0/9	<LQ	0/5	<LQ	0/5	<LQ

			(1 - 2)						
Atenolol	0.02	9/9	185 ± 51 (124 - 251)	9/9	28 ± 24 (2 - 67)	5/5	588 ± 156 (454 - 858)	5/5	176 ± 42 (126 - 236)
Propranolol	0.02	9/9	97 ± 27 (66 - 131)	9/9	5 ± 5 (1 - 15)	5/5	197 ± 46 (162 - 276)	5/5	14 ± 5 (10 - 23)
Carbamazepine	1.0	9/9	215 ± 85 (19 - 321)	8/9	41 ± 43 (<LQ - 113)	5/5	30 ± 2 (27 - 32)	4/5	8 ± 2 (<LQ - 11)
Oxazepam	1.2	8/8	139 ± 128 (20 - 354)	8/8	29 ± 24 (5 - 65)	5/5	409 ± 132 (251 - 615)	5/5	176 ± 31 (145 - 210)
Lorazepam	1.9	3/8	11 (<LQ - 27)	1/8	(<LQ - 6)	4/5	34 ± 2 (<LQ - 36)	5/5	18 ± 3 (15 - 23)
Bezafibrate	0.7	8/8	36 ± 42 (1 - 102)	6/8	8 ± 9 (<LQ - 26)	5/5	369 ± 330 (151 - 940)	5/5	187 ± 149 (84 - 447)
Fenofibrate	2.4	1/8	(<LQ - 4)	0/8	<LQ	0/8	<LQ	0/8	<LQ
Estrone	1.0	4/8	7 ± 2 (<LQ - 10)	5/8	9 ± 10 (<LQ - 26)	5/5	12 ± 3 (9 - 15)	5/5	5 ± 1 (4 - 7)
Testosterone	1.0	1/8	(<LQ - 1)	0/8	<LQ	2/5	(<LQ - 1)	0/5	<LQ
ΣPhPHs	-	-	2 729 ± 1 057 (1 358 - 5 158)	-	752 ± 517 (75 - 1 593)	-	9 892 ± 2 569 (6 844 - 13 910)	-	2 625 ± 1 007 (1 711 - 4 226)
<i>Other emerging micropollutants</i>									
Atrazine	0.2					5/5	4 ± 1 (3 - 5)	5/5	2 ± 1 (1 - 2)
Diuron	0.2					5/5	25 ± 5 (19 - 30)	5/5	4 ± 1 (2 - 5)
Isoproturon	0.2					5/5	34 ± 22 (11 - 62)	5/5	12 ± 6 (5 - 20)
PFOA	1.0					5/5	25 ± 9 (14 - 36)	5/5	37 ± 19 (16 - 57)
PFOS	1.0					5/5	44 ± 12 (24 - 56)	5/5	31 ± 13 (14 - 47)
Bisphenol A	10					5/5	259 ± 148 (142 - 513)	5/5	78 ± 24 (52 - 112)
NP	100					5/5	841 ± 681 (143 - 1 895)	3/5	286 (<LQ - 390)
t-OP	0.6					5/5	17 ± 5 (10 - 22)	5/5	16 ± 15 (4 - 39)
DEHP	100					4/4	1 413 ± 862 (919 - 2 704)	4/4	861 ± 489 (377 - 1 300)
DEP	100					5/5	991 ± 443 (441 - 1 644)	5/5	437 ± 149 (298 - 646)
DnBP	100					5/5	932 ± 631 (355 - 1 986)	5/5	607 ± 383 (309 - 1 280)
Acesulfame	50					4/4	8 725 ± 602 (7 900 - 9 300)	4/4	7 525 ± 665 (6 700 - 8 200)
Cyclamate	50					2/4	240 (<LQ - 430)	0/4	<LQ
Saccharin	50					4/4	1 355 ± 572 (840 - 2 100)	4/4	703 ± 284 (450 - 1 100)
Sucralose	250					4/4	7 150 ± 545 (6 500 - 7 800)	4/4	5 875 ± 222 (5 600 - 6 100)
Triclosan	10					3/3	135 (121 - 158)	3/3	103 (86 - 119)
Methyl paraben	2.8					3/3	65 (31 - 102)	3/3	11 (10 - 13)
Ethyl paraben	3.5					3/3	40 (27 - 57)	2/3	5 (<LQ - 7)
Propyl paraben	3.3					3/3	56 (37 - 81)	2/3	5 (<LQ - 5)
Benzyl paraben	3.0					1/3	(<LQ - 4)	1/3	(<LQ - 3)
Butyl paraben	2.8					2/3	10 (<LQ - 13)	0/3	<LQ
Fluorene	0.2					3/3	1.7 (0.3 - 4.2)	3/3	3.0 (2.6 - 3.4)
Phenanthrene	0.2					3/3	16.7	3/3	24.2

Anthracene	0.2
Fluoranthene	0.2
Pyrene	0.2
Benzo[a]anthracene	0.2
Chrysene	0.2
Benzo[b]fluoranthene	0.2
Benzo[k]fluoranthene	0.2
Benzo[a]pyrene	0.2
Indeno[123]pyrene	0.2
Dibenzo[ah]anthracene	0.2
Benzo[ghi]perylene	0.2

	(13.0 - 19.1)		(10.2 - 33.3)
3/3	0.6 (0.5 - 0.8)	3/3	16.7 (13.0 - 19.1)
3/3	3.2 (2.6 - 3.9)	3/3	2.6 (2.4 - 2.8)
3/3	2.4 (2.1 - 2.8)	3/3	1.6 (1.4 - 1.8)
0/3	<LQ	1/3	(<LQ - 0.9)
3/3	1.5 (1.2 - 1.6)	3/3	1.5 (0.7 - 1.9)
3/3	3.3 (2.2 - 4.0)	3/3	3.2 (1.5 - 4.2)
3/3	1.2 (0.9 - 1.4)	3/3	1.5 (0.5 - 2.5)
3/3	1.4 (0.9 - 1.7)	3/3	1.8 (0.7 - 3.0)
3/3	2.0 (1.0 - 2.6)	3/3	2.0 (0.8 - 3.3)
3/3	0.5 (0.3 - 0.6)	3/3	1.8 (0.3 - 4.3)
3/3	2.0 (1.1 - 2.6)	3/3	1.7 (0.7 - 2.3)

LQ = limit of quantification.  
N = number of quantification / campaigns performed.  
Av. ± SD = average ± standard deviation (calculated only when N > 3).



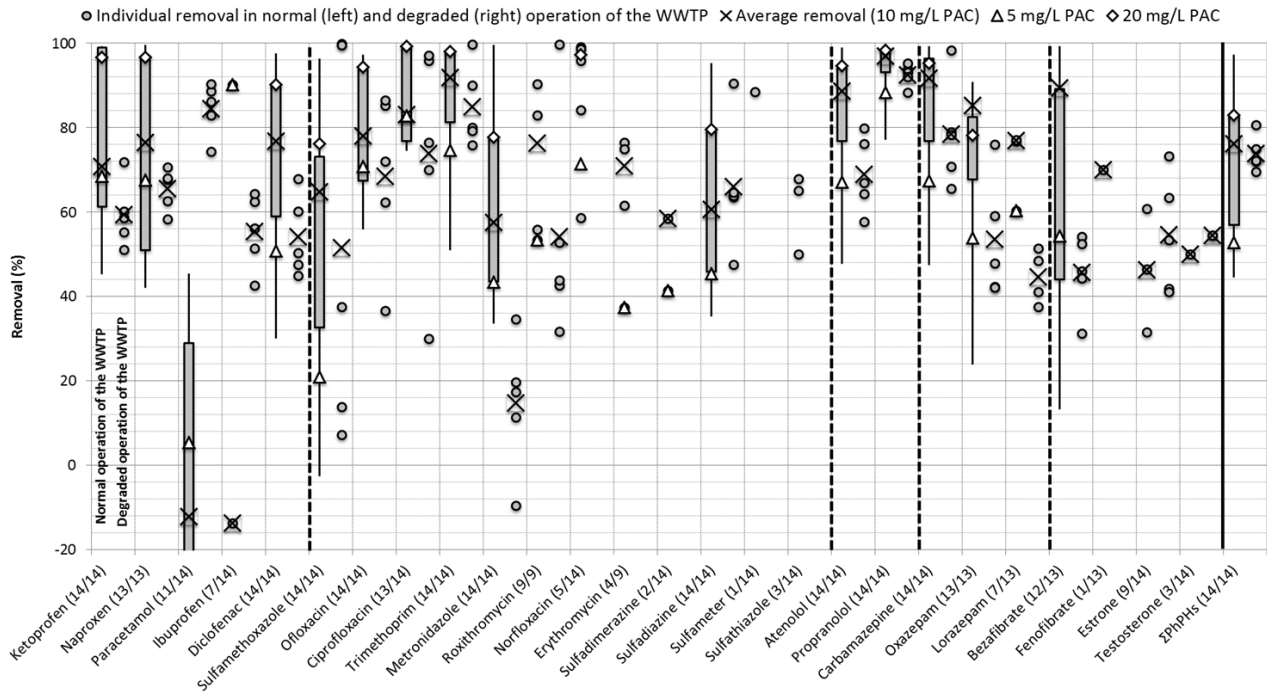
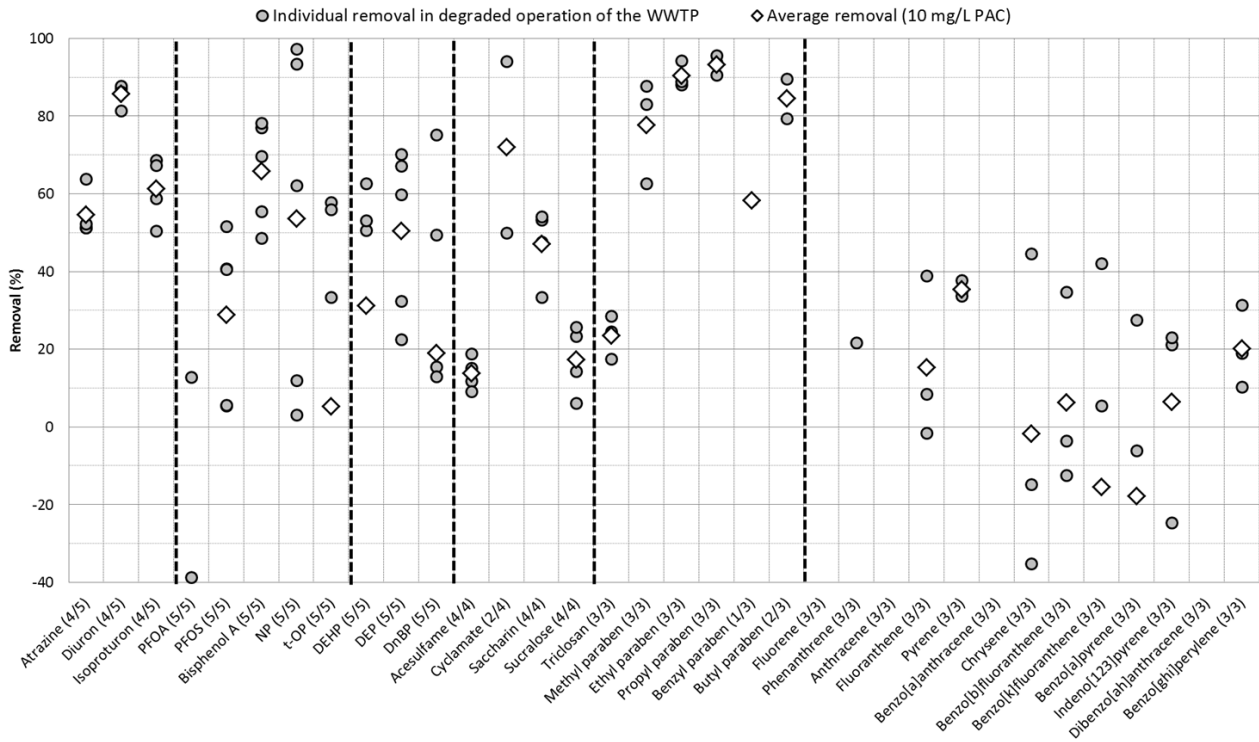


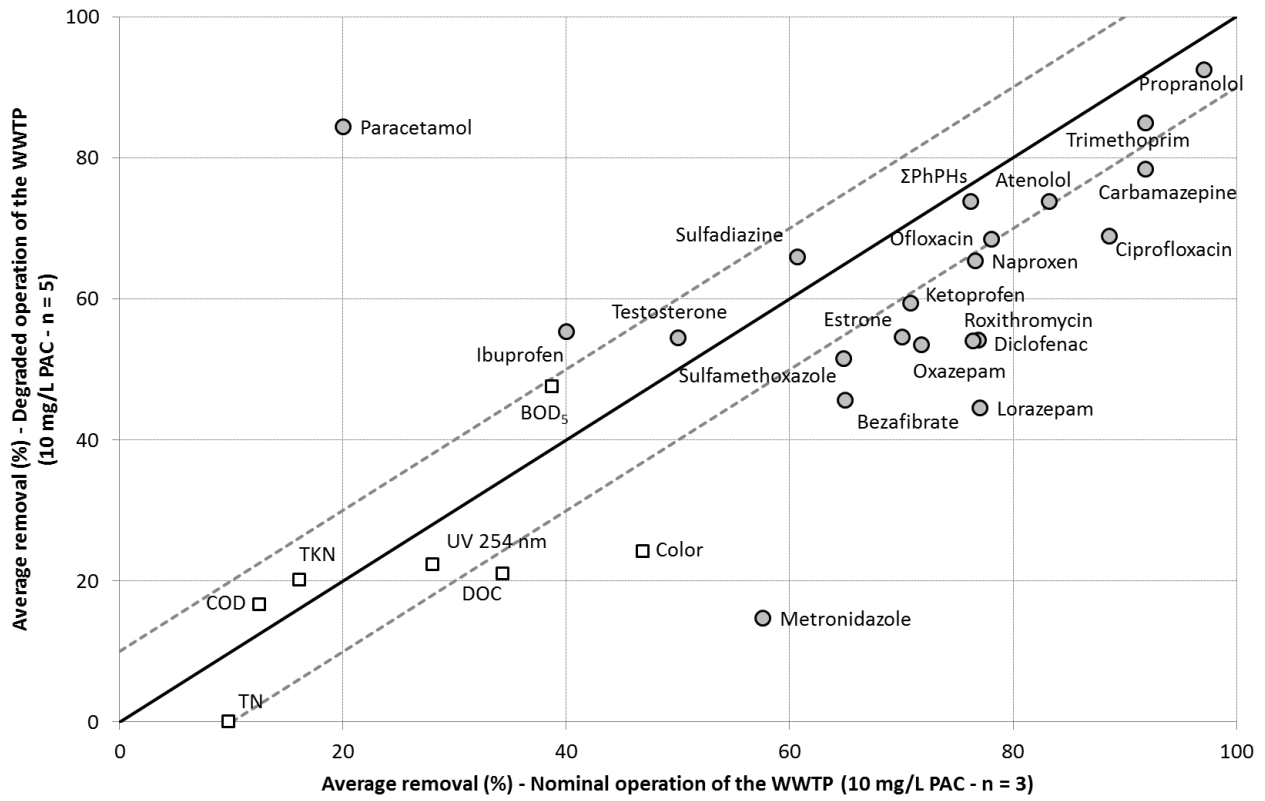
Figure 2 - Removals of pharmaceuticals and hormones (N=26) by PAC treatment during nominal (left) and degraded (right) WWTP configurations (min - Q1 - Q2 - Q3 - max or individual values) - occurrence in brackets

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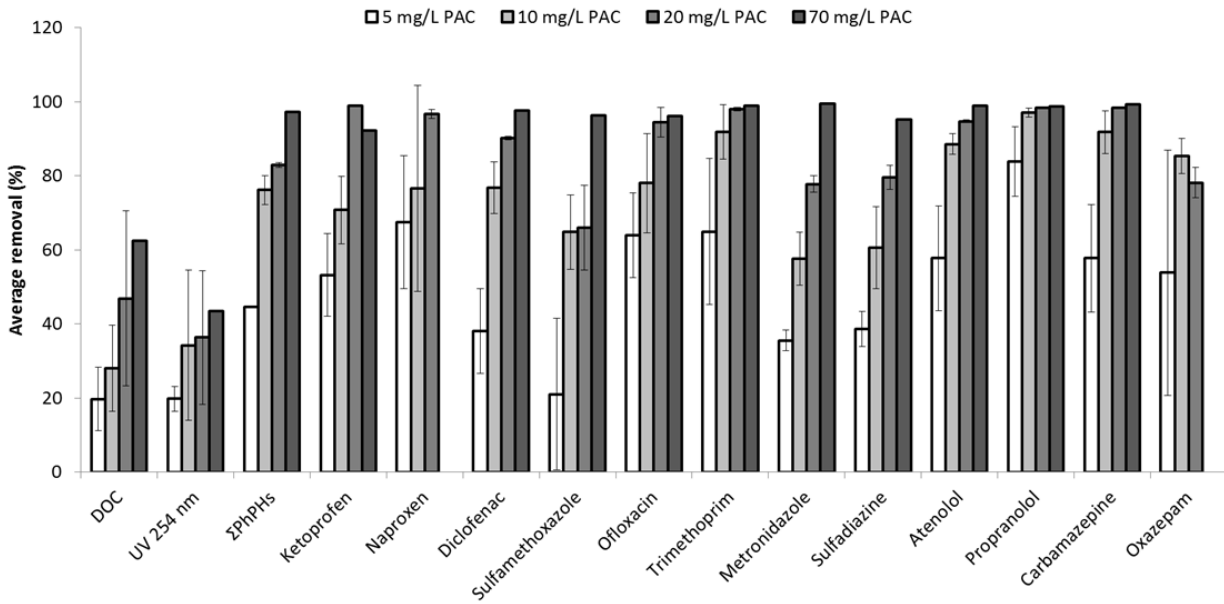


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Figure 3 - Removals of the other emerging micropollutants by PAC, in degraded configuration of the WWTP.



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**Figure 4 - Parameters influencing the efficiency of PAC to remove emerging micropollutants from treated wastewater - influence of the water quality (top) and the fresh PAC dose (bottom)**