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## Removal of emerging micropollutants from wastewater by activated carbon adsorption: Experimental study of different activated carbons and factors influencing the adsorption of micropollutants in wastewater

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1 Removal of emerging micropollutants from wastewater by activated carbon adsorption:  
2 experimental study of different activated carbons and factors influencing the adsorption of  
3 micropollutants in wastewater

4  
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17  
18 **HIGHLIGHTS**

- 19 • BET surface and bulk density of activated carbons are correlated to micropollutants adsorption,  
20 • The activated carbon dose and the contact time have a great influence on adsorption,  
21 • FeCl<sub>3</sub> has a positive influence on micropollutants adsorption by activated carbon (+10-15%),  
22 • Both the quantity and composition of organic matter impact the adsorption,  
23 • UV-254 removals are correlated to several micropollutants removals.

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France. (Email: *romain.mailler@siaap.fr*)

25 ABSTRACT

26

27 Activated carbon processes, initially designed for drinking water production, are tested for wastewater application in order  
28 to characterize their efficiency to remove micropollutants from wastewater treatment plants (WWTPs) discharges. In that  
29 purpose, a pilot was set up at the Seine Centre WWTP and is studied by the Paris sanitation service (SIAAP) and the  
30 Water Environment and Urban Systems laboratory (LEESU). The *in-situ* study raised several additional questions related  
31 to the structural and morphological properties of activated carbons, in order to select the proper material, the influence of  
32 operational parameters such as the activated carbon dose and the contact time, the role of organic matter concentration  
33 and composition, the presence of a residual concentration of methanol or the impact of ferric chloride addition. Thus,  
34 various complementary experiments were carried out at laboratory scale to improve the understanding of the  
35 micropollutants adsorption process on activated carbon, in particular on powdered activated carbon (PAC).

36

37 The results have highlighted a strong link between the efficiency of PACs and their specific surface (BET), which can be  
38 easily estimated by their bulk density. The study of the sorption process has also confirmed the strong influence of the  
39 PAC dose and the rapidity of the sorption kinetic. From an operational point of view, the ferric chloride injection seems  
40 to slightly improve most of the detected compounds adsorption, probably thanks to the coagulation of the dissolved  
41 organic matter colloidal fraction. In contrary, the presence in the water of a residual concentration of methanol seems to  
42 have no impact on the pharmaceuticals fate. The influence of the wastewater matrix where adsorption is performed is  
43 strong, with notably lower adsorption in settled water compared to various WWTP discharges. However, the dissolved  
44 organic carbon concentration is not always sufficient to explain sorption competitions in wastewater, and the composition  
45 and the distribution of the organic matter should be considered too. In particular, the carbon removal from biological  
46 treatments is the step that clearly modifies both the quantity and the composition of the organic matter. It has been  
47 observed that discharges from WWTPs operating with different biological processes (activated sludge, membrane  
48 bioreactor or biofiltration) have similar organic matter concentrations and compositions, and allows comparable removals  
49 of organic matter and micropollutants by adsorption. The lower performances on micropollutants observed in the settled  
50 water can be explained by the higher quantity of small protein-like molecules (fluorophores  $\delta$  and  $\gamma$ ), which compose the  
51 most competitive organic matter fraction for adsorption on activated carbon, compared to the other waters.

52

53

54 KEYWORDS

55 Adsorption; organic matter; pharmaceuticals; activated carbon; wastewater

56

## 57 INTRODUCTION

58

59 The presence of a large range of emerging micropollutants, particularly pharmaceuticals and hormones, personal care  
60 products or pesticides, has been highlighted in wastewater treatment plant (WWTP) discharges (Miège *et al.* 2009;  
61 Verlicchi *et al.* 2012; Loos *et al.* 2013; Mailler *et al.* 2015). Even if several hydrophobic, volatile or biodegradable  
62 compounds are strongly removed by conventional wastewater treatments (Ruel *et al.* 2012; Mailler *et al.* 2014b), most of  
63 micropollutants are not removed. Thus, various strategies of contamination reduction are assessed by the scientific  
64 community and water treatment engineers. Among them, the implementation of tertiary treatments dedicated to  
65 micropollutants elimination represents a relevant solution. In particular, adsorption on activated carbon appears to be  
66 efficient, very flexible and relatively cheap (Abegglen & Siegrist 2012), together with not producing oxidation by-  
67 products.

68

69 In this context, the Parisian public sanitation service (SIAAP) and the Water Environment and Urban Systems laboratory  
70 (LEESU) study, in collaboration with SAUR teams, the CarboPlus® process. This process is based on a fluidized bed of  
71 activated carbon (powder - PAC - or micro-grain -  $\mu$ GAC) to remove micropollutants by adsorption. A large-scale pilot  
72 based on this technology was set up at the Seine Centre WWTP (240 000 m<sup>3</sup>/days) to characterize the efficiency of  
73 activated carbon to remove a wide range of pollutants from WWTP discharges. The *in-situ* results are presented in (Mailler  
74 *et al.* 2015) for PAC.

75 In parallel to the *in situ* study, complementary laboratory scale experiments were conducted to i) better understand the  
76 relationships between activated carbon properties and the adsorption in wastewater and ii) to improve the understanding  
77 of the micropollutant adsorption mechanisms in wastewater application, in particular with PAC.

78

79 Activated carbon is characterized by different structural and morphological properties that can affect adsorption (Baudu  
80 *et al.* 2001; Li *et al.* 2002; Yu *et al.* 2008; Delgado *et al.* 2012). Thus, the first axis consists in studying the relationships  
81 between activated carbon properties and their efficiency to remove micropollutants. In particular, a focus is performed on  
82 the specific BET surface and the bulk density.

83

84 The second axis consists in studying the adsorption mechanism in wastewater representing a complex matrix. Indeed, the

85 literature highlighted that the matrix where adsorption is performed plays a crucial role in the fate of molecules (Ebie *et*  
86 *al.* 2001; Ternes *et al.* 2002; de Ridder *et al.* 2010; de Ridder *et al.* 2011), particularly the organic matter which competes  
87 with pollutants for adsorption through direct sites competition or pore blocking. In addition, most of the studies were  
88 conducted for drinking water production or in surface waters, and the adsorption mechanisms were poorly assessed in  
89 wastewater. Thus, the influences of both the activated carbon dose and the contact time on the performances were  
90 assessed, as well as the influence of the organic matter and chemicals that can be injected within the process for  
91 operational purposes.

92

93 This article summarizes the results from the laboratory scale experiments conducted within this project. First, the  
94 relationships between micropollutants removals and activated carbon properties are assessed. Then, the influence of the  
95 dose of carbon, the contact time, the organic matter quantity and quality, the presence of a residual concentration of  
96 methanol and the injection of FeCl<sub>3</sub> were studied.

97

98

## 99 MATERIALS AND METHODS

100

### 101 1. Activated carbon characterization

102

103 11 adsorbents, including micro and mesoporous PACs and  $\mu$ GAC, have been selected based on their technical datasheets  
104 provided by the producers. Among them, 3 are commercialized by DaCarb® (PB 170®, PB 170-400® and PC 1000® -  
105 France), 3 by Chemviron® (WP 235®, Carbsorb 28® and Cyclecarb 305® - Belgium), 2 by Norit® (W 35® and SA  
106 Super® - Netherlands) and 3 by Jacobi® (LP 39®, MP 25® and Hydro XP 17® - Sweden). These activated carbons are  
107 recognized for their high organic pollutants affinity, but their use in wastewater was poorly studied in the literature.

108

109 Several structural properties such as the specific BET surface (m<sup>2</sup>/g), the porous volume (mL/g), the pore size distribution  
110 and the bulk density (g/cm<sup>3</sup>) have been measured on the 11 activated carbons. In addition, the particle size distribution  
111 and the micropollutant elimination have been determined for 4 of them: PB 170®, WP 235®, W 35® and PC 1000®.

112

113 These structural properties have been analyzed at the University of Technology of Compiègne (UTC, France). The  
114 specific BET surface and the pore size distribution were measured with an ASAP 2010 Micromeritics analyzer equipped

115 with a degasing station and a gas isotherm adsorption analyses station (nitrogen), according to the conventional methods  
116 used to determine these parameters. Fresh activated carbon samples (100 mg) were degased at least 12 h before to be  
117 analyzed. Results correspond to the specific surface in  $\text{m}^2/\text{g}$  obtained with the BET (Brunauer, Emmett and Teller) method.  
118 The pore size distribution is determined with the BJH (Barrett, Joyner and Halenda) method, using the desorption curve  
119 of the same gas on the same analyzer. This method allows also calculating the microporous and mesoporous pore volumes.  
120 The bulk density was measured by weighting, with a high precision balance (0.01 mg), 50 to 100 mL of activated carbon,  
121 measured with a 100 mL graduated cylinder. The activated carbon is introduced by small doses (10 mg) and is compacted  
122 every 10 mL to minimize the vacuum between particles.

123 The particles size distribution of the 4 PACs was measured with a Mastersizer 2000 Malvern laser particle sizer. Every  
124 analysis corresponds to 15 000 light diffraction measures. 3 scans were performed at least per sample.

125

## 126 2. Pollutants and analytical procedures

127

128 For every sample, several parameters were measured in the dissolved phase: UV absorbance at 254 nm (UV-254),  
129 dissolved organic carbon (DOC) and concentrations of 16 pharmaceuticals and 2 pesticides (list and limit of quantification  
130 in supporting material - Table S1). Organic micropollutants were analyzed by the Institute of Analytical Sciences (ISA -  
131 Villeurbanne, France), while UV-254 and DOC were measured by the SIAAP laboratory (French accreditation -  
132 Colombes, France). Analytical protocols are validated and are given in (Mailler *et al.* 2015).

133

134 3D fluorescence spectrometry analyses were also performed by the LEESU. They allow generating a tridimensional  
135 matrix and to plot it on a 3D spectrum containing all excitation and emission spectra of the dissolved organic matter  
136 (DOM) present in a sample. This method gives the distribution of the different components of the DOM as they don't  
137 fluoresce in the same zones of the spectrum. The detailed description of 3D fluorescence spectrometry is given in (Hudson  
138 *et al.* 2007). Analyses have been performed with a Jasco FP-8300 spectrofluorometer equipped with a 1 cm quartz cell.

139

## 140 3. Laboratory experiments protocols

141

142 The laboratory experiments have been performed in the Seine Centre WWTP (Colombes, France) between April 2013  
143 and May 2015. Wastewater was punctually sampled from the WWTP discharges with 10 L glass bottles, properly rinsed  
144 and grilled, and used the same day for experiments. Then, samples were filtered on glass fibers filters (GF/F 0.7  $\mu\text{m}$ ) after

145 experiments, before to be sent to laboratories for analyses.

146

### 147 3.1. Efficiency comparison of 4 PACs

148

149 The efficiency of 4 PACs (PB 170®, WP 235®, W 35® and PC 1000® - Table 1) to remove micropollutants was assessed,  
150 by contacting individually 10 mg/L of each PAC with 1 L of Seine Centre WWTP (SEC) discharges during 45 min under  
151 strong mixing. After filtering, samples were conditioned and sent to ISA laboratory to analyze pharmaceuticals and  
152 pesticides.

153

### 154 3.2. PAC dose and adsorption kinetic

155

156 Regarding its performances, PB 170® was selected to characterize the relationship between PAC dose, contact time and  
157 micropollutant removal. First, 10 mg/L of this PAC were contacted with 1 L of SEC discharges under strong mixing  
158 during different contact times (5 - 10 - 30 - 45 - 60 min), which are close from the pilot contact time range. Then, 3 PAC  
159 doses (5 - 10 - 20 mg/L) were tested with 1 L of SEC discharges and during 45 min.

160

### 161 3.3. DOM and adsorption

162

163 The DOM has been identified to play a crucial role in the adsorption process because it induces a competition with the  
164 organic micropollutants for adsorption (Matsui *et al.* 2003; de Ridder *et al.* 2011; Delgado *et al.* 2012). These phenomena  
165 have been principally observed with surface water and natural organic matter, but some recent studies also studied it in  
166 wastewater (Margot *et al.* 2013; Altmann *et al.* 2014). In this context, it is necessary to determine the role of both the  
167 quantity and the quality of the DOM in the adsorption process. To this end, 7 types of wastewater featuring by different  
168 levels of organic matter (Table 1) have been contacted under strong mixing with PAC (10 mg/L of PB 170® during- 45  
169 min). Among the tested waters, 4 were WWTP discharges, from Seine Centre (SEC), Seine Aval (SAV), Seine Morée  
170 (SEM) and Seine Amont (SAM) WWTPs. The 3 other tested waters were outlet waters from the physico-chemical  
171 lamellar settling unit (SEC settled water) and the carbon biofiltration effluent (carbon removal) of SEC, as well as SEC  
172 settled water diluted with distilled water to reach a DOC level comparable to the WWTP discharges. The layouts of the  
173 different studied WWTPs are given in supporting material - Table S1, as well as the sampling points (red circles). The  
174 organic matter characteristics of these waters are different and given in Table 1. Among the 7 wastewaters, the

175 micropollutants adsorption has been assessed with SEC settled water, SEC carbon biofiltration effluent, SEC and SAV  
 176 discharges.

177

178 A 3D fluorescence spectrometry characterization has also been performed on these 7 waters, before and after contact with  
 179 PAC. The spectra interpretation follows the fluorophores defined in (Parlanti *et al.* 2002), as indicated for SEC settled  
 180 water and discharges in supporting material - Figure S2.  $\alpha$ ,  $\alpha'$  and  $\beta$  correspond to humic-like substances,  $\gamma$  and  $\delta$   
 181 respectively represents tyrosine-like and tryptophan-like proteins. Then, I1, I2, I3 and I4 indexes, respectively  
 182 corresponding to the ratios  $\alpha'/\alpha$ ,  $\beta/\alpha$ ,  $\gamma/\alpha$  and  $\delta/\alpha$ , were calculated to evaluate the distribution. Finally, the humification  
 183 index (HIX) and the biological activity index (BIX) were also evaluated (Zsolnay *et al.* 1999; Parlanti *et al.* 2002). The  
 184 different fluorophores, HIX and BIX are given in Table 1 for the 7 tested wastewaters.

185

186

**Table 1 - The 7 studied wastewaters and their main DOM characteristics**

	SEC settled water	SEC settled water - diluted	SEC carbon biofiltration effluent	SEC discharges	SAM discharges	SAV discharges	SEM discharges
Biological treatment	-	-	BF (C)	BF (C+N)	CAS (C+N)	CAS (C) BF (N)	MBR C+N
TOC (mgC/L)	32	7.8	-	7.3	7.2	-	5.5
DOC (mgC/L)	27	7.7	6.6	6.8	6.6	11	5.2
UV-254 (cm <sup>-1</sup> )	0.859	0.203	0.120	0.150	0.173	0.237	0.140
Fluo $\alpha$ (UA)	1 879	455	812	1 522	822	2 097	701
Fluo $\alpha'$ (UA)	2 019	442	741	1 262	712	2 041	730
Fluo $\beta$ (UA)	1 926	440	742	1 371	761	2 018	657
Fluo $\delta$ (UA)	4 949	1 080	665	1 348	678	1 685	622
Fluo $\gamma$ (UA)	4 194	907	354	1 077	448	590	231
HIX	1.0	1.2	3.4	3.2	3.6	5.0	6.4
BIX	0.85	0.90	0.97	0.96	0.99	0.95	0.96

SEC = Seine Centre WWTP; SAM = Seine Amont WWTP; SAV = Seine Aval; SEM = Seine Morée.  
 BF = biofiltration; CAS = conventional activated sludge; MBR = membrane bioreactor: C = carbon removal; N = nitrogen removal (nitrification + denitrification).  
 DOC = dissolved organic carbon, UV-254 = UV absorbance at 254 nm, Fluo = fluorophore, HIX = humification index, BIX = biological activity index.

187

188

#### 189 3.4. Influence of the residual methanol concentration in the WWTP discharges

190

191 A residual methanol concentration is present in both SEC and SAV discharges because of the post-denitrification stage.  
 192 Indeed, denitrifying microorganisms needs a carbon source and when the denitrification is performed after the carbon  
 193 removal and the nitrification, as in both SEC and SAV, the carbon content is too low (Rocher *et al.* 2012). Methanol is



194 then added during this stage as carbon source, but its consumption by the microorganisms is not complete. Operationally  
 195 speaking, it is interesting to study the impact of this residual concentration on the micropollutant adsorption by activated  
 196 carbon. Thus, the performances obtained with the SEC discharges have been compared to performances obtained with  
 197 the same water spiked with methanol (6 and 12 mgC/L). The adsorbability of methanol has also been studied and  
 198 preliminary tests demonstrated that no adsorption of methanol occurs when contacting 12 mgC/L of methanol in ultra-  
 199 pure water with 10 mgPAC/L.

200

### 201 3.5. Influence of the ferric chloride

202

203 The CarboPlus® process operating in PAC configuration requires the injection of FeCl<sub>3</sub> to stabilize the PAC bed and  
 204 prevent any leakage. This substance is known to destabilize particles by neutralization of the surface charges, which could  
 205 impact the adsorption of micropollutants. To evaluate the impact of FeCl<sub>3</sub>, 1 L of SEC discharges have been contacted  
 206 with PAC alone (10 mg/L), FeCl<sub>3</sub> alone (2.5 gFeCl<sub>3</sub>/m<sup>3</sup>) and both PAC and FeCl<sub>3</sub> under strong mixing during 45 min.

207

208

## 209 RESULTS AND DISCUSSION

210

### 211 1. Influence of PAC characteristics on its efficiency

212

213 Structural and morphological properties of the 4 tested PACs are given in the Table 2. The removals of the micropollutants  
 214 with a PAC dose of 10 mg/L during 45 min are also provided.

215

**Table 2 - Characterization and performances of the 4 PACs studied**

	PB 170®	WP 235®	W 35®	PC 1000®
Producer	DaCarb	Chemviron	Norit	DaCarb
Raw material	Wood	Coal	Peat	Coconut
Bulk density (g/cm <sup>3</sup> )	0.30	0.38	0.33	0.54
Specific BET surface (m <sup>2</sup> /g)	957 ± 28	909 ± 30	768 ± 19	458 ± 14
Pore size distribution (micro, meso, macroporous) <sup>1</sup>	54% - 35% - 11%	53% - 31% - 16%	45% - 45% - 10%	59% - 29% - 12%
Pore volume (micro + meso) (mL/g)	0.5066	0.4841	0.4876	0.2435
Particle size distribution (µm)	3.4 - 16.2 - 58.9	3.4 - 18.0 - 58.0	3.2 - 19.4 - 86.2	3.7 - 31.7 - 129.4

d10 - d50 - d90				
	Micropollutant removal (%) - (10 mg/L of PAC, 45 min of contact)			
16 micro-pollutants <sup>2</sup>	61%	53%	51%	32%
Atenolol	54%	44%	41%	21%
Carbamazepine	63%	44%	48%	16%
Ciprofloxacin	77%	63%	62%	49%
Diclofenac	32%	22%	28%	5%
Diuron	75%	66%	60%	24%
Norfloxacin	79%	69%	62%	58%
Ofloxacin	79%	71%	68%	46%
Propranolol	81%	76%	70%	46%
Roxithromycin	43%	38%	40%	21%
Trimethoprim	46%	36%	33%	10%
1 Distribution of surface. Micropore = < 2 nm, mesopores = < 50 nm and macropores = > 50 nm. 2 Sum of 16 pharmaceuticals = atenolol, bezafibrate, carbamaepine, ciprofloxacin, diclofenac, erythromycin, ketoprofen, lorazepam, metronidazole, naproxen, norfloxacin, ofloxacin, propranolol, roxithromycin, sulfamethoxazole and trimethoprim.				

216

217 Among the 4 PACs, the PB 170® and WP 235® have a similar mesoporous structure with close pore size distribution  
 218 and specific BET surface (900-1000 m<sup>2</sup>/g), while W 35® and especially PC 1000® have different pore surface  
 219 distributions and lower specific BET surfaces (supporting material - Figure S3; Table 2). W 35® is strongly  
 220 mesoporous with 45% of the BET surface resulting from mesopores, while PC 1000® is microporous with 59% of the  
 221 surface resulting from micropores. 3 of the tested PACs have similar bulk densities (0.30-0.40 g/cm<sup>3</sup>) while PC 1000®  
 222 is heavier (0.54 g/cm<sup>3</sup>). Regarding the particle size distribution, PB 170® and WP 235® are comparable while the two  
 223 other PACs have a larger particle size distribution and a higher median diameter. This is particularly notable for the PC  
 224 1000® which is characterized by median and d90 values twice higher than those of the PB 170® and WP 235®.

225

226 Even if only 1 punctual experiment was performed, a clear trend can be observed with most of the compounds. For  
 227 individual compounds, the PB 170® allows the highest removals for 15 of the 18 micropollutants and the PC 1000® is  
 228 always the worst efficient. The WP 235® and W 35® seem to have similar performances, slightly weaker than PB 170®.  
 229 Overall, the sum of the 16 pharmaceuticals is removed by 61%, 53%, 51% and 32% respectively by the PB 170®, WP  
 230 235®, W 35® and PC 1000®.

231

232 The micropollutant removal is well correlated with the specific BET surface (**Figure 1**): the higher the specific BET  
 233 surface, the higher the micropollutant removal. In addition, the specific BET surface is also correlated to the bulk  
 234 density of the PAC, a low bulk density corresponding to a high BET surface. This relationship has been verified with 7  
 235 other PACs differing by their nature, as the bulk density is very easy to measure and could therefore be a proxy of the  
 236 BET surface. Considering the 11 PAC, this link is still observed (**Figure 1**). Thus, the bulk density could be used as an

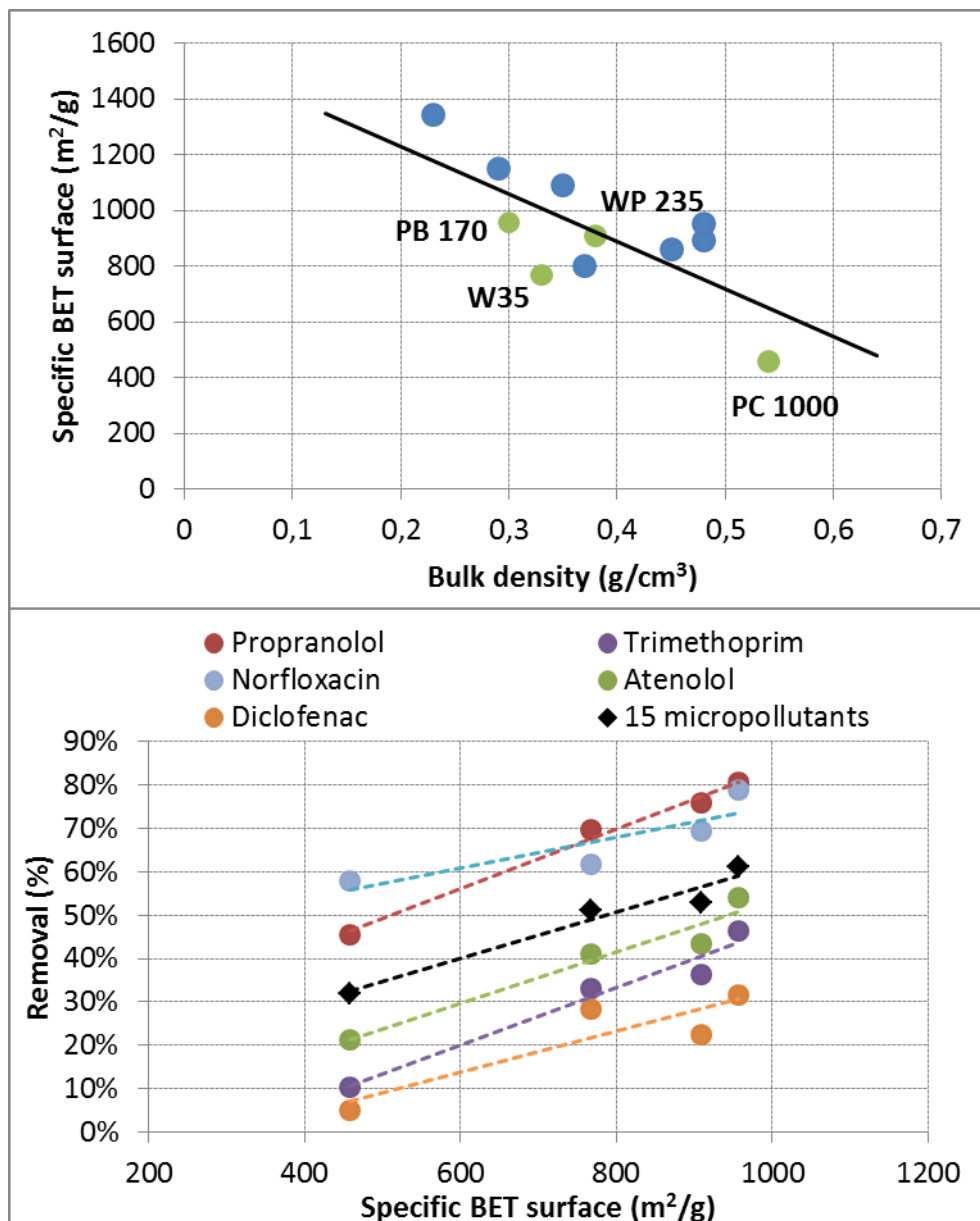
237 indicator to select activated carbons and estimate their BET surface and efficiency for micropollutants removal from  
238 wastewater.

239

240 The link between the efficiency of activated carbons and their specific BET surface (600-1500 m<sup>2</sup>/g) has already been  
241 observed in the literature (Çeçen & Aktas 2012), but the distribution of this surface between the different categories of  
242 pores (micro < 2 nm, meso 2-50 nm and macropores > 50 nm) has also to be considered. This is particularly important  
243 in presence of organic matter because it competes with micropollutants for adsorption, directly or by pore blocking  
244 (Newcombe *et al.* 2002; Yu *et al.* 2008). Thus, a mesoporous structure with a large pore size distribution should limit  
245 the competition with the DOM (Ebie *et al.* 2001).

246

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250  
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**Figure 1 - Correlations between the specific BET surface and the micropollutant removals obtained with a PAC, and link with its bulk density**

253

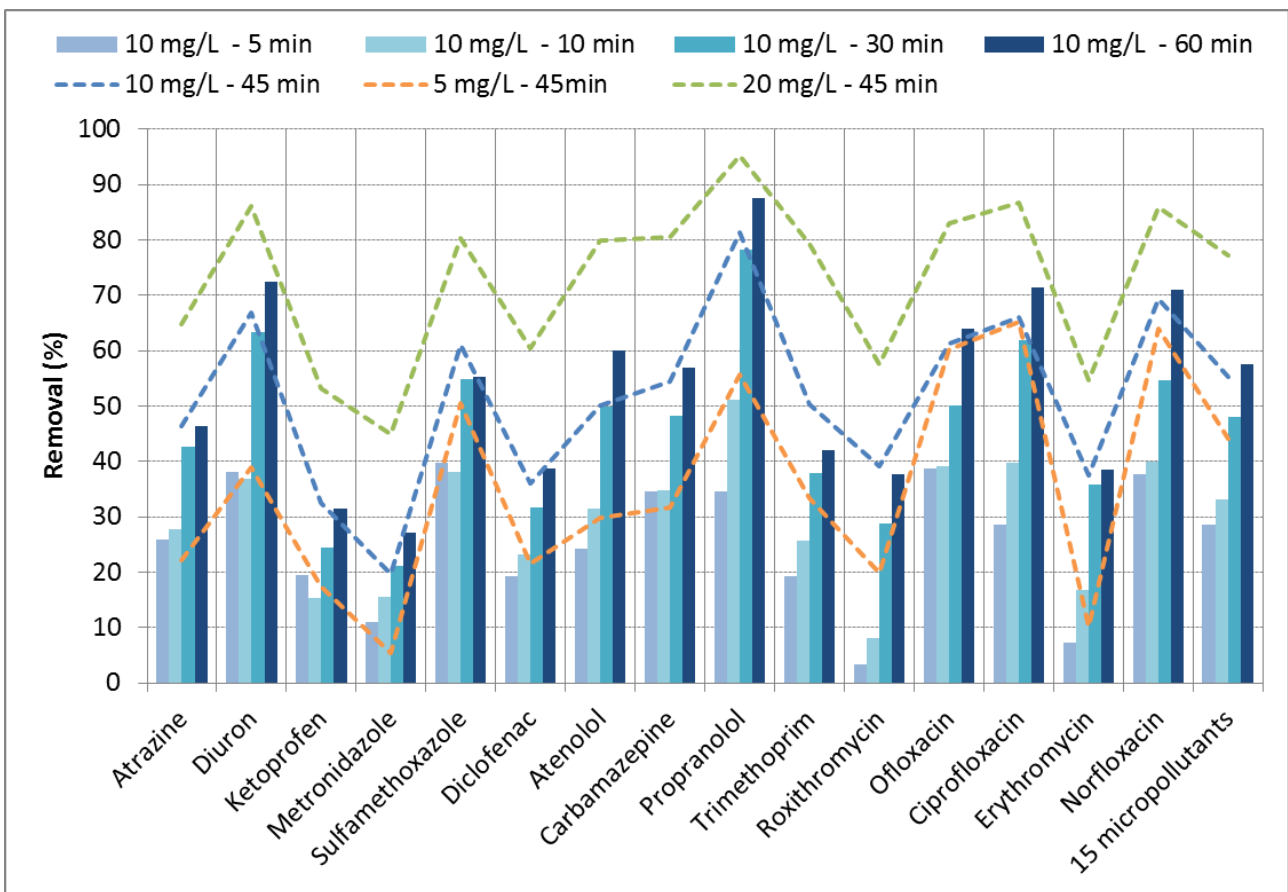
## 2. Adsorption of micropollutants on PAC

254

### 2.1. Influence of fresh PAC dose and adsorption kinetic

255

256 The Figure 2 displays the influence of the contact time and the PAC dose on the removal of micropollutants from Seine  
257 Centre discharges by PAC.  
258  
259



260

**Figure 2 - Micropollutants adsorption kinetic in the Seine Centre discharges and influence of the dose on removals**

261  
262  
263

264 According to the results (Figure 2), a higher dose of PAC logically results in higher micropollutant removals, i.e.  
265 carbamazepine (32-54-80%; removals at 5-10-20 mgPAC/L), diclofenac (22-36-60%), propranolol (56-81-95%) or  
266 sulfamethoxazole (51-61-80%). However, the relationship is not linear as doubling the PAC mass doesn't result in a  
267 doubling of the removals. Actually, the relationship is logarithmic resulting in the reaching of a plateau when increasing

268 the dose, as displayed in supporting material - Figure S4. Thus, the PAC dose in wastewater has a great influence on the  
269 removal, as already observed in the literature (Snyder et al. 2007; Boehler et al. 2012; Margot et al. 2013) or at large scale  
270 with the CarboPlus® pilot (Mailler *et al.* 2015). Considering the individual results of the micropollutants, this positive  
271 influence of the dose is statistically significant (test of Shapiro-Wilk, Fischer and Student - p-value < 0.05) between 5 and  
272 10 mgPAC/L (p-value = 0.016) and between 10 and 20 mgPAC/L (p-value = 0.0005).

273

274 Furthermore, the removals notably increase with the contact time (Figure 2), i.e. ciprofloxacin (29-40-62-66-71%;  
275 removals at 5-10-30-45-60 min contact times) or diclofenac (19-23-32-36-39%). However, the PAC is very fine (< 50  
276 µm), resulting in a relatively fast adsorption kinetic. As a consequence, although the equilibrium is not reached after 60  
277 min, differences of removal between 30, 45 and 60 min contact time for a same PAC dose are limited (< 10%) indicating  
278 the proximity of the equilibrium. Thus, the short contact times (30-60 min) employed in PAC tertiary treatments are  
279 suitable for an efficient adsorption of micropollutants. For several compounds (8/15), such as atrazine (26-46%; removals  
280 after 5 and 60 min), norfloxacin (38-71%), ofloxacin (39-64%) or sulfamethoxazole (40-55%), the removal achieved after  
281 5 min represents more than half of the removal after 60 min, confirming the very fast kinetic. In contrary, erythromycin  
282 (7-39%) or roxithromycin (3-38%) seem to have slower kinetics, probably because of their high molecular weight. These  
283 compounds will then be more sensitive to changes of contact time in adsorption processes.

284

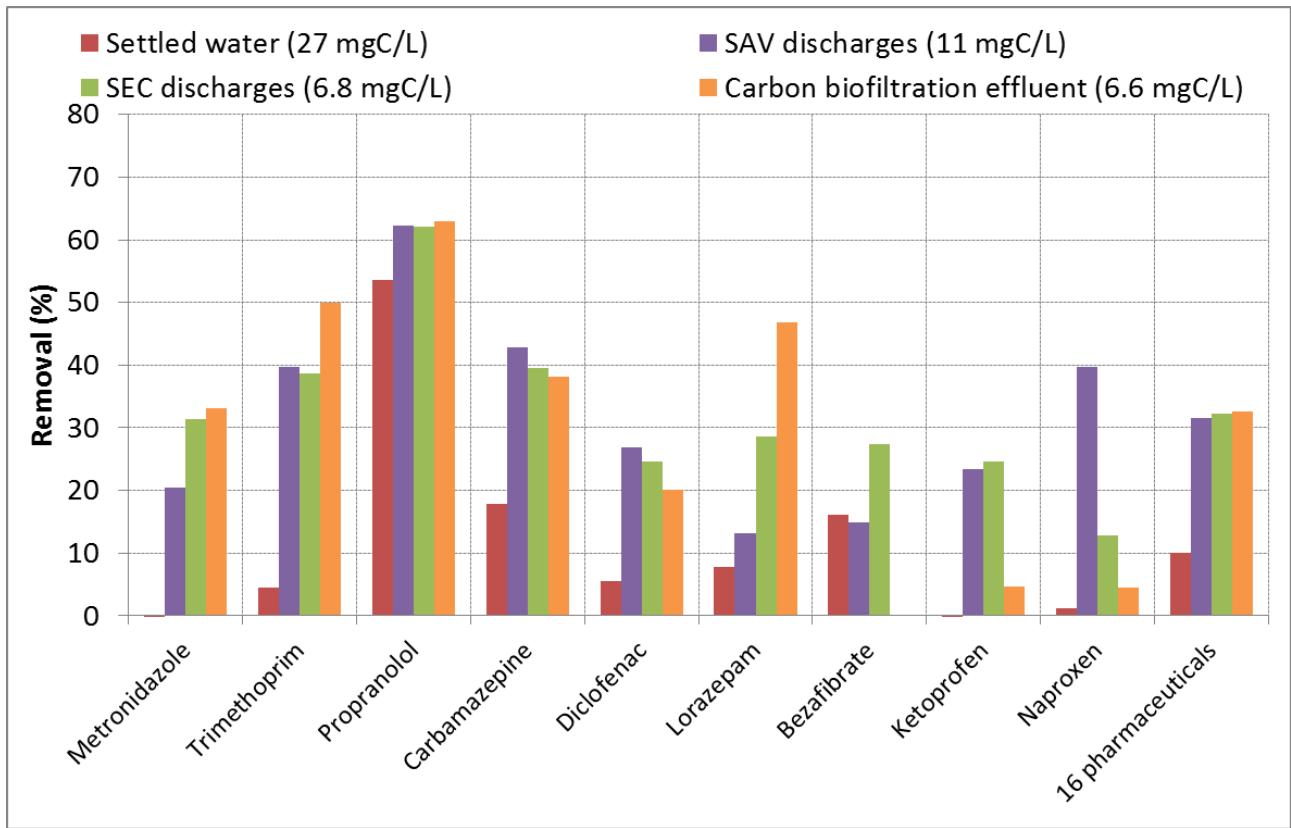
## 285 2.2. Influence of the matrix

### 286 2.2.1. Dissolved organic carbon

287

288 The Figure 3 displays the removals of micropollutants observed with different types of wastewater, sorted from the highest  
289 to the lowest DOC value.

290



291  
292 **Figure 3 - Pharmaceuticals removals by PAC adsorption from different types of wastewater**  
293

294 Removals observed with the SEC settled water are overall lower than those from the three other wastewaters. In particular,  
295 they are significantly lower (p-value = 0.001) than in the SEC discharges (water from the same WWTP), considering all  
296 the compounds displayed on Figure 3. Comparable removals are overall achieved with the 3 other waters, which have  
297 undergone an intense biological carbon treatment. For instance, the carbamazepine is removed at 18% in SEC settled  
298 water, against 38 to 42% in the other matrixes. Similarly, the trimethoprim removal increases from 5% in settled water to  
299 39-50% in the other waters.

300  
301 These results indicate that DOC value has a negative impact on micropollutant adsorption, as the removals observed in  
302 the SEC settled water, featuring the highest DOC concentration (27 mgC/L), are the lowest compare to the other waters.  
303 The negative influence of DOC on micropollutant adsorption from wastewater was also observed in the literature (de  
304 Ridder *et al.* 2011; Margot *et al.* 2013; Altmann *et al.* 2014). In contrary, DOC value seems to have a limited impact on  
305 propranolol behavior, a compound which is easily adsorbed by activated carbon as positively charged (Mailler *et al.*  
306 2015).

307  
308 According to what is previously stated, micropollutant removals should be lower in SAV discharges compared to those

309 in the SEC carbon biofiltration effluent and discharges, regarding the differences of DOC (11 vs. 6.6-6.8 mgC/L). This is  
310 observed for bezafibrate, lorazepam and metronidazole. However, removals are similar for the other compounds, in spite  
311 of slightly higher influent concentrations in the SAV discharges. Besides, considering the individual removals of  
312 compounds from Figure 3, the removals from SEC and SAV discharges are significantly similar (p-value = 0.175). The  
313 organic matter of SAV discharges should then be less competitive than organic matter from other discharges, what  
314 counterbalances the higher DOC.

315 This result indicates that the sole DOC level isn't sufficient to explain the variations of removals from water to water, the  
316 organic matter composition and nature have also to be considered. Considering that, the DOM nature and adsorption was  
317 assessed before and after contact with PAC for these 4 waters, as well as 3 additional wastewater matrixes.

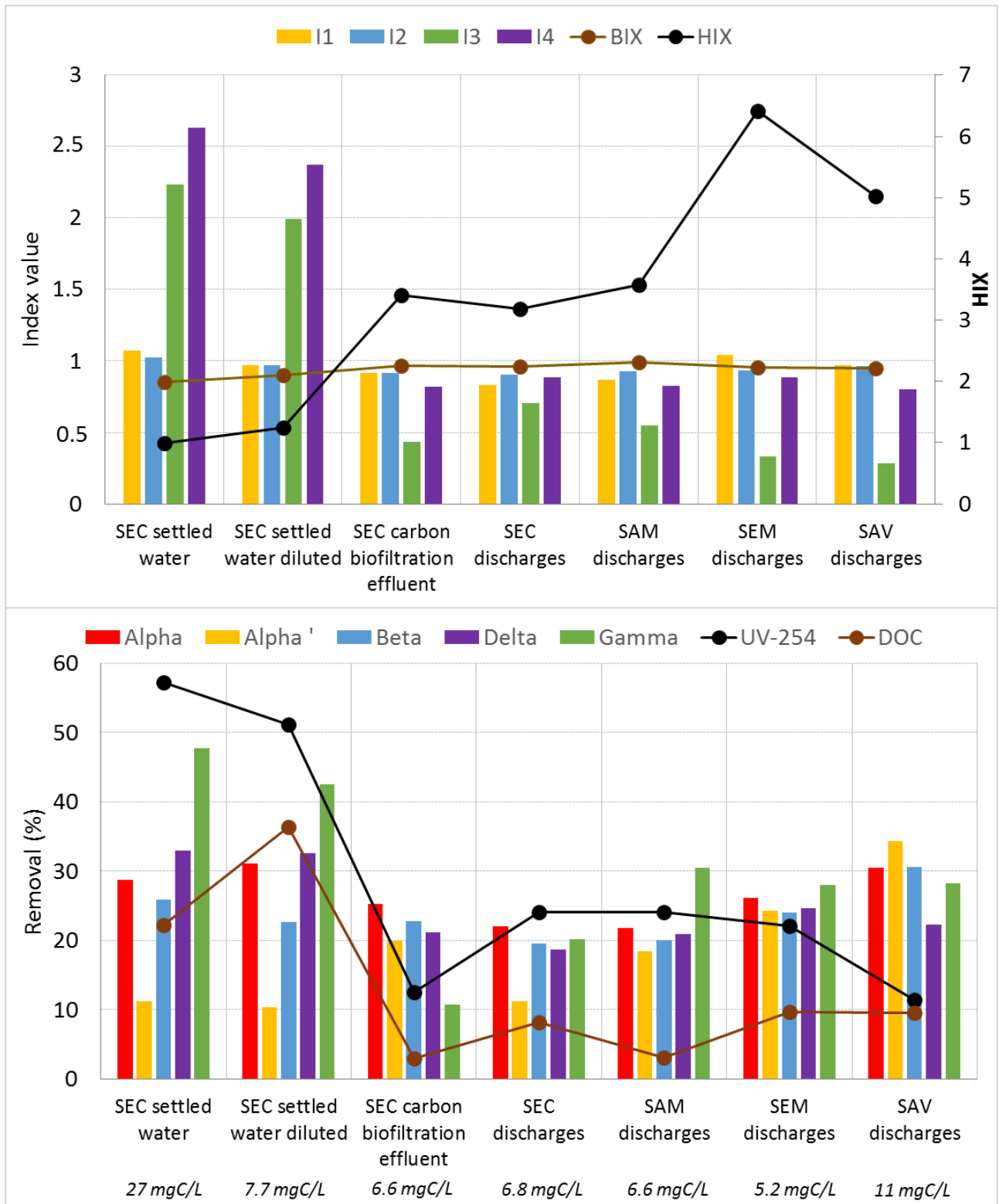
318

#### 319 *2.2.2. Composition and adsorption of the organic matter*

320

321 Figure 4 displays the composition (indexes from 3D fluorescence analysis) of the organic matter from 7 wastewater  
322 matrixes, as well as the organic matter removal by PAC adsorption (10 mgPAC/L - 45 min).

323



**Figure 4 - DOM adsorption and distribution using the defined indexes for the different studied wastewaters**

324

325

326

327

328

329

First of all, the 4 WWTP discharges (SEC, SAM, SEM and SAV) and the SEC carbon biofiltration effluent have a similar distribution of DOM with a large fraction of humic-like organic matter (peaks  $\alpha$ ,  $\alpha'$  and  $\beta$ ; indexes I1 and I2), and a smaller fraction of organic matter resulting from bacterial activity ( $\gamma$  and  $\delta$ ; I3 and I4), as shown on Figure 4 and in Table



330 1. In contrary, the DOM distribution is different in the SEC settled water with very high I3 and I4 indexes, characterizing  
331 protein molecules, compared to I1 and I2 indexes, characterizing the humic-like substances. This indicates that carbon  
332 biological treatments significantly remove DOC and fluorophores  $\delta$  and  $\gamma$  (see SEC settled water and carbon biofiltration  
333 effluent in Table 1), resulting in a significant modification of the DOM distribution (Figure 4). Together with this  
334 difference of DOM composition, the SEC settled water has higher DOC (27 mgC/L) and UV-254 (0.859 cm<sup>-1</sup>) values,  
335 highlighting a higher quantity of DOM.

336 In addition, the HIX increases along the different steps of wastewater treatment, as shown by the low HIX in the SEC  
337 settled water (1.0) and the higher HIX after the biological treatments (> 3). This suggests that small protein molecules ( $\delta$   
338 and  $\gamma$ ) are transformed into humic-like substances ( $\alpha$ ,  $\alpha'$  and  $\beta$ ) during biological treatments, explaining the HIX increase.  
339 The HIX from SAM and SEC discharges, as well as SEC carbon biofiltration effluent, are similar (3.2-3.6), while those  
340 from SAV and SEM discharges are higher (5.0-6.4), resulting from higher hydraulic retention times.

341

342 Regarding the removal of DOM by activated carbon, DOC and UV-254 removals are notably higher in the SEC settled  
343 water compared to the other ones. This is consistent as DOC and UV-254 are much higher in this water. This suggests  
344 that in this water, less sites will be available for micropollutants as more DOM is sorbed, what is consistent with  
345 micropollutants results (Figure 3). For the other wastewaters, the DOM removal is rather comparable (10-25% for DOC  
346 and 5-10% for UV-254).

347 In addition, fluorophores removals are rather similar in all wastewaters except in the SEC settled water. In the WWTP  
348 discharges, all the fluorophores are removed between 10 and 30%. In contrary, in SEC settled water, fluorophores  $\delta$  and  
349  $\gamma$  are predominant (I3 and I4) and are better removed (35-50%) than the other fluorophores. They are also better removed  
350 than in the other water. In consequence, these fluorophores will have the highest impact on the competition with  
351 micropollutants for adsorption. This is consistent with the study of (de Ridder *et al.* 2011) which identified the small size  
352 DOM as the most competing ones for adsorption. Moreover, the fluorophores removal pattern is the same in SEC diluted  
353 settled water, confirming that the distribution of DOM is as important in the adsorption process as the DOC value.

354

355 In this context, and considering that the carbon biological treatment significantly reduces the DOC and the quantity of  
356 fluorophores  $\delta$  and  $\gamma$  (the most competing DOM), the lower removals of micropollutants by PAC in the SEC settled water  
357 compared to the other waters are then consistent. Indeed, the competition is stronger in this water resulting from i) a  
358 higher quantity of DOM (DOC and UV-254) and ii) a different DOM distribution, with more small protein-like substances  
359 and less humic-like substances. In addition, I3 and I4 are lower in the SAV discharges than in SEC carbon biofiltration

360 effluent and discharges, together with a higher HIX. This means that this water has less very competitive DOM what  
361 counterbalances the higher DOC, resulting in similar micropollutants removals.

362

363 It can be concluded that, besides a low DOC, low I3 and I4 indexes, together with a high HIX, are positive for the  
364 minimization of DOM competition during the micropollutants adsorption.

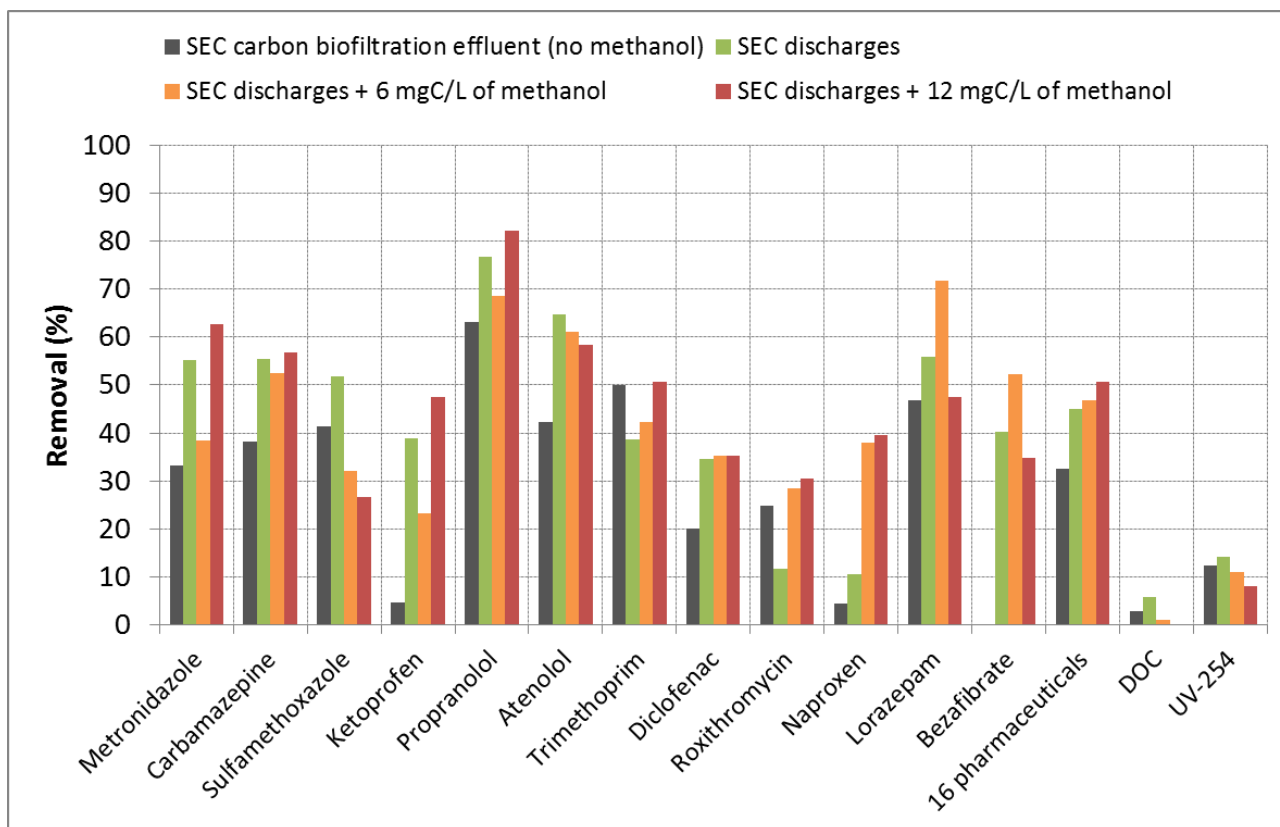
365

### 366 2.2.3. Presence and concentration of methanol

367

368 The micropollutant and organic matter removals obtained in presence of a residual concentration of methanol are  
369 presented in Figure 5.

370



371

372 **Figure 5 - Impact of a residual concentration of methanol in the WWTP discharges on the adsorption of**  
373 **pharmaceuticals by PAC**

374

375 The comparison of removals obtained in the carbon biofiltration effluent and in the SEC discharges allows assessing the  
376 impact of the methanol presence in the wastewater on the PAC adsorption (Figure 5). Its presence doesn't decrease the  
377 performances as the removals observed in the SEC discharges are similar or higher than those in the carbon biofiltration

378 effluent. The better removals in the SEC discharges could be explained i) by the methanol itself, and ii) by the carbon and  
379 nitrogen treatment achieved in the second and third biofiltration stages. but further experiments are needed to bring an  
380 answer.

381 Moreover, no clear trend is observed between the increase of the residual concentration of methanol and the  
382 micropollutant removals, except for sulfamethoxazole and naproxen for which the removal decrease and increase  
383 respectively. However, the results indicate that the increase of the methanol concentration doesn't lead to a significant  
384 degradation of the PAC performances for most compounds.

385

386 Thus, results have shown that the residual concentration of methanol doesn't affect negatively the removal of  
387 micropollutants by activated carbon (Figure 5). In contrary, its presence in biological treatment effluents could favor a  
388 biological activity in the tertiary treatments by activated carbon.

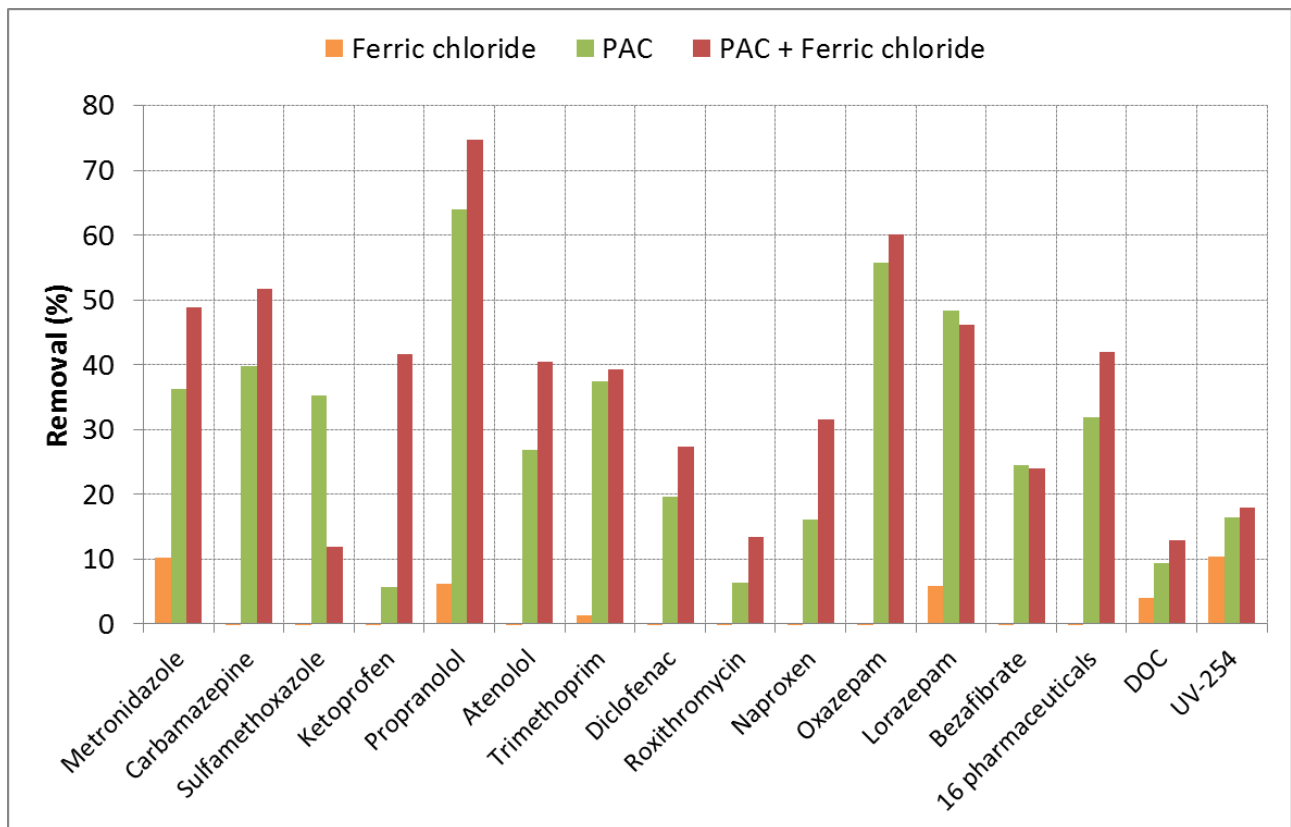
389

## 390 2.2. Influence of the injection of FeCl<sub>3</sub>

391

392 The ferric chloride influence on the fate of micropollutants in presence of PAC is illustrated on figure 7.

393



394

## Figure 6 - Influence of the presence of FeCl<sub>3</sub> on the pharmaceuticals removals by PAC adsorption

395  
396

397 Three types of behaviors are observed for micropollutants. For most compounds, such as carbamazepine, beta blockers  
398 or diclofenac, and for DOM (DOC and UV-254), a slightly higher removal (+ 5-15%) is obtained by coupling PAC and  
399 ferric chloride, probably by coagulation of the colloidal fraction. These differences are not significant taking uncertainties  
400 into account, but 10 compounds in 13, as well as DOC and UV-254, have a greater removal in presence of FeCl<sub>3</sub>. In  
401 contrary, no clear influence is observed for lorazepam and bezafibrate. Finally, sulfamethoxazole seems to be the only  
402 one with a lower removal (- 30%) in presence of ferric chloride.

403 (Margot *et al.* 2013) also observed a positive effect of the coagulant on micropollutant removals. However, the mechanism  
404 at the origin of this improvement is not identified. Supplementary tests are required to determine if coagulation,  
405 complexation or direct decrease of the competition with organic matter are involved.

406

407

## 408 CONCLUSIONS

409

410 The Parisian public sanitation service (SIAAP) and the Water Environment and Urban Systems laboratory (LEESU) study  
411 the CarboPlus® process at large scale, in collaboration with the SAUR teams. In parallel to the study of the large scale  
412 pilot, complementary laboratory scale experiments were carried out to improve the understanding of the micropollutants  
413 adsorption on activated carbon, in particular PAC.

414

415 These experiments allowed displaying the links between structural properties of activated carbons and their efficiency to  
416 remove micropollutants. In particular, it has been shown that the PAC performances are closely related to the specific  
417 BET surface, which can easily be estimated through the bulk density measure.

418

419 The strong influence of the PAC dose has also been confirmed, as well as the suitability of the adsorption kinetic (less  
420 than one hour) for WWTP application (operational requirements). In an operational point of view, the injection of FeCl<sub>3</sub>  
421 doesn't disrupt the adsorption process. A slight improvement is even observed for most compounds (+ 10-15%), except  
422 for sulfamethoxazole, probably through coagulation of the colloidal fraction of the DOM. In contrary, the residual  
423 concentration of methanol present in the WWTP discharges due to the post denitrification process seems to have no  
424 impact on the fate of most pharmaceuticals.

425

426 Then, this study highlighted the differences of micropollutants adsorption in the various wastewater matrixes. The DOC  
427 concentration is important considering the competition of adsorption but it isn't always sufficient to explain the  
428 performances reductions from water to water. It has been shown that the distribution of the different molecular  
429 components of the DOM should be considered in addition to the quantity of DOM. Indeed, small protein-like fluorophores  
430 have been identified as the most problematic for adsorption competition in wastewater, while a high HIX, highlighting  
431 the humification of the DOM, is favorable to micropollutants adsorption. The reduction of protein-like substances in  
432 wastewater is then a way to maximize the adsorption of micropollutants by activated carbon.

433

434

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