



HAL
open science

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

R. Mailler, J. Gasperi, Y. Coquet, C. Derome, A. Buleté, E. Vulliet, Adèle Bressy, G. Varrault, G. Chebbo, V. Rocher

► To cite this version:

R. Mailler, J. Gasperi, Y. Coquet, C. Derome, A. Buleté, et al.. 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. *Journal of Environmental Chemical Engineering*, 2016, 4 (1), <10.1016/j.jece.2016.01.018>. <hal-01266245>

HAL Id: hal-01266245

<https://enpc.hal.science/hal-01266245v1>

Submitted on 19 Jun 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

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
5 R. Mailler^{1A*}, J. Gasperi^{1*}, Y. Coquet², C. Derome¹, A. Buleté³, E. Vulliet³, A. Bressy⁴, G. Varrault¹, G.
6 Chebbo⁴ and V. Rocher⁵

7
8 ¹ LEESU (UMR MA 102, Université Paris-Est, AgroParisTech), Université Paris-Est Créteil, 61 avenue du
9 Général de Gaulle, 94010 Créteil Cedex, France. (E-mail: *maillerr@leesu.enpc.fr*; *gasperi@u-pec.fr*)

10 ² SAUR, Direction de la Recherche et du Développement, 1 rue Antoine Lavoisier, 78064 Guyancourt, France.

11 ³ Université de Lyon, Institut des Sciences Analytiques, UMR5280 CNRS, Université Lyon 1, ENS-Lyon, 5
12 rue de la Doua, 69100 Villeurbanne, France.

13 ⁴ LEESU (UMR MA 102, Université Paris-Est, AgroParisTech), École des Ponts ParisTech, 6-8 avenue Blaise
14 Pascal, Champs-sur-Marne, 77455 Marne-la-Vallée Cedex 2, France.

15 ⁵ SIAAP, Direction du Développement et de la Prospective, 82 avenue Kléber, 92700 Colombes, France.

16 * Corresponding authors

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 • FeCl₃ 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.

24

^{AA} Present address: SIAAP, Direction du Développement et de la Prospective, 82 avenue Kléber, 92700 Colombes,
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 δ and γ), 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 - μ 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 m³/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 FeCl₃ were studied.

97

98

99 MATERIALS AND METHODS

100

101 1. Activated carbon characterization

102

103 11 adsorbents, including micro and mesoporous PACs and μ 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 (m²/g), the porous volume (mL/g), the pore size distribution
110 and the bulk density (g/cm³) 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 m^2/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 μm) 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. α , α' and β correspond to humic-like substances, γ and δ
 181 respectively represents tyrosine-like and tryptophan-like proteins. Then, I1, I2, I3 and I4 indexes, respectively
 182 corresponding to the ratios α'/α , β/α , γ/α and δ/α , 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 ⁻¹)	0.859	0.203	0.120	0.150	0.173	0.237	0.140
Fluo α (UA)	1 879	455	812	1 522	822	2 097	701
Fluo α' (UA)	2 019	442	741	1 262	712	2 041	730
Fluo β (UA)	1 926	440	742	1 371	761	2 018	657
Fluo δ (UA)	4 949	1 080	665	1 348	678	1 685	622
Fluo γ (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 FeCl₃ 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 FeCl₃, 1 L of SEC discharges have been contacted
 206 with PAC alone (10 mg/L), FeCl₃ alone (2.5 gFeCl₃/m³) and both PAC and FeCl₃ 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 ³)	0.30	0.38	0.33	0.54
Specific BET surface (m ² /g)	957 ± 28	909 ± 30	768 ± 19	458 ± 14
Pore size distribution (micro, meso, macroporous) ¹	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 ²	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 m²/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/cm³) while PC 1000®
 222 is heavier (0.54 g/cm³). 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

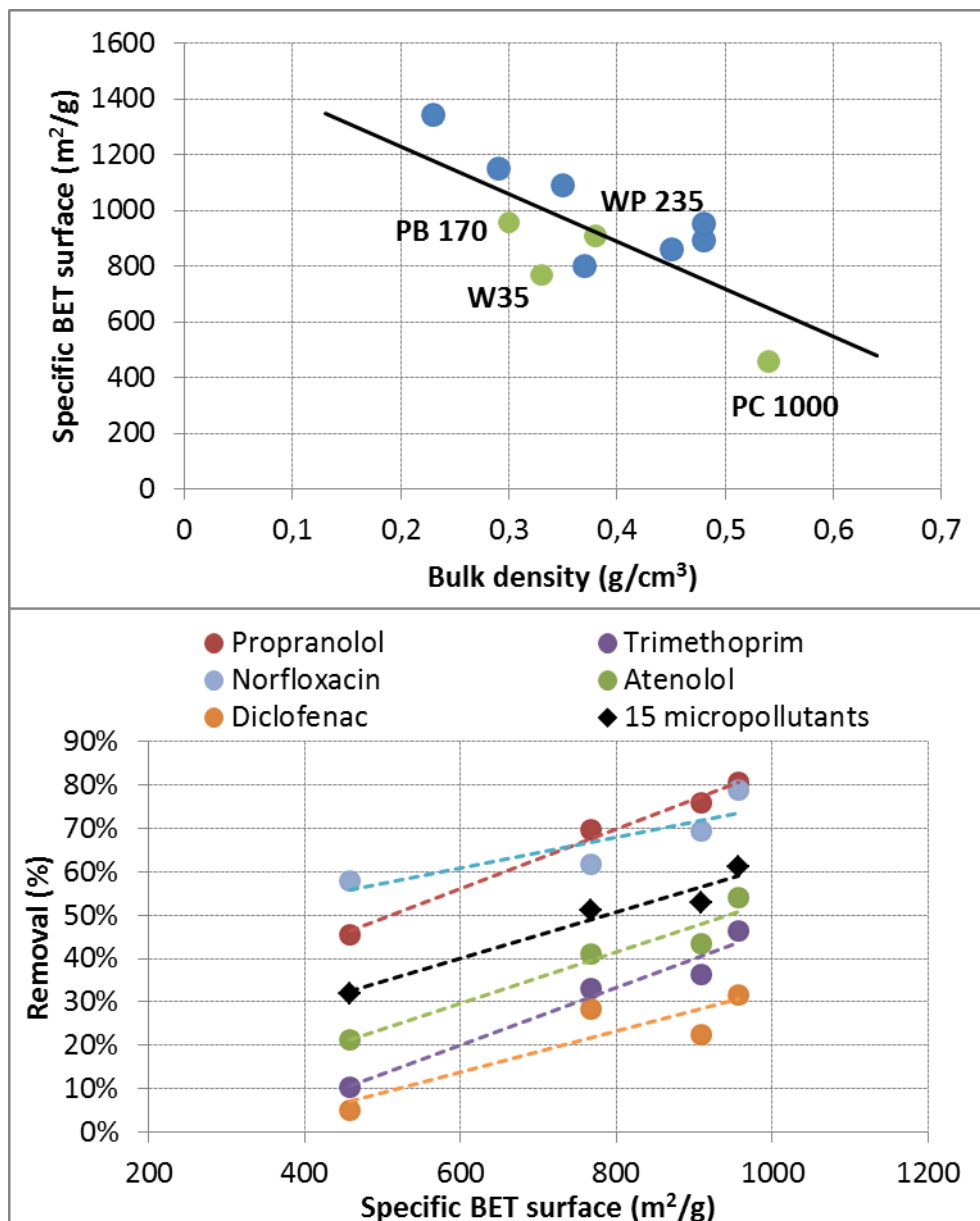
237 indicator to select activated carbons and estimate their BET surface and efficiency for micropollutants removal from
238 wastewater.

239

240 The link between the efficiency of activated carbons and their specific BET surface (600-1500 m²/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

247



248

249
250
251
252

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

253

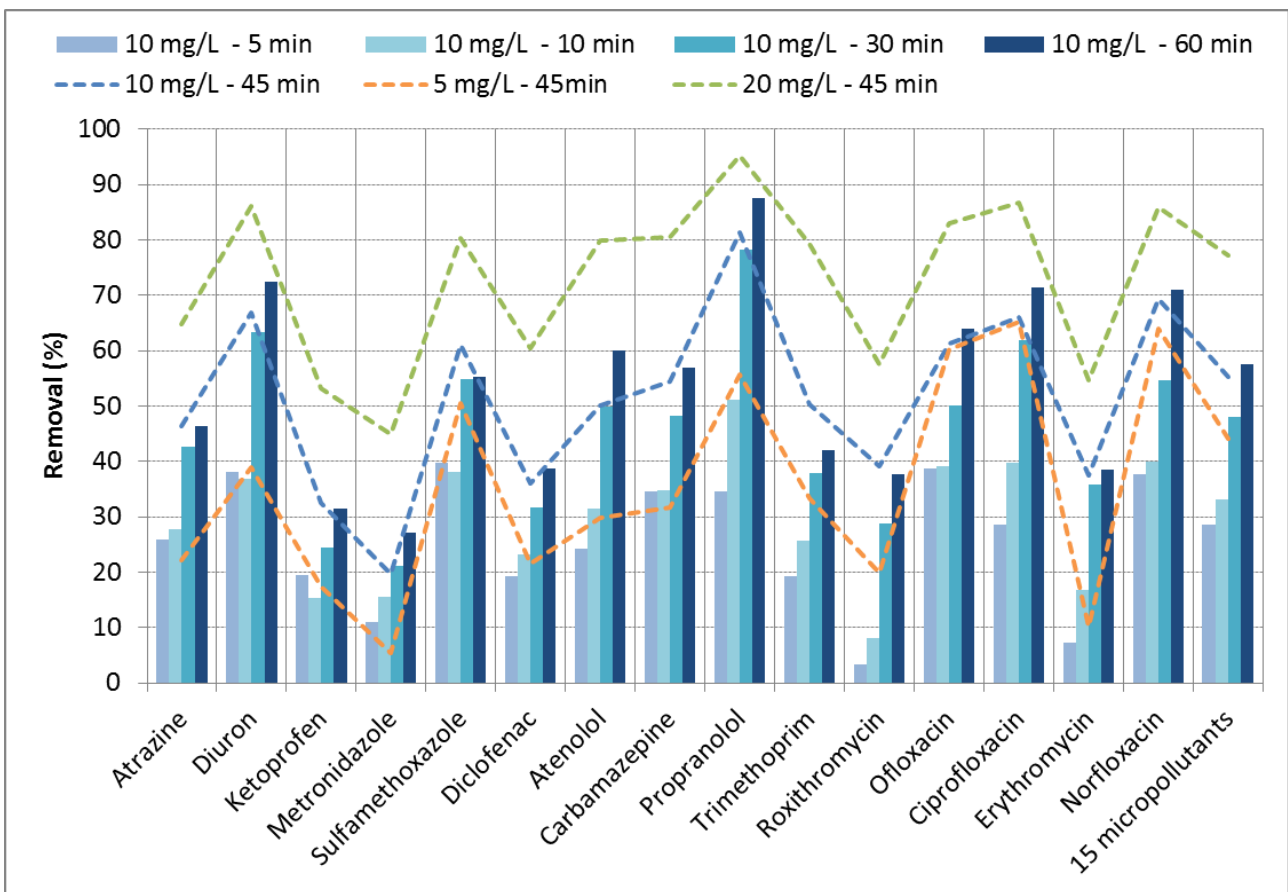
2. Adsorption of micropollutants on PAC

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

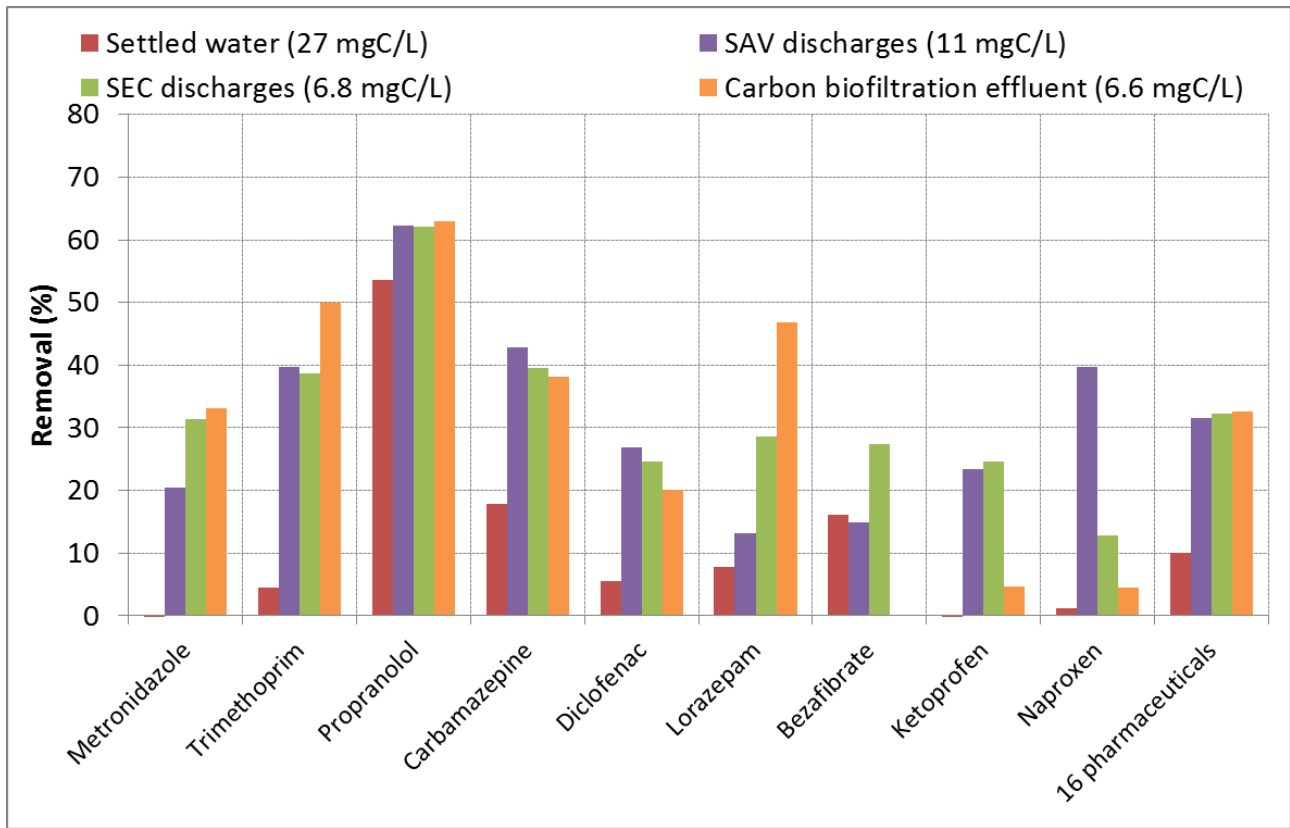
285 2.2. Influence of the matrix

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

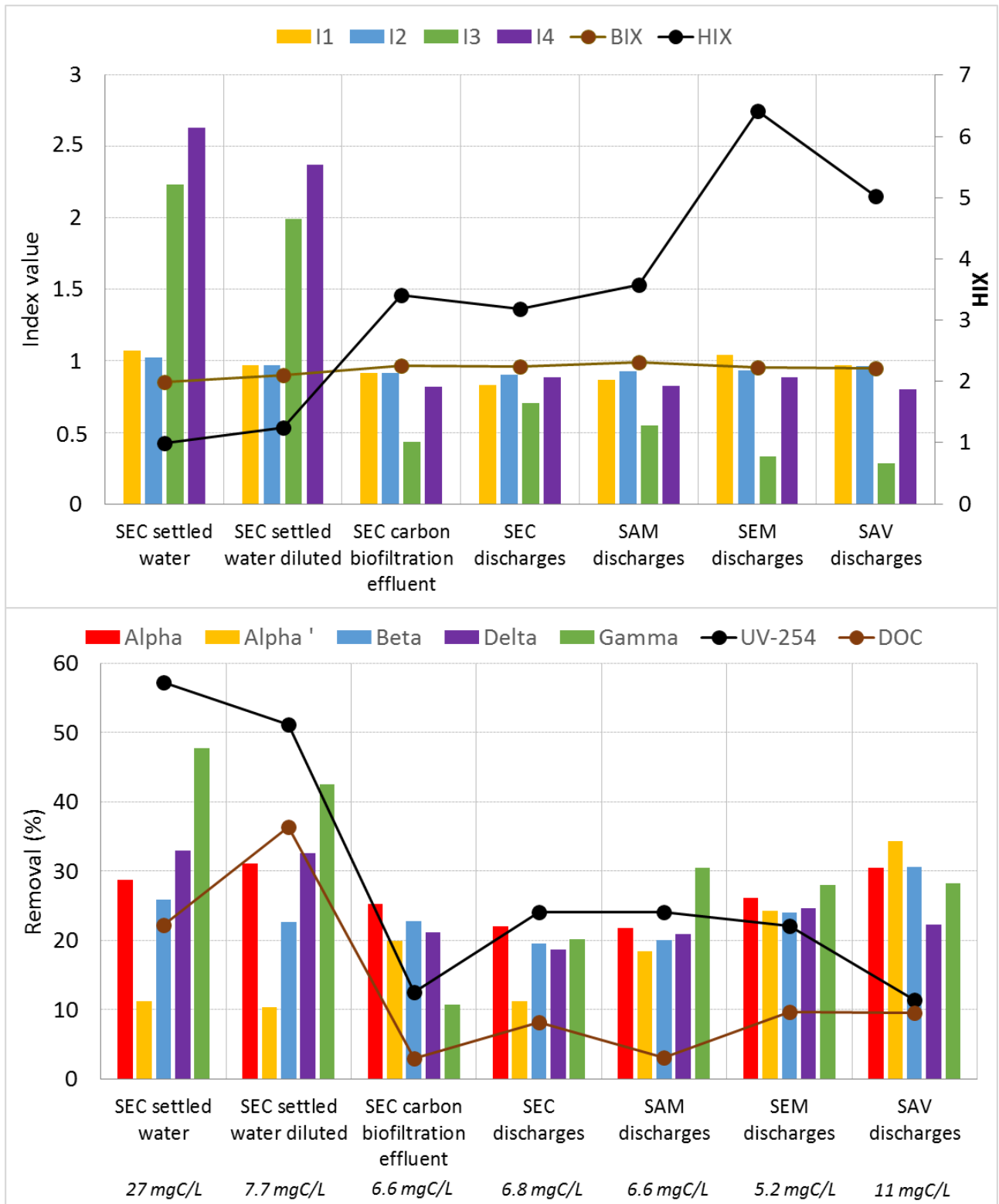


Figure 4 - DOM adsorption and distribution using the defined indexes for the different studied wastewaters

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 α , α' and β ; indexes I1 and I2), and a smaller fraction of organic matter resulting from bacterial activity (γ and δ ; 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 δ and γ (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⁻¹) 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 (δ
338 and γ) are transformed into humic-like substances (α , α' and β) 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 δ and
349 γ 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 δ and γ (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.

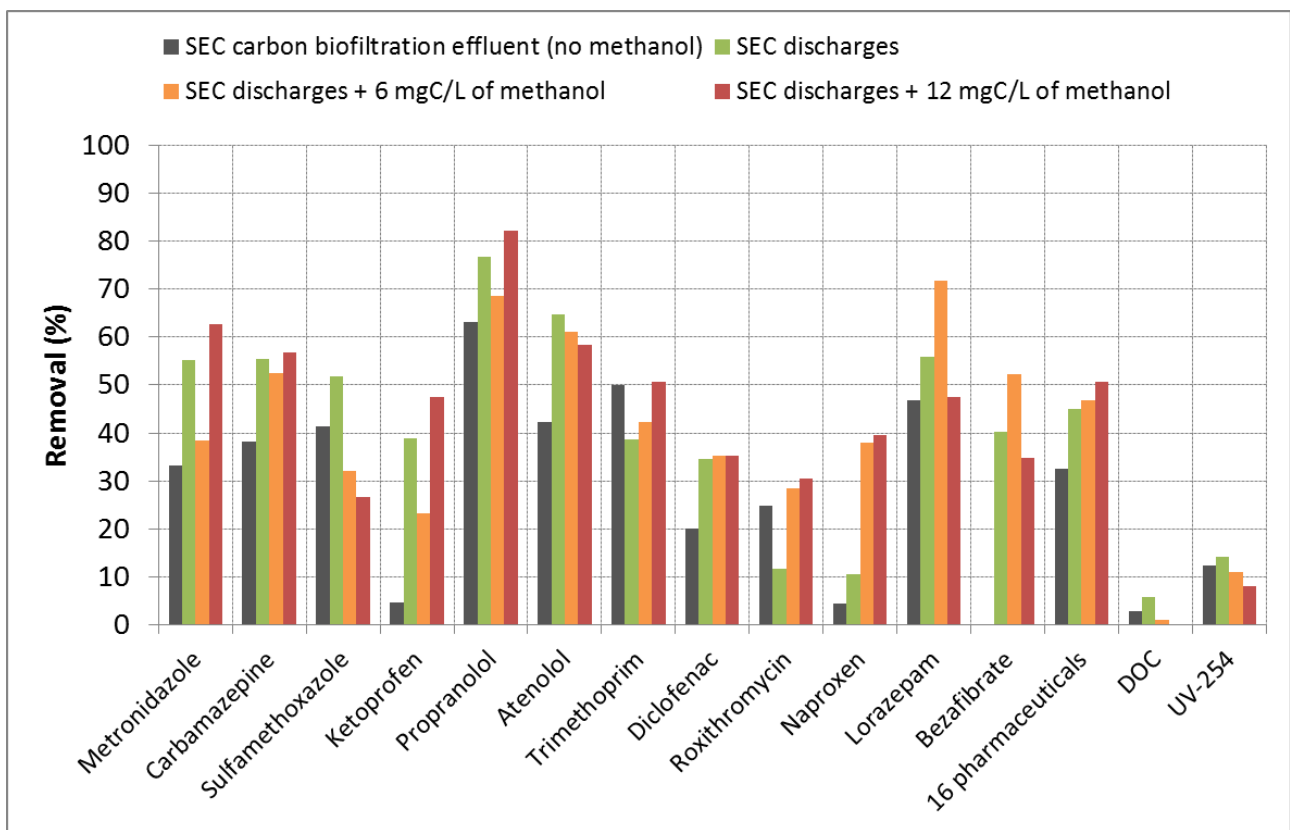
365

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.

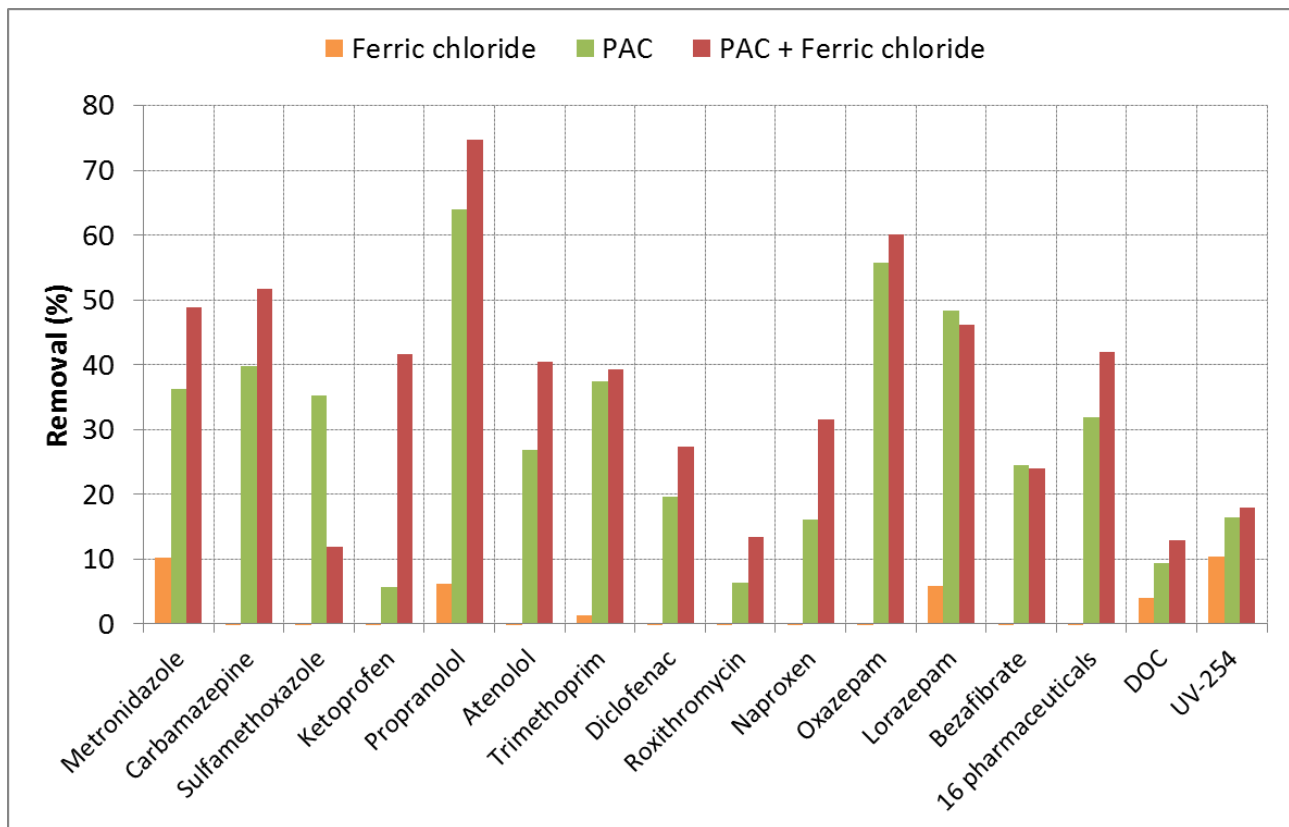
389

390 2.2. Influence of the injection of FeCl₃

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 FeCl₃ 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 FeCl₃. 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 FeCl₃
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

435 ACKNOWLEDGEMENT

436

437 This study has been performed within the framework of the OPUR research program. The authors would like to thank
438 Benjamin Cassier and Mélanie Gobin, as well as the SIAAP (Céline Briand), the SAUR (Séverine Bareilles), the ISA
439 (Antoine Vauchez, Mikaël Tournier, Florent Lafay and Loic Spinner), the LEESU and UTC teams for their technical
440 support and their active participation to the sampling campaigns and analyses.

441 REFERENCES

442

- 443 Abegglen C. and Siegrist H. (2012). *Micropolluants dans les eaux résiduares*
444 *urbaines. Etapes de traitement supplémentaire dans les stations*
445 *d'épuration. (in French).*
- 446 Altmann J., Ruhl A. S., Zietzschmann F. and Jekel M. (2014). Direct comparison
447 of ozonation and adsorption onto powdered activated carbon for
448 micropollutant removal in advanced wastewater treatment. *Water Research*
449 **55**(0), 185-93.
- 450 Baudu M., Guibaud G., Raveau D. and Lafrance P. (2001). Prediction of Adsorption
451 from Aqueous Phase of Organic Molecules as a Function of Some
452 Physicochemical Characteristics of Activated Carbons. *Water Quality*
453 *Research* **36**(4), 631-57.
- 454 Boehler M., Zwickenpflug B., Hollender J., Ternes T., Joss A. and Siegrist H.
455 (2012). *Removal of micropollutants in municipal wastewater treatment*
456 *plants by powder-activated carbon.* International Water Association,
457 London, Royaume-Uni.
- 458 Çeçen F. and Aktas Ö. (2012). *Activated carbon for water and wastewater*
459 *treatment integration of adsorption and biological treatment.* Wiley-VCH,
460 Weinheim, Germany.
- 461 de Ridder D. J., Verliefde A. R., Heijman S. G., Verberk J. Q., Rietveld L. C.,
462 van der Aa L. T., Amy G. L. and van Dijk J. C. (2011). Influence of
463 natural organic matter on equilibrium adsorption of neutral and charged
464 pharmaceuticals onto activated carbon. *Water Sci Technol* **63**(3), 416-23.
- 465 de Ridder D. J., Villacorte L., Verliefde A. R. D., Verberk J. Q. J. C., Heijman
466 S. G. J., Amy G. L. and van Dijk J. C. (2010). Modeling equilibrium
467 adsorption of organic micropollutants onto activated carbon. *Water*
468 *Research* **44**(10), 3077-86.
- 469 Delgado L. F., Charles P., Glucina K. and Morlay C. (2012). The removal of
470 endocrine disrupting compounds, pharmaceutically activated compounds and
471 cyanobacterial toxins during drinking water preparation using activated
472 carbon—A review. *Science of the Total Environment* **435-436**(0), 509-25.
- 473 Ebie K., Li F., Azuma Y., Yuasa A. and Hagishita T. (2001). Pore distribution
474 effect of activated carbon in adsorbing organic micropollutants from
475 natural water. *Water Research* **35**(1), 167-79.
- 476 Hudson N., Baker A. and Reynolds D. (2007). Fluorescence analysis of dissolved
477 organic matter in natural, waste and polluted waters—a review. *River*
478 *Research and Applications* **23**(6), 631-49.
- 479 Li L., Quinlivan P. A. and Knappe D. R. U. (2002). Effects of activated carbon
480 surface chemistry and pore structure on the adsorption of organic
481 contaminants from aqueous solution. *Carbon* **40**(12), 2085-100.
- 482 Loos R., Carvalho R., António D. C., Comero S., Locoro G., Tavazzi S.,
483 Paracchini B., Ghiani M., Lettieri T., Blaha L., Jarosova B., Voorspoels
484 S., Servaes K., Haglund P., Fick J., Lindberg R. H., Schwesig D. and
485 Gawlik B. M. (2013). EU-wide monitoring survey on emerging polar organic
486 contaminants in wastewater treatment plant effluents. *Water Research*
487 **47**(17), 6475-87.
- 488 Mailler R., Gasperi J., Coquet Y., Deshayes S., Zedek S., Cren-Olivé C.,
489 Cartiser N., Eudes V., Bressy A., Caupos E., Moilleron R., Chebbo G. and
490 Rocher V. (2014a). Study of a large scale powdered activated carbon pilot:
491 Removals of a wide range of emerging and priority micropollutants from
492 wastewater treatment plant effluents. *Water Research*(0).
- 493 Mailler R., Gasperi J., Coquet Y., Deshayes S., Zedek S., Cren-Olivé C.,
494 Cartiser N., Eudes V., Bressy A., Caupos E., Moilleron R., Chebbo G. and
495 Rocher V. (2015). Study of a large scale powdered activated carbon pilot:
496 Removals of a wide range of emerging and priority micropollutants from
497 wastewater treatment plant effluents. *Water Research* **72**(0), 315-30.
- 498 Mailler R., Gasperi J., Rocher V., Gilbert-Pawlik S., Geara-Matta D., Moilleron
499 R. and Chebbo G. (2014b). Biofiltration vs conventional activated sludge
500 plants: what about priority and emerging pollutants removal? *Environmental*
501 *Science and Pollution Research* **21**(8), 5379-90.
- 502 Margot J., Kienle C., Magnet A., Weil M., Rossi L., de Alencastro L. F.,
503 Abegglen C., Thonney D., Chèvre N., Schärer M. and Barry D. A. (2013).
504 Treatment of micropollutants in municipal wastewater: Ozone or powdered
505 activated carbon? *Science of the Total Environment* **461-462**(0), 480-98.
- 506 Matsui Y., Fukuda Y., Inoue T. and Matsushita T. (2003). Effect of natural
507 organic matter on powdered activated carbon adsorption of trace
508 contaminants: characteristics and mechanism of competitive adsorption.
509 *Water Research* **37**(18), 4413-24.

510 Miège C., Choubert J. M., Ribeiro L., Eusèbe M. and Coquery M. (2009). Fate of
511 pharmaceuticals and personal care products in wastewater treatment plants
512 - Conception of a database and first results. *Environmental Pollution*
513 **157**(5), 1721-6.

514 Newcombe G., Morrison J., Hepplewhite C. and Knappe D. R. U. (2002).
515 Simultaneous adsorption of MIB and NOM onto activated carbon: II.
516 Competitive effects. *Carbon* **40**(12), 2147-56.

517 Parlanti E., Morin B. and Vacher L. (2002). Combined 3D-spectrofluorometry, high
518 performance liquid chromatography and capillary electrophoresis for the
519 characterization of dissolved organic matter in natural waters. *Organic*
520 *Geochemistry* **33**(3), 221-36.

521 Rocher V., Paffoni C., Goncalves A., Guerin S., Azimi S., Gasperi J., Moilleron
522 R. and Pauss A. (2012). Municipal wastewater treatment by biofiltration:
523 comparisons of various treatment layouts. Part 1: assessment of carbon and
524 nitrogen removal. *Water Science and Technology* **65**(9), 1705-12.

525 Ruel S. M., Choubert J. M., Budzinski H., Miegé C., Esperanza M. and Coquery M.
526 (2012). Occurrence and fate of relevant substances in wastewater treatment
527 plants regarding Water Framework Directive and future legislations. *Water*
528 *Science and Technology* **65**(7), 1179-89.

529 Snyder S. A., Adham S., Redding A. M., Cannon F. S., DeCarolis J., Oppenheimer
530 J., Wert E. C. and Yoon Y. (2007). Role of membranes and activated carbon
531 in the removal of endocrine disruptors and pharmaceuticals. *Desalination*
532 **202**(1-3), 156-81.

533 Ternes T. A., Meisenheimer M., McDowell D., Sacher F., Brauch H.-J., Haist-Gulde
534 B., Preuss G., Wilme U. and Zulei-Seibert N. (2002). Removal of
535 Pharmaceuticals during Drinking Water Treatment. *Environmental Science &*
536 *Technology* **36**(17), 3855-63.

537 Verlicchi P., Al Aukidy M. and Zambello E. (2012). Occurrence of pharmaceutical
538 compounds in urban wastewater: Removal, mass load and environmental risk
539 after a secondary treatment—A review. *Science of the Total Environment*
540 **429**(0), 123-55.

541 Yu Z., Peldszus S. and Huck P. M. (2008). Adsorption characteristics of selected
542 pharmaceuticals and an endocrine disrupting compound—Naproxen,
543 carbamazepine and nonylphenol—on activated carbon. *Water Research* **42**(12),
544 2873-82.

545 Zietzschmann F., Altmann J., Ruhl A. S., Dünnebier U., Dommisch I., Sperlich A.,
546 Meinel F. and Jekel M. (2014). Estimating organic micro-pollutant removal
547 potential of activated carbons using UV absorption and carbon
548 characteristics. *Water Research* **56**(0), 48-55.

549 Zsolnay A., Baigar E., Jimenez M., Steinweg B. and Saccomandi F. (1999).
550 Differentiating with fluorescence spectroscopy the sources of dissolved
551 organic matter in soils subjected to drying. *Chemosphere* **38**(1), 45-50.

552

553