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1 Removal of a wide range of emerging pollutants from wastewater treatment plant
2 discharges by micro-grain activated carbon in fluidized bed as tertiary treatment at
3 large pilot scale

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18
19 HIGHLIGHTS

- 20
21 • Pharmaceuticals and hormones are well removed (> 80%) by micro-grain activated carbon (μ GAC)
22 • 50 to > 90% removals are also achieved for alkylphenols, bisphenol A, parabens, pesticides and sweeteners
23 • UV absorbance at 254 nm, dissolved organic carbon and micropollutant removals are well correlated
24 • Elimination of NH_4^+ , NO_2^- and total suspended solids occurs with μ GAC
25 • Performances obtained with μ GAC are similar to those with powdered activated carbon
26
27

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1 ABSTRACT

2

3 Among the solutions to reduce micropollutant discharges into the aquatic environment, the implementation of tertiary
4 wastewater treatments is seriously considered by wastewater treatment plant (WWTP) managers and scientists. In that
5 purpose, activated carbon adsorption is a promising technique and a large scale pilot, based on a fluidized bed
6 technology, has been tested at the Seine Centre WWTP (240 000 m³/d - Paris, France) both with powdered (PAC) and
7 micro-grain activated carbon (μGAC). Thus, conventional wastewater quality parameters (n = 11), pharmaceuticals and
8 hormones (PPHs; n = 62) and other emerging pollutants (n = 57) have been monitored in μGAC configuration during
9 13 campaigns.

10

11 A significant correlation has been established between dissolved organic carbon (DOC), PPHs and UV absorbance at
12 254 nm (UV-254) removals. This confirms that UV-254 could be used as a tertiary treatment performance indicator to
13 monitor the process. This parameter allowed identifying that the optimal μGAC retention time (SRT) is 90-100 days.

14

15 The μGAC configuration substantially improves the overall quality of the WWTP discharges by reducing biological
16 (38-45%) and chemical oxygen demands (21-48%), DOC (13-44%) and UV-254 (22-48%). In addition, total suspended
17 solids (TSS) are retained by the μGAC bed and a biological activity (nitrification) leads to a total elimination of NO₂⁻.

18

19 For micropollutants, PPHs have a good affinity for μGAC and high (> 60%) or very high (> 80%) removals are
20 observed for most of the quantified compounds (n = 22/32), i.e. atenolol (92-97%), carbamazepine (80-94%),
21 ciprofloxacin (75-95%), diclofenac (71-97%), oxazepam (74-91%) or sulfamethoxazole (56-83%). In addition,
22 alkylphenols, artificial sweeteners, benzotriazole, bisphenol A, personal care products (triclocarban and parabens) and
23 pesticides have removals lying in the 50 - > 90% range.

24

25 Overall, μGAC allows obtaining performances comparable to PAC at the same activated carbon dose. Indeed, the
26 average removal of the 13 PPHs found at a high occurrence (> 75%) in WWTP discharges is similar at 20 g/m³ of
27 μGAC (78-89%) and PAC (85-93%). In addition, this recycled μGAC operation leads to several operational advantages
28 (no FeCl₃, reactivable, high SRT) and has a stronger impact on the overall wastewater quality.

29

30

1 **KEYWORDS**

2

3 Emerging pollutants; pharmaceuticals and hormones; adsorption; micro-grain activated carbon; wastewater tertiary
4 treatment;

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6

7 **INTRODUCTION**

8

9 The presence of a wide range of priority and emerging pollutants in the aquatic environment and wastewater treatment
10 plant (WWTP) discharges has been confirmed by many studies (Deblonde et al. 2011, Gasperi et al. 2008, Giger et al.
11 2003, Heberer 2002, Jelić et al. 2012, Lange et al. 2012, Loos et al. 2013, Luo et al. 2014, Miège et al. 2009, Rogers
12 1996, Verlicchi et al. 2012). In particular, pharmaceuticals and hormones (PPHs), preservatives from personal care
13 products (PCPs), pesticides, phthalates or artificial sweeteners are quantified at ng/L to µg/L levels. These compounds
14 are harmful for the aquatic environment and/or humans (Bolong et al. 2009, Daughton and Ternes 1999).

15

16 45 compounds are listed in the European Union Water Framework Directive (EC 2013) as priority substances with
17 environmental quality standards (EQS) to respect in the aquatic environment, and 10 others are listed on the
18 complementary watch list (Decision 2015/495, published on the 24th of March 2015). European or national regulations
19 could evolve in the near future by adding new compounds and setting additional or lowering existing EQS. Moreover,
20 the EAWAG Institute in Switzerland has recently proposed environmental quality criteria, similar to EQS, for several
21 other emerging compounds such as PPHs and pesticides (Götz et al. 2010, Kase et al. 2011).

22

23 Different strategies of contamination reduction are considered by stakeholders and water quality managers, such as
24 source reduction or wastewater treatment improvement. Several studies have highlighted the persistence of many
25 compounds, including PPHs and PCPs, in conventional treatments (Choubert et al. 2011, Clara et al. 2007, Clara et al.
26 2005, Sipma et al. 2010). Thus, the implementation of specific tertiary treatments is seriously considered by wastewater
27 managers and decision makers. Among them, activated carbon adsorption is promising but very few studies have
28 studied its application to wastewater (Altmann et al. 2014, Boehler et al. 2012, Löwenberg et al. 2014, Mailler et al.
29 2015b, Reungoat et al. 2012, Ruel et al. 2011).

30

1 In this context, a large scale activated carbon pilot has been set up at the Seine Centre WWTP, treating wastewater from
2 Paris conurbation and supervised by the Paris public sanitation service (SIAAP). The study of this pilot, performed by
3 the SIAAP and the Laboratory of Water Environment and Urban Systems (LEESU) during two years (2013-2015), was
4 organized in two phases. First, the performances were evaluated with powdered activated carbon (PAC) on 119
5 micropollutants (N = 14; N for the number of campaigns). The full description of the results obtained can be found in
6 (Mailler et al. 2015b). Then, the pilot performances were assessed with micro-grain activated carbon (μ GAC) on the
7 same micropollutants (N = 13). This μ GAC has an intermediary particle size (200-600 μ m - supporting material Table
8 S1) between PAC (< 100 μ m) and grain activated carbon (> 800 μ m), is reactivable (carried out by the μ GAC supplier
9 and included in the selling price) and produced from used activated carbon. This leads to various operational advantages
10 compared to PAC, such as the reduction of the solid wastes to handle, the non-necessity to inject FeCl_3 to prevent
11 activated carbon leakages, or the overall higher simplicity of operation, for a similar costs (\approx 1 000 €/ton).

12
13 This article aims at synthetizing the performances of this wastewater tertiary treatment operating with μ GAC. First, the
14 quality of the pilot influents (WWTP discharges) is discussed regarding both the conventional wastewater quality
15 parameters and the micropollutant concentrations. Then, the micropollutant removals obtained with the pilot at two
16 μ GAC doses (10 and 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$) are presented, as well as those of conventional wastewater quality parameters. In
17 addition, the influence of the μ GAC dose on performances and the optimal μ GAC residence time (SRT) are also
18 discussed, as well as the use of UV absorbance at 254 nm (UV-254) as a performance indicator. Finally, a comparison
19 of the performances between μ GAC and PAC is performed.

20
21 Such results are of high interest and very relevant considering the poverty of the literature about the removal of
22 micropollutants from wastewater by activated carbon. In particular, the study of this large scale pilot, both in PAC and
23 μ GAC, is one of the first about fluidized activated carbon treatment in wastewater.

24 25 26 MATERIALS AND METHODS

27 28 1. WWTP description

29
30 The tertiary treatment pilot has been set up at the Seine Centre WWTP (Colombes, France), supervised by the Paris

1 public sanitation service (SIAAP). This plant treats 240 000 m³/day (900 000 population equivalent) of mainly domestic
2 wastewater from Paris conurbation. The treatment is ensured by three major steps: pre, primary and biological
3 treatment. After the pretreatment (screening, grit and oil removal units), a physicochemical lamellar settling unit
4 (Densadeg®) removes a great part of the particulate and colloidal pollution thanks to the addition of ferric chloride and
5 anionic polymer. Finally, the removal of nutrients (carbon - nitrogen - phosphorus) is performed by a three stages
6 biofiltration treatment. The first stage (Biofor® filters - biolite media) performs the carbon removal in aerobic
7 conditions, the second stage (Biostyr® filters - biostyrene media) ensures a total nitrification in aerobic conditions and
8 the third stage (Biofor® filters - biolite media) allows the denitrification of water in anoxic conditions (Rocher et al.
9 2012). The layout of the Seine Centre WWTP is given in supporting material - Figure S1.

10 11 12 2. The CarboPlus® process

13
14 The studied tertiary treatment pilot is based on the CarboPlus® process, developed by the company SAUR. This
15 process allows operating with different kinds of activated carbons such as PAC (Mailler et al. 2015b), or µGAC as in
16 this study. The µGAC is a material with an intermediary size between PAC (< 100 µm) and granular activated carbon
17 (> 800 µm). The selected µGAC is the Cyclecarb 305® from Chemviron Carbon, which is produced from recycled
18 activated carbon and is reactivable. This mesoporous product is characterized by a bulk density of 0.53 kg/m³, a median
19 particle size of 423.5 µm and a specific BET surface of 860 ± 20 m²/g (supporting material - Table S1), which is close
20 to those of products tested in the PAC study (Mailler et al. 2015b). In addition, the distribution of this surface by pore
21 size is similar for both activated carbons (supporting material - Figure S3).

22
23 The CarboPlus® process consists in a reactor where water flows upstream through a high mass fluidized bed of µGAC.
24 A continuous dose of fresh µGAC is injected into the system to ensure the renewal of adsorbent. At steady state, a
25 similar quantity of used µGAC is extracted from the reactor to keep the total mass of the bed constant. Moreover, the
26 total mass of the bed can be adjusted by regulating the µGAC extraction. In contrary to the same process in PAC
27 configuration, no coagulant and flocculant are needed to maintain the bed shape. A layout of the CarboPlus® process is
28 given in supporting material - Figure S2.

29
30 The studied pilot is a 5 m high reactor with a surface of about 5 m², and is fed with the WWTP discharges (third

1 biofiltration stage effluents) at a fixed flow rate of 1 400 m³/day. The hydraulic velocity inside the reactor is 15 m/h. At
2 steady state, the concentration of μ GAC in the bed reaches 300 g/L with a μ GAC bed depth of 1.5-2.5 m depending on
3 the μ GAC dose. The contact time between μ GAC and water can then be estimated between 10 and 20 min. In this case,
4 the extraction of μ GAC started after 120 days of operation.

7 3. Structure of the study and sampling strategy

8
9 The performances of the pilot have been assessed for two μ GAC doses (10 and 20 g $_{\mu$ GAC}/m³). In order to follow the
10 ramp-up of the process and to determine the optimal μ GAC retention time (SRT), the choice has been made for both
11 doses to start with an empty reactor and to inject the continuous fresh dose normally without extracting any μ GAC until
12 reaching the optimal performances on dissolved organic matter (DOC) and UV absorbance at 254 nm (UV-254). This
13 corresponds to the ramp-up phase. Thus, the μ GAC extraction started after a stabilization of both DOC and UV-254
14 removals. After reaching this point, the pilot was operated normally, corresponding to the stabilized phase and the
15 ramp-up phase duration corresponds to the average SRT.

16
17 To determine the process performances, a total of 13 campaigns have been performed. 8 campaigns were carried out at
18 a fresh μ GAC dose of 20 g $_{\mu$ GAC}/m³ - 3 during the ramp-up phase and 5 during the stabilized phase - and 5 campaigns
19 were performed at 10 g $_{\mu$ GAC}/m³ - all during the stabilized phase.

20
21 24 h composite samples of 20 L were collected in glass bottles, properly cleaned, by automatic refrigerated (4°C)
22 samplers. These samplers are equipped with Teflon® pipes to avoid any contamination or sorption. When samples were
23 completed, glass bottles were collected, carefully homogenized, filtered on 0.7 μ m GF/F filters (Whatmann®) and sub-
24 samples were conditioned for analyses. Analyses were performed on dissolved phase. All samples were analyzed within
25 48 h after sampling, due to transport time to the laboratories involved, except for sweeteners. As recommended by the
26 laboratory performing the artificial sweeteners analyses (internal tests), these samples were acidified (1% volumetric
27 HCl) and stored in fridge (4°C) until analyses.

30 4. Pollutants and analytical procedures

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In all samples, conventional wastewater quality parameters were analyzed by the SIAAP laboratory, which is accredited by the French authorities (COFRAC), to characterize the overall quality of the water. The monitored parameters are the dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand in 5 days (BOD₅), UV absorbance at 254 nm (UV-254), total Kjeldahl nitrogen (TKN), NH₄⁺, NO₂⁻, NO₃⁻, total phosphorus (TP), PO₄³⁻ and total suspended solids (TSS). The limits of quantification (LQ) and the analytical standards are given in supporting material - Table S2. In addition, UV-254 and DOC were used to calculate the SUVA (specific UV absorbance = 100 x UV-254/DOC) for every sample to assess the evolution of the organic matter aromaticity.

A total of 119 priority and emerging pollutants were monitored in the dissolved phase (Table 1). The detailed list of the studied compounds is given in supporting material - Table S3 with their limits of detection (LD) and quantification (LQ). The analyses were performed by the Institute of Analytical Sciences (ISA - Villeurbanne, France) of CNRS (n = 83; n for the number of compounds), the Laboratory of Water Environment and Urban Systems (LEESU - Créteil, France) (n = 15), the Laboratory CARSO (Poitiers, France) (n = 13), the Central Laboratory of the Police Prefecture (LCPP) (n = 4) and the Water Technology Center (TZW - Karlsruhe, Germany) (n = 4).

The 83 compounds from ISA were analyzed in all samples and include 5 analgesics, 31 antibiotics, 2 beta blockers, 1 diuretic, 10 hormones, 2 hypolipemians, 4 psychoactive drugs, 3 chlorinated solvents, 2 perfluorinated acids (PFAs) and 23 pesticides (Table 1). The remaining compounds (n = 36) were analyzed for 6 to 8 campaigns during stabilized phase (supporting material - Table S3). The detail of the campaigns performed for each compound is given in supporting material - Table S3.

For ISA, analytical methods were adapted from (Vulliet et al. 2011) for PPHs and PFAs, and from (Barrek et al. 2009) for the others. These analytical methods were revalidated with the Seine Centre discharges matrix, resulting in updated LD and LQ. For the other substances (LEESU, LCPP and TZW), the detailed methods are given in (Gasperi et al. 2014) for PCPs, in (Bergé et al. 2014) for phthalates, in (Cladière et al. 2013) for alkylphenols and bisphenol A, and in (Scheurer et al. 2009) for artificial sweeteners.

Table 1 - Studied pollutants and analytical methods

Groups	n ^a	N ^b	Extraction method ^c	Analysis ^d	Reference	LQ ^e
<i>Institute of Analytical Sciences - ISA (N=83)</i>						

Analgesics/anti-inflammatory	5	13	SPE <i>StrataX® or Oasis HLB® cartridges</i>	LC-MSMS	(Vulliet et al. 2011)	9.8 - 193
Antibiotics	31					1 - 900
Beta blockers	2					3.3 - 23
Chlorinated solvents	3		SPE <i>StrataX® cartridges</i>	GC-MS	(Barrek et al. 2009)	5.1 - 8.0
Diuretics	1		SPE <i>StrataX® or Oasis HLB® cartridges</i>	LC-MS/MS	(Vulliet et al. 2011)	414
Hormones	10					1.2 - 700
Hypolipemians	2					6.3 - 38.4
Perfluorinated acids	2		SPE <i>StrataX® cartridges</i>			7.2 - 7.4
Pesticides	23		SPE <i>Oasis HLB® cartridges</i>	LC-MS/MS GC-MS	(Barrek et al. 2009)	3.0 - 233
Psychoactive drugs	4		SPE <i>StrataX® or Oasis HLB® cartridges</i>	LC-MS/MS	(Vulliet et al. 2011)	0.1 - 9.6
<i>Laboratory of Water Environment and Urban Systems - LEESU (N=15)</i>						
Alkylphenols	7	7	SPE <i>Oasis HLB® cartridges</i>	LC-MS/MS	(Cladière et al. 2013)	2 - 25
Other chemicals	1					10
Personal care products	7	7			(Gasperi et al. 2014)	2.8 - 10
<i>Laboratory CARSO (N=13)</i>						
Other chemicals	1	7	<i>Measured performed by an external contractor Analytical methods not communicated</i>			50
Pesticides	5					20 - 50
Psychoactive drugs	2					200 - 500
X-ray agents	5					50 - 500
<i>Central Laboratory of the Police Prefecture - LCPP (N=4)</i>						
Phthalates	4	8	SPE <i>Oasis HLB® cartridges</i>	GC-MS	(Bergé et al. 2014)	90
<i>Water Technology Center - TZW (N=4)</i>						
Artificial sweeteners	4	6	SPE <i>Bakerbond SDB1 cartridges</i>	LC-MS/MS	(Scheurer et al. 2009)	50 - 250
<i>Total micropollutants</i>	119					
^a n = number of substances. ^b N = number of campaigns performed. ^c SPE = solid phase extraction. ^d Analytical methods: LC = liquid chromatography, GC = gas chromatography, GC-MS = GC with mass spectrometry, LC-MS/MS = LC with tandem mass spectrometry. ^e LQ = limit of quantification.						

5. Data treatment and presentation

For the evaluation of the pilot efficiency to remove micropollutants, only the campaigns sampled in stabilized phase were considered. Removals were calculated only when the compounds were quantified in the pilot influents. Thus, two cases were encountered regarding the pilot effluent concentrations: i) the compound was also quantified in the pilot effluents and ii) the compound concentration in the pilot effluents was below LQ or LD. In the first case, removals were normally calculated. In the second case, the removal was estimated by considering a concentration of LQ/2 in the pilot effluents.

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As the number of data for micropollutant concentrations in stabilized phase is relatively limited for both assessed μGAC doses ($n = 5$ for $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$; $n = 5$ for $10 \text{ g}_{\mu\text{GAC}}/\text{m}^3$), it was chosen to present all the calculated removals for a compound on the same figure. In tables, only the stabilized phase was considered and average \pm standard deviation (SD) with minimum and maximum values are presented. Average \pm SD were calculated for compounds with at least 3 values. For the others, only minimum and maximum values are presented.

In order to evaluate the evolution of the pilot performances on micropollutants, the average removal of the 13 PPHs detected at high occurrences in the WWTP discharges, both in μGAC and PAC configurations, was considered to compare the results in μGAC and PAC configurations.

RESULTS AND DISCUSSION

1. Pilot influent wastewater quality

Conventional wastewater parameters

The concentrations of the conventional wastewater quality parameters are given in Table 2. In the pilot influents, the quality of water is relatively good, particularly for organic matter. Low concentrations are measured for DOC ($6.9 \pm 1.6 \text{ mgC/L}$), COD ($27 \pm 16 \text{ mgO}_2/\text{L}$) and BOD₅ ($3.8 \pm 1.8 \text{ mgO}_2/\text{L}$). Organic matter is particularly important in the adsorption processes because it competes with micropollutants for adsorption sites and/or prevents them from accessing to them by pore blocking (Kilduff and Wigton 1998, Matsui et al. 2003, Pelekani and Snoeyink 1999). Indeed, the negative influence of DOC concentration has been highlighted in several studies (Delgado et al. 2012, Mailler et al. 2015b, Margot et al. 2013).

Levels for organic matter (DOC, UV-254 and BOD₅) are very similar to those measured in the same pilot influents during the PAC operation phase (2013, (Mailler et al. 2015b)). The comparison of μGAC results with those of PAC, later presented, is then very relevant and interesting as performed on waters of similar overall quality. In addition, they are lower than those reported in other studies about activated carbon adsorption in wastewater, including those from

1 (Margot et al. 2013) (DOC = 7.3 ± 1.9 mgC/L), (Altmann et al. 2014) (DOC = 9.6-11.4 mgC/L) or (Löwenberg et al.
2 2014) (DOC = 8.8 ± 1.2 mgC/L). In contrary, (Boehler et al. 2012) tested activated carbon on a wastewater with similar
3 DOC (DOC = 5.6-8.9 mgC/L).

4
5 Regarding the other parameters (Table 2), TSS (4.7 ± 2.6 mg/L) are very low in the Seine Centre discharges resulting
6 from the high removal (98%) achieved by this WWTP (Mailler et al. 2014, Rocher et al. 2012). For the same reason,
7 nitrogen species concentrations are limited, especially for NH_4^+ (0.5 ± 0.4 mgN/L), highlighting the total nitrification
8 performed. Low levels of NO_2^- (1.04 ± 0.76 mgN/L) and NO_3^- (9.7 ± 2.7 mgN/L) were also observed as a result of the
9 efficient denitrification step. Finally, total phosphorus and PO_4^{3-} are most of the time found below their LQ, respectively
10 0.3 and 0.1 mgP/L (Table 2).

11
12

13 *PPHs*

14

15 32 PPHs (on 62 monitored) were quantified in the pilot influents (Table 2). Among them, 19 compounds have a high
16 occurrence ($> 75\%$) including atenolol, carbamazepine, diclofenac, gabapentin, iopromide, lorazepam, ofloxacin,
17 oxazepam or sulfamethoxazole. In contrary, acetaminophen, ibuprofen and iothalamic acid have a low occurrence ($<$
18 25%) in the pilot influents.

19 The remaining compounds ($n = 10$) have been quantified at moderate occurrences (25-75%), including bezafibrate,
20 estrone, iopamidol, naproxen or tetracycline. Moreover, 30 PPHs were never quantified in the pilot influents, including
21 20 antibiotics, 7 hormones, fenofibrate, fluvoxamine and primidone. The complete list of these molecules is given in
22 Table 2.

23

24 Regarding concentrations in the pilot influents (Table 2), the PPH pattern in the pilot influents is similar to the one
25 previously observed in this WWTP (Mailler et al. 2015b), excepted few compounds that are more concentrated in this
26 study such as atenolol, diclofenac or carbamazepine.

27

28 14 compounds were measured at average concentrations lower than 100 ng/L. Among them, 17- β -estradiol (14 ± 4
29 ng/L), estrone (6 ± 2 ng/L) and lorazepam (15 ± 10 ng/L) are found at very low levels (< 20 ng/L) in the pilot influents.

30 However, carbamazepine, lorazepam, norfloxacin and propranolol are characterized by a high occurrence ($> 75\%$)

1 despite their low concentrations.

2

3 17 compounds are measured at average concentrations higher than 100 ng/L, such as atenolol (448 ± 400 ng/L),
4 ciprofloxacin (184 ± 95 ng/L), erythromycin (190 ± 88 ng/L), ibuprofen (170 ± 211 ng/L), ketoprofen (147 ± 87 ng/L),
5 naproxen (449 ± 120 ng/L), ofloxacin (953 ± 438 ng/L) or oxazepam (239 ± 110 ng/L). 7 substances have particularly
6 high concentrations ($> 1\,000$ ng/L): diclofenac ($1\,120 \pm 1\,400$ ng/L), gabapentin ($2\,360 \pm 1\,470$ ng/L),
7 sulfamethoxazole ($1\,430 \pm 1\,450$ ng/L) and 4 of the 5 studied X-ray agents. Among the X-ray agents, iohexol ($8\,600 \pm$
8 $5\,130$ ng/L) and iomeprol ($28\,600 \pm 16\,900$ ng/L) concentrations are significantly higher than those observed for the
9 other PPHs. Overall, a group of 13 compounds (Table 2) is characterized by both a high occurrence ($> 75\%$) and lies in
10 the 100 to $> 1\,000$ ng/L range in the pilot influents. These substances have to be carefully considered in the
11 performances evaluation, especially for comparing with other tertiary treatments.

12

13 The concentrations observed are overall consistent with those reported in the literature for WWTP effluents (Deblonde
14 et al. 2011, Loos et al. 2013, Luo et al. 2014, Margot et al. 2013, Miège et al. 2009, Verlicchi et al. 2012). In particular,
15 for X-ray agents, atenolol, diclofenac, gabapentin, roxithromycin or trimethoprim, such high concentrations in WWTP
16 effluents are not surprising as they are known to be particularly recalcitrant to conventional WWTPs (Margot et al.
17 2013, Radjenović et al. 2009, Sipma et al. 2010). Then, the very low occurrences as well as low concentrations of
18 hormones, acetaminophen, bezafibrate, ibuprofen and naproxen can be explained by their relatively good
19 biodegradability ($k_{\text{bio}} > 1$ L/gTSS/d) by biological treatments (Joss et al. 2006, Pomiès et al. 2013) implying high
20 removals by WWTP biological treatments (Margot et al. 2013, Nakada et al. 2007, Radjenović et al. 2009, Sipma et al.
21 2010). Moreover, the studied WWTP performs very efficient carbon removal, nitrification and denitrification by
22 biofiltration (Mailler et al. 2014, Rocher et al. 2012), as highlighted by the overall quality of the pilot influents (Table
23 2), what is favorable to micropollutant removal. However, several differences can be identified. For example,
24 tetracycline was measured at much higher concentrations in the literature (Deblonde et al. 2011, Miège et al. 2009). In
25 contrary, ofloxacin and sulfamethoxazole are measured at higher levels than in other studies (Deblonde et al. 2011,
26 Loos et al. 2013, Margot et al. 2013). Finally, ketoprofen, oxazepam, ofloxacin and propranolol were detected at much
27 higher occurrence than in the study of (Margot et al. 2013), which studied a tertiary PAC treatment at large scale with a
28 high number of campaigns. These differences should result from differences of countries consumptions and/or a specific
29 behavior of these compounds within the biofiltration process.

30

1

2 *Other emerging pollutants*

3

4 28 compounds (in 57) were never quantified, i.e. butyl benzyl phthalate (BBP), benzyl paraben, chlorinated solvents (n
5 = 3), cyclamate and pesticides (n = 23).

6 29 other emerging pollutants (in 57), including 6 priority substances from (EC 2013), were quantified in the pilot
7 influents (Table 2). AMPA, benzotriazole, bisphenol A, DEHP, DnBP, ethyl paraben, glyphosate, methyl paraben,
8 triclosan and triclocarban, as well as 5 alkylphenols (4-NP, NP1EO, NP2EO, NP1EC and t-OP) and 3 sweeteners
9 (acesulfame, saccharin and sucralose) were found at high occurrences (> 75%), while butyl paraben, OP2EO, PFOA,
10 PFOS and propyl paraben were quantified at low occurrences (< 25%). The remaining pollutants (n = 9) have a
11 moderate occurrence (25-75%), including priority substances diuron and terbutryn.

12

13 Most of the compounds (n = 17/29) were measured below 100 ng/L, including bisphenol A (26 ± 8 ng/L), glyphosate
14 (84 ± 38 ng/L), mecoprop (37 ± 19 ng/L), terbutryn (33 ± 10 ng/L), all the PCPs (n = 7), most of the alkylphenols (n =
15 6/7) and PFOS (≤ 92 ng/L). In particular, butyl paraben (≤ 10 ng/L), PFOA (≤ 10 ng/L), propyl paraben (≤ 4 ng/L), 4-
16 NP (90 ± 86 ng/L), t-OP (11 ± 7 ng/L), OP2EO (<LQ - 15 ng/L) and triclocarban (7 ± 3 ng/L) were measured at very
17 low levels (< 20 ng/L).

18 12 emerging pollutants were measured above 100 ng/L in average, such as DEHP (501 ± 379 ng/L), diuron (524 ± 623
19 ng/L), NP1EO (183 ± 375 ng/L) or saccharin (231 ± 106 ng/L). Acesulfame ($2\,570 \pm 1\,000$ ng/L), benzotriazole ($2\,810$
20 ± 481 ng/L), DnBP ($2\,990 \pm 4\,060$ ng/L) and sucralose ($8\,200 \pm 1\,060$ ng/L) were found at particularly high levels in
21 the pilot influents with average concentrations higher than 1 000 ng/L. Such low occurrences and concentrations for
22 alkylphenols, PCPs and chlorinated solvents in the pilot influents are consistent considering their very high removals by
23 the conventional WWTPs reported in the literature (Choubert et al. 2011, Clara et al. 2007, Mailler et al. 2014).
24 Similarly, the high concentrations found for benzotriazole, phthalates and artificial sweeteners are consistent regarding
25 other studies (Bergé et al. 2014, Lange et al. 2012, Loos et al. 2013).

Table 2 - Concentrations of conventional wastewater parameters and micropollutants in wastewater by μGAC

	Pilot influents		Pilot effluents - 20 $\mu\text{GAC}/\text{m}^3$		Pilot ffluents - 10 $\mu\text{GAC}/\text{m}^3$		
	LQ	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>							
BOD ₅ (mgO ₂ /L)	0.5	13/13	3.8 \pm 1.8 (1.4 - 8.0)	5/5	2.6 \pm 1.6 (0.8 - 5.0)	5/5	2.2 \pm 0.6 (1.8 - 3.3)
COD (mgO ₂ /L)	4.0	13/13	27 \pm 16 (16 - 81)	5/5	12 \pm 3 (9 - 17)	5/5	17 \pm 2 (15 - 19)
DOC (mgC/L)	0.5	13/13	6.9 \pm 1.6 (4.4 - 11)	5/5	3.7 \pm 0.5 (2.8 - 4.3)	5/5	5.8 \pm 0.9 (4.2 - 6.7)
NH ₄ ⁺ (mgN/L)	0.3	7/13	0.5 \pm 0.4 (<LQ - 1.6)	2/5	(<LQ - 1.3)	0/5	<LQ
NO ₂ ⁻ (mgN/L)	0.02	13/13	1.04 \pm 0.76 (0.24 - 2.30)	4/5	0.06 \pm 0.05 (<LQ - 0.13)	2/5	(<LQ - 0.02)
NO ₃ ⁻ (mgN/L)	0.4	13/13	9.7 \pm 2.7 (5.8 - 15.0)	5/5	11.3 \pm 2.0 (9.0 - 14.5)	5/5	10.1 \pm 2.2 (7.8 - 13.1)
TKN (mgN/L)	0.5	13/13	1.3 \pm 0.5 (0.7 - 2.7)	4/5	0.9 \pm 0.7 (<LQ - 1.9)	5/5	0.9 \pm 0.3 (0.6 - 1.3)
PO ₄ ³⁻ (mgP/L)	0.1	5/13	0.19 \pm 0.08 (<LQ - 0.33)	1/5	(<LQ - 0.11)	4/5	0.24 \pm 0.08 (<LQ - 0.34)
TP (mgP/L)	0.3	3/13	0.48 \pm 0.04 (<LQ - 0.50)	0/5	<LQ	1/5	(<LQ - 0.40)
TSS (mg/L)	2.0	8/13	4.7 \pm 2.6 (<LQ - 11)	2/5	(<LQ - 3)	0/5	<LQ
UV-254 (cm ⁻¹)	-	13/13	0.126 \pm 0.012 (0.098 - 0.142)	5/5	0.067 \pm 0.004 (0.063 - 0.072)	4/4	0.092 \pm 0.011 (0.073 - 0.097)
<i>Pharmaceuticals and hormones</i>							
Acetaminophen	130	1/13	(<LQ - 6 420)	0/5	<LQ	0/5	<LQ
Atenolol	23	11/13	448 \pm 400 (<LQ - 1 335)	0/5	<LQ	0/5	<LQ
Bezafibrate	38	5/13	44 \pm 6 (<LQ - 56)	0/5	<LQ	0/5	<LQ
Carbamazepine	0.1	13/13	74 \pm 65 (21 - 277)	5/5	4 \pm 3 (2 - 9)	5/5	65 \pm 23 (46 - 104)
Ciprofloxacin	28	13/13	184 \pm 95 (89 - 395)	2/5	(<LQ - 63)	1/5	(<LQ - 74)
Diclofenac	171	13/13	1 120 \pm 1 400 (<LQ - 4 240)	0/5	<LQ	0/5	<LQ
Erythromycin	3.7	13/13	190 \pm 88 (10 - 373)	5/5	40 \pm 32 (11 - 94)	5/5	156 \pm 28 (130 - 188)
17- α -estradiol	7.1	4/13	23 \pm 11 (<LQ - 39)	2/5	(<LQ - 16)	0/5	<LQ
17- β -estradiol	7.1	4/13	14 \pm 4 (<LQ - 19)	2/5	(<LQ - 14)	0/5	<LQ
Estrone	1.2	4/13	6 \pm 2 (<LQ - 19)	0/5	<LQ	0/5	<LQ
Furosemide	414	2/13	(<LQ - 482)	0/5	<LQ	0/5	<LQ
Gabapentin	200	7/7	2 340 \pm 1 360 (400 - 4 900)	3/3	1 390 (810 - 1 760)	4/4	1 830 \pm 1 100 (220 - 2 700)
Ibuprofen	10	3/13	170 \pm 211 (<LQ - 413)	1/5	(<LQ - 18)	1/5	(<LQ - 44)
Iohexol	500	6/7	8 930 \pm 4 840 (<LQ - 15 900)	2/3	(<LQ - 5 400)	4/4	5 130 \pm 3 520 (560 - 10 300)
Iomeprol	500	6/7	29 900 \pm 16 100 (<LQ - 50 000)	3/3	8 660 (870 - 16 500)	4/4	15 100 \pm 8 310 (2 200 - 24 300)
Iopamidol	500	5/7	1 520 \pm 590 (<LQ - 2 390)	1/3	(<LQ - 503)	4/4	1 239 \pm 576 (725 - 2 210)
Iopromide	50	7/7	5 190 \pm 2 720 (782 - 9 480)	3/3	1 070 \pm 670 (300 - 1 500)	4/4	4 003 \pm 1 715 (2040 - 6 710)
Iothalamic acid	500	1/7	(<LQ - 1 200)	1/3	(<LQ - 1 100)	0/4	<LQ
Ketoprofen	16	10/13	147 \pm 87 (<LQ - 288)	0/5	<LQ	4/5	61 \pm 36 (<LQ - 105)
Lorazepam	0.5	13/13	15 \pm 10 (4 - 28)	0/5	<LQ	2/5	(<LQ - 6)
Naproxen	193	4/13	449 \pm 120 (<LQ - 563)	0/5	<LQ	0/5	<LQ

		Pilot influents		Pilot effluents - 20 g _μ GAC/m ³		Pilot effluents - 10 g _μ GAC/m ³	
	LQ	N	Concentration (ng/L) Av. ± SD (min - max)	N	Concentration (ng/L) ** Av. ± SD (min - max)	N	Concentration (ng/L) ** Av. ± SD (min - max)
Norfloxacine	43	12/13	98 ± 35 (<LQ - 151)	2/5	(<LQ - 64)	0/5	<LQ
Ofloxacin	4.6	13/13	953 ± 438 (363 - 2 275)	5/5	143 ± 38 (105 - 189)	5/5	363 ± 109 (180 - 461)
Oxazepam	10	13/13	239 ± 110 (138 - 547)	5/5	39 ± 18 (21 - 68)	5/5	159 ± 91 (107 - 320)
Propranolol	3.3	13/13	44 ± 45 (5 - 142)	0/5	<LQ	1/5	(<LQ - 17)
Roxithromycin	11	11/13	464 ± 578 (<LQ - 1 565)	1/5	(<LQ - 146)	0/5	<LQ
Sulfadiazine	15	10/13	83 ± 73 (<LQ - 239)	0/5	<LQ	0/5	<LQ
Sulfadimethoxine	5.2	3/13	79 ± 121 (<LQ - 219)	4/5	60 ± 102 (<LQ - 213)	0/5	<LQ
Sulfamethoxazole	1.0	13/13	1 430 ± 1 450 (320 - 6 290)	5/5	506 ± 326 (183 - 1 060)	5/5	596 ± 213 (281 - 828)
Sulfathiazole	1.3	7/13	1.8 ± 0.4 (<LQ - 2.4)	0/5	<LQ	0/5	<LQ
Tetracycline	10.9	6/13	47 ± 20 (<LQ - 74)	0/5	<LQ	3/5	33 ± 2 (<LQ - 34)
Trimethoprim	8.1	10/13	181 ± 254 (<LQ - 774)	0/5	<LQ	0/5	<LQ
<i>Pesticides</i>							
AMPA	50	7/7	735 ± 330 (232 - 1 316)	3/3	753 ± 345 (352 - 970)	4/4	720 ± 103 (605 - 839)
Diuron	7.4	6/13	524 ± 623 (<LQ - 1 745)	0/5	<LQ	0/5	<LQ
Glyphosate	50	6/7	84 ± 38 (<LQ - 151)	1/3	(<LQ - 119)	1/4	(<LQ - 88)
Mecoprop	20	6/7	37 ± 19 (<LQ - 69)	1/3	(<LQ - 21)	1/4	(<LQ - 25)
Terbutryn	20	4/7	33 ± 10 (<LQ - 46)	0/3	<LQ	0/4	<LQ
<i>Alkylphenols</i>							
4-NP	25	7/7	90 ± 86 (32 - 244)	3/4	31 ± 4 (<LQ - 35)	3/3	41 ± 3 (38 - 43)
NP1EO	10	7/7	183 ± 375 (10 - 1 031)	3/4	41 ± 30 (<LQ - 74)	3/3	30 ± 9 (20 - 35)
NP2EO	4	7/7	79 ± 124 (13 - 355)	4/4	17 ± 9 (6 - 26)	3/3	34 ± 32 (6 - 71)
NP1EC	2	7/7	148 ± 99 (89 - 371)	4/4	54 ± 44 (21 - 119)	3/3	82 ± 8 (74 - 89)
t-OP	4.4	6/7	11 ± 7 (<LQ - 24)	3/4	6 ± 8 (<LQ - 8)	0/3	<LQ
OP1EO	12	4/7	27 ± 25 (<LQ - 65)	0/4	<LQ	0/3	<LQ
OP2EO	3	1/7	(<LQ - 15)	0/4	<LQ	0/3	<LQ
<i>Phthalates</i>							
DEHP	50	8/8	501 ± 379 (150 - 1 171)	4/4	367 ± 234 (91 - 619)	4/4	1 075 ± 922 (285 - 2 189)
DEP	50	5/8	331 ± 227 (<LQ - 641)	4/4	342 ± 154 (196 - 547)	0/4	<LQ
DnBP	50	8/8	2 990 ± 4 060 (233 - 10 720)	4/4	1 550 ± 1 290 (245 - 2 690)	4/4	8 494 ± 4 566 (5 265 - 11 722)
<i>Personal care products</i>							
Butyl paraben	2.8	1/4	(<LQ - 10)	0/4	<LQ		
Ethyl paraben	3.5	4/4	44 ± 62 (4 - 136)	3/4	15 ± 12 (<LQ - 28)		
Methyl paraben	2.8	4/4	61 ± 80 (21 - 204)	4/4	23 ± 15 (10 - 46)		
Propyl paraben	3.3	1/4	(<LQ - 4)	0/4	<LQ		
Triclocarban	3.0	4/4	7 ± 3 (4 - 11)	0/4	<LQ		
Triclosan	10.0	4/4	104 ± 10 (94 - 121)	4/4	87 ± 22 (622 - 1 327)		

		Pilot influents		Pilot effluents - 20 g _μ GAC/m ³		Pilot effluents - 10 g _μ GAC/m ³	
	LQ	N	Concentration (ng/L) Av. ± SD (min - max)	N	Concentration (ng/L) ** Av. ± SD (min - max)	N	Concentration (ng/L) ** Av. ± SD (min - max)
<i>Artificial sweeteners</i>							
Acesulfame	50	6/6	2 570 ± 1 000 (2 300 - 4 300)	3/3	1 270 ± 570 (800 - 1 900)	3/3	1 767 ± 513 (1 200 - 2 200)
Saccharin	50	6/6	231 ± 106 (170 - 300)	1/3	(<LQ - 100)	3/3	160 ± 75 (81 - 230)
Sucralose	250	6/6	8 200 ± 1 060 (6 400 - 9 400)	3/3	3 230 ± 590 (2 800 - 3 900)	3/3	6 000 ± 557 (5 400 - 6 500)
<i>Other compounds</i>							
Benzotriazole	100	7/7	2 810 ± 480 (1 600 - 3 340)	0/3	<LQ	4/4	354 ± 52 (290 - 430)
Bisphenol A	10	6/7	26 ± 8 (<LQ - 35)	1/4	(<LQ - 11)	3/3	21 ± 9 (13 - 30)
PFOA	7.4	1/13	(<LQ - 10)	0/5	<LQ	0/4	<LQ
PFOS	7.2	2/13	(<LQ - 92)	0/5	<LQ	0/4	<LQ
<p><i>Compounds never quantified (n = 15):</i> 1,2,4-trichlorobenzene, androstenediene, atrazine, BBP, benzyl paraben, cyclamate, dicyclanile, marbofloxacin, metaldehyde, metronidazole, oxytetracycline, pentachlorophenol, primidone, progesterone, testosterone,</p> <p><i>Compounds never detected (n = 43):</i> alachlor, aldrin, ampicillin, chlorfenvinphos, chlorpyrifos, chlortetracycline, danofloxacin, DDD pp, DDE pp, DDT op, DDT pp, difloxacin, econazole, endosulfan α, endosulfan β, endrin, enrofloxacin, estriol, fenofibrate, fofenicol, fluvoxamine, gestodene, HCH α, HCH β, HCH δ, HCH γ, hexachlorobenzene, hexachlorobutadiene, isodrin, isoproturon, levonorgestrel, monensin, narasin, norethindrone, orbifloxacin, penicilline G, simazine, sulfabenzamide, sulfadimerazine, sulfameter, sulfanilamide, trifluralin and tylosin.</p> <p>In bold: PPHs selected for the calculation of the average removal of 13 PPHs (performances indicator) - high occurrence (> 75%) and also monitored in PAC configuration.</p>							

2. Efficiency of the μ GAC

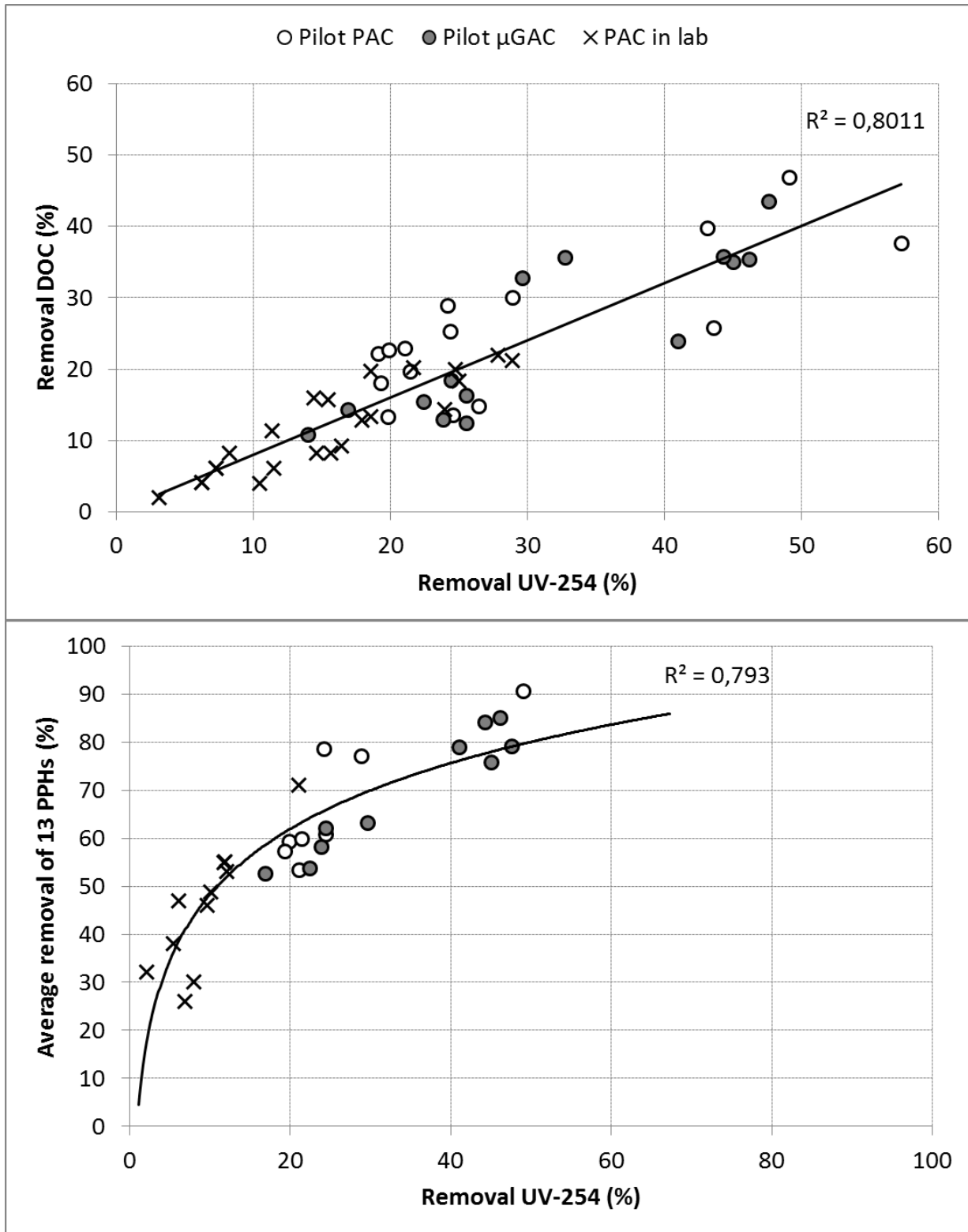
2.1. Relation between UV-254, DOC and PPHs

During the ramp-up phase, the performances of the pilot were assessed using UV-254 and COD. UV-254 is a parameter that is very easy and quick to measure either in continuous (sensor) or in punctual (spectrophotometer UV-Vis). Since a good correlation between UV-254 and several micropollutant removals has been highlighted in the literature (Altmann et al. 2014, Zietzschmann et al. 2014), correlations between UV-254 and DOC or between UV-254 and PPHs were also examined. These correlations are plotted in Figure 1. The correlations have been calculated using values from the pilot operating with PAC (Mailler et al. 2015b) and μ GAC (this study), and values from batch tests performed in complement to the *in situ* campaigns to better understand adsorption mechanisms (Mailler et al. 2015a).

The linear correlation obtained between UV-254 and DOC removals is both significant (p-value < 0.0001) and strongly positive ($r_{\text{Spearman}} = 0.871$), what is consistent as UV-254 reflects all molecules with aromatic rings, which are a fraction of the organic matter (DOC). The relation suggests that both the aromatic and the non-aromatic fractions of the organic matter are adsorbed. However, the aromatic fraction is better removed than the whole organic matter, as the UV-254 removal is always higher than the DOC removal. This is confirmed by the SUVA (specific UV absorbance) which is always lower in the pilot effluents ($2.0 \pm 0.4 \text{ L}/(\text{mgC}\cdot\text{m})$) than in influents ($1.7 \pm 0.3 \text{ L}/(\text{mgC}\cdot\text{m})$) of the pilot. In addition, the removal increase of the aromatic fraction is similar to the removal increase of the whole organic matter, as highlighted by the linear relation.

The 13 PPHs (in bold in Table 2) found at a high occurrence (> 75%) in the pilot influents in both PAC and μ GAC configurations of the pilot (Figure 1) were selected as an indicator of the process performances. The correlation found between UV-254 and the average removal of these 13 PPHs is also significant (p-value < 0.0001) and strongly positive ($r_{\text{Spearman}} = 0.948$). Unlike the previous correlation, this one is logarithmic, highlighting that PPHs and organic matter have a different affinity for activated carbon, especially at low UV-254 removals. Similar significant (p-value < 0.0001) correlations are found between UV-254 and several individual PPHs (supporting material - Figure S5) such as atenolol ($r_{\text{Spearman}} = 0.926$), carbamazepine ($r_{\text{Spearman}} =$

1 0.821), diclofenac ($r_{\text{Spearman}} = 0.900$) or trimethoprim ($r_{\text{Spearman}} = 0.766$). This indicates that UV-254 removal is a
 2 good proxy of the PPHs removal and can then be used as a performances indicator for tertiary treatments..



3
 4 13 PPHs: atenolol, carbamazepine, ciprofloxacin, diclofenac, erythromycin, ketoprofen, lorazepam, norfloxacin,
 5 ofloxacin, oxazepam, propranolol, roxithromycin, and sulfamethoxazole.
 6
 7

Figure 1 - Correlations between UV-254, DOC and PPHs removals in WWTP discharges

1 2.2. Ramp-up phase

2

3 Online monitoring of UV-254 (sensors) was used for the determination of the optimal μGAC retention time (SRT). As
4 UV-254 removal is well correlated to the PPHs removal (Figure 1), it was used to evaluate the overall performances of
5 the pilot during the ramp-up phase. Figure 2 displays the increase of the pilot performances during the ramp-up phase
6 until reaching the stabilized phase. A technical problem with the UV-254 sensors at $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ prevented to obtain a
7 complete curve for this configuration. The stabilized phase starts when UV-254 removal reaches a plateau: the timing is
8 then determined *a posteriori*.

9 This SRT is relatively low for PAC in general (5-7 days) but is much higher for μGAC (Figure 2), which is composed
10 of particles ten times larger than those of PAC, resulting in significantly slower saturation kinetics for μGAC .

11

12 As regards the Figure 2, the UV-254 removal increases in time both at 10 and $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$. This removal reaches a
13 maximum of 25-30% at $10 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ against 45-55% at $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$. The maximum removal of UV-254 and
14 micropollutants are reached after a SRT of 90-100 days for both configurations. Indeed, the UV-254 removal is stable
15 after this period of operation with maximum temporary removal variations of 5% between 90th and 160th day for both
16 doses. This SRT can then be considered as the optimal SRT, although the effective SRT applied during the study was
17 120 days, and the μGAC shape (total mass of μGAC , concentration and depth of the bed) at this time has to be taken as
18 the reference. This result confirms that the campaigns performed after the 90th day of operation are part of the stabilized
19 phase.

20

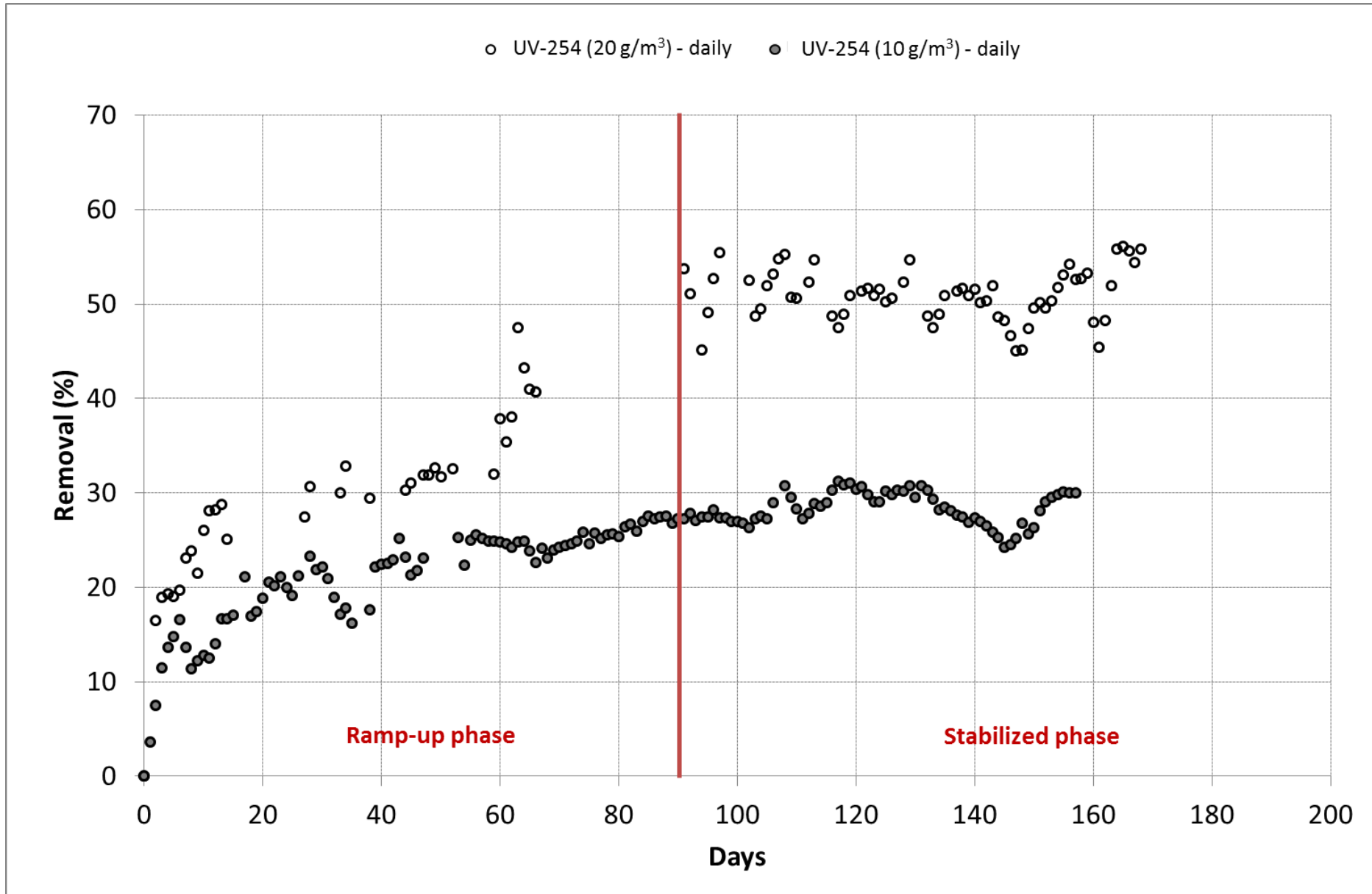


Figure 2 - Ramp-up phase of the CarboPlus® process for both assessed doses (10 and 20 g_{μGAC}/m³)

1

2

1 2.3. Efficiency in stabilized phase

2

3 *Conventional wastewater quality parameters*

4

5 The removals of conventional wastewater quality parameters within the μGAC tertiary treatment are given in
6 Table 3. Overall, the quality of the WWTP discharges is improved during μGAC treatments, with removals
7 observed for most of the parameters. The impact on phosphorous pollution was not determined due to the very
8 low levels of PO_4^{3-} and TP ($< \text{LQ}$).

9

10 DOC ($35 \pm 7\%$), COD ($43 \pm 3\%$) and UV-254 ($45 \pm 3\%$) are notably eliminated at $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$. At $10 \text{ g}_{\mu\text{GAC}}/\text{m}^3$,
11 these parameters are significantly less removed (p-value < 0.05 ; tests of Shapiro-Wilk, Fischer, t or Mann-
12 Whitney), i.e. DOC ($15 \pm 2\%$), COD ($26 \pm 3\%$) and UV-254 ($24 \pm 1\%$). This can be mainly explained by a
13 decrease of the number of adsorption site available which is linked to the fresh activated carbon dose. Such
14 performances on these parameters are similar to those obtained with PAC treatments a similar doses (Altmann et
15 al. 2014, Boehler et al. 2012, Mailler et al. 2015b, Margot et al. 2013). Significantly similar (p-value < 0.05)
16 removals are obtained between the both μGAC doses for BOD_5 and TSS. In particular, TSS are reduced by the
17 μGAC bed with high removals ($72 \pm 30\%$, both doses considered) when calculable, indicating a capacity of the
18 process to retain a fraction of the particulate pollution. This TSS retention capacity is similar with both doses
19 (Table 3) and is confirmed in supporting material - Figure S4 which displays the TSS concentrations measured
20 by sensors in both influents and effluents of the pilot during the whole study at a time interval of 1 h. As regards
21 the nitrogen species (Table 3), a clear biological activity is occurring in the reactor in stabilized phase. Indeed, a
22 removal of TKN ($42 \pm 16\%$, both doses considered), NH_4^+ ($47 \pm 20\%$) and NO_2^- ($95 \pm 1\%$) is observed while
23 NO_3^- ($< 3\%$) is rather produced. This suggests that nitrification is occurring in the reactor. This is not surprising
24 considering the high SRT (90-100 days) leading to the formation of a biofilm in the reactor. The very high
25 removal of NO_2^- is particularly interesting for WWTP manager since such tertiary treatment could be also used
26 to improve the nitrite treatment and reduce the discharges in the aquatic environment of this problematic
27 regulated parameter.

28

29 **Table 3 - Removals of conventional wastewater quality parameters with μGAC in stabilized phase**

Parameter ¹	20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$					Av. \pm SD ²
	C4	C5	C6	C7	C8	

	02/06/14	01/07/14	17/07/14	26/08/14	23/09/14	
	Removal (%) ³					
BOD ₅	57	48	0	29	43	35 ± 22
COD	41	39	44	48	43	43 ± 3
DOC	35	35	36	44	24	35 ± 7
NH ₄ ⁺	NC	19	19	55	69	40 ± 25
NO ₂ ⁻	65	98	98	98	97	92 ± 13
NO ₃ ⁻	3	-7	-14	-13	-26	-13 ± 10
TKN	29	72	72	30	36	48 ± 20
TSS	67	NC	NC	72	NC	NC
UV-254	45	46	44	48	41	45 ± 3
	10 g _{μGAC} /m ³					
Parameter ¹	C9 13/01/15	C10 27/01/15	C11 10/02/15	C12 24/02/15	C13 24/03/15	Av. ± SD ²
	Removal (%)					
BOD ₅	40	38	38	44	18	36 ± 10
COD	29	26	21	25	29	26 ± 3
DOC	15	16	13	13	18	15 ± 2
NH ₄ ⁺	55	53	NC	NC	58	55 ± 3
NO ₂ ⁻	99	99	98	96	98	98 ± 1
NO ₃ ⁻	-30	-21	-11	-8	-9	-16 ± 10
TKN	40	38	31	36	40	37 ± 4
TSS	75	67	80	NC	NC	74 ± 7
UV-254	22	24	24	26	24	24 ± 1
¹ BOD ₅ = biological oxygen demand in 5 days; COD = chemical oxygen demand; DOC = dissolved organic carbon; TKN = total Kjeldahl nitrogen; TSS = total suspended solids; UV-254 = UV absorbance at 254 nm. ² Average ± standard deviation. ³ Removal in italics: <LQ in the pilot effluents; NC = not calculated (<LQ in both influents and effluents of the pilot).						

1

2

3 *PPHs*

4

5 The removals obtained with the μGAC treatment in both 10 and 20 g_{μGAC}/m³ configurations are given in Figure 3 for all
6 PPHs quantified and for the average of the 13 PPHs selected as performance indicator. Furosemide is not represented
7 because it was not quantified during stabilized phases (only ramp-up phase). The compounds for which all the removals
8 were estimated (<LQ in the pilot effluents) as previously explained, are marked with an asterisk (*).

9 Overall, while 32 PPHs were quantified in the pilot influents, only 18 were still measured quantified in the pilot
10 effluents at 20 g_{μGAC}/m³ and 16 at 10 g_{μGAC}/m³ (Table 2).

11 4 types of behaviors can be observed within the μGAC treatment: very good (> 80%), good (60-80%), moderate (30-
12 60%) and low (< 30%) removals.

13

14 At 20 g_{μGAC}/m³, 5 compounds have low removals (< 30%), particularly gabapentin (7-33%; min-max) and
15 sulfadimethoxine (< 0-23%). Iothalamic acid, 17-α- and 17-β-estradiols were very occasionally detected but when
16 detected, the compounds are not or very poorly removed (< 20%). In contrary, 16 PPHs are very well and steadily

1 removed (> 80%) by the process, such as diclofenac (71-97%), ofloxacin (76-90%) or oxazepam (74-91%). Among
2 them, 8 compounds have a particularly high affinity for μGAC (> 90%), i.e. atenolol (92-97%), carbamazepine (80-
3 94%), ciprofloxacin (75-95%), estrone (88-90%), ketoprofen (82-95%), lorazepam (95-99%), propranolol (94-98%) and
4 roxithromycin (80-99%). In addition, acetaminophen and ibuprofen are eliminated up to 95%. 5 compounds have good
5 removals (60-80%) with μGAC , including erythromycin (43-77%), iopromide (60-67%) and sulfamethoxazole (56-
6 83%). The remaining PPHs ($n = 4$) have moderate removals (30-60%). Indeed, bezafibrate (53-55%), iohexol (57-58%),
7 iomeprol (28-37%) and iopamidol (55%) have a moderate affinity for μGAC . The average removal of the 13 PPHs at
8 $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ is around 85% (78-89%).

9
10 At $10 \text{ g}_{\mu\text{GAC}}/\text{m}^3$, the efficiency of the pilot is reduced. The removals of erythromycin (3-47%), iopamidol (9-42%),
11 iopromide (39-57%) and sulfamethoxazole (12-24%) move from moderate or good to low or moderate removals.
12 Similarly, carbamazepine (40-62%), ketoprofen (14-82%) and oxazepam (33-51%) move to the moderate removals
13 category, while ciprofloxacin (70-85%), ofloxacin (58-73%) and roxithromycin (28-73%) are now in the good removals
14 category. In addition, tetracycline, which was not quantified in any campaign of the $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ configuration, is rather
15 well removed (39-90%). Finally, good or very good removals are still observed for atenolol (51-92%), lorazepam (82-
16 99%), norfloxacin (58-86%) and propranolol (77-98%). The average removal of the 13 PPHs at $10 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ of fresh
17 μGAC is around 60% (57-68%).

18
19 By comparing the removals obtained with both μGAC doses (Figure 3 and Figure 5), it is clear that this operation
20 parameter has a crucial influence on performances. Indeed, for the compounds with calculable removals in both
21 configurations ($n = 21$), a clear reduction of the performances is observed (Figure 3) for most of them ($n = 14$), while
22 bezafibrate, ciprofloxacin, gabapentin, iohexol, iomeprol, lorazepam, norfloxacin, propranolol and trimethoprim have
23 rather similar removals with both doses. In particular, a significant difference ($p\text{-value} < 0.05$; tests of Shapiro-Wilk,
24 Fischer, t or Mann-Whitney) between removals at 10 and $20 \text{ g}_{\mu\text{GAC}}/\text{m}^3$ is found for the average removal of 13 PPHs ($p\text{-}$
25 $\text{value} = 4.3 \times 10^{-6}$), carbamazepine ($p\text{-value} = 2.8 \times 10^{-6}$), diclofenac ($p\text{-value} = 0.020$), erythromycin ($p\text{-value} = 0.003$),
26 iopromide ($p\text{-value} = 0.042$), ketoprofen ($p\text{-value} = 0.015$), ofloxacin ($p\text{-value} = 3.2 \times 10^{-4}$), oxazepam ($p\text{-value} =$
27 0.020), roxithromycin ($p\text{-value} = 0.024$) and sulfamethoxazole ($p\text{-value} = 0.020$). Contrariwise, ciprofloxacin ($p\text{-value} =$
28 0.886), gabapentin ($p\text{-value} = 0.860$), lorazepam ($p\text{-value} = 0.835$), norfloxacin ($p\text{-value} = 0.867$) and propranolol ($p\text{-}$
29 $\text{value} = 0.095$) have significantly similar ($p\text{-value} > 0.05$) removals in both configuration.

30

1 Thus, if an objective of 80% removal in average for PPHs is stated, an operation of the CarboPlus® μ GAC treatment is
2 suited when operating at 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$. Since the adsorption of micropollutants by activated carbon is greatly dependent
3 of the dose (Mailler et al. 2015b, Margot et al. 2013, Snyder et al. 2007), an increase of the μ GAC dose could improve
4 the performances. A great improvement can then be expected by increasing the μ GAC dose to 30 $\text{g}_{\mu\text{GAC}}/\text{m}^3$, in particular
5 for compounds moderately (30-60%) or well (60-80%) removed at lower doses (diclofenac, erythromycin or
6 sulfamethoxazole).

7

8

9 *Other emerging pollutants*

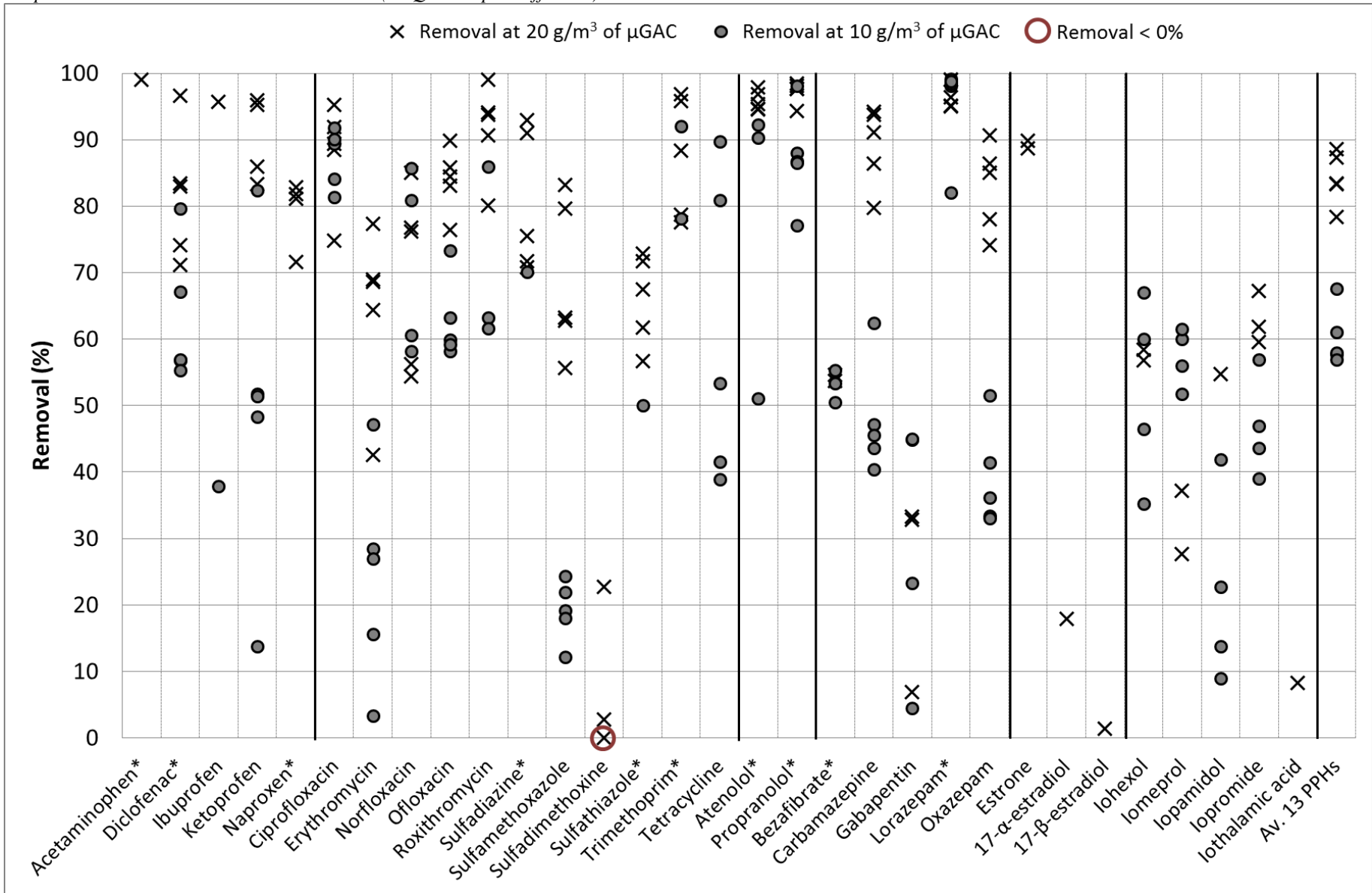
10

11 Similarly to PPHs, different fates are encountered with the other emerging pollutants (Figure 4). At 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$, few
12 compounds (n = 5) are not or poorly eliminated (< 30%) by the pilot such as AMPA (< 0-26%), glyphosate (0-50%),
13 DEHP (< 0-85%), DEP (3-20%) and DnBP (< 0-38%). Most of other emerging pollutants monitored (n = 13) have a
14 relatively good affinity (> 60%) with the μ GAC, i.e. benzotriazole (97-99%), bisphenol A (56-83%), mecoprop (52-
15 77%), NP1EO (64-93%), NP1EC (64-82%), terbutryn (57-70%) or triclocarban (63-86%). In particular, diuron, 4-NP
16 and PFOS, listed as priority substances, have removals lying in the 50-99% range. This indicates that the μ GAC
17 treatment allows the removal of a large range of pollutants with various physical and chemical properties. In addition,
18 the remaining pollutants (n = 6), such as triclosan (30-38%), ethyl paraben (0-85%), methyl paraben (28-77%) or t-OP
19 (44-80%), are characterized by moderate removals (30-60%) at 10 and 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$, suggesting that they can be
20 adsorbed but they have not a high adsorbability. In that case, the performances of the process for these compounds
21 could be improved by the application of a higher dose, offering a higher number of adsorption sites.

22

23 The fate of several other emerging pollutants is greatly dependent to the μ GAC dose. In particular, benzotriazole is
24 significantly better removed at 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$ than at 10 $\text{g}_{\mu\text{GAC}}/\text{m}^3$ (p-value = 0.0004), as well as acesulfame (p-value =
25 0.005), bisphenol A (p-value = 0.043), NP1EC (p-value = 0.001), NP1EO (p-value = 0.037), saccharin (p-value =
26 0.011) and sucralose (p-value = 0.009). In contrary, no significant impact of the μ GAC dose is observed for 4-NP,
27 NP2EO, t-OP, OP1EO, pesticides and phthalates.

1 *Compounds which removals were all estimated (<LQ in the pilot effluents).



2
3 Figure 3 - Removals of PPHs (n = 31) by μGAC treatment in stabilized phase at 10 and 20 g_{μGAC}/m³

1 *Compounds which removals were all estimated (<LQ in the pilot effluents).

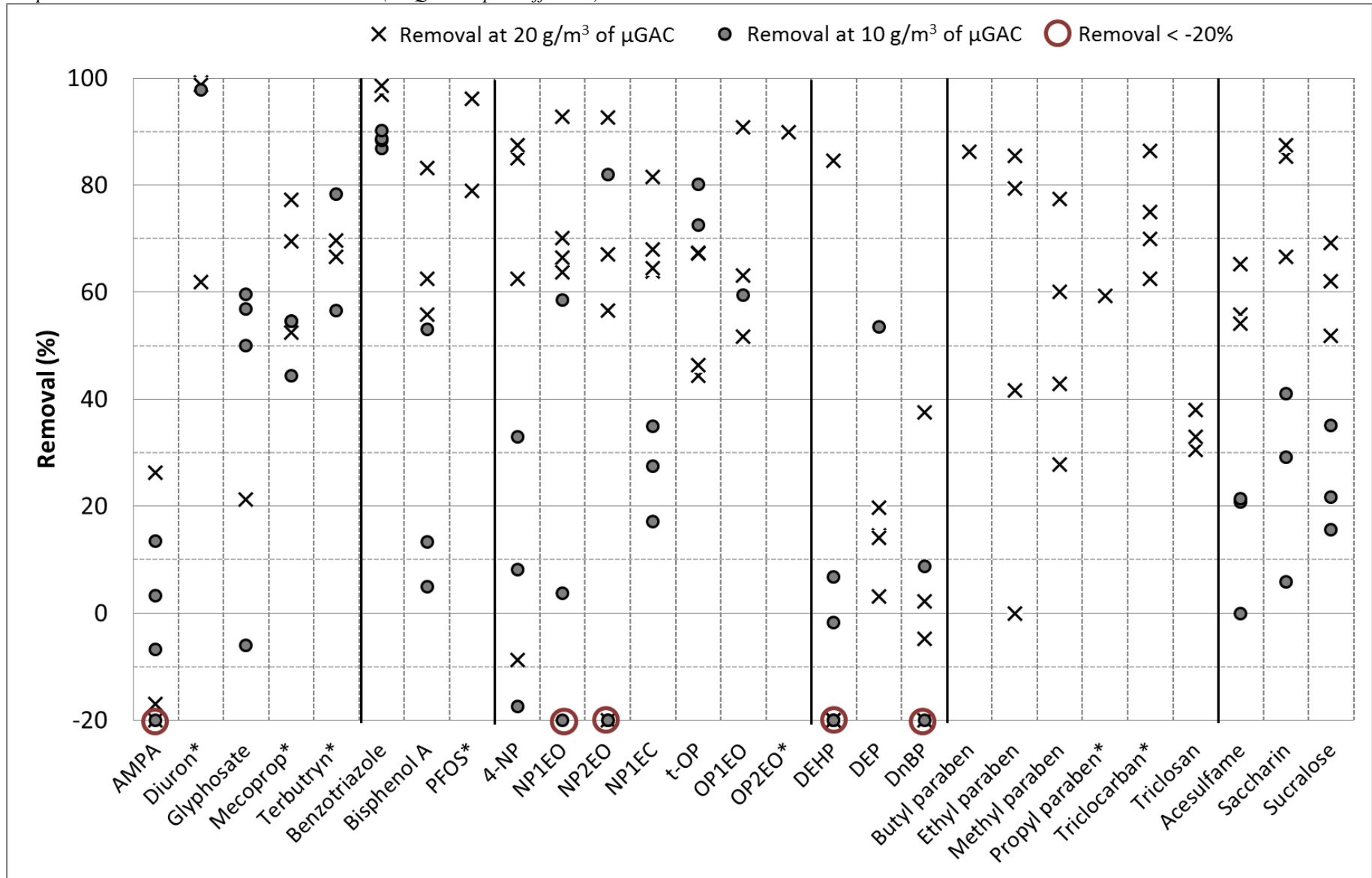


Figure 4 - Removals of the other emerging pollutants within μGAC treatment

2

3

3. Comparison of CarboPlus® operating with μ GAC and PAC

Such results are, to the best of authors' knowledge, the first displaying the efficiency of a μ GAC or GAC process operating in fluidized bed in wastewater. Consequently, no comparison is possible with the literature, but a comparison with the same pilot operating with PAC can be assessed (Mailler et al. 2015b). The removals obtained with this pilot in PAC configuration were similar to those in the literature with PAC contact reactor followed by a separation step (Altmann et al. 2014, Boehler et al. 2012, Löwenberg et al. 2014, Margot et al. 2013).

Conventional wastewater quality parameters were considered followed by the 13 PPHs quantified at high occurrence (Table 2), monitored both in μ GAC and PAC configurations. Finally, the other emerging pollutants are discussed.

Conventional wastewater quality parameters

Regarding conventional wastewater quality parameters, two groups can be distinguished: those impacted (DOC and UV-254) and those not impacted (BOD₅, COD, nitrogen species and TSS) by the activated carbon dose (10 or 20 g/m³), whether PAC or μ GAC. For the parameters not impacted by the dose applied, the pilot has a similar efficiency with μ GAC or PAC, i.e. removals of 38-45% for BOD₅. In contrary, COD or nitrogen species are better removed by μ GAC, resulting from the biological activity induced by the high SRT, particularly for TKN, NO₂⁻ and NH₄⁺ (Figure 5). Moreover, TSS were not removed at all by the PAC treatment (Mailler et al. 2015b), but are efficiently retained by the μ GAC bed (Table 3). This means that μ GAC is able to remove a fraction of the micropollutants in the particulate phase (not monitored in this study), in contrary to PAC. Regarding the parameters impacted by the activated carbon dose (organic matter), UV-254 is similarly removed for both activated carbon configurations at both 10 g/m³ and 20 g/m³. For DOC, a different trend is highlighted as PAC is slightly more efficient than μ GAC at similar doses, both at 10 and 20 g/m³. DOC results can be explained by FeCl₃ and polymer additions during PAC treatment which induce a coagulation and flocculation of the organic matter.

PPHs

Different types of behaviors are encountered regarding PPHs removal with PAC or μ GAC (Figure 5). First, atenolol, diclofenac and propranolol have very similar removals between μ GAC and PAC for the same dose. In contrary, carbamazepine, erythromycin, ketoprofen, norfloxacin and ofloxacin are rather slightly better removed by PAC than

1 μ GAC for the same dose, but the differences are limited ($< 20\%$) and not significant. Then, oxazepam and
2 sulfamethoxazole are better removed with PAC at a dose of 10 g/m^3 , but this is not the case anymore at a dose of 20
3 g/m^3 as removals are equivalent between PAC and μ GAC. For these compounds, the dose of μ GAC seems to have a
4 greater impact than the dose of PAC. Finally, lorazepam and roxithromycin are rather better removed by μ GAC than
5 PAC at a similar dose. These tendencies should be taken with caution regarding the limited removal differences.

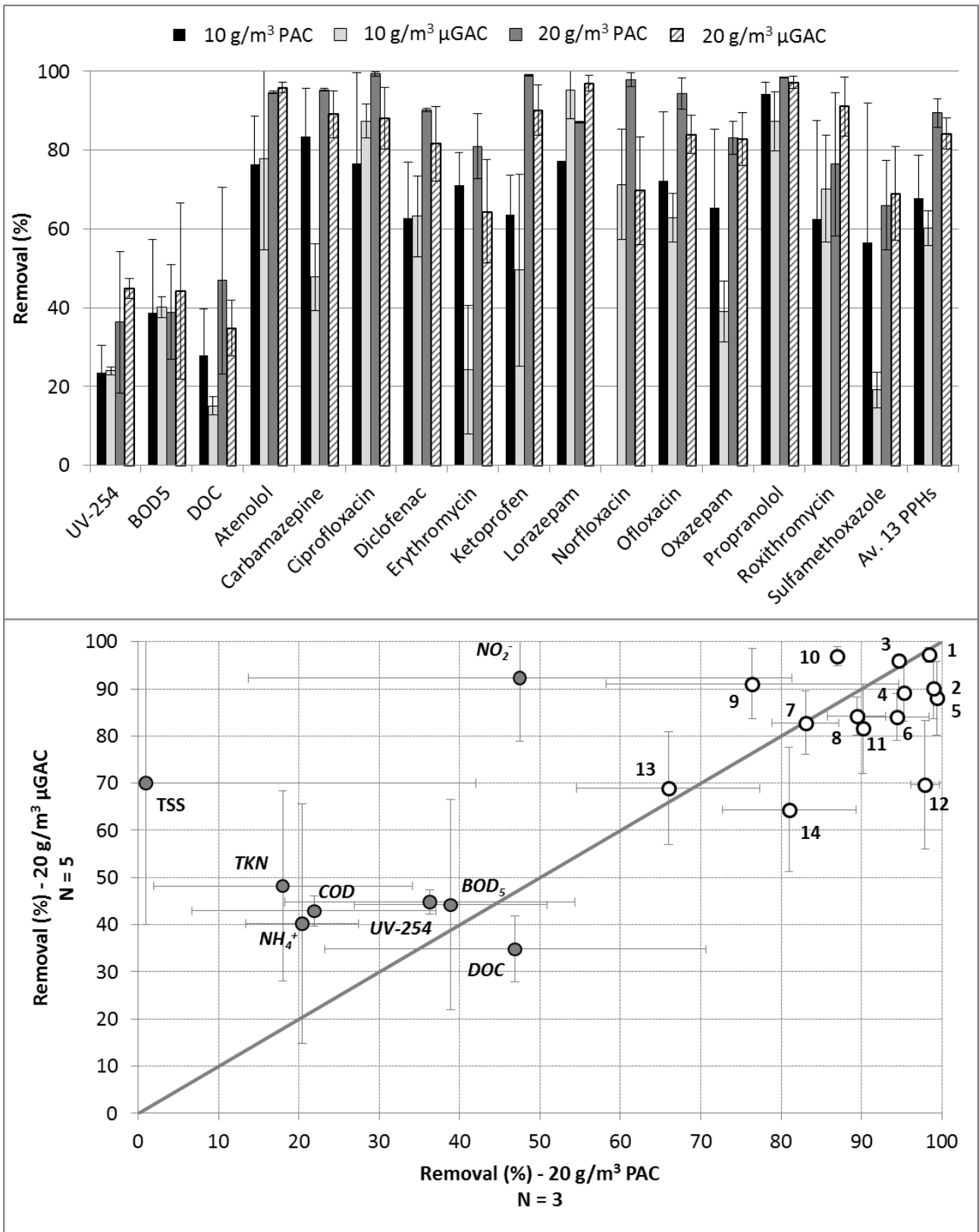
6
7 Overall, μ GAC can be considered as efficient as PAC for PPHs removal at a similar fresh activated carbon dose.
8 Indeed, the average removal of the 13 PPHs is similar with 20 g/m^3 of both PAC ($88 \pm 4\%$) and μ GAC ($81 \pm 4\%$), as
9 well as with 10 g/m^3 of both PAC ($68 \pm 11\%$) and μ GAC ($60 \pm 4\%$). Moreover, by comparing the average removals of
10 the 13 individual PPHs, and as displayed in Figure 5, the pilot performances are significantly similar between μ GAC
11 and PAC operating at a dose of 20 g/m^3 (p-value = 0.218) or 10 g/m^3 (p-value = 0.275).

12
13 The slightly better performances (10-20%) obtained with PAC compared to μ GAC for several compounds could be
14 explained by various factors such as the nature of μ GAC which is reactivated (loss of sorption sites), in contrary to
15 PAC, or the higher hydraulic velocity with μ GAC. However, this is more likely due to the application of FeCl_3 in PAC
16 configuration to handle correctly the bed, which improves the colloidal pollution elimination by
17 coagulation/flocculation, in contrary to μ GAC. Such improvement of the dissolved pollution elimination by FeCl_3
18 addition has already been highlighted in the literature (Gasperi et al. 2012, Mailler et al. 2015a, Margot et al. 2011).

19 20 *Other emerging pollutants*

21
22 For the other emerging pollutants, comparison was assessed for 18 compounds monitored in both μ GAC (10 and 20
23 g/m^3) and PAC (only 10 g/m^3) configurations, including bisphenol A, diuron, 4-NP, t-OP, PCPs, PFAs, phthalates and
24 sweeteners (Figure 4) (Mailler et al. 2015b). Overall, the results are consistent between PAC and μ GAC as pesticides,
25 bisphenol A and parabens are removed ($> 50\%$) in both configurations. In addition, 4-NP and phthalates have very
26 variable removals both with PAC and μ GAC. However, at a similar dose of 10 g/m^3 , acesulfame (9-19% vs. 0-21%;
27 PAC vs. μ GAC), diuron (81-86% vs. 51-99%), saccharin (33-54% vs. 6-41%) and sucralose (6-26% vs. 16-35%) have
28 similar removals with both activated carbons, while bisphenol A (49-78% vs. 5-53%) and parabens are rather better
29 removed by PAC. Thus, unlike for PPHs, no clear trend is observed for the other emerging pollutants but μ GAC can be
30 considered as efficient as PAC and the several differences observed should be due to the sensitiveness of these

1 compounds to the FeCl₃ injection within PAC.



2

3 1 = propranolol, 2 = ketoprofen, 3 = atenolol, 4 = carbamazepine, 5 = ciprofloxacin, 6 = ofloxacin, 7 = oxazepam, 8 =
 4 average removal of 13 PPHs, 9 = roxithromycin, 10 = lorazepam, 11 = diclofenac, 12 = norfloxacin, 13 =
 5 sulfamethoxazole, 14 = erythromycin.

6 **Figure 5 - Comparison of the CarboPlus® performances operating with PAC and μGAC**

1 CONCLUSIONS

2

3 PAC tertiary wastewater treatments have already been studied in the literature (Boehler et al. 2012, Löwenberg et al.
4 2014, Margot et al. 2013), especially in the configuration contact reactor followed by a separation step (membrane or
5 sand filtration). The CarboPlus® process is based on a high mass fluidized bed of activated carbon with continuous
6 injection of a fresh dose and without any additional separation step. The high efficiency of this technology to remove a
7 wide range of micropollutants has been previously highlighted with PAC (Mailler et al. 2015b). In this study, the
8 tertiary treatment of WWTP discharges by μ GAC has been evaluated for conventional wastewater quality parameters,
9 PPHs and other micropollutants in this study.

10

11 First, the relationships between UV-254, organic matter (DOC) and several PPHs (average removal or individual
12 compound removal) has been confirmed by compiling data from both the PAC and μ GAC studies. UV-254 removal is a
13 good proxy of the PPHs removal and can then be used as a performances indicator for tertiary treatments. This
14 parameter is much easier and cheaper to measure than micropollutants. The monitoring of this parameter allowed
15 determining an optimal μ GAC retention time of 80-90 days, both at 10 and 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$.

16

17 The μ GAC fluidized bed treatment improves the overall quality of WWTP discharges, with removals of 30-35% for
18 DOC, 40-45% for UV-254, 38-45% for BOD_5 and 40-45% for COD. In addition, TSS are strongly retained by the
19 μ GAC bed, and nitrification occurs in stabilized phase allowing a total elimination of NO_2^- . Regarding micropollutants,
20 μ GAC removes PPHs efficiently (> 80%), particularly atenolol, carbamazepine, ciprofloxacin, ketoprofen, lorazepam,
21 ofloxacin, oxazepam or propranolol. Several other PPHs are also substantially removed (> 50%) such as diclofenac,
22 erythromycin, sulfamethoxazole or X-ray agents. Alkylphenols, artificial sweeteners, benzotriazole, bisphenol A, PCPs,
23 pesticides and PFOS have also a good affinity for μ GAC, while phthalates are not or poorly eliminated. The fresh
24 μ GAC dose is a crucial parameter and greatly influences the pilot performances. Thus, the average removal of the 13
25 PPHs selected as performances indicator reaches 78-89% at 20 $\text{g}_{\mu\text{GAC}}/\text{m}^3$ against 57-68% at 10 $\text{g}_{\mu\text{GAC}}/\text{m}^3$.

26

27 Overall, μ GAC allows obtaining performances comparable to PAC treatments at a same fresh activated carbon dose,
28 even if slightly higher removals are observed with PAC for several compounds. The differences are explained by the
29 nature of μ GAC, which is reactivated, and more likely by the injection of FeCl_3 with PAC. However, μ GAC removes
30 NO_2^- and TSS, in contrary to PAC. In addition, the μ GAC configuration leads to several operational advantages over

1 PAC for a similar cost ($\approx 1\ 000$ €/ton), such as the ease of operation, the non-necessity to use FeCl_3 and polymer and
2 the reactivability of the adsorbent. In this context, μGAC seems to be more suited than PAC for wastewater treatment,
3 although the cost has to be evaluated in both cases to allow a choice.

4

5

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7

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13

14

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