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

R. Mailler[1A]*, J. Gasperi[1]*, Y. Coquet[2], A. Buleté[3], E. Vulliet[3], S. Deshayes[1,4], S. Zedek[1], C. Mirande-Bret[1], V. Eudes[4], A. Bressy[5], E. Caupos[1], R. Moilleron[1], G. Chebbo[5] and V. Rocher[6]

[1] LEESU (UMR MA 102, Université Paris-Est, AgroParisTech), Université Paris-Est Créteil, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France. (E-mail: *gasperi@u-pec.fr*)

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

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

[4] LCPP (Laboratoire Central de la Préfecture de Police), 39 bis rue de Dantzig, 75015 Paris, France.

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

[6] SIAAP, Direction du Développement et de la Prospective, 82 avenue Kléber, 92700 Colombes, France.

* Corresponding authors

HIGHLIGHTS

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

[A] Present address: SIAAP, Direction du Développement et de la Prospective, 82 avenue Kléber, 92700 Colombes, France. (Email: romain.mailler@siaap.fr)

ABSTRACT

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

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

The µGAC configuration substantially improves the overall quality of the WWTP discharges by reducing biological (38-45%) and chemical oxygen demands (21-48%), DOC (13-44%) and UV-254 (22-48%). In addition, total suspended solids (TSS) are retained by the µGAC bed and a biological activity (nitratation) leads to a total elimination of NO_2^-.

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

Overall, µGAC allows obtaining performances comparable to PAC at the same activated carbon dose. Indeed, the average removal of the 13 PPHs found at a high occurrence (> 75%) in WWTP discharges is similar at 20 g/m^3 of µGAC (78-89%) and PAC (85-93%). In addition, this recycled µGAC operation leads to several operational advantages (no $FeCl_3$, reactivable, high SRT) and has a stronger impact on the overall wastewater quality.

KEYWORDS

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

INTRODUCTION

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

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

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

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

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

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

MATERIALS AND METHODS

1. WWTP description

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

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

2. The CarboPlus® process

The studied tertiary treatment pilot is based on the CarboPlus® process, developed by the company SAUR. This process allows operating with different kinds of activated carbons such as PAC (Mailler et al. 2015b), or µGAC as in this study. The µGAC is a material with an intermediary size between PAC (< 100 µm) and granular activated carbon (> 800 µm). The selected µGAC is the Cyclecarb 305® from Chemviron Carbon, which is produced from recycled activated carbon and is reactivable. This mesoporous product is characterized by a bulk density of 0.53 kg/m^3, a median particle size of 423.5 µm and a specific BET surface of 860 ± 20 m^2/g (supporting material - Table S1), which is close to those of products tested in the PAC study (Mailler et al. 2015b). In addition, the distribution of this surface by pore size is similar for both activated carbons (supporting material - Figure S3).

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

The studied pilot is a 5 m high reactor with a surface of about 5 m^2, and is fed with the WWTP discharges (third

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

3. Structure of the study and sampling strategy

The performances of the pilot have been assessed for two µGAC doses (10 and 20 $g_{\mu GAC}/m^3$). In order to follow the ramp-up of the process and to determine the optimal µGAC retention time (SRT), the choice has been made for both doses to start with an empty reactor and to inject the continuous fresh dose normally without extracting any µGAC until reaching the optimal performances on dissolved organic matter (DOC) and UV absorbance at 254 nm (UV-254). This corresponds to the ramp-up phase. Thus, the µGAC extraction started after a stabilization of both DOC and UV-254 removals. After reaching this point, the pilot was operated normally, corresponding to the stabilized phase and the ramp-up phase duration corresponds to the average SRT.

To determine the process performances, a total of 13 campaigns have been performed. 8 campaigns were carried out at a fresh µGAC dose of 20 $g_{\mu GAC}/m^3$ - 3 during the ramp-up phase and 5 during the stabilized phase - and 5 campaigns were performed at 10 $g_{\mu GAC}/m^3$ - all during the stabilized phase.

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

4. Pollutants and analytical procedures

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 (BOD_5), UV absorbance at 254 nm (UV-254), total Kjeldahl nitrogen (TKN), NH_4^+, NO_2^-, NO_3^-, total phosphorus (TP), PO_4^{3-} 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 hypolipemiants, 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]
Institute of Analytical Sciences - ISA (N=83)						

Analgesics/anti-inflammatory	5	13	SPE *StrataX® or Oasis HLB® cartridges*	LC-MSMS	(Vulliet et al. 2011)	9.8 - 193
Antibiotics	31					1 - 900
Beta blockers	2					3.3 - 23
Chlorinated solvents	3		SPE *StrataX® cartridges*	GC-MS	(Barrek et al. 2009)	5.1 - 8.0
Diuretics	1		SPE *StrataX® or Oasis HLB® cartridges*	LC-MS/MS	(Vulliet et al. 2011)	414
Hormones	10					1.2 - 700
Hypolipemiants	2					6.3 - 38.4
Perfluorinated acids	2		SPE *StrataX® cartridges*			7.2 - 7.4
Pesticides	23		SPE *Oasis HLB® cartridges*	LC-MS/MS GC-MS	(Barrek et al. 2009)	3.0 - 233
Psychoactive drugs	4		SPE *StrataX® or Oasis HLB® cartridges*	LC-MS/MS	(Vulliet et al. 2011)	0.1 - 9.6
Laboratory of Water Environment and Urban Systems - LEESU (N=15)						
Alkylphenols	7	7	SPE *Oasis HLB® cartridges*	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
Laboratory CARSO (N=13)						
Other chemicals	1	7	*Measured performed by an external contractor Analytical methods not communicated*			50
Pesticides	5					20 - 50
Psychoactive drugs	2					200 - 500
X-ray agents	5					50 - 500
Central Laboratory of the Police Prefecture - LCPP (N=4)						
Phthalates	4	8	SPE *Oasis HLB® cartridges*	GC-MS	(Bergé et al. 2014)	90
Water Technology Center - TZW (N=4)						
Artificial sweeteners	4	6	SPE *Bakerbond SDB1 cartridges*	LC-MS/MS	(Scheurer et al. 2009)	50 - 250
Total micropollutants	*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.

As the number of data for micropollutant concentrations in stabilized phase is relatively limited for both assessed µGAC doses (n = 5 for 20 $g_{µGAC}/m^3$; n = 5 for 10 $g_{µGAC}/m^3$), 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 ± standard deviation (SD) with minimum and maximum values are presented. Average ± 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 ± 1.6 mgC/L), COD (27 ± 16 mgO_2/L) and BOD_5 (3.8 ± 1.8 mgO_2/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 BOD_5) 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

(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. 2014) (DOC = 8.8 ± 1.2 mgC/L). In contrary, (Boehler et al. 2012) tested activated carbon on a wastewater with similar DOC (DOC = 5.6-8.9 mgC/L).

Regarding the other parameters (Table 2), TSS (4.7 ± 2.6 mg/L) are very low in the Seine Centre discharges resulting from the high removal (98%) achieved by this WWTP (Mailler et al. 2014, Rocher et al. 2012). For the same reason, nitrogen species concentrations are limited, especially for NH_4^+ (0.5 ± 0.4 mgN/L), highlighting the total nitrification 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 efficient denitrification step. Finally, total phosphorus and PO_4^{3-} are most of the time found below their LQ, respectively 0.3 and 0.1 mgP/L (Table 2).

PPHs

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

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

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

14 compounds were measured at average concentrations lower than 100 ng/L. Among them, 17-β-estradiol (14 ± 4 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. However, carbamazepine, lorazepam, norfloxacin and propranolol are characterized by a high occurrence (> 75%)

despite their low concentrations.

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

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

Other emerging pollutants

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

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

Most of the compounds (n = 17/29) were measured below 100 ng/L, including bisphenol A (26 ± 8 ng/L), glyphosate (84 ± 38 ng/L), mecoprop (37 ± 19 ng/L), terbutryn (33 ± 10 ng/L), all the PCPs (n = 7), most of the alkylphenols (n = 6/7) and PFOS (≤ 92 ng/L). In particular, butyl paraben (≤ 10 ng/L), PFOA (≤ 10 ng/L), propyl paraben (≤ 4 ng/L), 4-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 low levels (< 20 ng/L).

12 emerging pollutants were measured above 100 ng/L in average, such as DEHP (501 ± 379 ng/L), diuron (524 ± 623 ng/L), NP1EO (183 ± 375 ng/L) or saccharin (231 ± 106 ng/L). Acesulfame (2 570 ± 1 000 ng/L), benzotriazole (2 810 ± 481 ng/L), DnBP (2 990 ± 4 060 ng/L) and sucralose (8 200 ± 1 060 ng/L) were found at particularly high levels in the pilot influents with average concentrations higher than 1 000 ng/L. Such low occurrences and concentrations for alkylphenols, PCPs and chlorinated solvents in the pilot influents are consistent considering their very high removals by the conventional WWTPs reported in the literature (Choubert et al. 2011, Clara et al. 2007, Mailler et al. 2014). Similarly, the high concentrations found for benzotriazole, phthalates and artificial sweeteners are consistent regarding 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 $g_{µGAC}/m^3$		Pilot ffluents - 10 $g_{µGAC}/m^3$	
	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)
Conventional wastewater parameters							
BOD_5 (mgO_2/L)	0.5	13/13	3.8 ± 1.8 (1.4 - 8.0)	5/5	2.6 ± 1.6 (0.8 - 5.0)	5/5	2.2 ± 0.6 (1.8 - 3.3)
COD (mgO_2/L)	4.0	13/13	27 ± 16 (16 - 81)	5/5	12 ± 3 (9 - 17)	5/5	17 ± 2 (15 - 19)
DOC (mgC/L)	0.5	13/13	6.9 ± 1.6 (4.4 - 11)	5/5	3.7 ± 0.5 (2.8 - 4.3)	5/5	5.8 ± 0.9 (4.2 - 6.7)
NH_4^+ (mgN/L)	0.3	7/13	0.5 ± 0.4 (<LQ - 1.6)	2/5	(<LQ - 1.3)	0/5	<LQ
NO_2^- (mgN/L)	0.02	13/13	1.04 ± 0.76 (0.24 - 2.30)	4/5	0.06 ± 0.05 (<LQ - 0.13)	2/5	(<LQ - 0.02)
NO_3^- (mgN/L)	0.4	13/13	9.7 ± 2.7 (5.8 - 15.0)	5/5	11.3 ± 2.0 (9.0 - 14.5)	5/5	10.1 ± 2.2 (7.8 - 13.1)
TKN (mgN/L)	0.5	13/13	1.3 ± 0.5 (0.7 - 2.7)	4/5	0.9 ± 0.7 (<LQ - 1.9)	5/5	0.9 ± 0.3 (0.6 - 1.3)
PO_4^{3-} (mgP/L)	0.1	5/13	0.19 ± 0.08 (<LQ - 0.33)	1/5	(<LQ - 0.11)	4/5	0.24 ± 0.08 (<LQ - 0.34)
TP (mgP/L)	0.3	3/13	0.48 ± 0.04 (<LQ - 0.50)	0/5	<LQ	1/5	(<LQ - 0.40)
TSS (mg/L)	2.0	8/13	4.7 ± 2.6 (<LQ - 11)	2/5	(<LQ - 3)	0/5	<LQ
UV-254 (cm^{-1})	-	13/13	0.126 ± 0.012 (0.098 - 0.142)	5/5	0.067 ± 0.004 (0.063 - 0.072)	4/4	0.092 ± 0.011 (0.073 - 0.097)
Pharmaceuticals and hormones							
Acetaminophen	130	1/13	(<LQ - 6 420)	0/5	<LQ	0/5	<LQ
Atenolol	23	11/13	448 ± 400 (<LQ - 1 335)	0/5	<LQ	0/5	<LQ
Bezafibrate	38	5/13	44 ± 6 (<LQ - 56)	0/5	<LQ	0/5	<LQ
Carbamazepine	0.1	13/13	74 ± 65 (21 - 277)	5/5	4 ± 3 (2 - 9)	5/5	65 ± 23 (46 - 104)
Ciprofloxacin	28	13/13	184 ± 95 (89 - 395)	2/5	(<LQ - 63)	1/5	(<LQ - 74)
Diclofenac	171	13/13	1 120 ± 1 400 (<LQ - 4 240)	0/5	<LQ	0/5	<LQ
Erythromycin	3.7	13/13	190 ± 88 (10 - 373)	5/5	40 ± 32 (11 - 94)	5/5	156 ± 28 (130 - 188)
17-α-estradiol	7.1	4/13	23 ± 11 (<LQ - 39)	2/5	(<LQ - 16)	0/5	<LQ
17-β-estradiol	7.1	4/13	14 ± 4 (<LQ - 19)	2/5	(<LQ - 14)	0/5	<LQ
Estrone	1.2	4/13	6 ± 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 ± 1 360 (400 - 4 900)	3/3	1 390 (810 - 1 760)	4/4	1 830 ± 1 100 (220 - 2 700)
Ibuprofen	10	3/13	170 ± 211 (<LQ - 413)	1/5	(<LQ - 18)	1/5	(<LQ - 44)
Iohexol	500	6/7	8 930 ± 4 840 (<LQ - 15 900)	2/3	(<LQ - 5 400)	4/4	5 130 ± 3 520 (560 - 10 300)
Iomeprol	500	6/7	29 900 ± 16 100 (<LQ - 50 000)	3/3	8 660 (870 - 16 500)	4/4	15 100 ± 8 310 (2 200 - 24 300)
Iopamidol	500	5/7	1 520 ± 590 (<LQ - 2 390)	1/3	(<LQ - 503)	4/4	1 239 ± 576 (725 - 2 210)
Iopromide	50	7/7	5 190 ± 2 720 (782 - 9 480)	3/3	1 070 ± 670 (300 - 1 500)	4/4	4 003 ± 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 ± 87 (<LQ - 288)	0/5	<LQ	4/5	61 ± 36 (<LQ - 105)
Lorazepam	0.5	13/13	15 ± 10 (4 - 28)	0/5	<LQ	2/5	(<LQ - 6)
Naproxen	193	4/13	449 ± 120 (<LQ - 563)	0/5	<LQ	0/5	<LQ

		Pilot influents		Pilot effluents - 20 $g_{\mu GAC}/m^3$		Pilot effluents - 10 $g_{\mu GAC}/m^3$	
	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)
Norfloxacin	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
Pesticides							
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
Alkylphenols							
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
Phthalates							
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)
Personal care products							
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 $g_{\mu GAC}/m^3$		Pilot effluents - 10 $g_{\mu GAC}/m^3$	
	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)
Artificial sweeteners							
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)
Other compounds							
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

Compounds never quantified (n = 15): 1,2,4-trichlorobenzene, androstenediene, atrazine, BBP, benzyl paraben, cyclamate, dicyclanile, marbofloxacin, metaldehyde, metronidazole, oxytetracycline, pentachlorophenol, primidone, progesterone, testosterone,

Compounds never detected (n = 43): 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, flofenicol, 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.

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.

2. Efficiency of the µGAC

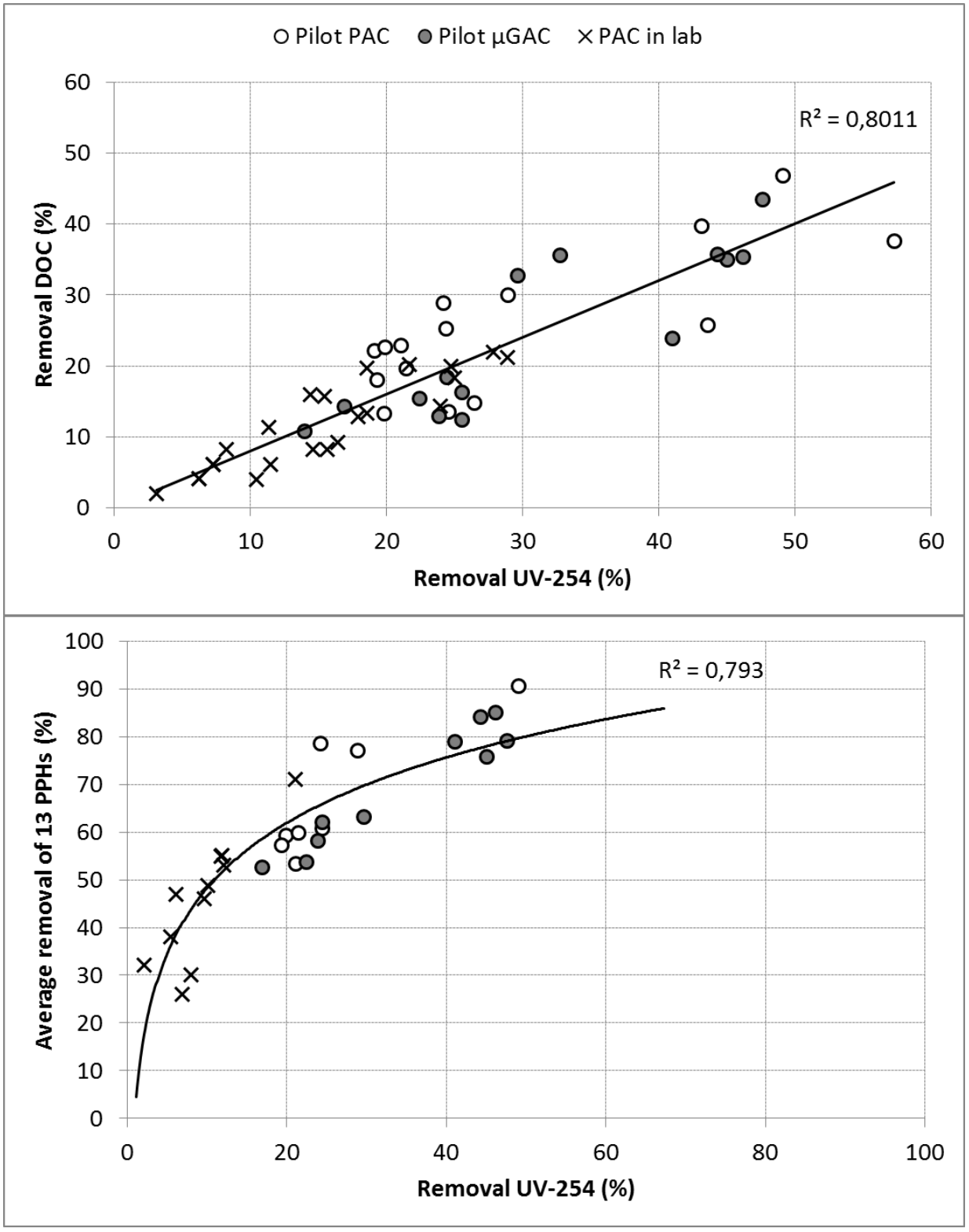
2.1. Relation between UV-254, DOC and PPHs

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 µGAC (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 ($r_{Spearman}$ = 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 ± 0.4 L/(mgC.m)) than in influents (1.7 ± 0.3 L/(mgC.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 µGAC 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 ($r_{Spearman}$ = 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 ($r_{Spearman}$ = 0.926), carbamazepine ($r_{Spearman}$ =

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



13 PPHs: atenolol, carbamazepine, ciprofloxacin, diclofenac, erythromycin, ketoprofen, lorazepam, norfloxacin, ofloxacin, oxazepam, propranolol, roxithromycin, and sulfamethoxazole.

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

2.2. Ramp-up phase

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

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

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

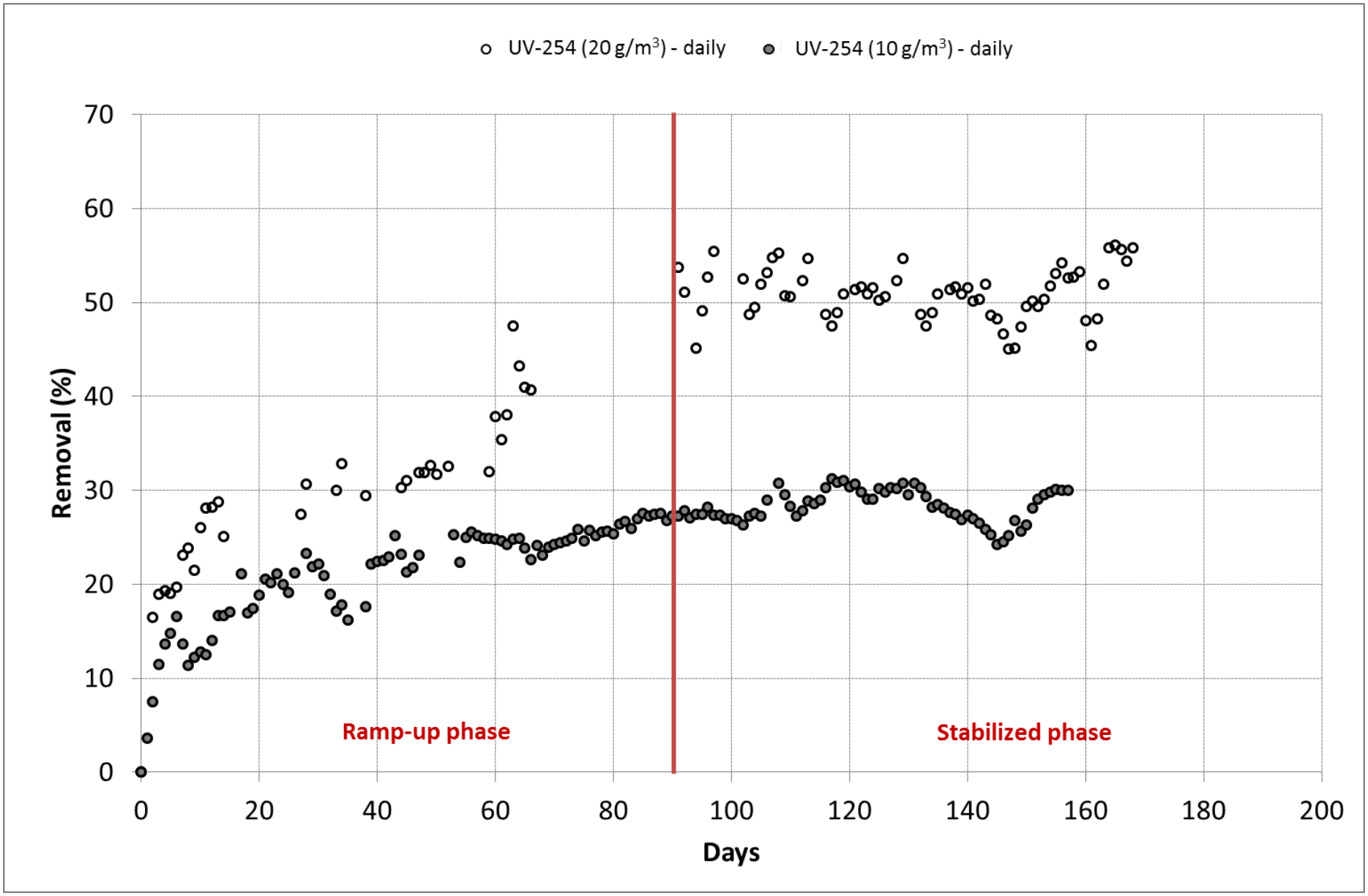


Figure 2 - Ramp-up phase of the CarboPlus® process for both assessed doses (10 and 20 $g_{\mu GAC}/m^3$)

2.3. Efficiency in stabilized phase

Conventional wastewater quality parameters

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

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

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

20 $g_{µGAC}/m^3$						
Parameter [1]	C4	C5	C6	C7	C8	Av. ± SD [2]

	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 $g_{\mu GAC}/m^3$						
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).

PPHs

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

Overall, while 32 PPHs were quantified in the pilot influents, only 18 were still measured quantified in the pilot effluents at 20 $g_{\mu GAC}/m^3$ and 16 at 10 $g_{\mu GAC}/m^3$ (Table 2).

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

At 20 $g_{\mu GAC}/m^3$, 5 compounds have low removals (< 30%), particularly gabapentin (7-33%; min-max) and sulfadimethoxine (< 0-23%). Iothalamic acid, 17-α- and 17-β-estradiols were very occasionally detected but when detected, the compounds are not or very poorly removed (< 20%). In contrary, 16 PPHs are very well and steadily

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

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

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

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

Other emerging pollutants

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

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

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

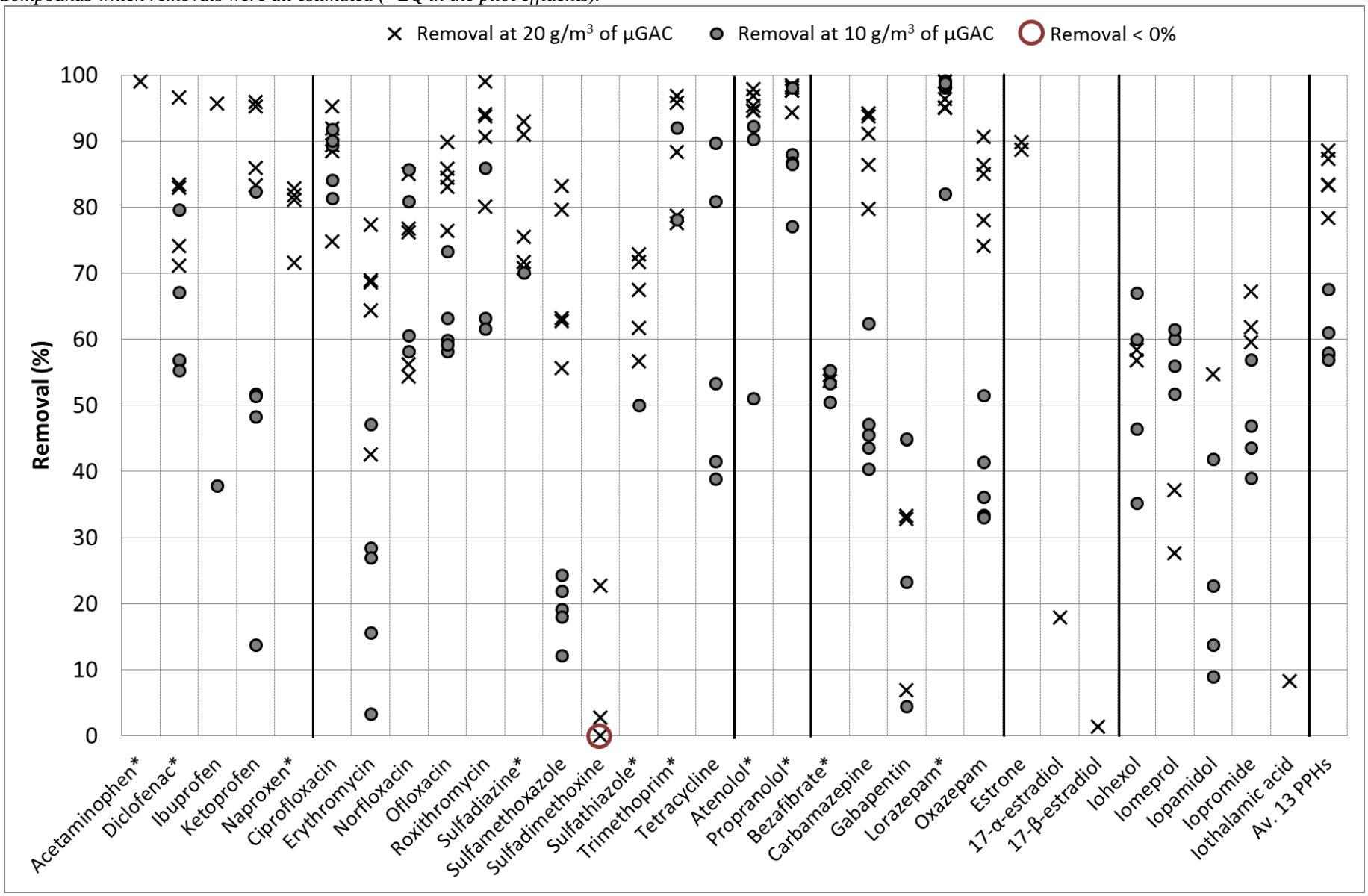


Figure 3 - Removals of PPHs (n = 31) by µGAC treatment in stabilized phase at 10 and 20 $g_{\mu GAC}/m^3$

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

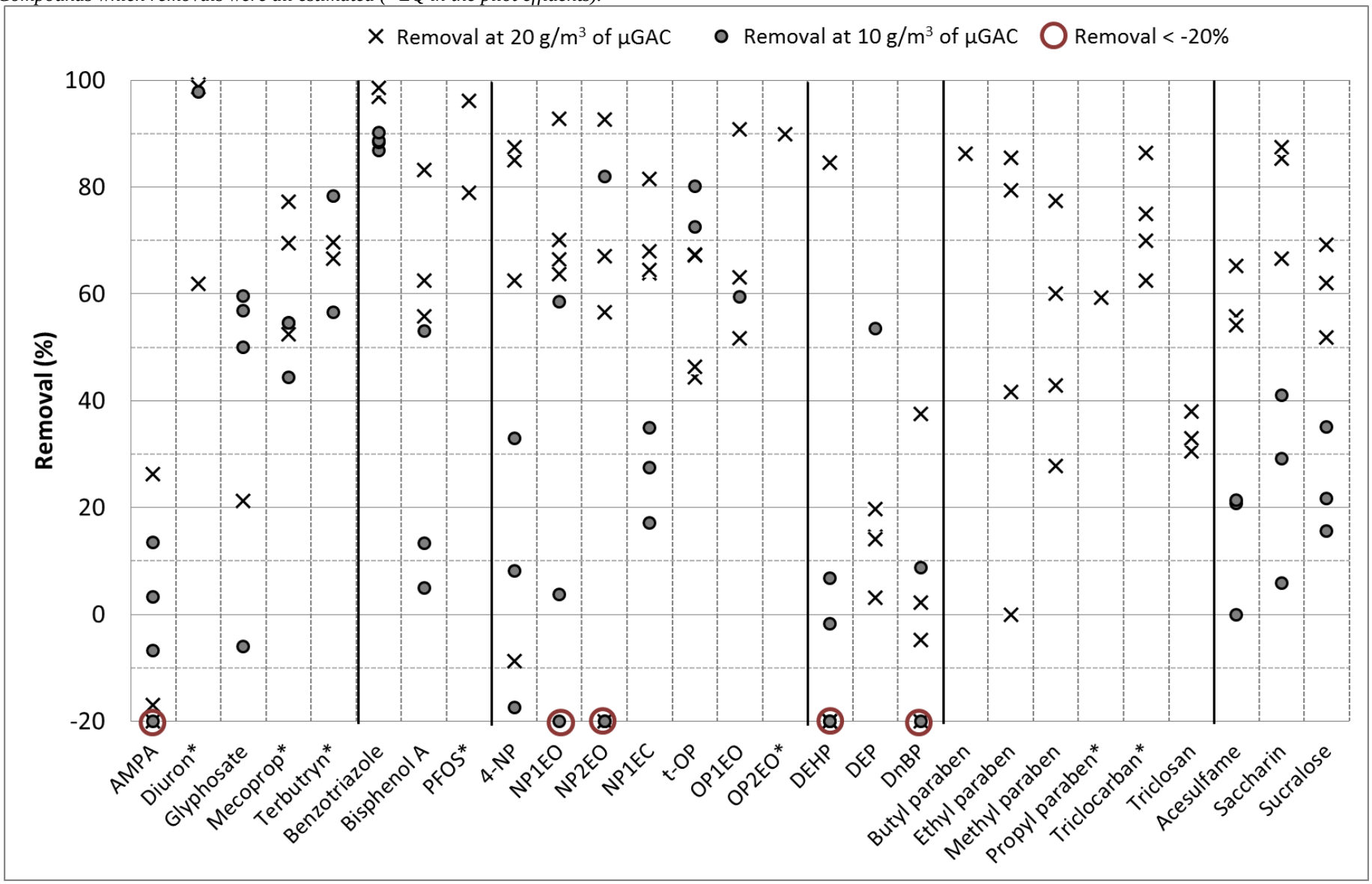


Figure 4 - Removals of the other emerging pollutants within µGAC treatment

3. Comparison of CarboPlus® operating with µGAC and PAC

Such results are, to the best of authors' knowledge, the first displaying the efficiency of a µGAC 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 µGAC 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 (BOD_5, COD, nitrogen species and TSS) by the activated carbon dose (10 or 20 g/m^3), whether PAC or µGAC. For the parameters not impacted by the dose applied, the pilot has a similar efficiency with µGAC or PAC, i.e. removals of 38-45% for BOD_5. In contrary, COD or nitrogen species are better removed by µGAC, resulting from the biological activity induced by the high SRT, particularly for TKN, NO_2^- and NH_4^+ (Figure 5). Moreover, TSS were not removed at all by the PAC treatment (Mailler et al. 2015b), but are efficiently retained by the µGAC bed (Table 3). This means that µGAC 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/m^3 and 20 g/m^3. For DOC, a different trend is highlighted as PAC is slightly more efficient than µGAC at similar doses, both at 10 and 20 g/m^3. DOC results can be explained by $FeCl_3$ 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 µGAC (Figure 5). First, atenolol, diclofenac and propranolol have very similar removals between µGAC and PAC for the same dose. In contrary, carbamazepine, erythromycin, ketoprofen, norfloxacin and ofloxacin are rather slightly better removed by PAC than

µGAC for the same dose, but the differences are limited (< 20%) and not significant. Then, oxazepam and 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 g/m^3 as removals are equivalent between PAC and µGAC. For these compounds, the dose of µGAC seems to have a greater impact than the dose of PAC. Finally, lorazepam and roxithromycin are rather better removed by µGAC than PAC at a similar dose. These tendencies should be taken with caution regarding the limited removal differences.

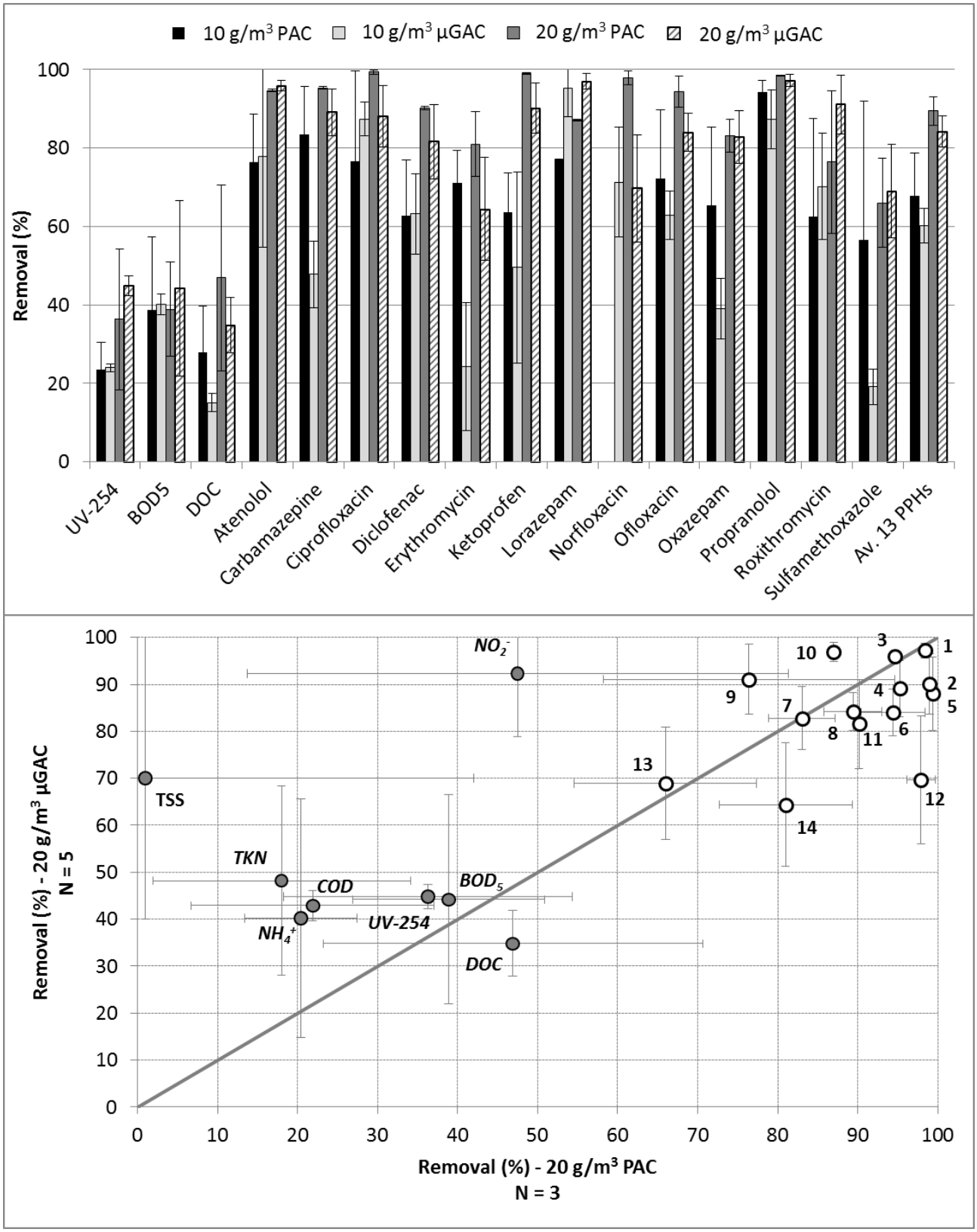
Overall, µGAC can be considered as efficient as PAC for PPHs removal at a similar fresh activated carbon dose. Indeed, the average removal of the 13 PPHs is similar with 20 g/m^3 of both PAC (88 ± 4%) and µGAC (81 ± 4%), as well as with 10 g/m^3 of both PAC (68 ± 11%) and µGAC (60 ± 4%). Moreover, by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

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

Other emerging pollutants

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

compounds to the $FeCl_3$ injection within PAC.



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

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

CONCLUSIONS

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

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

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

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

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

ACKNOWLEDGEMENT

This study has been performed within the framework of the OPUR research program. The authors would like to thank the SIAAP (Céline Briand), the LEESU (Damien Lherm, Mélanie Gobin and Yen Pham), the ISA (Antoine Vauchez, Mikael Tournier, Florent Lafay and Loic Spinner) and the SAUR (Séverine Bareilles) teams for their technical support and their active participation to the sampling campaigns. Similarly, authors thank the technical teams of the Laboratory CARSO and the Water Technology Centre (TZW) for their participation to analyses.

LIST OF REFERENCES

Altmann, J., Ruhl, A.S., Zietzschmann, F. and Jekel, M. (2014) Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. Water Research 55(0), 185-193.

Barrek, S., Cren-Olivé, C., Wiest, L., Baudot, R., Arnaudguilhem, C. and Grenier-Loustalot, M.-F. (2009) Multi-residue analysis and ultra-trace quantification of 36 priority substances from the European Water Framework Directive by GC-MS and LC-FLD-MS/MS in surface waters. Talanta 79(3), 712-722.

Bergé, A., Gasperi, J., Rocher, V., Gras, L., Coursimault, A. and Moilleron, R. (2014) Phthalates and alkylphenols in industrial and domestic effluents: Case of Paris conurbation (France). Science of the Total Environment 488-489(0), 26-35.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A. and Siegrist, H. (2012) Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. Water Sci Technol 66(10), 2115-2121.

Bolong, N., Ismail, A.F., Salim, M.R. and Matsuura, T. (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 239(1-3), 229-246.

Choubert, J.M., Ruel, S.M., Esperanza, M., Budzinski, H., Miege, C., Lagarrigue, C. and Coquery, M. (2011) Limiting the emissions of micro-pollutants: what efficiency can we expect from wastewater treatment plants? Water Science and Technology 63(1), 57-65.

Cladière, M., Gasperi, J., Lorgeoux, C., Bonhomme, C., Rocher, V. and Tassin, B. (2013) Alkylphenolic compounds and bisphenol A contamination within a heavily urbanized area: case study of Paris. Environmental Science and Pollution Research 20(5), 2973-2983.

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H. (2005) Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Research 39(19), 4797-4807.

Clara, M., Scharf, S., Scheffknecht, C. and Gans, O. (2007) Occurrence of selected surfactants in untreated and treated sewage. Water Research 41, 4339-4348.

Daughton, C.G. and Ternes, T.A. (1999) Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environmental Health

Perspectives 107, 907-938.
Deblonde, T., Cossu-Leguille, C. and Hartemann, P. (2011) Emerging pollutants in wastewater: A review of the literature. International Journal of Hygiene and Environmental Health 214(6), 442-448.
Delgado, L.F., Charles, P., Glucina, K. and Morlay, C. (2012) The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon—A review. Science of the Total Environment 435-436(0), 509-525.
EC (2013) Directive 2013/39/EU of the European Parliament amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. JO-EU L226/1.
Gasperi, J., Garnaud, S., Rocher, V. and Moilleron, R. (2008) Priority pollutants in wastewater and combined sewer overflow. Science of the Total Environment 407(1), 263-272.
Gasperi, J., Laborie, B. and Rocher, V. (2012) Treatment of combined sewer overflows by ballasted flocculation: Removal study of a large broad spectrum of pollutants. Chemical Engineering Journal 211-212(0), 293-301.
Gasperi, J., Geara, D., Lorgeoux, C., Bressy, A., Zedek, S., Rocher, V., El Samrani, A., Chebbo, G. and Moilleron, R. (2014) First assessment of triclosan, triclocarban and paraben mass loads at a very large regional scale: Case of Paris conurbation (France). Science of the Total Environment 493(0), 854-861.
Giger, W., Alder, A.C., Golet, E.M., Kohler, H.P.E., McArdell, C.S., Molnar, E., Siegrist, H. and Suter, M.J.F. (2003) Occurrence and fate of antibiotics as trace contaminants in wastewaters, sewage sludges, and surface waters. Chimia 57(9), 485-491.
Götz, C., Stamm, C., Fenner, K., Singer, H., Schärer, M. and Hollender, J. (2010) Targeting aquatic microcontaminants for monitoring: exposure categorization and application to the Swiss situation. Environmental Science and Pollution Research 17(2), 341-354.
Heberer, T. (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters 131(1-2), 5-17.
Jelić, A., Gros, M., Petrović, M., Ginebreda, A. and Barceló, D. (2012) Emerging and Priority Pollutants in Rivers. Guasch, H., Ginebreda, A. and Geiszinger, A. (eds), pp. 1-23, Springer Berlin Heidelberg.
Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A. and Siegrist, H. (2006) Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Research 40(8), 1686-1696.
Kase, R., Eggen, R.I.L., Junghans, M., Götz, C. and Hollender, J. (2011) Waste Water - Evaluation and Management. Einschlag, P.F.S.G. (ed), InTech.
Kilduff, J.E. and Wigton, A. (1998) Sorption of TCE by Humic-Preloaded Activated Carbon: Incorporating Size-Exclusion and Pore Blockage Phenomena in a Competitive Adsorption Model. Environmental Science & Technology 33(2), 250-256.
Lange, F., Scheurer, M. and Brauch, H.-J. (2012) Artificial sweeteners—a recently recognized class of emerging environmental contaminants: a review. Analytical and Bioanalytical Chemistry 403(9), 2503-2518.
Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D. and Gawlik, B.M. (2013) EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Research 47(17), 6475-6487.
Löwenberg, J., Zenker, A., Baggenstos, M., Koch, G., Kazner, C. and Wintgens, T. (2014) Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: Process performance and removal efficiency. Water Research 56(0), 26-36.
Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S. and Wang, X.C. (2014) A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment 473-474(0), 619-641.
Mailler, R., Gasperi, J., Rocher, V., Gilbert-Pawlik, S., Geara-Matta, D., Moilleron, R. and Chebbo, G. (2014) Biofiltration vs conventional activated sludge plants: what about priority and emerging pollutants removal? Environmental Science and Pollution Research 21(8), 5379-5390.
Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault, G., Chebbo, G. and Rocher, V. (2015a) Elimination des polluants émergents dans les rejets de STEP. Partie 2 : étude expérimentale des processus de sorption sur le charbon actif. Techniques Sciences et Méthodes, A paraître.

Mailler, R., Gasperi, J., Coquet, Y., Deshayes, S., Zedek, S., Cren-Olivé, C., Cartiser, N., Eudes, V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G. and Rocher, V. (2015b) Study of a large scale powdered activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents. Water Research 72(0), 315-330.
Margot, J., Magnet, A., Thonney, D., Chèvre, N., De Alencastro, F. and Rossi, L. (2011) Treatment of micropollutants in wastewater - Final report on Vidy (Lausannes) WWTP pilot tests, p. 128, FOEN, Switzerland (in French).
Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M. and Barry, D.A. (2013) Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Science of the Total Environment 461-462(0), 480-498.
Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003) Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. Water Research 37(18), 4413-4424.
Miège, C., Choubert, J.M., Ribeiro, L., Eusèbe, M. and Coquery, M. (2009) Fate of pharmaceuticals and personal care products in wastewater treatment plants - Conception of a database and first results. Environmental Pollution 157(5), 1721-1726.
Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N. and Takada, H. (2007) Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. Water Research 41, 4373-4382.
Pelekani, C. and Snoeyink, V.L. (1999) Competitive adsorption in natural water: role of activated carbon pore size. Water Research 33(5), 1209-1219.
Pomiès, M., Choubert, J.-M., Wisniewski, C. and Coquery, M. (2013) Modelling of micropollutant removal in biological wastewater treatments : A review. Science of the Total Environment 443, 733-748.
Radjenović, J., Petrović, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43(3), 831-841.
Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W. and Keller, J. (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. Water Research 46(3), 863-872.
Rocher, V., Paffoni, C., Goncalves, A., Guerin, S., Azimi, S., Gasperi, J., Moilleron, R. and Pauss, A. (2012) Municipal wastewater treatment by biofiltration: comparisons of various treatment layouts. Part 1: assessment of carbon and nitrogen removal. Water Science and Technology 65(9), 1705-1712.
Rogers, H.R. (1996) Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. Science of the Total Environment 185(1-3), 3-26.
Ruel, S.M., Choubert, J.M., Esperanza, M., Miege, C., Navalon Madrigal, P., Budzinski, H., Le Menach, K., Lazarova, V. and Coquery, M. (2011) On-site evaluation of the removal of 100 micro-pollutants through advanced wastewater treatment processes for reuse applications. Water Science and Technology 63(11), 2486-2497.
Scheurer, M., Brauch, H.-J. and Lange, F. (2009) Analysis and occurrence of seven artificial sweeteners in German waste water and surface water and in soil aquifer treatment (SAT). Analytical and Bioanalytical Chemistry 394(6), 1585-1594.
Sipma, J., Osuna, B., Collado, N., Monclus, H., Ferrero, G., Comas, J. and Rodriguez-Roda, I. (2010) Comparison of removal of pharmaceuticals in MBR and activated sludge systems. Desalination 250, 653-659.
Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C. and Yoon, Y. (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination 202(1-3), 156-181.
Verlicchi, P., Al Aukidy, M. and Zambello, E. (2012) Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment——A review. Science of the Total Environment 429(0), 123-155.
Vulliet, E., Cren-Olivé, C. and Grenier-Loustalot, M.-F. (2011) Occurrence of pharmaceuticals and hormones in drinking water treated from surface waters. Environmental Chemistry Letters 9(1), 103-114.
Zietzschmann, F., Altmann, J., Ruhl, A.S., Dünnbier, U., Dommisch, I., Sperlich, A., Meinel, F. and Jekel, M. (2014) Estimating organic micro-pollutant removal potential of activated carbons using UV absorption and carbon characteristics.

Water Research 56(0), 48-55.