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## Fluorescence excitation/emission matrices as a tool to monitor the removal of organic micropollutants from wastewater effluents by adsorption onto activated carbon

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1 **Title**

2 Fluorescence excitation/emission matrices as a tool to monitor the removal of organic micropollutants from  
3 wastewater effluents by adsorption onto activated carbon

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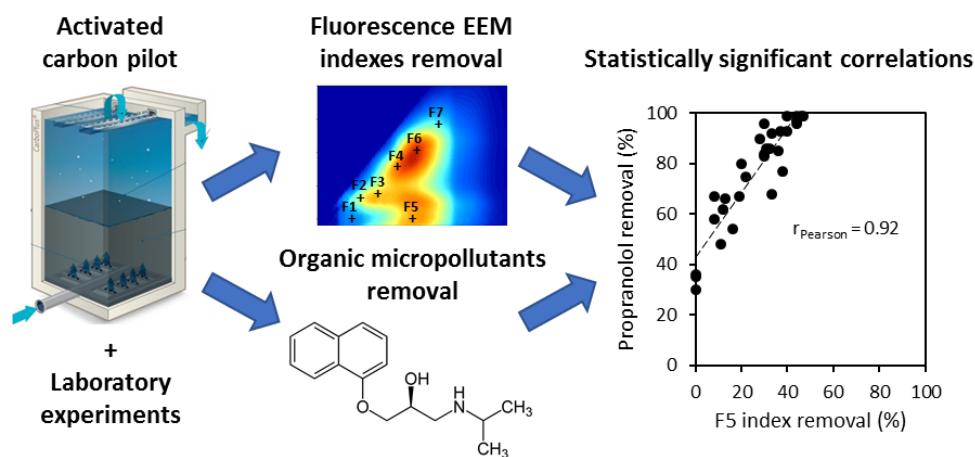
17 **Highlights**

- 18 • Removal of 28 micropollutants and fluorescence EEM indexes was investigated.
- 19 • 7 fluorescence EEM indexes specific to adsorption were found using PARAFAC analysis.
- 20 • Correlations were found between the removal of spectroscopic indexes and most OMPs.
- 21 • UV<sub>254</sub> provided much less accurate correlations than most fluorescence indexes.
- 22 • OMPs interactions with fluorescing DOM likely promoted their co-adsorption.

23

24

## 25 Graphical abstract



26

## 27 Abstract

28 Monitoring the removal of organic micropollutants (OMPs) in advanced wastewater treatment facilities  
29 requires expensive and time-consuming analytical methods that cannot be installed online. Spectroscopic  
30 techniques such as fluorescence excitation/emission spectroscopy were demonstrated to offer the potential  
31 for monitoring OMPs removal in conventional wastewater treatment plants or ozonation pilots but their  
32 application to activated carbon (AC) adsorption processes was only investigated at lab scale and not in real  
33 treatment facilities. In this study, indexes from fluorescence emission/excitation matrices (EEMs) were used  
34 to find correlations with the removal of 28 OMPs from a large-scale AC pilot in fluidized bed employed for  
35 wastewater advanced treatment, as well as from batch experiments. Differences in OMPs removal could be  
36 observed depending on the operational conditions (i.e. pilot or batch experiments, contact time, type of AC)  
37 and the physico-chemical properties of the molecules. 7 PARAFAC components were derived from the  
38 fluorescence EEMs of 60 samples obtained before and after adsorption. Positive correlations were obtained  
39 between the removal of fluorescence indexes and most OMPs, and correlation coefficients were much higher  
40 than the ones obtained with  $UV_{254}$ , confirming the interesting potential of fluorescence spectroscopy to  
41 accurately monitor adsorption performances at the industrial scale. The highest correlation coefficients were  
42 obtained for OMPs having the best removals while the ones that were refractory to adsorption, as well as to  
43 interactions with DOM, exhibited weak correlations. These results suggest that interactions between OMPs  
44 and fluorescing DOM and their subsequent co-adsorption onto AC were at the origin of the correlations

45 found. Lower correlations were also found for the most biodegradable OMPs, which indicated that the  
46 occurrence of biological effects could make the monitoring of these compounds more challenging.

## 47 **Keywords**

48 Wastewater advanced treatment; Activated carbon; Organic micropollutants; Fluorescence EEM; PARAFAC

## 49 **1. Introduction**

50 Many organic micropollutants (OMPs), such as household chemicals, personal care products, pesticides or  
51 pharmaceuticals are rejected from human activities and are found in raw wastewaters. Some OMPs with  
52 specific properties (e.g. biodegradable, hydrophobic or volatile compounds) can be removed during  
53 conventional wastewater treatments, but most OMPs are not completely removed by physical and biological  
54 treatments and are detected at non-negligible concentrations (i.e. ng/L up to  $\mu\text{g/L}$ ) after treatment (Loos et  
55 al., 2013; Margot et al., 2013). The presence of OMPs in wastewater effluents can lead to adverse effects on  
56 water bodies and living organisms (Luo et al., 2014). To deal with this issue, several advanced treatment  
57 technologies can be used for the removal of OMPs from wastewater effluents, including oxidation processes  
58 (Bourgin et al., 2018), membrane separation (Snyder et al., 2007) and activated carbon (AC) adsorption  
59 (Benstoem et al., 2017; Margot et al., 2013).

60 The efficiency of a given technology is generally assessed by the determination of OMPs removal rates. The  
61 average removal of quantified OMPs is a common indicator used to estimate the overall performance of a  
62 process towards the removal of micropollutants (e.g. the 80% targeted by the Swiss legislation). OMPs  
63 removals are calculated from concentrations before and after treatment that are determined by targeted  
64 chemical analysis. Those analyses are time-consuming, require multiple sample preparation steps (large  
65 volume sampling, preconcentration, elimination of interfering substances), heavy and expensive equipment  
66 for detection steps (e.g. liquid chromatography coupled to mass spectrometry) as well as qualified personnel.  
67 Thus, there is a need for complementary tools such as spectroscopic methods that could be installed online  
68 to improve the control of advanced wastewater treatment facilities (i.e. dosage of reagents, exhaustion of a  
69 granular AC bed, membrane clogging) by using surrogate models (Korshin et al., 2018). UV absorbance and  
70 fluorescence spectroscopy are widely used for the study of dissolved organic matter (DOM) in wastewater

71 treatment plants (WWTP) (Carstea et al., 2016; Goffin et al., 2018). Different methods have been developed  
72 to interpret data from fluorescence excitation/emission matrix (EEM) spectroscopy and to track DOM  
73 changes, in terms of quality and quantity, in aquatic ecosystems and water treatment facilities (Chen et al.,  
74 2003; Coble, 1996; Parlanti et al., 2000). Efforts have been made to monitor various families of OMPs by  
75 using the direct fluorescence signal of organic molecules (e.g., polycyclic aromatic hydrocarbons, pesticides,  
76 pharmaceuticals, volatile organic compounds) (Carstea et al., 2016; Ferretto et al., 2014) but the high  
77 concentrations of bulk DOM in wastewater hinders the direct detection of trace levels of OMPs (Wasswa et  
78 al., 2019). EEMs can nevertheless be used as surrogates for the prediction of OMPs removal, for example  
79 during primary and secondary wastewater treatment (SgROI et al., 2017), because OMPs and DOM undergo  
80 common elimination mechanisms. In this context, the removal of specific components related to aromatic  
81 proteins and tyrosine-like substances was successfully correlated with the elimination of easily removed  
82 OMPs, while another component related to humic-like substances was correlated with some moderately  
83 removed OMPs.

84 Both UV absorbance at 254 nm ( $UV_{254}$ ) and fluorescence EEM spectroscopy have been used for over ten  
85 years as surrogate parameters to monitor OMPs removal during ozonation of wastewater effluents (Chys et  
86 al., 2017; Gerrity et al., 2012; Nanaboina and Korshin, 2010; Park et al., 2017). Spectroscopic methods were  
87 also applied for the monitoring of OMP removals by AC adsorption. Satisfactory linear correlations were  
88 obtained between the removal of  $UV_{254}$  and the removal of specific OMPs or the average removal of several  
89 OMPs and for different types of AC (powdered – PAC, micro-grain –  $\mu$ GAC and granular activated carbon  
90 – GAC) (SgROI et al., 2018; Zietzschmann et al., 2014a, 2016). Compared to  $UV_{254}$ , better correlations were  
91 obtained using total fluorescence (TF, calculated as the total volume integrated under an EEM) for the  
92 removal of 13 OMPs by GAC filtration using rapid small-scale columns (Anumol et al., 2015), because of  
93 its higher sensitivity and selectivity. Ziska et al. (2016) also successfully developed surrogate models for the  
94 removal of 14 OMPs with PAC in batch reactors using power functions based on  $UV_{254}$  or TF, again showing  
95 better sensitivity of TF. This was attributed to the greater affinity of fluorophores for AC than UV-absorbing  
96 matter.

97 Recently, SgROI et al. (2018) used PARAFAC analysis to study the breakthrough of DOM through GAC  
98 rapid small-scale columns. Both  $UV_{254}$  and PARAFAC fluorescence components were successful in

99 predicting the breakthrough of 11 OMPs. A better sensitivity was observed with fluorescence indicators  
100 (PARAFAC components) than with UV<sub>254</sub>. To our knowledge, no study reported the use of fluorescence  
101 indexes to predict OMPs removal by AC processes at the industrial scale. Apart from the study of SgROI et  
102 al. (2018), only UV<sub>254</sub> and TF were employed in models to predict OMPs behavior and no other EEM data  
103 processing methods were used (e.g. fluorescence regional integration, peak-picking or PARAFAC analysis).  
104 Moreover, the physico-chemical mechanisms and potential biological effects underlying the correlations  
105 between the removal of OMPs and spectroscopic indexes are not known and are often overlooked in the  
106 literature.

107 The aim of this study was to find correlations between the removal of fluorescence EEM indexes and OMPs  
108 from wastewater effluents by adsorption onto AC at the industrial scale and to show that 3D fluorescence is  
109 a promising tool for the monitoring of OMPs, especially since online applications of fluorescence  
110 spectroscopy are being developed. Data were gathered both from a pilot used for wastewater advanced  
111 treatment with  $\mu$ GAC at the industrial scale and from batch experiments using PAC. Experimental conditions  
112 covered a range of various conditions to obtain statistically significant variations of OMPs removal. 28 OMPs  
113 exhibiting a wide range of physico-chemical properties were targeted based on their occurrence in the  
114 wastewater effluent. Correlation coefficients between each OMP and each fluorescence index were explored  
115 and discussed by considering the various effects of interactions between DOM and OMPs and their  
116 implication on the adsorption processes and the monitoring of OMPs. The occurrence of biological processes  
117 in adsorption-based treatments has been reported but their contribution to the elimination of OMPs is difficult  
118 to estimate, especially at the industrial scale (Piai et al., 2019; Zietzschmann et al., 2019). The potential  
119 influence of biodegradation on the correlations was thus also investigated. Finally, the perspective of building  
120 models for the prediction of OMPs elimination was discussed.

## 121 **2. Materials and methods**

### 122 *2.1. AC pilot tests*

123 The AC industrial pilot (CarboPlus<sup>®</sup>, Saur, Figure S1 in supplementary information) was based on a 1,000  
124 kg bed of micro-grain AC being continuously renewed by equivalent addition (daily) and extraction (weekly)  
125 (Guillossou et al., 2019; Mailler et al., 2016a). A dose of 10 g of fresh AC per m<sup>3</sup> of wastewater effluent was

126 applied daily, corresponding to 8.6 kg of AC per day for a flow rate of 860 m<sup>3</sup>/day. Once a week, after  
 127 washing the filter to remove the retained suspended solids, 60 kg of AC was removed from the bed to  
 128 maintain a constant age and mass of AC over time. This mode of operation ensures that fresh AC is available  
 129 at all times, thus guaranteeing a high and continuous adsorption efficiency. The bed was fluidized in a 5 m  
 130 high and 2.39 m<sup>2</sup> surface reactor with an ascendant fluid velocity of 15 m/h and an average hydraulic  
 131 retention time of about 20 min. The pilot was continuously fed with denitrified water (sampled after the third  
 132 biofiltration stage) from the Seine-Centre WWTP (Colombes, France). The plant is operated by the Paris  
 133 public sanitation service (SIAAP) and treats wastewater for 800,000 inhabitants with a flow of 240,000  
 134 m<sup>3</sup>/day. The treatment is composed of a pre-treatment step (screening, grit and oil removal) followed by  
 135 primary treatment (physico-chemical lamellar settling, removal of suspended particles, colloids and  
 136 phosphorus) and biological treatment (3 stages of biofiltration, removal of carbon, nitrification and  
 137 denitrification).

138 17 sampling campaigns (each consisting of one 24h composite sample from the inlet of the pilot and one  
 139 from the outlet) were carried out between 2015 and 2019 with the industrial pilot (Table 1). The pilot was  
 140 successively operated using two  $\mu$ GACs, CycleCarb 305 (Chemviron Carbon) from 2015 to 2017 (sampling  
 141 campaigns #1-12) and Norit 3040 (Cabot) from 2018 to 2019 (sampling campaigns #13-17). The first 16  
 142 sampling campaigns occurred while the AC bed was being continuously renewed (nominal condition) and  
 143 one last occurred at a time of no renewal for approximately 60 days (renewal of the bed was stopped to study  
 144 the kinetics of OMPs removal in the absence of fresh AC and to obtain lower values of removal rates from  
 145 the pilot). For each campaign, the WWTP effluent and the pilot effluent were sampled, consisting in 20 L of  
 146 24 h composite samples collected by automatic samplers equipped with Teflon<sup>®</sup> pipes in cleaned glass bottles  
 147 refrigerated at 4 °C. The properties of the AC are available in Table S1 and conventional wastewater quality  
 148 parameters during each sampling campaigns are provided in Table S2 (supplementary information).

149 Table 1. Details about sampling campaigns performed on the AC industrial pilot, type of  $\mu$ GAC used, and operating  
 150 conditions.

Sampling campaign	Year	Period	Activated carbon used	Producer	Operating conditions
1-2	2015	February			Equivalent extraction and injection
3-7	2016	September – December	CycleCarb 305	Chemviron	
8-12	2017	September – December			

13-16	2018	September – December	Norit 3040	Cabot	No extraction nor injection
17	2019	January - February			

151 *2.2. Batch experiments*

152 13 adsorption experiments (experiments #18-30) were carried out using various types of PAC at a dose of  
153 10 mg/L between 2018 and 2019 at the laboratory (i.e. batch tests) (Table 2). PAC was prepared from  $\mu$ GAC  
154 crushed and sieved to retain a fraction between 50 and 63  $\mu$ m in order to ensure fast adsorption kinetics.  
155 Wastewater effluent was sampled from the Seine Centre WWTP at two different stages with a similar quality:  
156 nitrified water before the third biofiltration stage (i.e. denitrification stage) and denitrified water after the  
157 third biofiltration stage (i.e. similar to AC pilot tests). 8 different PACs and two contact times (30 min and  
158 72 h) were used for adsorption experiments. For each experiment, samples were collected before and after  
159 adsorption in cleaned glass bottles for analyses. The properties of the PAC are available in Table S1 and  
160 conventional wastewater quality parameters during each experiment are provided in Table S2  
161 (supplementary information).

162 Table 2. Details about batch experiments performed at the laboratory, type of PAC used, and operating conditions.  
163 \* $\mu$ GAC was crushed to PAC before adsorption to ensure fast adsorption kinetics. The retained fraction ranged from 50  
164 to 63  $\mu$ m.

Experiment #	Date	Wastewater quality	PAC	Producer	Contact time with wastewater	Reference for PAC properties
18			CycleCarb 305*	Chemviron		
19			PC 100 300*	DaCarb		
20			AquaSorb 2000*	Jacobi		
21	19/03/19	Nitrified water	AquaSorb 630*	Jacobi	30 min	(Guillossou et al., 2020a)
22			ReSorb MC*	Jacobi		
23			Norit GAC 2442*	Cabot		
24			Norit REACT 2442*	Cabot		
25	02/07/18		CycleCarb 305*	Chemviron		
26	07/08/19		CycleCarb 305*	Chemviron		
27					30 min	
28	05/08/19	Denitrified wastewater	PB 170	DaCarb	30 min	(Mailler et al., 2016c)
29					72 h	
30					72 h	

165 *2.3. Analytical procedures*



166 28 OMPs (20 pharmaceuticals, 5 pesticides, 2 hormones and 1 perfluorinated acid) were analyzed within 48  
167 h at the Institute of Analytical Sciences (ISA – Villeurbanne, France) by liquid chromatography coupled to  
168 tandem mass spectroscopy. Prior to analysis, all samples were homogenized and filtered on 0.7  $\mu\text{m}$  GF/F  
169 glass filters (Whatman). More information on the analytical methods can be found in the literature (Vulliet  
170 et al., 2011). Details about OMPs physico-chemical properties and the analytical procedures are provided in  
171 the supporting material (Table S3, supplementary information).

172 Dissolved organic carbon (DOC) was analyzed for each experiment and sampling campaign by the certified  
173 SIAAP laboratory after filtration on 0.45  $\mu\text{m}$  polyvinylidene fluoride filters (Milex<sup>®</sup>, Merck) (limit of  
174 quantification = 0.3 mgC/L). Spectroscopic measurements were performed at room temperature directly after  
175 sampling and filtration on 0.45  $\mu\text{m}$  polyvinylidene fluoride filters (Milex<sup>®</sup>, Merck).  $\text{UV}_{254}$  was measured  
176 using a spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific). EEMs (fluorescence  
177 excitation/emission matrix) were obtained using a spectrofluorometer (FP-8300, 150-W Xenon lamp, Jasco)  
178 with the scanning range from excitation wavelength 240 nm to 450 nm at an interval of 5 nm and emission  
179 wavelength from 250 nm to 600 nm at an interval of 2 nm. If the  $\text{UV}_{254}$  was higher than 0.080  $\text{cm}^{-1}$ , the  
180 samples were diluted with ultrapure water to avoid inner filter effects due to adsorbing species present in the  
181 wastewater (Alberts and Takács, 2004). Since  $\text{UV}_{254}$  of wastewater effluents was always  $< 0.15 \text{ cm}^{-1}$ , low  
182 dilution factors ( $< 2$ ) were used to minimize sources of errors (Kothawala et al., 2013). EEMs of ultrapure  
183 water were subtracted from the sample EEMs and normalized by the Raman peak of ultrapure water at an  
184 excitation wavelength of 350 nm to obtain fluorescence data in Raman units (R.U.), and fluorescence  
185 intensities were corrected with dilution factors when needed (Lawaetz and Stedmon, 2009).

#### 186 2.4. Fluorescence data treatment

187 Three methods were used to process fluorescence data (Table S4). All of them were performed using a peak-  
188 picking approach, which consists of extracting fluorescence intensities measured at specific pairs of Ex/Em  
189 (excitation/emission) wavelengths from measured EEMs. The first extraction method used Ex/Em  
190 wavelengths defined by Parlanti et al. (2000) ( $\alpha$ ,  $\alpha'$  and  $\beta$  indexes related to humic-like components,  $\gamma$  and  $\delta$   
191 indexes related to protein-like components) as they are frequently used in the literature for a large range of  
192 aquatic environments. A second peak-picking approach was chosen based on Ex/Em maximum localization

193 of 6 PARAFAC components (C1-C3 related to protein-like components and C4-C6 related to humic-like  
194 components) previously obtained with raw wastewater from the same WWTP than the one studied in this  
195 work (Goffin et al. 2018). Finally, a set of Ex/Em wavelengths was based on Ex/Em maximum localization  
196 of 7 PARAFAC components (F1-F7) obtained in this study. The PARAFAC analysis was performed using  
197 MATLAB® with the DrEEM toolbox (Murphy et al., 2013) from 30 WWTP effluent samples before and  
198 after adsorption onto AC ( $n = 60$ ). Further details on the procedure used for PARAFAC analysis are presented  
199 in Goffin et al. (2018). EEMs contours plots and Ex/Em loadings of the seven fluorescent components  
200 identified in this study are presented in Figure S2.

### 201 2.5. Data processing

202 OMPs removal was calculated following the approach of Choubert et al. (2017), which stated that the  
203 uncertainty of OMP concentrations in wastewater generally ranges between 30% and 100% when the  
204 measured value is lower than 2.5 to 10 times the limit of quantification (LOQ) of the compound. Therefore,  
205 when a compound was quantified at levels above 5 times the LOQ in the WWTP effluent and above the LOQ  
206 in the pilot effluent, the removal was conventionally calculated. When a compound concentration was above  
207 5 times the LOQ in the WWTP effluent but below the LOQ in the pilot effluent, the removal was estimated  
208 using  $LOQ/2$ . Removals were not calculated when concentrations in both the WWTP and the pilot effluent  
209 ranged between the LOQ and 5 times the LOQ.

210 The relationships between the removal of OMPs and spectroscopic indexes was examined using the R  
211 software (R Core Team, 2007). Pearson correlations with a p-value higher than 0.05 were discarded to ensure  
212 that results were statistically significant.

## 213 3. Results and discussion

### 214 3.1. OMPs removal

215 Out of the 28 OMPs analyzed, 7 molecules (ciprofloxacin, clothianidin, imidacloprid, estrone, estradiol,  
216 thiacloprid and thiamethoxam) were detected less than 10 times among the 30 wastewater effluent samples  
217 analyzed before adsorption. The results for these molecules were therefore not presented to only retain  
218 statistically significant results. Concentrations of OMPs in the wastewater effluent typically ranged from  
219 ng/L levels up to several  $\mu\text{g/L}$  (e.g., acetaminophen or sulfamethoxazole) at the time of each sampling

220 campaign or batch experiment (Table S5, supplementary information). The removal of the 21 OMPs selected  
221 and the average removal for each experiment/sampling campaigns (17 sampling campaigns on the pilot and  
222 13 batch experiments) are presented in Table 3. Various removals were observed depending on the  
223 experimental conditions (i.e. pilot-scale or batch experiments, contact time and type of AC used) and the  
224 affinity of OMPs toward AC (Figure S3-S6). The average removals obtained from the industrial pilot (61%  
225 in average, sampling campaigns #1-16) were higher than those obtained at lab-scale (30% in average,  
226 experiments #18-28) for a close contact time (20 min and 30 min, respectively). The performances observed  
227 in the pilot were higher due to the large mass of AC permanently present in the bed (1,000 kg) and the amount  
228 of available adsorption site, similarly to a GAC filter. Most importantly, the dose of fresh AC added daily  
229 (8.7 kg) was previously demonstrated to be the major parameter controlling the adsorption efficiency (40%  
230 removals at a 5 mg/L dose and up to >95% at a 70 mg/L dose) (Mailler et al., 2016b, 2015). When the AC  
231 bed was not renewed for 2 months (sampling campaign #17), a decrease in adsorption performance was thus  
232 observed (from 61% to 35%) due to the absence of fresh AC and the progressive saturation of the adsorption  
233 sites. At lab-scale, the average removal increased from 30% to 79% when the contact time increased from  
234 30 min (experiments 18-28) to 72 h (experiments 29 and 30). It is well known that when the contact time  
235 increases, the molecules can diffuse from the liquid phase and adsorb onto the AC more easily (Moreno-  
236 Castilla, 2004). The presence of DOM hinders the diffusion of OMPs into the AC porosity, which therefore  
237 need more time to adsorb (Newcombe et al., 2002).

238 Table 3. Experimental conditions, removal (%) of each OMP and the average removal for each experiment/sampling campaign.

Experiment /Sampling campaign	Experimental conditions	ACN	ACD	ATE	CAR	DIC	DIU	ERY	IBU	KET	LOR	NAP	NOR	OFL	OXA	PFOS	PRO	ROX	SDZ	SMZ	TET	TRI	Average
1	Pilot - Nominal condition				40			16		14	99			58	51		68			0	42		43
2					46	55	98	27		51	95			73	36		77	62		18	39		56
3		57	63	79	53	46	93	48		36	24	12	95	74	47	21	96	22	39	33	99	88	56
4		74	60	78	51	50	98	28		64	44	46	81	65	49	9	90	32	33	21	98	86	58
5			72	66	38	37	98	25		67	45	47	85	57	40	0	83	16	36	16	22	79	49
6		37	61	66	46	42	95	29		64	38	52		63	48	39	86	0	43	34	50	80	51
7		0	57	70	38	45	95	27		71	37	51		56	38	33	84	0	35	6	34	84	45
8		89	99	85	75	63	99	38	99	67	69	73	95	83	71	64	97	52	50	41		89	75
9		94	99	84	76	66	98	55	99	71	72	75	93	79	71	51	96	57	53	62	88	93	78
10		79	99	72	59	55	93	31	98	69	44	58	91	67	52	36	93	17	39	37		85	64
11		86	99	63	50	38	87	20	99	49	22	53		62	33	43	85	30	52	4		76	55
12		77	99	63	55	34	83	33		73	40	53	92	65	43	32	86	13	40	27		80	57
13		99		92	84	60	97	33	70	85	72	78	77	84	74	30	99	34	92	56		96	74
14		99		94	84	63	96	38	70	93	63	81	72	79	70	57	99	16		61		93	74
15		99		83	71	53	98	18		81	98	67	94	70	62	55	93	18	96	51	68	98	72
16		99		84	73	50		53	93	72	98	46	95	71	53	50	92	20	96	53	68	90	71
17	Pilot - No renewal	99		51	24	17	65	6		75	6	33	0	25	0		54	0		22	32	78	31
18	Laboratory - 30 min	21		26	25	25	43	27		20	16	30		39	24	23	36	27	17	27		30	27
19		24		24	23	20	32	19		20	24	23		7	22	28	30	23	13	22		19	22
20		25		28	23	21	35	16		11	8	31		23	11	37	35	5	23	15		25	22
21		41		43	38	33	64	27		25	23	39		42	28	31	58	11	0	33		45	34
22		30		35	43	36	70	30		38	35	42		42	45	30	66	20	2	19		54	37
23		50		31	25	17	45	10		12	0	23		33	18	37	48	6	30	22		35	26
24		42		41	37	35	61	15		25	26	33		40	28	36	62	14	31	17		46	35
25				42	38	18		17		29	16	35		37	35	18	67	33		17			31
26		33	35	46	42	46	66	33	34	7	32	35	31	47	36	19	80	24	18	20	1	51	35
27		9	25	34	41	11	61	20	4	0	2	3		47	23	0	67	0	6	25		45	22
28	35	58	49	48	38	60	35	17	28	40	48		55	41	25	75	22	19	26		59	41	
29	Laboratory - 72 h	89	86	91	93	77	98	79	36	70	59	93		98	86	84	99	68	16	42		96	77
30		90	83	92	95	80	98	83	64	80	68	99		98	88	68	99	76	52	43		98	82

239 ACN: Acetaminophen; ACD: Acetamiprid; ATE: Atenolol; CAR: Carbamazepine; DIC: Diclofenac; DIU: Diuron; ERY: Erythromycin; IBU: Ibuprofen; KET: Ketoprofen; LOR:  
 240 Lorazepam; NAP: Naproxen; NOR: Norfloxacin; OFL: Ofloxacin; OXA: Oxazepam; PRO: Propranolol; ROX: Roxithromycin; SDZ: Sulfadiazine; SMZ: Sulfamethoxazole; TET:  
 241 Tetracycline; TRI: Trimethoprim.

242

243 5 OMPs (acetamiprid, diuron, norfloxacin, propranolol and trimethoprim) were better eliminated than the  
244 others, both in the industrial pilot and in laboratory (Figure S3, supplementary information). Among these  
245 OMPs, some have physico-chemical properties that may promote their adsorption, such as a small molecular  
246 size (acetamiprid and diuron) or a positive charge (norfloxacin, propranolol and trimethoprim) in WWTP  
247 effluent (Alves et al., 2018; Margot et al., 2013). On the contrary, 5 OMPs (erythromycin, PFOS,  
248 roxithromycin, sulfadiazine and sulfamethoxazole) were less eliminated than the others (Figure S4,  
249 supplementary information). Erythromycin and roxithromycin are large molecules and thus could be  
250 subjected to steric hindrance when they diffuse to adsorption sites and could compete with DOM for  
251 adsorption sites in large micropores and mesopores. Sulfadiazine and sulfamethoxazole are negatively  
252 charged and thus can be subjected to repulsive electrostatic interactions with the adsorbed DOM (also  
253 negatively charged). PFOS is also a large and negatively charged molecule exhibiting a low removal, despite  
254 the presence of a long hydrophobic chain which should allow hydrophobic interactions with the surface of  
255 the AC. 6 OMPs (atenolol, carbamazepine, diclofenac, naproxen, ofloxacin and oxazepam) had a removal  
256 close to the average removal of all OMPs (Figure S5, supplementary information). Interestingly, several  
257 OMPs (acetaminophen, ibuprofen, lorazepam and sulfadiazine) clearly exhibited higher removals in the pilot  
258 (in optimal conditions) than in batch experiments after 72h of contact time (Table 3, Figure S6). Since some  
259 biological activity has been indirectly observed in the industrial pilot through the occurrence of nitrification  
260 (Guillossou et al., 2019; Mailler et al., 2016a), this could be due to the occurrence of biodegradation in the  
261 AC bed of the industrial pilot. Although it is recognized that degradation/biosorption by biomass processes  
262 (e.g. biological activated carbon filters, sand filters, fixed bed, moving bed) have a limited efficiency  
263 regarding the removal of most OMPs (<16%) (Bourgin et al., 2018; Falås et al., 2016), biodegradation could  
264 still be significant for the most biodegradable compounds. Except lorazepam, these molecules (i.e.  
265 acetaminophen, ibuprofen and sulfadiazine) were indeed demonstrated to be highly removed by conventional  
266 WWTP (>78%) and thus to be easily amenable to biodegradation (Ben et al., 2018; Guillossou et al., 2019;  
267 Verlicchi et al., 2012). Other easily biodegradable compounds (e.g., naproxen, erythromycin) did not follow  
268 the same behavior and were less eliminated in the pilot than after 72h in batch experiments. Other elimination  
269 processes (e.g. different adsorption kinetics, interactions with DOM or other components of wastewater  
270 effluents) might thus compensate the effect of biodegradation.

271 More detailed information on the performances of the AC pilot and the influence of OMPs physico-chemical  
 272 properties on their adsorption can be found in previous studies (Guillossou et al., 2019, 2020a; Mailler et al.,  
 273 2016a).

### 274 3.2. Spectroscopic indexes removal

275 7 components were obtained from fluorescence EEMs ( $n = 60$ ) using PARAFAC analysis (Figure S2). F1,  
 276 F2 and F3 indexes were located at excitation/emission wavelengths associated with aromatic proteins (Ex/Em  
 277 250/302 nm), tyrosine-like (Ex/Em 280/316 nm) and tryptophan-like (Ex/Em 285/354 nm) components,  
 278 respectively. F4 (Ex/Em 325/384 nm), F5 (Ex/Em 250/420 nm), F6 (Ex/Em 345/432 nm) and F7 (Ex/Em  
 279 385/472 nm) indexes were related to humic and fulvic-like components (Table S4, SI) (Chen et al., 2003).  
 280 F7 exhibited a second peak of lower intensity (Ex/Em 270/472 nm), also related to fulvic-like compounds.  
 281 A significant loss of intensity was observed in all regions of EEMs after adsorption, illustrating the efficiency  
 282 of AC in removing fluorescing DOM (Figure S7, supplementary information). The removal of DOC, UV<sub>254</sub>  
 283 and all fluorescence indexes was, like the removal of OMPs, higher in the industrial pilot in nominal  
 284 configuration and at lab-scale for a longer contact time (Table 4). Apart from the F1 index, close to the  
 285 background noise of fluorescence EEMs, the removal of UV<sub>254</sub> and DOC was most of the time lower than  
 286 those of fluorescence indexes, indicating that fluorescing moieties of DOM were preferentially eliminated.

287 Table 4. Removal (%  $\pm$  standard deviation) of DOC, UV<sub>254</sub> and fluorescence indexes in the industrial pilot and at lab-  
 288 scale.

Index	Pilot – Nominal configuration (experiments #1-16)	Pilot – No renewal (experiment #17)	Laboratory – 30 min (experiments #18- 28)	Laboratory – 72 h (experiments #29- 30)
DOC	21 ( $\pm$ 7)	15	12 ( $\pm$ 6)	27 / 32
UV <sub>254</sub>	23 ( $\pm$ 6)	8	12 ( $\pm$ 3)	28 / 29
TF	38 ( $\pm$ 5)	20	12 ( $\pm$ 7)	48 / 50
F1	13 ( $\pm$ 48)	0	-24 ( $\pm$ 67)	83 / 84
F2	40 ( $\pm$ 6)	35	20 ( $\pm$ 11)	48 / 50
F3	44 ( $\pm$ 6)	31	22 ( $\pm$ 11)	47 / 50
F4	38 ( $\pm$ 6)	22	10 ( $\pm$ 7)	42 / 43
F5	36 ( $\pm$ 5)	16	10 ( $\pm$ 8)	46 / 47
F6	37 ( $\pm$ 7)	21	13 ( $\pm$ 7)	48 / 49
F7	40 ( $\pm$ 5)	20	6 ( $\pm$ 10)	50 / 52

289 Similar trends in the removal of fluorescence indexes were observed both in the industrial pilot and at lab  
 290 scale. Slightly higher removals were obtained for tryptophan-like (F2) and tyrosine-like (F3) indexes (Table  
 291 4). Other organic compounds (i.e. humic-like and fulvic-like material, F4-F7) were slightly less removed,

292 especially at lab-scale after 30 min. Similar results were obtained with indexes derived from other studies  
293 (Goffin et al., 2018; Parlanti et al., 2000) (Table S6).

294 Humic-like indexes (F4-F7) were more affected by the absence of AC renewal (and thus saturation of the  
295 adsorption sites) than protein-like indexes (F1-F3). For example, the reduction of the F5 index went from  
296 36% (sampling campaigns #1-16) to 16% (sampling campaigns #17) while the F2 index only decreased from  
297 40% to 35%. These results could indicate that protein-like components are less sensitive to adsorption  
298 phenomena, but also that they could be more easily biodegraded. However, these results would need to be  
299 confirmed with more data in the absence of fresh AC.

### 300 *3.3. Correlations between OMPs removal and spectroscopic indexes*

301 A regression analysis was performed to examine relationships between the removal of OMPs and  
302 spectroscopic indexes. Correlation coefficients ( $r_{\text{Pearson}}$ ) from the statistically significant regressions ( $p$ -value  
303  $< 0.05$ ) are reported in Table 5. Positive correlations were obtained between the removal of spectroscopic  
304 indexes and all OMPs, indicating that an increase in the elimination of fluorescing DOM (i.e. represented by  
305 the elimination of the indexes) did not hinder the elimination of OMPs (e.g. through competitive  
306 mechanisms). The adsorption of fluorescing DOM thus did not block all micropores where OMPs are  
307 preferentially adsorbed (Li et al., 2002). These positive correlations also suggested that OMPs and DOM,  
308 despite different physicochemical properties (e.g. molecular weight or electric charge), followed similar  
309 adsorption kinetics and mechanisms and/or that they interacted and were adsorbed together. The formation  
310 of DOM-OMPs complexes in the dissolved phase and their subsequent adsorption on PAC was indeed  
311 reported in similar conditions (Guillossou et al., 2020b). In complex wastewater matrix, interactions between  
312 OMPs and extracellular polymeric substances (EPS) have also been reported through adsorption by the  
313 proteinaceous components of EPS or some binding with metal ions (Yu, 2020; Zhang et al., 2018). This  
314 could also play a role in the common adsorption observed between OMPs and fluorescence indexes, since  
315 the soluble EPS fraction show fluorescence signals in both protein-like and humic-like regions (Ni et al.,  
316 2009; Sheng and Yu, 2006).

317

318 Table 5. Correlation coefficient ( $r_{\text{Pearson}}$ , p-value <0.05) values for the linear regressions between the removal of DOC,  
 319 UV<sub>254</sub>, fluorescence indexes and the removal of OMPs. The highest value for each OMP is written in bold type. TF =  
 320 Total Fluorescence. n = number of data for each OMP.

OMP	n	DOC	UV <sub>254</sub>	TF	Index						
					F1	F2	F3	F4	F5	F6	F7
ACN	26	0.66	0.64	0.74	0.59	<b>0.82</b>	0.69	0.76	0.71	0.76	0.70
ACD	15	0.89	0.81	0.86	0.57	0.86	<b>0.90</b>	0.89	0.83	0.86	0.82
ATE	28	0.62	0.77	0.93		0.78	0.83	<b>0.94</b>	<b>0.94</b>	0.93	0.93
CAR	30	0.63	0.78	0.83	0.40	0.69	0.70	0.83	<b>0.85</b>	<b>0.85</b>	0.79
DIC	29	0.57	0.81	<b>0.86</b>	0.44	0.72	0.77	0.82	<b>0.86</b>	0.85	0.81
DIU	27	0.58	0.74	<b>0.93</b>		0.77	0.87	0.92	0.92	0.89	<b>0.93</b>
ERY	30	0.49	0.53	0.59	0.38	0.45	0.44	0.53	<b>0.60</b>	0.58	0.56
IBU	12	0.67	0.78	0.68		0.76	0.76	<b>0.78</b>	0.64	0.67	0.65
KET	30	0.55	0.66	0.77		0.76	0.73	<b>0.79</b>	0.75	0.73	0.76
LOR	30		<b>0.75</b>	0.70		0.54	0.58	<b>0.72</b>	0.71	<b>0.72</b>	0.67
NAP	28	0.57	<b>0.85</b>	0.79		0.68	0.71	0.75	0.78	<b>0.81</b>	0.73
NOR	13	0.68	0.57	0.73		0.59	0.62	0.65	0.73	0.59	<b>0.78</b>
OFL	30	0.63	0.80	0.92	0.38	0.71	0.81	0.90	<b>0.93</b>	0.92	0.89
OXA	30	0.56	0.77	0.81		0.62	0.68	0.78	<b>0.82</b>	0.81	0.76
PFOS	27	0.54	<b>0.73</b>	0.56	0.47	<b>0.63</b>	0.54	0.50	0.54	0.58	0.47
PRO	30	0.60	0.71	0.90		0.68	0.82	0.91	<b>0.92</b>	0.89	0.90
ROX	29	0.39	<b>0.55</b>	0.46				0.38	0.48	<b>0.50</b>	0.39
SDZ	25	0.49	0.59	0.60		0.62	0.54	<b>0.69</b>	0.60	0.61	0.60
SMZ	30	0.37	0.49	0.49		0.50	0.41	<b>0.54</b>	0.49	0.49	0.45
TET	12	<b>0.81</b>				<b>0.71</b>					
TRI	27	0.63	0.73	0.94		0.80	0.86	<b>0.95</b>	0.93	0.92	<b>0.95</b>
Average removal		0.70	0.84	0.92	0.43	0.82	0.83	0.92	0.92	0.91	0.89

321

322 All the studied indexes provided statistically significant correlations with most OMPs (i.e. p-values < 0.05),  
 323 despite the use of different brands of AC and various grain sizes, which suggests that these results could be  
 324 transposed to other activated carbons. The correlation coefficients between the removal of OMPs and TF,  
 325 frequently used in OMPs adsorption studies, were similar to results obtained with other indexes (especially  
 326 F4 and F5). Despite being less specific than indexes derived from peak-peaking, TF is a promising  
 327 spectroscopic index to be used in future prediction models of OMPs removal. Interestingly, there were no  
 328 significant differences between the correlation coefficients obtained with the indexes obtained by PARAFAC  
 329 analysis and other indexes from the literature (Goffin et al., 2018; Parlanti et al., 2000) (Table S7), because  
 330 of the proximity of their Ex/Em wavelengths. This indicates that the development of specific EEMs indexes  
 331 does not appear essential to improve the correlation results in the case of adsorption studies. However, the  
 332 removal of DOC and more importantly of UV<sub>254</sub> (the most used spectroscopic index in OMPs adsorption

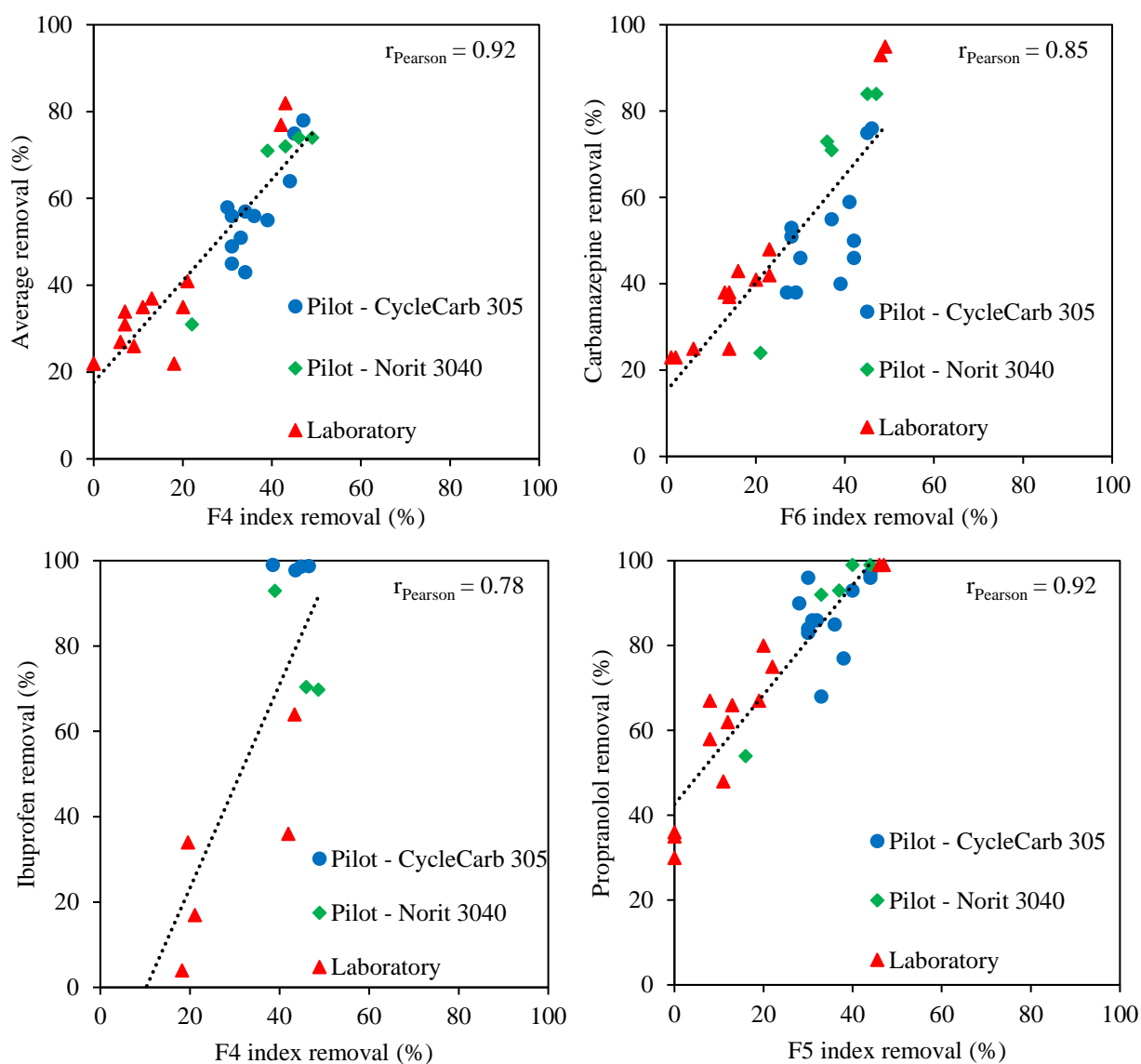


333 studies), were much less correlated with OMPs removal than most fluorescence indexes. Fluorescence  
334 spectroscopy thus offers the advantage of being more specific to several fractions of DOM with various  
335 chemical structures as compared to  $UV_{254}$ , which is mostly related to DOM aromaticity (Leenheer and Croué,  
336 2003). Fluorescence EEMs thus take into account numerous DOM fractions that interact with OMPs, or that  
337 follow similar adsorption mechanisms despite their different molecular properties.

338 Strong correlations ( $r_{\text{Pearson}} > 0.90$ ) were obtained between the removal of TF and fluorescence indexes related  
339 to humic and fulvic-like compounds (F4, F5, F6 and F7) and the removal of 6 OMPs (acetamiprid, atenolol,  
340 diuron, ofloxacin, propranolol and trimethoprim) (Figure S8). The average removal was also best correlated  
341 ( $r_{\text{Pearson}} = 0.92$ ) with humic-like fluorescence indexes from recent biological activity (F4, F5) (Figure 1).  
342 Moderate correlations ( $r_{\text{Pearson}} > 0.80$ ) were also obtained between these indexes and the removal of  
343 carbamazepine, diclofenac, ibuprofen, ketoprofen, naproxen, norfloxacin and oxazepam (Figure 1, Figure  
344 S8). The best correlations for acetaminophen and tetracycline were obtained with the indexes related to  
345 tyrosine-like compound ( $\gamma$  and F2), while the highest correlation coefficient for PFOS was obtained with  
346  $UV_{254}$  ( $r_{\text{Pearson}} = 0.73$ ). Weaker correlations ( $r_{\text{Pearson}} < 0.80$ ) were found for erythromycin, lorazepam,  
347 roxithromycin, sulfadiazine or sulfamethoxazole with any index. Interestingly, the most biodegradable  
348 OMPs (acetaminophen, ibuprofen, lorazepam and sulfadiazine) which exhibited higher removals in the pilot  
349 than in batch experiments also showed low correlation coefficients with spectroscopic indexes ( $r_{\text{Pearson}} < 0.82$ )  
350 (Table 5), which confirms that other processes than adsorption influenced their elimination. Monitoring these  
351 specific OMPs might thus prove more challenging. The occurrence of biodegradation might also explain the  
352 lower correlation coefficients globally obtained with protein-like indexes. Overall, even if some  
353 biodegradation could be expected for the most biodegradable compounds, robust correlations were obtained  
354 between the average removal and humic-like indexes, which indicated that biological effects had a low  
355 influence on the whole pool of OMPs. High correlation coefficients obtained with several OMPs (e.g.,  
356 atenolol, trimethoprim) also suggested that these specific molecules were mostly eliminated by adsorption  
357 processes.

358

359



362 Fig. 1. Statistically significant correlations between the removal of selected OMPs and fluorescence EEM indexes  
 363 obtained by PARAFAC analysis.

364  
 365  
 366 *3.4 Interactions between OMPs, fluorescing DOM and AC*

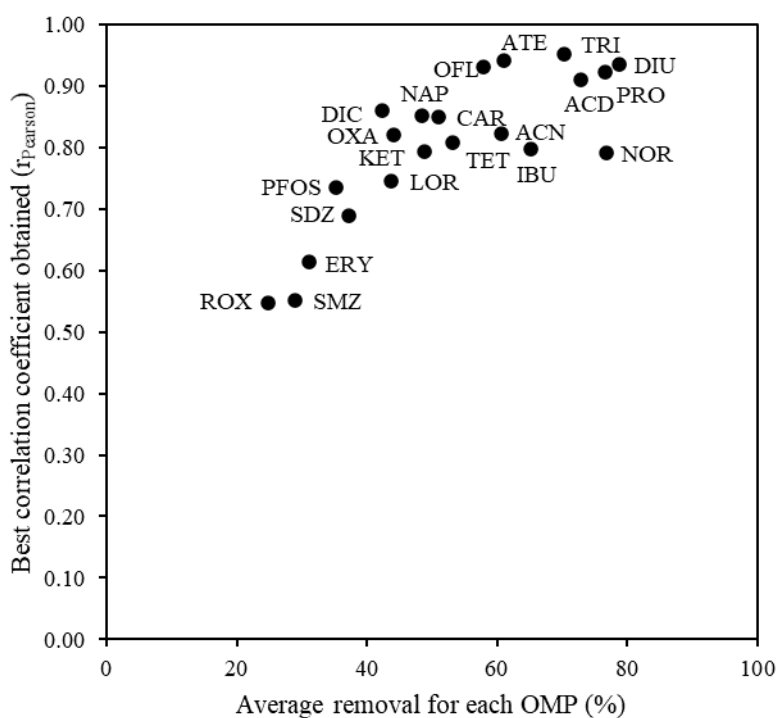
367 There was no apparent link between a specific physico-chemical property of OMPs and the indexes with  
 368 which they were correlated. Complex interactions (e.g. electrostatic, hydrophobic and van der Waals) exist  
 369 between AC, OMPs and DOM, and a single property cannot account for all these phenomena. For example,  
 370 the removal of both atenolol and ofloxacin was well correlated ( $r_{\text{Pearson}} > 0.90$ ) with the removal of the F4  
 371 component (humic-like from recent biological activity), but atenolol is positively charged while ofloxacin is  
 372 negatively charged in wastewater effluents. As mentioned earlier, the correlations observed between OMPs  
 373 and fluorescing DOM could be due to similar adsorption kinetics and mechanisms and/or to DOM-OMPs

374 interactions and co-adsorption. The hypothesis of similar adsorption mechanisms and kinetics of both OMPs  
375 and DOM can be first considered since it is known that smaller fractions of DOM can compete with OMPs  
376 for adsorption sites (Newcombe et al., 2002; Zietzschmann et al., 2014b). Such competition was associated  
377 with higher proportions of small acid and neutral compounds of DOM and was assumed to result from the  
378 similar molecular size range of these DOM compounds and most OMPs, which in turn targeted similar  
379 adsorption sites (Zietzschmann et al., 2014b). It is however uncertain if such competition would lead to  
380 correlations between the removals of DOM and OMPs, especially when considering their respective  
381 concentrations (i.e. mg/L levels of DOM compounds and ng/L- $\mu$ g/L levels of OMPs). Moreover, OMPs with  
382 different molecular properties and different adsorption behaviors were affected differently by these  
383 competition effects (Zietzschmann et al., 2014b). In our study, it is also not possible to infer that the obtained  
384 correlations were due to common molecular sizes since fluorophores cannot be associated with specific  
385 ranges of molecular size. Additional experiments would thus be needed to evaluate the relevance of  
386 competition effects with small fractions of DOM to the adsorption of OMPs presented in this study.

387 The occurrence of interactions between fluorescing DOM or EPS and OMPs could also explain the observed  
388 correlations. Such interactions (e.g. hydrogen bonding, hydrophobic, van der Waals or dipole-dipole  
389 interactions) were demonstrated between various OMPs and several types and fractions of natural DOM  
390 (Caupos et al., 2015; Mott, 2002; Yamamoto et al., 2003), effluent DOM (Guillossou et al., 2020b; Ilani et  
391 al., 2005) and EPS (Yu, 2020; Zhang et al., 2018). Hernandez-Ruiz et al. (2012) used fluorescence quenching  
392 to examine whether some OMPs could interact with fluorescent moieties of DOM and found that bisphenol-  
393 A interacted with microbial byproduct-like and humic acid-like fluorophores while carbamazepine and  
394 ibuprofen interacted with fulvic acid-like fluorophores. The impact of these DOM-OMPs associations on the  
395 adsorption processes and the occurrence of co-adsorption was recently observed for ciprofloxacin and humic  
396 acid adsorption onto AC and various resins (Jin et al., 2018), as well as for effluent DOM and various OMPs  
397 adsorption on AC (Guillossou et al., 2020b). This DOM-OMPs co-adsorption hypothesis is reinforced by the  
398 fact that the best correlations were obtained for the OMPs reaching the highest removals (e.g. diuron and  
399 propranolol), while the OMPs that were more refractory to adsorption exhibited weaker correlations (e.g.  
400 roxithromycin and sulfadiazine) (Figure 2). The latter OMPs indeed have physico-chemical properties that  
401 are unfavorable to interactions with DOM (i.e. a negative charge for sulfadiazine and sulfamethoxazole) or

402 to diffusion through AC porosity (i.e. a large size erythromycin and roxithromycin) due to the presence of  
403 DOM. Their lower interactions with DOM or the competition with DOM during adsorption (i.e. adsorption  
404 of DOM favored over adsorption of the OMP) can thus explain the weaker correlations. This result indicates  
405 that fluorescence EEM could be a suitable tool for the online monitoring of OMPs that are more easily  
406 removed by adsorption on AC, but not for OMPs that are more refractory to adsorption.

407



408

409 Fig. 2. Best correlation coefficient ( $r_{\text{Pearson}}$ ) obtained between a fluorescence index and an OMP removal compared to  
410 the average removal of each OMP for all the experiments performed (industrial pilot + laboratory).

411

### 412 3.5. Toward a prediction of OMPs removal?

413 Fluorescence spectroscopy appears as an effective tool for the online monitoring of the average removal of  
414 OMPs during adsorption processes, which could facilitate the supervision of advanced wastewater treatment  
415 facilities. The large variety of physico-chemical properties of selected OMPs suggests that fluorescence  
416 spectroscopy could be used to predict the removal of other OMPs found in wastewater, notably the 12  
417 compounds suggested as indicator substances for wastewater treatment in Switzerland (Office fédéral de  
418 l'environnement, Division Eaux, 2014). Fluorescence spectroscopy appeared much more accurate than  $UV_{254}$   
419 for the prediction of OMPs removal. While  $UV_{254}$  is currently the only spectroscopic option for high-

420 frequency monitoring, the online measurement of fluorescence is currently under development and would  
421 provide more information and accuracy for the monitoring of OMPs adsorption. Considering the lower  
422 correlations obtained with highly biodegradable compounds or with OMPs refractory to adsorption, it is  
423 worth noting that such application appears more accurate with the average concentration of OMPs and that  
424 monitoring specific OMPs could be more challenging.

425 Robust model development for accurate high-frequency monitoring would require a larger number of  
426 samples to allow training and validation of regression models (Chys et al., 2017). In addition to simple linear  
427 regression models, a large dataset would allow to study multiple linear regression models combining different  
428 spectroscopic indexes to predict OMPs removal. These models could have greater predictive power than  
429 simple models as suggested by several studies (Carstea et al., 2016; Goffin et al., 2019; Henderson et al.,  
430 2009). The combination of different indexes related to different fractions of DOM could account for the  
431 possible interactions between OMPs and DOM more accurately, and thus improve the prediction of their  
432 removal. The adsorption-specific fluorescence indexes (i.e. specific PARAFAC components) found in this  
433 study may also be more accurate than generic indexes for this type of models.

#### 434 **Conclusion**

- 435 • Out of 28 targeted OMPs, 21 were detected in wastewater over a significant number of sampling  
436 campaigns ( $n > 10$ ). Differences in OMPs removal in an industrial pilot and in batch experiments  
437 were observed depending on the operational conditions (i.e. pilot or batch experiments, contact time,  
438 type of AC) and the physico-chemical properties of the molecules to be eliminated.
- 439 • Robust positive correlations were obtained between the removal of spectroscopic indexes obtained  
440 by PARAFAC analysis and most OMPs. This indicates that these correlations show the potential of  
441 being used to monitor the removal of OMPs in a wide range of operational conditions. Overall, the  
442 average removal of all OMPs was well correlated ( $r_{\text{pearson}} = 0.92$ ) with humic-like fluorescing DOM,  
443 and correlations were much more accurate than with  $UV_{254}$ .
- 444 • These positive correlations suggested that OMPs and DOM followed similar adsorption mechanisms  
445 or more likely that they interacted and were adsorbed together. However, there was no apparent link  
446 between a specific OMPs physico-chemical property and the indexes with which they were

447 correlated. The most biodegradable OMPs and OMPs refractory to adsorption exhibited lower  
448 correlations, so their monitoring in full-scale adsorption processes might be more challenging,  
449 especially in the presence of biomass.

450 • An even higher number of samples in the dataset, especially originating from data acquired in even  
451 more various experimental conditions, would confirm the observed trends and could be used to build  
452 robust regression models by performing cross-validation. This study is nonetheless demonstrating  
453 that the application of fluorescence spectroscopy to the monitoring of adsorption processes at the  
454 industrial scale can accurately track the evolution of OMPs.

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## 459 **References**

- 460 Alberts, J.J., Takács, M., 2004. Comparison of the natural fluorescence distribution among size fractions of  
461 terrestrial fulvic and humic acids and aquatic natural organic matter. *Org. Geochem.* 35, 1141–1149.  
462 <https://doi.org/10.1016/j.orggeochem.2004.06.010>
- 463 Alves, T.C., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A., Gonzalez-Olmos, R.,  
464 2018. Influencing factors on the removal of pharmaceuticals from water with micro-grain activated  
465 carbon. *Water Res.* <https://doi.org/10.1016/j.watres.2018.07.037>
- 466 Anumol, T., Sgroi, M., Park, M., Roccaro, P., Snyder, S.A., 2015. Predicting trace organic compound  
467 breakthrough in granular activated carbon using fluorescence and UV absorbance as surrogates.  
468 *Water Res.* 76, 76–87. <https://doi.org/10.1016/j.watres.2015.02.019>
- 469 Ben, W., Zhu, B., Yuan, X., Zhang, Y., Yang, M., Qiang, Z., 2018. Occurrence, removal and risk of organic  
470 micropollutants in wastewater treatment plants across China: Comparison of wastewater treatment  
471 processes. *Water Res.* 130, 38–46. <https://doi.org/10.1016/j.watres.2017.11.057>
- 472 Benstoem, F., Nahrstedt, A., Boehler, M., Knopp, G., Montag, D., Siegrist, H., Pinnekamp, J., 2017.  
473 Performance of granular activated carbon to remove micropollutants from municipal wastewater—  
474 A meta-analysis of pilot- and large-scale studies. *Chemosphere* 185, 105–118.  
475 <https://doi.org/10.1016/j.chemosphere.2017.06.118>
- 476 Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., von Gunten, U.,  
477 Siegrist, H., McArdell, C.S., 2018. Evaluation of a full-scale wastewater treatment plant upgraded  
478 with ozonation and biological post-treatments: Abatement of micropollutants, formation of  
479 transformation products and oxidation by-products. *Water Res.* 129, 486–498.  
480 <https://doi.org/10.1016/j.watres.2017.10.036>
- 481 Carstea, E.M., Bridgeman, J., Baker, A., Reynolds, D.M., 2016. Fluorescence spectroscopy for wastewater  
482 monitoring: A review. *Water Res.* 95, 205–219. <https://doi.org/10.1016/j.watres.2016.03.021>
- 483 Caupos, E., Touffet, A., Mazellier, P., Croue, J.-P., 2015. Partitioning of the pesticide trifluralin between  
484 dissolved organic matter and water using automated SPME-GC/MS. *Environ. Sci. Pollut. Res.* 22,  
485 4201–4212. <https://doi.org/10.1007/s11356-014-3614-0>

- 486 Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence Excitation-Emission Matrix  
487 Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environ. Sci. Technol.* 37,  
488 5701–5710.
- 489 Choubert, J.-M., Martin Ruel, S., Miege, C., Coquery, M., 2017. Rethinking micropollutant removal  
490 assessment methods for wastewater treatment plants – how to get more robust data? *Water Sci.*  
491 *Technol.* 75, 2964–2972. <https://doi.org/10.2166/wst.2017.181>
- 492 Chys, M., Audenaert, W.T.M., Deniere, E., Mortier, S.T.F.C., Van Langenhove, H., Nopens, I., Demeestere,  
493 K., Van Hulle, S.W.H., 2017. Surrogate-Based Correlation Models in View of Real-Time Control  
494 of Ozonation of Secondary Treated Municipal Wastewater—Model Development and Dynamic  
495 Validation. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.7b04905>
- 496 Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission  
497 matrix spectroscopy. *Mar. Chem.* 51, 325–346.
- 498 Falås, P., Wick, A., Castronovo, S., Habermacher, J., Ternes, T.A., Joss, A., 2016. Tracing the limits of  
499 organic micropollutant removal in biological wastewater treatment. *Water Res.* 95, 240–249.  
500 <https://doi.org/10.1016/j.watres.2016.03.009>
- 501 Ferretto, N., Tedetti, M., Guigue, C., Mounier, S., Redon, R., Goutx, M., 2014. Identification and  
502 quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using  
503 fluorescence excitation–emission matrices and parallel factor analysis. *Chemosphere* 107, 344–353.  
504 <https://doi.org/10.1016/j.chemosphere.2013.12.087>
- 505 Gerrity, D., Gamage, S., Jones, D., Korshin, G.V., Lee, Y., Pisarenko, A., Trenholm, R.A., von Gunten, U.,  
506 Wert, E.C., Snyder, S.A., 2012. Development of surrogate correlation models to predict trace organic  
507 contaminant oxidation and microbial inactivation during ozonation. *Water Res.* 46, 6257–6272.  
508 <https://doi.org/10.1016/j.watres.2012.08.037>
- 509 Goffin, A., Guérin, S., Rocher, V., Varrault, G., 2018. Towards a better control of the wastewater treatment  
510 process: excitation-emission matrix fluorescence spectroscopy of dissolved organic matter as a  
511 predictive tool of soluble BOD5 in influents of six Parisian wastewater treatment plants. *Environ.*  
512 *Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-018-1205-1>
- 513 Goffin, A., Guérin-Rechdaoui, S., Rocher, V., Varrault, G., 2019. An environmentally friendly surrogate  
514 method for measuring the soluble chemical oxygen demand in wastewater: use of three-dimensional  
515 excitation and emission matrix fluorescence spectroscopy in wastewater treatment monitoring.  
516 *Environ. Monit. Assess.* 191, 421. <https://doi.org/10.1007/s10661-019-7570-5>
- 517 Guillosoou, R., Le Roux, J., Mailler, R., Morlay, C., Vulliet, E., Nauleau, F., Rocher, V., Gasperi, J., 2020a.  
518 Influence of the properties of 7 micro-grain activated carbons on organic micropollutants removal  
519 from wastewater effluent. *Chemosphere* 243, 125306.  
520 <https://doi.org/10.1016/j.chemosphere.2019.125306>
- 521 Guillosoou, R., Le Roux, J., Mailler, R., Pereira-Derome, C.S., Varrault, G., Bressy, A., Vulliet, E., Morlay,  
522 C., Nauleau, F., Rocher, V., Gasperi, J., 2020b. Influence of dissolved organic matter on the removal  
523 of 12 organic micropollutants from wastewater effluent by powdered activated carbon adsorption.  
524 *Water Res.* 172, 115487. <https://doi.org/10.1016/j.watres.2020.115487>
- 525 Guillosoou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J., Rocher, V., 2019.  
526 Organic micropollutants in a large wastewater treatment plant: What are the benefits of an advanced  
527 treatment by activated carbon adsorption in comparison to conventional treatment? *Chemosphere*  
528 218, 1050–1060. <https://doi.org/10.1016/j.chemosphere.2018.11.182>
- 529 Henderson, R.K., Baker, A., Murphy, K.R., Hambly, A., Stuetz, R.M., Khan, S.J., 2009. Fluorescence as a  
530 potential monitoring tool for recycled water systems: A review. *Water Res.* 43, 863–881.  
531 <https://doi.org/10.1016/j.watres.2008.11.027>
- 532 Hernandez-Ruiz, S., Abrell, L., Wickramasekara, S., Chefetz, B., Chorover, J., 2012. Quantifying PPCP  
533 interaction with dissolved organic matter in aqueous solution: Combined use of fluorescence  
534 quenching and tandem mass spectrometry. *Water Res.* 46, 943–954.  
535 <https://doi.org/10.1016/j.watres.2011.11.061>
- 536 Ilani, T., Schulz, E., Chefetz, B., 2005. Interactions of Organic Compounds with Wastewater Dissolved  
537 Organic Matter: Role of Hydrophobic Fractions. *J Env. QUAL* 34, 11.
- 538 Jin, J., Feng, T., Gao, R., Ma, Y., Wang, W., Zhou, Q., Li, A., 2018. Ultrahigh selective adsorption of  
539 zwitterionic PPCPs both in the absence and presence of humic acid: Performance and mechanism. *J.*  
540 *Hazard. Mater.* 348, 117–124. <https://doi.org/10.1016/j.jhazmat.2018.01.036>

541 Korshin, G.V., Sgroi, M., Ratnaweera, H., 2018. Spectroscopic surrogates for real time monitoring of water  
542 quality in wastewater treatment and water reuse. *Curr. Opin. Environ. Sci. Health* 2, 12–19.  
543 <https://doi.org/10.1016/j.coesh.2017.11.003>

544 Kothawala, D.N., Murphy, K.R., Stedmon, C.A., Weyhenmeyer, G.A., Tranvik, L.J., 2013. Inner filter  
545 correction of dissolved organic matter fluorescence: Correction of inner filter effects. *Limnol.*  
546 *Oceanogr. Methods* 11, 616–630. <https://doi.org/10.4319/lom.2013.11.616>

547 Lawaetz, A.J., Stedmon, C.A., 2009. Fluorescence Intensity Calibration Using the Raman Scatter Peak of  
548 Water. *Appl. Spectrosc.* 63, 936–940.

549 Leenheer, J.A., Croué, J.-P., 2003. Characterizing Aquatic Dissolved Organic Matter. *Environ. Sci. Technol.*  
550 37, 18A-26A. <https://doi.org/10.1021/es032333c>

551 Li, L., Quinlivan, P.A., Knappe, D.R.U., 2002. Effects of activated carbon surface chemistry and pore  
552 structure on the adsorption of organic contaminants from aqueous solution. *Carbon* 40, 2085–2100.  
553 [https://doi.org/10.1016/S0008-6223\(02\)00069-6](https://doi.org/10.1016/S0008-6223(02)00069-6)

554 Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M.,  
555 Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg,  
556 R.H., Schwesig, D., Gawlik, B.M., 2013. EU-wide monitoring survey on emerging polar organic  
557 contaminants in wastewater treatment plant effluents. *Water Res.* 47, 6475–6487.  
558 <https://doi.org/10.1016/j.watres.2013.08.024>

559 Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on  
560 the occurrence of micropollutants in the aquatic environment and their fate and removal during  
561 wastewater treatment. *Sci. Total Environ.* 473–474, 619–641.  
562 <https://doi.org/10.1016/j.scitotenv.2013.12.065>

563 Mailler, R., Gasperi, J., Coquet, Y., Buleté, A., Vulliet, E., Deshayes, S., Zedek, S., Mirande-Bret, C., Eudes,  
564 V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2016a. Removal of a wide range  
565 of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon  
566 in fluidized bed as tertiary treatment at large pilot scale. *Sci. Total Environ.* 542, Part A, 983–996.  
567 <http://dx.doi.org/10.1016/j.scitotenv.2015.10.153>

568 Mailler, R., Gasperi, J., Coquet, Y., Buleté, A., Vulliet, E., Deshayes, S., Zedek, S., Mirande-Bret, C., Eudes,  
569 V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2016b. Removal of a wide range  
570 of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon  
571 in fluidized bed as tertiary treatment at large pilot scale. *Sci. Total Environ.* 542, Part A, 983–996.  
572 <https://doi.org/10.1016/j.scitotenv.2015.10.153>

573 Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault, G., Chebbo,  
574 G., Rocher, V., 2016c. Removal of emerging micropollutants from wastewater by activated carbon  
575 adsorption: Experimental study of different activated carbons and factors influencing the adsorption  
576 of micropollutants in wastewater. *J. Environ. Chem. Eng.* 4, 1102–1109.  
577 <https://doi.org/10.1016/j.jece.2016.01.018>

578 Mailler, R., Gasperi, J., Coquet, Y., Deshayes, S., Zedek, S., Cren-Olivé, C., Cartiser, N., Eudes, V., Bressy,  
579 A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2015. Study of a large scale powdered  
580 activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from  
581 wastewater treatment plant effluents. *Water Res.* 72, 315–330.  
582 <https://doi.org/10.1016/j.watres.2014.10.047>

583 Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thoney, D.,  
584 Chèvre, N., Schäfer, M., Barry, D.A., 2013. Treatment of micropollutants in municipal wastewater:  
585 Ozone or powdered activated carbon? *Sci. Total Environ.* 461–462, 480–498.  
586 <https://doi.org/10.1016/j.scitotenv.2013.05.034>

587 Moreno-Castilla, C., 2004. Adsorption of organic molecules from aqueous solutions on carbon materials.  
588 *Carbon* 42, 83–94. <https://doi.org/10.1016/j.carbon.2003.09.022>

589 Mott, H.V., 2002. Association of hydrophobic organic contaminants with soluble organic matter: evaluation  
590 of the database of Kdoc values. *Adv. Environ. Res.* 6, 577–593.

591 Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., 2013. Fluorescence spectroscopy and multi-way  
592 techniques. *PARAFAC. Anal. Methods* 5, 6557–6566. <https://doi.org/10.1039/C3AY41160E>

593 Nanaboina, V., Korshin, G.V., 2010. Evolution of Absorbance Spectra of Ozonated Wastewater and Its  
594 Relationship with the Degradation of Trace-Level Organic Species. *Environ. Sci. Technol.* 44, 6130–  
595 6137. <https://doi.org/10.1021/es1005175>

596 Newcombe, G., Morrison, J., Hepplewhite, C., Knappe, D.R.U., 2002. Simultaneous adsorption of MIB and  
597 NOM onto activated carbon II. Competitive effects. *Carbon* 40, 2147–2156.



598 Ni, B.-J., Fang, F., Xie, W.-M., Sun, M., Sheng, G.-P., Li, W.-H., Yu, H.-Q., 2009. Characterization of  
599 extracellular polymeric substances produced by mixed microorganisms in activated sludge with gel-  
600 permeating chromatography, excitation–emission matrix fluorescence spectroscopy measurement  
601 and kinetic modeling. *Water Res.* 43, 1350–1358. <https://doi.org/10.1016/j.watres.2008.12.004>  
602 Office fédéral de l’environnement, Division Eaux, 2014. Rapport explicatif concernant la modification de  
603 l’ordonnance sur la protection des eaux.

604 Park, M., Anumol, T., Daniels, K.D., Wu, S., Ziska, A.D., Snyder, S.A., 2017. Predicting trace organic  
605 compound attenuation by ozone oxidation: Development of indicator and surrogate models. *Water*  
606 *Res.* 119, 21–32. <https://doi.org/10.1016/j.watres.2017.04.024>  
607 Parlanti, E., Wörz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved organic matter fluorescence spectroscopy  
608 as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Org.*  
609 *Geochem.* 31, 1765–1781. [https://doi.org/10.1016/S0146-6380\(00\)00124-8](https://doi.org/10.1016/S0146-6380(00)00124-8)  
610 Piai, L., Dykstra, J., Adishakti, M.G., Blokland, M., Langenhoff, A., van der Wal, A., 2019. Diffusion of  
611 hydrophilic organic micropollutants in granular activated carbon with different pore sizes. *Water*  
612 *Res.* <https://doi.org/10.1016/j.watres.2019.06.012>

613 R Core Team, 2007. R: A language and environment for statistical computing. R Foundation for Statistical  
614 Computing, Vienna, Austria.

615 Sgroi, M., Anumol, T., Roccaro, P., Vagliasindi, F.G.A., Snyder, S.A., 2018. Modeling emerging  
616 contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing  
617 components of dissolved organic matter. *Water Res.* <https://doi.org/10.1016/j.watres.2018.09.018>  
618 Sgroi, M., Roccaro, P., Korshin, G.V., Greco, V., Sciuto, S., Anumol, T., Snyder, S.A., Vagliasindi, F.G.A.,  
619 2017. Use of fluorescence EEM to monitor the removal of emerging contaminants in full scale  
620 wastewater treatment plants. *J. Hazard. Mater., Special Issue on Emerging Contaminants in*  
621 *engineered and natural environment* 323, Part A, 367–376.  
622 <https://doi.org/10.1016/j.jhazmat.2016.05.035>

623 Sheng, G.-P., Yu, H.-Q., 2006. Characterization of extracellular polymeric substances of aerobic and  
624 anaerobic sludge using three-dimensional excitation and emission matrix fluorescence spectroscopy.  
625 *Water Res.* 40, 1233–1239. <https://doi.org/10.1016/j.watres.2006.01.023>  
626 Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C., Yoon,  
627 Y., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and  
628 pharmaceuticals. *Desalination* 202, 156–181. <https://doi.org/10.1016/j.desal.2005.12.052>  
629 Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban  
630 wastewater: Removal, mass load and environmental risk after a secondary treatment—A review. *Sci.*  
631 *Total Environ., Special Section - Arsenic in Latin America, An Unrevealed Continent: Occurrence,*  
632 *Health Effects and Mitigation* 429, 123–155. <https://doi.org/10.1016/j.scitotenv.2012.04.028>  
633 Vulliet, E., Cren-Olivé, C., Grenier-Loustalot, M.-F., 2011. Occurrence of pharmaceuticals and hormones in  
634 drinking water treated from surface waters. *Environ. Chem. Lett.* 9, 103–114.  
635 <https://doi.org/10.1007/s10311-009-0253-7>

636 Wasswa, J., Mladenov, N., Pearce, W., 2019. Assessing the potential of fluorescence spectroscopy to monitor  
637 contaminants in source waters and water reuse systems. *Environ. Sci. Water Res. Technol.* 5, 370–  
638 382. <https://doi.org/10.1039/C8EW00472B>  
639 Yamamoto, H., Liljestrand, H.M., Shimizu, Y., Morita, M., 2003. Effects of Physical–Chemical  
640 Characteristics on the Sorption of Selected Endocrine Disruptors by Dissolved Organic Matter  
641 Surrogates. *Environ. Sci. Technol.* 37, 2646–2657. <https://doi.org/10.1021/es026405w>  
642 Yu, H.-Q., 2020. Molecular Insights into Extracellular Polymeric Substances in Activated Sludge. *Environ.*  
643 *Sci. Technol.* 54, 7742–7750. <https://doi.org/10.1021/acs.est.0c00850>  
644 Zhang, H., Jia, Y., Khanal, S.K., Lu, H., Fang, H., Zhao, Q., 2018. Understanding the Role of Extracellular  
645 Polymeric Substances on Ciprofloxacin Adsorption in Aerobic Sludge, Anaerobic Sludge, and  
646 Sulfate-Reducing Bacteria Sludge Systems. *Environ. Sci. Technol.* 52, 6476–6486.  
647 <https://doi.org/10.1021/acs.est.8b00568>

648 Zietzschmann, F., Altmann, J., Ruhl, A.S., Dünnebier, U., Dommisch, I., Sperlich, A., Meinel, F., Jekel, M.,  
649 2014a. Estimating organic micro-pollutant removal potential of activated carbons using UV  
650 absorption and carbon characteristics. *Water Res.* 56, 48–55.  
651 <https://doi.org/10.1016/j.watres.2014.02.044>  
652 Zietzschmann, F., Aschermann, G., Jekel, M., 2016. Comparing and modeling organic micro-pollutant  
653 adsorption onto powdered activated carbon in different drinking waters and WWTP effluents. *Water*  
654 *Res.* 102, 190–201. <https://doi.org/10.1016/j.watres.2016.06.041>

655 Zietzschmann, F., Dittmar, S., Splettstößer, L., Hunsicker, J., Dittmann, D., Meinel, F., Rößler, A., Metzger,  
656 S., Jekel, M., Ruhl, A.S., 2019. Fast empirical lab method for performance projections of large-scale  
657 powdered activated carbon re-circulation plants. *Chemosphere* 215, 563–573.  
658 <https://doi.org/10.1016/j.chemosphere.2018.10.055>  
659 Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F., Jekel, M., 2014b. Impact of  
660 EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated  
661 wastewater. *Water Res.* 65, 297–306. <https://doi.org/10.1016/j.watres.2014.07.043>  
662 Ziska, A.D., Park, M., Anumol, T., Snyder, S.A., 2016. Predicting trace organic compound attenuation with  
663 spectroscopic parameters in powdered activated carbon processes. *Chemosphere* 156, 163–171.  
664 <https://doi.org/10.1016/j.chemosphere.2016.04.073>  
665