

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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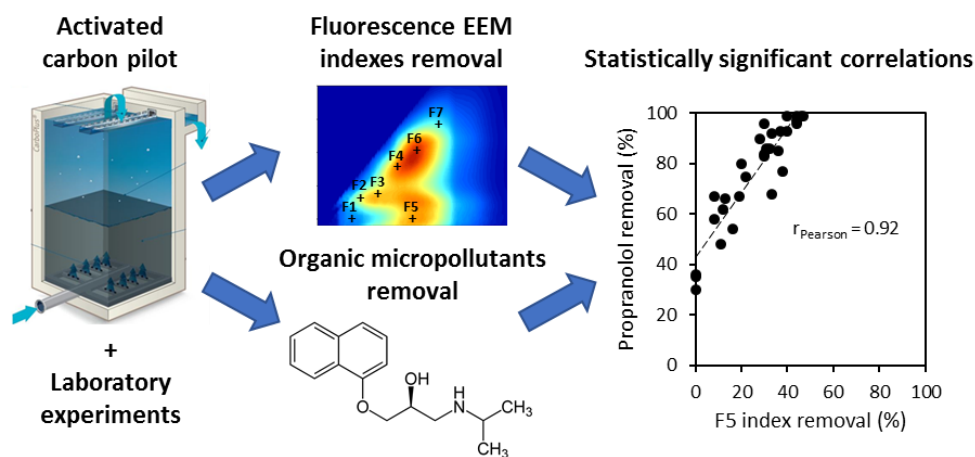
17 **Highlights**

- 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 • UV₂₅₄ 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 – μ 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 UV₂₅₄. 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 UV₂₅₄ 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 μ 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[®], 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 m³ of wastewater effluent was

126 applied daily, corresponding to 8.6 kg of AC per day for a flow rate of 860 m³/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 m² 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 m³/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 μ 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[®] 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 μ 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 μ GAC
154 crushed and sieved to retain a fraction between 50 and 63 μ 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 * μ GAC was crushed to PAC before adsorption to ensure fast adsorption kinetics. The retained fraction ranged from 50
164 to 63 μ 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 μm 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 μm polyvinylidene fluoride filters (Milex[®], 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 μm polyvinylidene fluoride filters (Milex[®], Merck). 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 UV_{254} was higher than 0.080 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 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) (α , α' and β indexes related to humic-like components, γ and δ
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.

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, UV₂₅₄
 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 UV₂₅₄ 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, UV₂₅₄ 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 ₂₅₄	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_{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_{Pearson} , p-value <0.05) values for the linear regressions between the removal of DOC,
 319 UV₂₅₄, 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 ₂₅₄	TF	Index						
					F1	F2	F3	F4	F5	F6	F7
ACN	26	0.66	0.64	0.74	0.59	0.82	0.69	0.76	0.71	0.76	0.70
ACD	15	0.89	0.81	0.86	0.57	0.86	0.90	0.89	0.83	0.86	0.82
ATE	28	0.62	0.77	0.93		0.78	0.83	0.94	0.94	0.93	0.93
CAR	30	0.63	0.78	0.83	0.40	0.69	0.70	0.83	0.85	0.85	0.79
DIC	29	0.57	0.81	0.86	0.44	0.72	0.77	0.82	0.86	0.85	0.81
DIU	27	0.58	0.74	0.93		0.77	0.87	0.92	0.92	0.89	0.93
ERY	30	0.49	0.53	0.59	0.38	0.45	0.44	0.53	0.60	0.58	0.56
IBU	12	0.67	0.78	0.68		0.76	0.76	0.78	0.64	0.67	0.65
KET	30	0.55	0.66	0.77		0.76	0.73	0.79	0.75	0.73	0.76
LOR	30		0.75	0.70		0.54	0.58	0.72	0.71	0.72	0.67
NAP	28	0.57	0.85	0.79		0.68	0.71	0.75	0.78	0.81	0.73
NOR	13	0.68	0.57	0.73		0.59	0.62	0.65	0.73	0.59	0.78
OFL	30	0.63	0.80	0.92	0.38	0.71	0.81	0.90	0.93	0.92	0.89
OXA	30	0.56	0.77	0.81		0.62	0.68	0.78	0.82	0.81	0.76
PFOS	27	0.54	0.73	0.56	0.47	0.63	0.54	0.50	0.54	0.58	0.47
PRO	30	0.60	0.71	0.90		0.68	0.82	0.91	0.92	0.89	0.90
ROX	29	0.39	0.55	0.46				0.38	0.48	0.50	0.39
SDZ	25	0.49	0.59	0.60		0.62	0.54	0.69	0.60	0.61	0.60
SMZ	30	0.37	0.49	0.49		0.50	0.41	0.54	0.49	0.49	0.45
TET	12	0.81				0.71					
TRI	27	0.63	0.73	0.94		0.80	0.86	0.95	0.93	0.92	0.95
Average removal		0.70	0.84	0.92	0.43	0.82	0.83	0.92	0.92	0.91	0.89

321

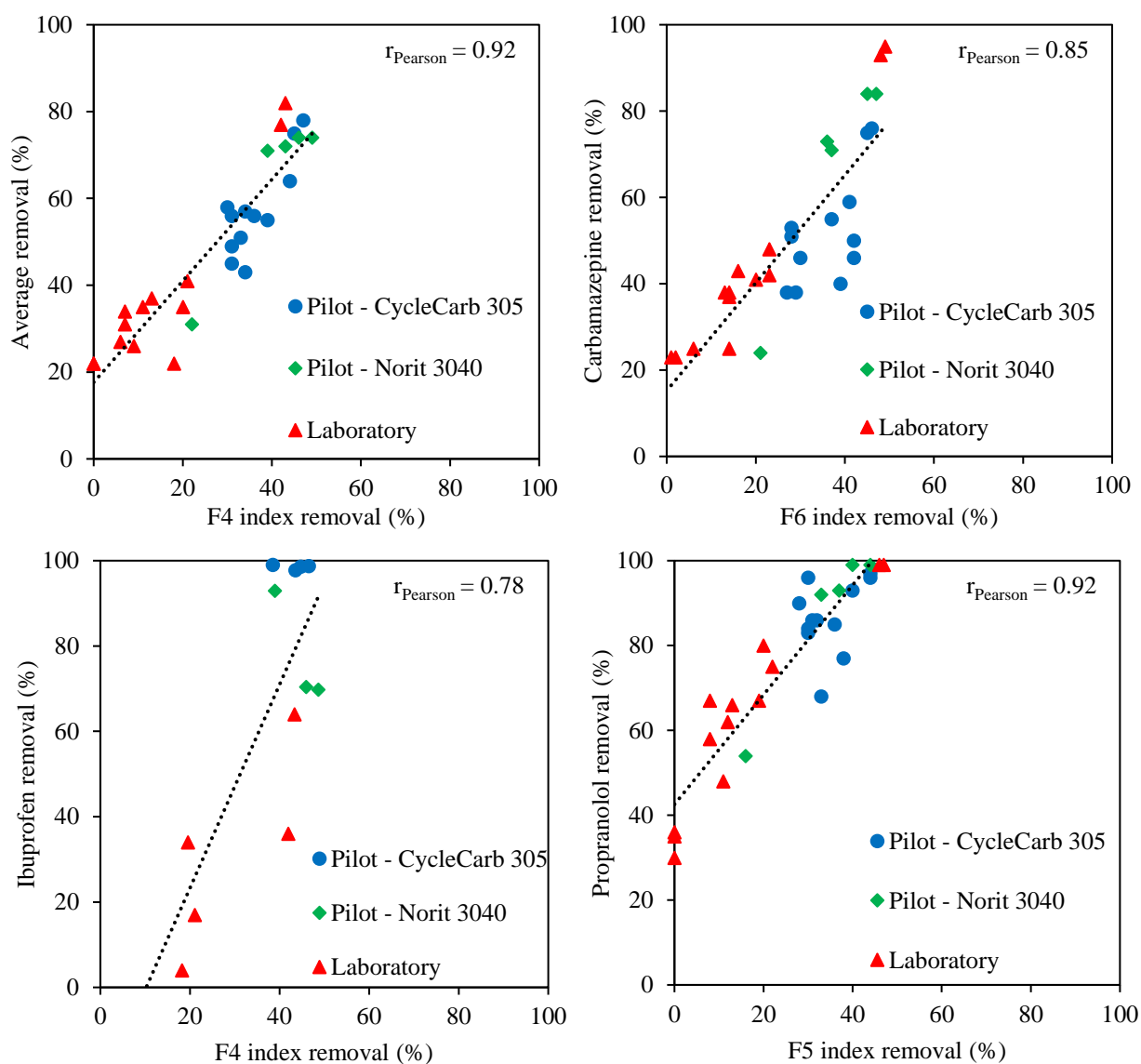
322 All the studied indexes provided statistically significant correlations with most OMPs (i.e. p-values < 0.05),
 323 despite the use of different brands of AC and various grain sizes, which suggests that these results could be
 324 transposed to other activated carbons. The correlation coefficients 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 UV₂₅₄ (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 (γ 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*

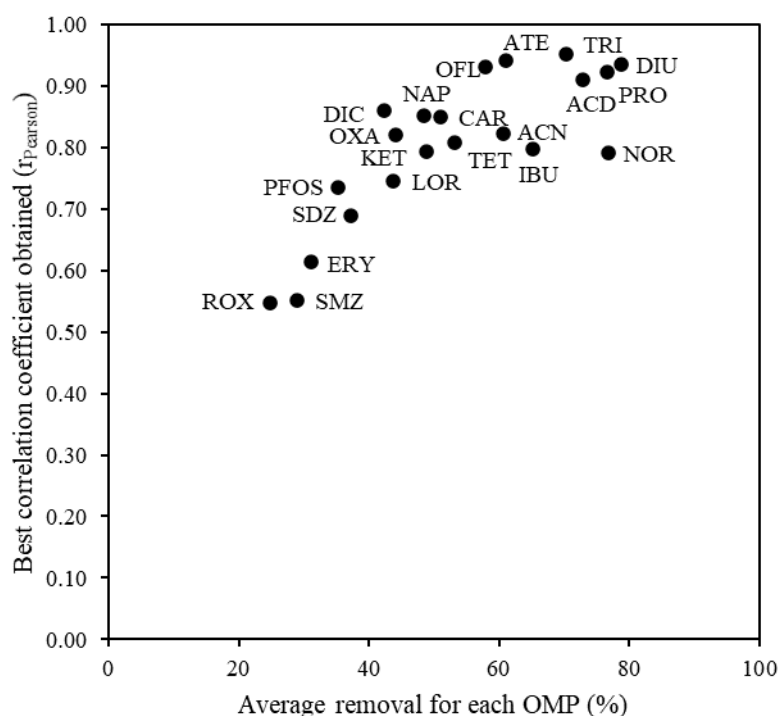
367 There was no apparent link between a specific physico-chemical property of OMPs and the indexes with
 368 which they were correlated. Complex interactions (e.g. electrostatic, hydrophobic and van der Waals) exist
 369 between AC, OMPs and DOM, and a single property cannot account for all these phenomena. 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- μ 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_{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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