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## **Fate of emerging and priority micropollutants during the sewage sludge treatment - Part 2: Mass balances of organic contaminants on sludge treatments are challenging**

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1 Fate of emerging and priority micropollutants during the sewage sludge treatments: case study of  
2 Paris conurbation - part 2: mass balances of organic contaminants on sludge treatments are  
3 challenging.

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14

## 15 **Highlights**

- 16 • 71 OCs mass balances were performed in full-scale sludge treatment facilities
- 17 • Screw decanter was selected as reference as its action is only physical
- 18 • Several OCs mass balances are frequently not correct in screw decanter
- 19 • The frequency of correct mass balances is significantly correlated to logKow

- 1
- Removal of the 71 OCs are reported in full-scale sludge digestion process

1 **Fate of emerging and priority micropollutants during the sewage sludge treatments -**  
2 **part 2: mass balances of organic contaminants on sludge treatments are challenging.**

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13

14 **Abbreviations**

15 AP, alkylphenols (n=4 including t-OP, ter-octylphenol, NP1EO, nonylphenol  
16 monoethoxylate, NP2EO, nonylphenol diethoxylate, NP, nonylphenol)

17

18 DMin, DMout, dry matter content of the sludge at the input and output of the process

19

20 LAS, linear alkylbenzene sulfonates (sum of the four congeners LAS-C10, LAS-C11, LAS-  
21 C12, LAS-C13)

22 LQ/LD, limit of quantification/limit of detection

23 OC, organic contaminants

24 PAE, phthalates (n=4 including DEP, diethyl phthalate, DnBP Di-n-butyl phthalate, BBP,  
25 benzylbutyl phthalate, DEHP, diethylhexyl phthalate)

26 PAH, polycyclic aromatic hydrocarbons (sum of 13 congeners including fluor, fluoranthene,  
27 BbF, benzo(b)fluoranthene, BaP, benzo(a)pyrene)

28 PCB, polychlorobiphenyls [sum of 20 congeners including PCB28 (3Cl), PCB180 (7Cl),  
29 PCB209 (10Cl)]

30 PFA, perfluorinated acids (n=2 including PFOA, perfluorooctanoic acids and PFOS,  
31 perfluorooctanesulfonic acids

32 PHP, pharmaceutical products

33 Qin, Qout, input and output flows of the process

34 SIAAP, Greater Paris sanitation authority

35 SRT, solid retention time

36 STP, sludge treatment plant

37 TSS, total suspended solid

38 WWTP, wastewater treatment plants

39 **Abstract**

40 This paper analyzes the fate of 71 priority and emerging organic contaminants all along the  
41 treatment trains of sewage sludge treatment facilities in Paris including dewatering by  
42 centrifugation, thermal drying and anaerobic digestion. It aimed at proposing and applying a  
43 mass balances calculation methodology to each process and pollutant. This data validation  
44 strategy demonstrated the complexity to perform representative inlet/outlet sampling and  
45 analysis campaigns at industrial scales regarding organic compounds and to propose options  
46 to overcome this issue. Centrifugation and drying processes only implied physical  
47 mechanisms as phase separation and water elimination. Hence, correct mass balance were  
48 expected observed for organic contaminants if sampling and analysis campaigns were  
49 representative. This was the case for hydrophobic and neutral compounds. For the other more  
50 hydrophilic and charged compounds, the mass balances were scarcely correct. Thus, the  
51 conventional sampling and analytical practices used with sludge should be questioned and  
52 adapted to better take into account the high heterogeneity of sludge and the evolution of  
53 matrix effect within sludge treatment processes on micropollutant determination. For the  
54 biological anaerobic digestion process where degradations can occur and removals can be  
55 observed, the mass balances were deeply interpreted for 60 contaminants. This process  
56 contributed to the elimination above 70% of 21 detected compounds including 16  
57 pharmaceuticals, 2 phthalates, 2 hormones and 1 perfluorinated compound. Removals of  
58 domperidone, propranolol, escitalopram, lidocaine, verapamil and cefoperazone under this  
59 condition were reported for the first time.

60

61 **Key-words**

62 Sewage sludge; organic compounds; mass balances; screw decanter; thermal drying;  
63 anaerobic digestion

64

65

66 **1. Introduction**

67 Wastewater treatment plants (WWTP) produce an important quantity of sewage sludge by  
68 treating suspended solids, organic matter and nutrients from human activities. Actually, about  
69 1 million ton dry matter (DM) of sludge are produced each year in France, against a total of  
70 11 million tons DM of sludge in all Europe (Kelessidis and Stasinakis, 2012).

71

72 Sludge are treated and conditioned before land application, incineration or landfilling (Fytili  
73 and Zabaniotou, 2008; Mininni et al., 2015). In France (> 70% of the DM mass), as well as in  
74 Europe in general (> 50%), the main pathway for sludge management is still land application.

75 The sewage sludge treatment aims to reduce fermentescibility, nuisances (particularly odour),  
76 pathogens content and vector attraction potential as well as to reduce bulk and improve their  
77 physical characteristics to aid handling, dewatering and acceptability for use on agricultural  
78 land. Current practices in Europe are based on the requirements of the 1986 Directive on the

79 use of sewage sludge in agriculture (86/278/EEC) that was transposed to national laws with  
80 specific limits on heavy metals, organic contaminants and pathogens in various member states  
81 (Mininni et al., 2015). In the new EU regulation on fertilising products (2019/1009), sewage  
82 sludge composts and digestates are unauthorized Component Material Categories which could  
83 prevent their use in agriculture with the product status.

84

85 A wide range of organic contaminants (OC) sorbs on sewage sludge during wastewater  
86 treatment (Clara et al., 2007; Mailler et al., 2014; Ruel et al., 2012) leading to their  
87 contamination by various compounds such as alkylphenols (AP), phthalates (PAE), polycyclic  
88 aromatic hydrocarbons (PAH), pharmaceuticals products (PHP), hormones or organotins  
89 (Bergé et al., 2012, 2013; Clarke and Smith, 2011; Mailler et al., 2017; Meng et al., 2016;  
90 Verlicchi and Zambello, 2015). Data on OC occurrence in sludge are nowadays extensive and  
91 diverse in the literature but the impact of sludge treatments on OC concentrations is difficult  
92 to assess considering that most studies do not distinguish different types of sludge from a  
93 given sludge treatment plant (STP); they mostly aimed at characterizing the contamination of  
94 raw and/or final treated sludge disregarding the type of sludge treatment. In addition, sludge  
95 sampling practises are still unsophisticated due to technical field constraints, they are mostly  
96 punctual samples taken from pipe or storage tank stitchings. Sludge being a very  
97 heterogeneous material, this lead to a sampling representativeness issue, in particular when  
98 assessing pollutants with highly variable properties such as hydrophilic and polar OC. Finally,



99 sludge treatment includes physical, chemical and microbiological manipulation and may  
100 involve mechanical dewatering, heating, chemical reactions and microbiological  
101 transformation processes that may influence the loss, or potential formation, of OC by  
102 volatilisation, biological or abiotic transformation, bound residues formation or extraction  
103 with excess liquors that returned to the inlet of the WWTP (Mailler et al., 2017).

104

105 In this context, a study was conducted aiming at i) featuring OC pattern of the different types  
106 of sludge from Paris conurbation and the contamination of residual waters from thermal  
107 drying and centrifugation, ii) assessing the industrial scale efficiency of four widespread  
108 sludge treatment processes to remove/decrease these contaminations based on mass balances  
109 and iii) questioning the representativeness of conventional sampling and micropollutant  
110 analysis in sludge practises. The first objective was treated in the part 1 paper (Mailler et al.,  
111 2017) while this part 2 paper deals with the second and third objectives, based on the same  
112 database.

113 Therefore, centrifugation, anaerobic digestion, thermal drying and cooking + press filtration  
114 were considered. A total of 71 OC including Water Framework Directive priority pollutants,  
115 PHP, hormones, perfluorinated acids (PFA), linear alkylbenzene sulfonate (LAS), AP, PAE,  
116 PAH and polychlorobiphenyls (PCB) were investigated (SI Table 1). As the objective of this  
117 study was also to apply mass balances calculations at industrial scale for each sludge

118 treatment process, OC in the residual water from thermal drying and centrifugation were  
119 monitored too.

120

121 The novelty of this paper is the of mass balances calculation at full-scale to this large  
122 spectrum of pollutants within three widespread sludge treatment processes, i.e. dewatering by  
123 centrifugation, anaerobic digestion and thermal drying, to question the sampling and  
124 analytical conventional practises and to analyse the behaviour of OC in those processes. Such  
125 mass balance analysis is an effective way to understand and model the fate of numerous OC  
126 in sludge treatment trains but to the best of our knowledge, its application to various  
127 treatments and OC is not available in the literature, especially based on sludge produced at  
128 real industrial scale STPs. In addition, sampling and analytical practises applied for  
129 micropollutant determination in sewage sludge were never questioned.

130

131

## 132 **2. Materials and methods**

133 The data presented in this study are calculated based on OC contents found in campaigns  
134 carried out in 2013-2014 and published in Mailler et al. (2017).

### 135 **2.1. Sludge treatment plants monitored**

136 STPs from three SIAAP WWTPs were sampled: Seine Aval, Seine Centre and Seine  
137 Gresillons. They treat sludge produced by the treatment of wastewater from Paris  
138 conurbation. The Seine Centre plant has a treatment capacity of 240,000 m<sup>3</sup> of wastewater per  
139 day. Its sludge treatment consists in dewatering of mixed biological and physicochemical

140 settling sludge by centrifugation (Guinard D6LP30HBHF screw decanter) with cationic  
141 polymer addition ( $\approx 5.5$  kg polyacrylamide polymer/ton dry matter (DM)) resulting in a  
142 production of almost 21,000 tons DM of centrifuged sludge per year (SIAAP source). The  
143 residence time in screw decanters is very short, estimated to be several minutes. The  
144 centrifuged sludge is then incinerated. The Seine Aval plant has a treatment capacity of  
145 1,700,000 m<sup>3</sup> of wastewater per day (biggest in Europe) and produces more than 55,000 tons  
146 DM of treated sludge per year (SIAAP source). After thickening, sludge is digested in two-  
147 stage mesophilic (37°C) anaerobic digesters, which transforms an important part of organic  
148 matter (about 40%) into biogas, with a total residence time of 15-20 days. Then digested  
149 sludge is dewatered by high pressure and temperature cooking followed by press filtration  
150 (Porteous process). The Seine Gresillons plant has a treatment capacity of 300,000 m<sup>3</sup> of  
151 wastewater per day. Sludge treatment consists in a thickening by centrifugation (GEA UCD-  
152 536-50-34 screw decanter) with cationic polymer addition ( $\approx 4.5$  kg polyacrylamide  
153 polymer/ton DM), an anaerobic digestion (mesophilic or thermophilic digesters), a dewatering  
154 of digested sludge by centrifugation (GEA UCD-536-50-34 screw decanter) with cationic  
155 polymer addition ( $\approx 10$  kg polyacrylamide polymer/ton DM) and then a thermal drying (thin  
156 film rotating dryer VOMM or belt dryer ANDRITZ) step. The residence time in thermal  
157 dryers is very short, estimated to be several minutes. A part of the thermal drying process  
158 used in this plant operates at a high temperature (255-280°C for thin film rotating dryer  
159 VOMM) compared to conventional dryers used for the other part of thermal drying (125°C

160 for belt dryer ANDRITZ). The characteristics of each WWTP and STP, and the full layout of  
161 each STP, are given in supporting material of Mailler et al. (2017).

162

## 163 **2.2. Data set and monitored pollutants**

164 Different types of sludge have been sampled (punctual samples in the storage tank  
165 considering the estimated residence time in the processes) within the three studied STPs in  
166 April-May 2013 and April 2014 (3 to 4 consecutive weeks in 2 consecutive years in order to  
167 assess the OC content variability). The complete sampling strategy is described in Mailler et  
168 al. (2017). In this second paper, the OC concentration data on raw sludge and centrifuged  
169 sludge samples (n = 7), as well as residual water from centrifugation (n = 3), from Seine  
170 Centre WWTP are considered and treated together to evaluate the mass balance of OC in the  
171 dewatering centrifugation process. Sampling considered the very short residence time.  
172 Similarly, OC data on raw and digested sludge samples (n = 7) from Seine Aval, that were  
173 sampled considering a solid retention time of 16 days, are considered together to evaluate the  
174 mass balance of the mesophilic anaerobic digestion process. Finally, OC data on centrifuged  
175 sludge and thermal dried sludge samples (n = 6), as well as residual water samples from  
176 thermal drying (n = 3), from Seine Gresillons are considered together to evaluate the mass  
177 balance of the thermal drying process respectively. Similarly to centrifugation, the short  
178 residence time was considered during sampling.

179 71 emerging OC, including PHP (n = 18), hormones (n = 6), PFA (n = 2), LAS (n = 4), PAH

180 (n = 13), PCB (n = 20), AP (n = 4) and PAE (n = 4), have been analyzed in sludge samples  
181 (inlet and outlet of processes) and in residual water samples from centrifugation and from  
182 thermal drying. The 4 PAE and t-OP were only measured in 2014. The 66 other compounds  
183 were analyzed in 2013 and 2014 just after sampling. Due to its high DM content, the liquid  
184 samples from centrifugation were either extracted entirely or separation of dissolved and  
185 particulate phases was made before extraction of each sub-sample. The liquid samples from  
186 thermal drying were directly extracted. For sludge samples, the total OC concentration was  
187 measured after freeze drying and grinding of the raw samples. Briefly, analytical methods are  
188 based on specific extraction methods (QuEChERS, Accelerated Solvent Extraction, Solid  
189 Phase Extraction) coupled to Liquid Chromatography-tandem mass spectrometer detector for  
190 PHP and PFA, to Liquid Chromatography-fluorescence detector for PAH and nonylphenols,  
191 to Gas Chromatography-mass spectrometer detector for hormones, phthalates and  
192 octylphenols and to Gas Chromatography-high resolution mass spectrometer detector for  
193 PCB. The complete list and analytical procedures information are given in Mailler et al.  
194 (2017).

195

### 196 **2.3. Mass balance assessment**

197 A data validation strategy based on mass balance assessment was performed on the three  
198 sludge treatment processes. First, the daily process DM performances during sampling  
199 campaigns were compared to 3 to 4 months of operation to check that days of sampling are

200 representative of a normal operation of processes. Then the DM mass balances were  
201 calculated in order to check the efficiency of processes and the representativeness of punctual  
202 samples. The verification of DM mass balance is a crucial prerequisite to validate the  
203 representativeness of samples, considering that getting reliable data on operational parameters  
204 was very challenging at industrial scale. If DM mass balance is validated, OC mass balance is  
205 calculated for compounds detected in both input and output sludge samples during at least one  
206 campaign considering the following rules.

207 *Centrifugation:* The raw sludge mass load was calculated using the sludge daily volumetric  
208 flow ( $\text{m}^3/\text{d}$ ) and the average DM content ( $\text{g DM/L}$ ) of the day measured by the WWTP in  
209 routine. The mass load of centrifuged sludge was estimated using the daily DM flow ( $\text{t DM/d}$ )  
210 of the campaign under consideration, the wet mass flow ( $\text{t wet sludge/d}$ ) and the average DM  
211 content ( $\text{g DM/L}$ ) of the day measured by the WWTP in routine. To quantify the mass load of  
212 the residual water, its daily volumetric flow ( $\text{m}^3/\text{d}$ ) was first calculated considering a DM  
213 balance in the centrifugation process (difference between DM mass flow in raw sludge and  
214 centrifuged sludge) and then multiplied by the average particulate content measured in the  
215 residual water by the WWTP in routine. SI Table 2 explains the calculations made to assess  
216 OC mass loads in the centrifugation process of Seine Centre. Once the OC mass loads were  
217 calculated, OC mass balances were established: considering the sampling and analytical  
218 uncertainties, a mass balance was considered correct / valid if the difference between input  
219 and output mass flows was +/- 30%.

220 *Thermal drying:* the mass loads of centrifuged sludge were calculated using the sludge daily  
221 volumetric flow ( $\text{m}^3/\text{d}$ ) and the average DM content ( $\text{g DM/L}$ ) of the day measured by the  
222 WWTP in routine. The residual water mass loads were calculated using the water daily  
223 volumetric flow ( $\text{m}^3/\text{d}$ ) estimated by considering that only water is removed from sludge and  
224 using the difference of DM content between dried and centrifuged sludge and the sludge daily  
225 volumetric flow. Regarding the extremely low suspended solids concentrations content in the  
226 residual water compared to sludge, this simplification is acceptable. The mass loads of  
227 thermal dried sludge were calculated using their daily volumetric flows ( $\text{m}^3/\text{d}$ ) estimated as  
228 the difference between the centrifuged sludge and residual water volumetric flows. SI Table 2  
229 explains the calculations realized to evaluate OC mass loads in the thermal drying process of  
230 Seine Gresillons. Same criteria of +/- 30% was used to say if OC mass balance is correct or  
231 not.

232 *Anaerobic digestion:* mass loads were not calculated for this process considering that the  
233 volumetric flow is equal in the inlet and outlet of the anaerobic digestion unit. Then,  
234 concentrations in  $\text{ng/L}$  were considered to evaluate mass balances and removals of OC  
235 directly. Removals were calculated for each sampling period because sampling took into  
236 account the HRT of the unit. If output concentrations were lower than the LD, this latter was  
237 used to calculate the removal.

238

239

### 240 **3. Results and discussion**

241 Three different types of sludge treatment process were assessed in this work. The way to  
242 assess their role in the fate of OC was fully different. Indeed, centrifugation and thermal  
243 drying are physical processes implying respectively phase separation and water elimination.  
244 Except volatilization and thermal degradation that could theoretically occur in thermal drying,  
245 no removal of OC should be observed on both processes considering the very short residence  
246 time, only OC distribution between aqueous and solid phases (OC content was measured in  
247 both phases) should be observed with correct mass balances. For the biological process, as  
248 anaerobic conditions may favor OC transformation, removals can be calculated.

249

#### 250 **3.1. Mass balance of OC in dewatering by centrifugation**

##### 251 **3.1.1. DM mass balance**

252 Due to the lack of data on the volumetric flow of the residual water, we assumed a correct  
253 DM mass balance to calculate it. In this kind of process with very short residence time, loss of  
254 DM is assumed negligible which guarantee the feasibility of our calculation. Moreover, this  
255 sampling strategy and methodology of calculation were validated by Mailler et al. (2014)  
256 demonstrating a conservative mass balance for trace metals, i.e. for zinc with  $731 \pm 133$  and  
257  $729 \pm 142$  mg/kg DM respectively for inlet and outlet sludge samples as no zinc was found in  
258 the aqueous phase. In order to validate the process performances, the conventional operation  
259 parameters measured during the sampling periods were compared to the average data



260 measured in routine by SIAAP in the corresponding three months (Table 1). The results  
 261 confirmed the normal operation of the process during the sampling period and the  
 262 representativeness of samples. This process is very repeatable in each period with a stable DM  
 263 concentration factor of  $5.4 \pm 0.3$  in 2013 and very efficient with an aqueous phase containing  
 264 less than 4% of the initial DM in 2013 (Table 1). Similar stability and efficiency were  
 265 observed in 2014. Mass balances were thus calculated for the detected OC.

266

267 **Table 1** Performances of the centrifugation processes during the sampling period and  
 268 comparison with average values from the daily operation monitoring of the facilities on the  
 269 corresponding 3 or 4 months' period. CS for centrifuged sludge, RS for raw sludge, CW for  
 270 residual water of centrifugation

Parameter	Proportion of DM			
	Concentration factor	lost in residual water	$Q_{out\_CS}$	$Q_{out\_CW}$
Equation	$DM_{out\_CS}/DM_{in\_RS}$	$TSS_{out\_CW}/DM_{in\_RS}$ $\times 100$	$Q_{in\_RS}/\text{concentration}$ factor	$Q_{in\_RS} - Q_{out\_CS}$
Unit	-	in %	in m <sup>3</sup> /d	in m <sup>3</sup> /d
April, 9 <sup>th</sup> , 2013	5.4	2.0	245	1067
April, 30 <sup>th</sup> , 2013	5.3	3.5	317	1360
May, 14 <sup>th</sup> , 2013	5.3	5.3	285	1222
May, 22 <sup>th</sup> , 2013	5.9	3.1	325	1583
June, 11 <sup>th</sup> , 2013	5.3	5.0	296	1281

April, 1 <sup>st</sup> , 2014	6.0	2.7	213	1079
April, 8 <sup>th</sup> , 2014	4.8	1.9	453	1715
April, 15 <sup>th</sup> , 2014	4.5	3.2	405	1429
<b>Average ± STD (5 d of sampling in 2013)</b>	<b>5.4 ±0.25</b>	<b>3.7 ±1.3</b>	<b>293 ±31</b>	<b>1302 ±189</b>
<i>Average ± STD of daily operation data in april, may, june 2013</i>	<i>5.2 ±0.4</i>	<i>3.2 ±1</i>	<i>264 ±64</i>	<i>1111 ±270</i>
<b>Average ± STD (3 d of sampling in 2014)</b>	<b>5.1 ±0.8</b>	<b>2.6 ±0.6</b>	<b>357 ±127</b>	<b>1407 ±318</b>
<i>Average ± STD of daily operation data in march, april, may, june 2014</i>	<i>5.3 ±0.5</i>	<i>3.6 ±2.1</i>	<i>269 ±84</i>	<i>1131 ±318</i>

271

272

273

### 3.1.2. OC mass balance

274 For several compounds (n=11), essentially PHP and PFA, no mass balance could be

275 calculated because OC concentration in either raw sludge or centrifuged sludge or both was

276 lower than the LQ. This was the case for ivermectine in both year and for azithromycin,

277 cefoperazone, escitalopram, glybencyclamide, lidocaine, miconazole, PFOA, propranolol,

278 sulfamethoxazole, verapamil, in 2014. Five of these compounds (azithromycin, lidocaine,

279 PFOA, propranolol, verapamil) were quantified in the residual water whereas they were not  
 280 detected in the inlet or/and outlet of the centrifugation process. In this water matrix, the LQ  
 281 was determined really low with a lower matrix effect than in the solid matrices, explaining  
 282 their quantification.

283 An OC mass balance was calculated for all the sampling campaigns for 59 (2013) and 56  
 284 (2014) compounds, and for 6 (2013) and 4 (2014) more compounds for at least one campaign  
 285 (SI Tables 3 and 4). The reason for no calculation was the same as mentioned above. Once  
 286 validation of mass balances was assessed (SI table 4), the compounds were grouped according  
 287 to the frequency of calculation of a correct mass balance (Table 2) and this parameter was  
 288 plotted against physicochemical properties in order to explain the difficulties to get correct  
 289 mass balance (Fig 1).

290

291 **Table 2** Classification of the compounds according to the frequency of calculation of a correct  
 292 mass balance and according to the range of concentration (if inferior or superior to 5 times the  
 293 LQ) on the centrifugation and thermal drying processes. Underlined compounds are those  
 294 found in the residual waters of each process. For families like PAH or PCB, calculation was  
 295 also done on the sum ( $\Sigma$ ) of all congeners. For compounds abbreviation see SI Table 1.

	Centrifugation	Thermal drying
	<b>Frequency &gt; 0.7 (group 1)</b>	
$\mu P_{in}$ and $\mu P_{out} > 5 \times LQ$	<u>NP</u> , <u>BBP</u> , <u>LAS-C11</u> , <u>PFOS</u> ,	<u>NP</u> , BaP, BbF, $\Sigma$ PAH (13),

	mico, <u>LAS-C10</u>	Fluor, LAS-C10, LAS-C13
<5 × LQ	EE2, <u>BbF</u> , E1, <u>BaP</u> , <u>PCB209</u>	E1, PCB180, PCB209, ΣPCB (20)

**0.3 < Frequency < 0.7 (group 2)**

	<u>Fluor</u> , <u>DEHP</u> , <u>esci</u> , <u>vera</u> , <u>lora</u> , <u>t-OP</u> , <u>DEP</u> , <u>DnBP</u> , <u>domp</u>	cbz, cip, nor, ofl, para, <u>azi</u> , mico, LAS-C11, LAS-C12, <u>tram</u>
$\mu P_{in}$ and $\mu P_{out} > 5 \times LQ$		

<5 × LQ	$\alpha E2$ , <u>PCB28</u> , <u>PCB180</u> , ( <u>ΣPCB (20)</u> , <u>ΣPAH (13)</u> )	$\alpha E2$ , EE2, PCB28
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**Frequency < 0.3 (group 3)**

	<u>LAS-C12</u> , <u>LAS-C13</u> , cbz, <u>propra</u> , <u>cip</u> , <u>nor</u> , <u>para</u> , glyben, <u>ofl</u>	<u>propra</u> , <u>esci</u> , glyben, lora, <u>vera</u> , <u>domp</u>
$\mu P_{in}$ and $\mu P_{out} > 5 \times LQ$		

<5 × LQ	<u>tram</u> , PFOA, <u>lido</u> , cefo, <u>azi</u> , smx	<u>PFOS</u> , <u>lido</u>
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298

**Fig 1** Impact of both logKow and charge at pH 7 of compounds on the frequency of calculation of correct mass balances in centrifugation (a and

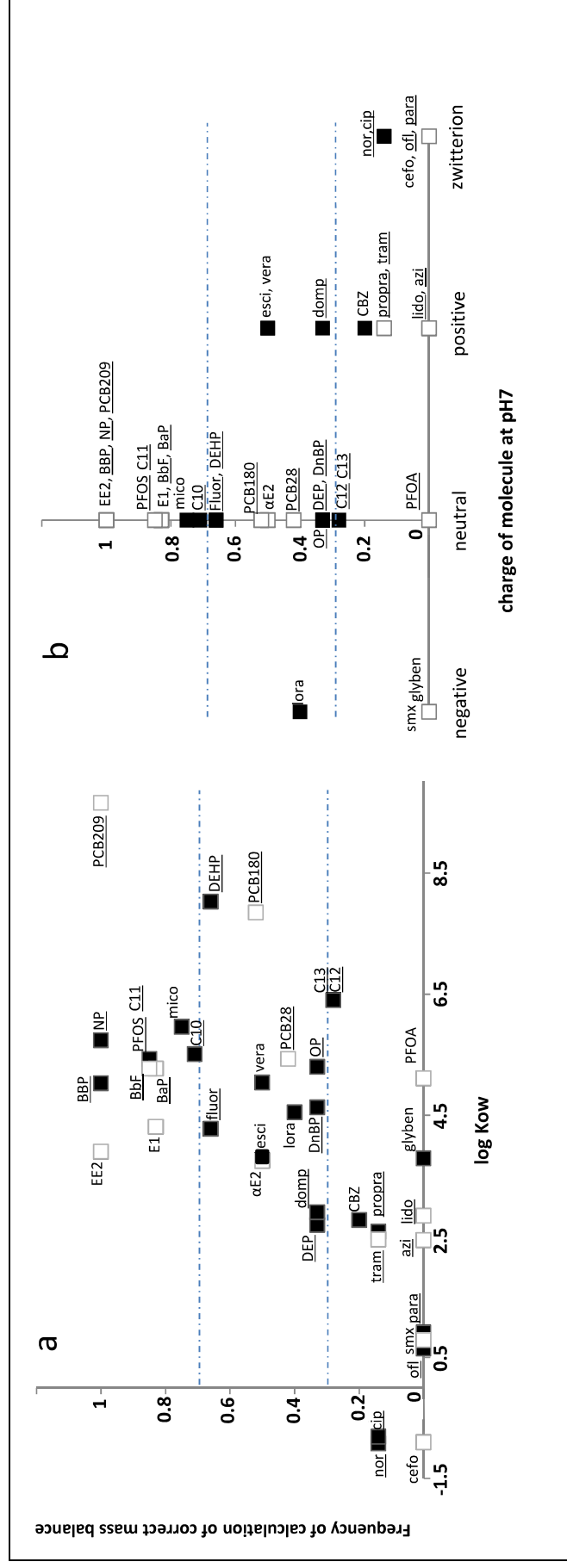
299

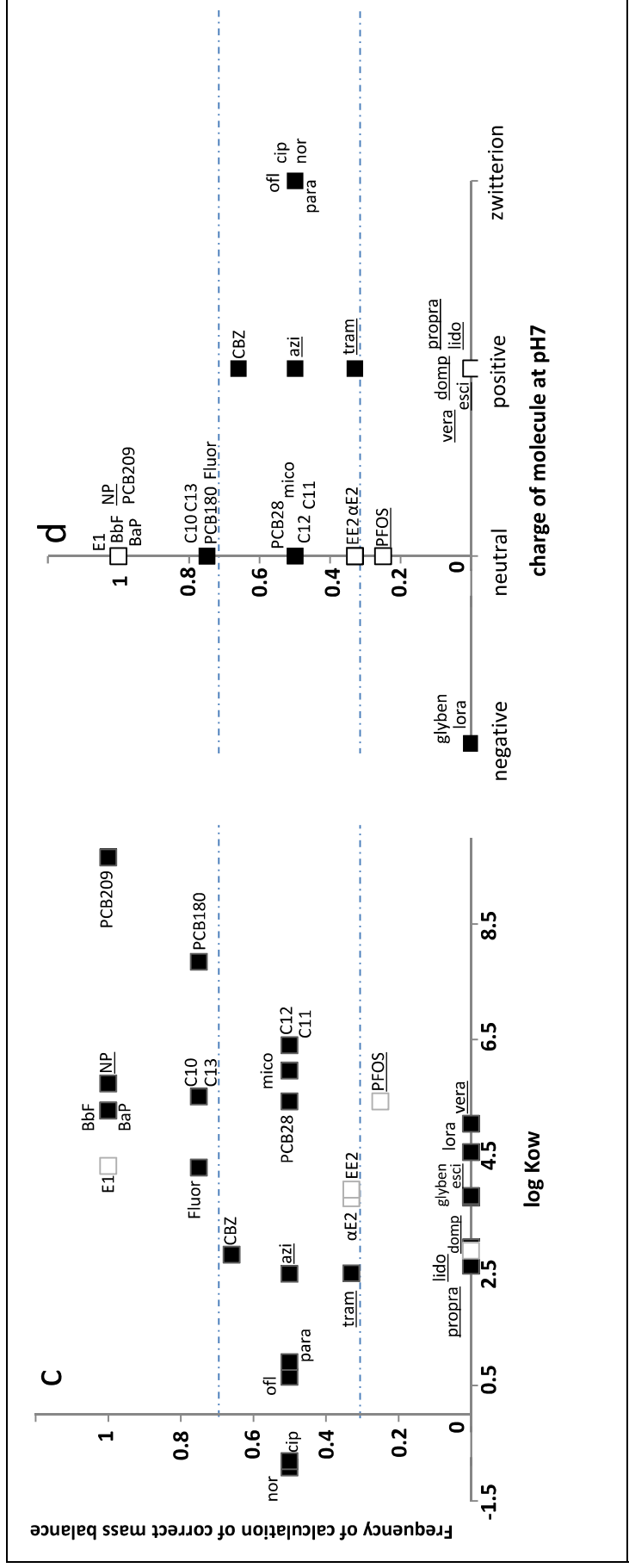
b) and thermal drying (c and d). Black square for compounds that are always quantified above 5 times the LQ, white square if one measure is

300

below 5 times LQ. Underlined compounds are those found in the residual water of centrifugation or thermal drying. For compounds abbreviation

301 see SI Table 1.





303 As previously discussed, the centrifugation process was very conservative for DM and trace  
304 metals. As shown in figure 1 and table 3, mass balances were also frequently correct for 11  
305 compounds including NP, some hormones, some PAH and PCB, BBP (one of the phthalates  
306 with the highest level in sludge), 2 LAS, one PHP (miconazole) and one PFA (PFOA). These  
307 compounds from group 1 are all neutral compounds together with log Kow above 3.5. They  
308 present concentration either lower than  $5 \times \text{LQ}$  (hormones) or greater than  $5 \times \text{LQ}$  (NP). They  
309 also present fluctuating concentrations in raw sludge (BbF load range between 2 and 28 g/d,  
310 SI table 3). Eight of these compounds were quantified in the residual water at less than 5% of  
311 the inlet mass of the centrifuge decanters, mainly because they were sorbed on the remaining  
312 suspended solids; this underlines the low contribution of this aqueous fraction to their mass  
313 balance assessment. However, if the inlet mass is high, this OC fraction present in the residual  
314 water may represent a non-negligible input on the total load of the WWTP; this point has to  
315 be considered to assess the global performances of WWTP.

316 The group 2 was characterized by an intermediate frequency (between 30 and 70%) of  
317 calculation of a correct mass balance. Among the compounds, some persistent hydrophobic  
318 compounds like PCB, DEHP, fluor and t-OP, had sometimes incorrect mass balances (SI table  
319 4) due to higher mass in the outlet. The other OCs of group 2 are 4 PHP (escitalopram,  
320 verapamil, loratidine, domperidone) with concentrations greater than 5 times the LQ and  
321 presenting positive and negative mass balances, the same was observed for  $\alpha\text{E2}$  whose  
322 concentrations were however close to the LQ. In this group 2, compounds have high logKow

323 between 2.5 and 8 and only 4 compounds out of 12 are charged.

324 The group 3 with mass balances frequently not correct includes compounds that are more  
325 hydrophilic (11/15 with  $\log K_{ow} < 3$ ), mainly charged (12/15) and have concentrations close to  
326 the LQ (6/15) (figure 1). This unbalanced mass was mainly due to higher mass load in inlet  
327 than outlet. Moreover, in this group, compounds like tramadol, propranolol, lidocaine and  
328 azithromycin were quantified in the residual water at high proportion up to 90% of the outlet  
329 for azithromycin, meaning that it is essential in this case to measure the compounds in the  
330 residual water. It also includes 4 hydrophobic OCs: the two highly concentrated high  
331 molecular weight LAS and PFOA, which were very poorly quantified, and the negatively  
332 charged glybencyclamide (with quantification of higher mass loads in the outlet). The mass  
333 balance of the 3 hydrophilic well quantified fluoroquinolones was never correct even if they  
334 are easily sorbed to sludge thanks to their charge (cation exchange and bridging).  
335 Carbamazepine and propranolol, hydrophobic compounds and positively charged at pH7,  
336 accurately quantified at 100 times the LQ, are also present in the group 3 and presented higher  
337 mass load in the inlet than in the outlet of the centrifuge decanters. For the last 5 PHP and  
338 PFOA, their presence at concentration very close to the LQ may explain that the mass balance  
339 was never correct.

340 Spearman (non-normal distributions) correlation tests (XL Stat software) were performed and  
341 indicated significant positive correlations ( $p\text{-value} < 0.05$ ) between  $\log K_{ow}$  and the frequency  
342 of calculation of correct mass balances within screw decanter, both for compound detected



343 below ( $r = 0.673$ ) and above 5 time the LQ ( $r = 0.675$ ). For the compounds charge, a negative  
344 correlation is significant only for compounds detected above 5 time the LQ ( $r = -0.426$ ). Other  
345 properties like molar mass or topological surface area were tested but they did not provide  
346 further explanation.

347

348 These results demonstrated the complexity to establish OC mass balance in the centrifugation  
349 process for compounds with concentration near the LQ (due to uncertainties). The presence of  
350 positive or/and negative charges in the molecules could also explain this difficulty of mass  
351 balance calculation. Indeed, the addition of cationic polymers during centrifugation may  
352 change the interactions between OC and organic matter, that could induce changes in  
353 extracting yield and analysis (matrix effect) that are not compensated by the addition of  
354 deuterated compounds (no ageing). Analytical practices should then be adapted to consider  
355 this, with for example method validation for each type of matrix. In addition, the sampling  
356 strategy should be questioned, even if it was validated based on DM and by comparing to the  
357 average operation in a longer period (insufficient validations). Indeed, sludge is a very  
358 variable and heterogeneous material and OC concentrations in sludge are then very variable.  
359 The punctual samples considering the sludge residence time in the process could be sufficient  
360 for either highly concentrated or stable parameters such as DM, trace metals or some  
361 hydrophobic OC but insufficient for trace and less stable parameters such as hydrophilic and  
362 charged OC whose interactions with matrix would change according to the applied conditions.

363 The implementation of more thorough sampling strategy should be evaluated in order to  
364 reduce sample heterogeneity by (1) implementing 24h composite sampling systems adapted to  
365 sludge, (2) increasing the number of composite samples for one batch, , and (3) collecting  
366 multiple samples from a type of sludge taken from various sampling spots to get a more  
367 representative composite punctual sample.

368

369

## 370 **3.2. Mass balance of OC in thermal drying**

### 371 **3.2.1. DM mass balance**

372 The drying process was very repeatable in each sampling week of 2013 with a stable DM  
373 concentration factor of  $3.5 \pm 0.2$  and its performances were very similar to those calculated on  
374 a three months' period (Table 3, SI Table 5). The calculated DM mass balance was correct  
375 with a difference between inlet and outlet always lower than 30% (SI fig 1). The TSS  
376 concentration in the residual water, only measured in 2014, underlined a very high efficiency  
377 of separation with residual water containing extremely low concentrations of DM. The  
378 measured and calculated operation data presented a higher variability in 2014 compared to  
379 2013. In 2014, the first campaign could not be considered due to the impossibility to obtain  
380 the volumetric flow data for the centrifuged sludge inlet. Moreover, the DM mass balance  
381 calculated for the second campaign was not correct with a difference between inlet and outlet  
382 DM greater than 57%, highlighting a clear sampling representativeness issue. For these

383 reasons, OCs mass balances were calculated for all weeks in 2013 and only one week in 2014.

384

385 **Table 3** Performances of the thermal drying processes during the sampling period and

386 comparison with average values from the daily operation monitoring of the facilities on the

387 corresponding 3 or 4 months' period. nm, not measured; TDS for thermal dried sludge; CS for

388 centrifuged sludge; TDW for residual water of thermal drying process.

Parameter	Concentration factor	Proportion of DM		
		lost in residual water	$Q_{out\_TDS}$	$Q_{out\_TDW}$
Equation	$DM_{out\_TDS}/DM_{in\_CS}$	$TSS_{out\_TDW}/DM_{in\_CS} \times 100$	$Q_{in\_CS} - Q_{out\_TDW}$	$Q_{in\_CS} \times [DM_{out\_TDS} - DM_{in\_CS}]$
Unit	-	in %	in m <sup>3</sup> /d	in m <sup>3</sup> /d
April, 9 <sup>th</sup> , 2013	3.4	nm	19.5	33.4
April, 30 <sup>th</sup> , 2013	3.6	nm	14.6	27.1
May, 14 <sup>th</sup> , 2013	3.3	nm	18.7	34.1
May, 22 <sup>th</sup> , 2013	-	nm	-	-
June, 11 <sup>th</sup> , 2013	3.6	nm	21.8	44.0
April, 1 <sup>st</sup> , 2014	2.0	0.010	-	-
April, 8 <sup>th</sup> , 2014	2.6	0.025	13.5	17.0
April, 15 <sup>th</sup> , 2014	3.6	0.003	32.5	41.8
<b>Average ± STD (5</b>				
<b>d of sampling in</b>	<b>3.5 ±0.2</b>	<b>-</b>	<b>18.6 ±3.0</b>	<b>34.6 ±7.0</b>
<b>2013)</b>				

*Average ± STD of  
daily operation data  
in*

	3.5 ±0.3	-	16.2 ±6.	28.5 ±11.0
--	----------	---	----------	------------

*april, may, june  
2013*

**Average ± STD (3**

<b>d of sampling in</b>	<b>2.7 ±0.8</b>	<b>0.014 ±0.010</b>	-	-
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**2014)**

*Average ± STD of  
daily operation data  
in*

	3.5 ±0.4	-	-	-
--	----------	---	---	---

*march, april, may,  
june 2014*

389

390

391

**3.2.2. OC mass balance**

392

For 5 compounds in 2013 (cefoperazone, ivermectine, sulfamethoxazole, PFOA, NP2EO) and

393

15 compounds in 2014 (azithromycin, carbamazepine, cefoperazone, domperidone,

394

escitalopram, glybencyclamide, ivermectine, lidocaine, loratidine, miconazole, propranolol,

395

sulfamethoxazole, tramadol, verapamil, PFOA), no OC mass balance could be calculated

396

because OC concentration in either centrifuged sludge (inlet of thermal drying process) or

397

thermal dried sludge or both were lower than the LQ. However, six of them (PFOA,

398 azithromycin, lidocaine, sulfamethoxazole, tramadol, verapamil) were quantified in the  
399 residual water extracted from the process even if not quantified in sludge, 4 of them were  
400 similarly quantified in the residual water of the centrifugation process. As previously stated,  
401 in such aqueous matrix, the LQ is very low with a lower matrix effect than in the solid matrix,  
402 allowing OC quantification at lower levels. This means they were present in the sludge but  
403 not quantified.

404 An OC mass balance is calculated for all the considered sampling weeks for 51 (2013) and 56  
405 (2014) compounds and for 10 more compounds in 2013 for at least one week (SI Table 3).

406 The reason for no calculation is the same as previously mentioned. Once the validation of  
407 mass balances was assessed (SI Table 6), the compounds were grouped according to the  
408 frequency of quantification of a correct mass balance (Table 3). It is important to note that  
409 only one or two mass balances were calculated for some compounds due to data lower than  
410 LQ (azithromycin, estrone, glybencyclamide, loratidine, miconazole) or lack of data  
411 (phthalates). By comparison, more compounds presented correct mass balances (Table 3) in  
412 thermal drying process than in centrifugation process but trends observed by linking it to  
413 physicochemical properties were less interpretable (Fig 1). Spearman (non-normal  
414 distributions) correlation tests were performed and indicated a significant positive correlation  
415 ( $p$ -value  $< 0.05$ ) only between  $\log K_{ow}$  and the compounds detected above 5 time the LQ ( $r =$   
416 0.437). Due to possible volatilization during this thermal process, other properties like  
417 volatility (expressed by means of Henry constant or vapor pressure) were considered but it did

418 not provide further explanation. The number of molecules quantified in the residual water is  
419 low (11/71) and their concentrations contribution to mass balances were low, the fraction  
420 being lower than 0.5% of the input mass except once for tramadol at 10% (SI Table 6).  
421 Compounds with correct mass balances included neutral persistent organic molecules such as  
422 all PAH, all PCB, surfactants, phthalates and one hormone. The group with intermediate  
423 frequency of correct mass balance gathered hydrophilic and hydrophobic compounds, either  
424 neutral, zwitterion or positively charged, mainly highly concentrated, except for hormones.  
425 For 7 negatively and positively charged PHP and PFOS, the mass balance was frequently not  
426 correct with mainly higher mass load measured in the output of the dryer (5/8), even for  
427 compounds with concentration largely above 5 time the LQ (6/8). In this group 3, 6  
428 compounds were quantified in the residual water. It seems thus difficult to link the OC  
429 behavior during drying process to their physicochemical properties except for very  
430 hydrophobic and neutral compounds for which mass balances are frequently correct. Some  
431 heat sensitive molecules could be altered during this process resulting in a lower outlet mass,  
432 which is only observed for 3 compounds in the group 3. For compounds that interact with  
433 organic matter thanks to cation exchange and bridging, the change in organic matter structure  
434 that could occur during this high temperature process may modify the interactions with OC  
435 and thus interfere with the extraction and analysis efficiency. This could explain the behavior  
436 observed for the charged compounds in the group 3, which were also quantified in the  
437 residual water.

438

439 **3.3. Removal of OC in anaerobic digestion**

440 As shown in SI Table 7, average removals of both DM and volatile solids calculated in the 3  
441 or 4 weeks of sampling were similar to removals observed in digestion during the  
442 corresponding three months' period, attesting of the good performances of the anaerobic  
443 digestion and its time stability. Considering that the volumetric flow is equal in the inlet and  
444 outlet of the anaerobic digestion unit, concentrations in ng/L were directly considered to  
445 assess mass balances and calculate removals of OC.

446 Two (in 2013) and 4 (in 2014) samples were considered to calculate OC removal on the  
447 anaerobic digestion unit. For 2 compounds, glybencyclamide and ivermectine, no removal  
448 was calculated due to inlet and outlet concentrations near and lower than the LQ (SI Table 8).  
449 In 2014, 5 more compounds, PFOA, sulfamethoxazole, azithromycin, cefoperazone and  
450 loratidine also presented inlet and outlet concentrations under the LQ, the same for  
451 carbamazepine but only for one week. In 2013, for these compounds, removals could be  
452 calculated but concentrations remained low which suggests to consider these removals with  
453 caution due to high uncertainty. One compound, miconazole, presented inlet concentrations  
454 lower than the LQ but outlet concentrations largely above the LQ for the 4 weeks in 2014  
455 whereas it was the contrary for the 2 weeks in 2013. Thus, its high removal calculated in 2013  
456 has to be also considered with caution (Table 4).

457

458 **Table 4** Class of removals of OC during anaerobic digestion. Underlined molecules are only  
 459 present in one class of removal. In brackets: number of weeks in which removal was  
 460 calculated out of 6 available data. For PAH (sum 13), PCB (sum 20), LAS (sum 4). \*data on  
 461 miconazole have to be considered with caution due to high removals in 2013 and negative  
 462 mass balances in 2014. For compounds abbreviation see SI Table 1.

<b>Class of removal</b>	<b>Compounds with low concentrations</b>	<b>Compounds with high concentrations</b>
<b>In %</b>	<b>[OC] &lt; 5*LQ</b>	<b>[OC] &gt; 5*LQ</b>
Removal < 30	E3(3), T(1), $\alpha$ EE2(1), $\alpha$ E2(2), $\beta$ E2(2)	para(1), cbz(1), ofl(1), nor(2), cip(1), LAS(2), NP2EO(2), <u>PAH(2)</u> , PCB(3), DEHP(1), BBP(2), DEP(1)
30 < Removal < 70	E1(4), E3(3), T(5), $\alpha$ EE2(1), $\alpha$ E2(2), $\beta$ E2(1)	PFOS(2), para(1), cbz(1), propra(1), esci(1), lido(1), vera(1), ofl(2), nor(1), cip(3), LAS(1), NP2EO(3), PCB(1), DEHP(1), BBP(2), DEP(1), DnBP(3)
Removal > 70	<u>lora(1)</u> , $\alpha$ EE2(3), E1(2)	PFOS(4), para(4), cbz(2), propra(5), esci(5), lido(4), <u>mico(3)*</u> , <u>trama(5)</u> , vera(4), <u>domp(6)</u> , ofl(2), nor(2), cip(1), DEP(1), DnBP(1)

463  
 464 For several persistent compounds (NP, LAS, PAH, PCB,  $\alpha$ E2,  $\beta$ E2), all quantified greatly



465 above the LQ (except hormones), the outlet concentrations were often greater than the inlet  
466 ones, preventing to calculate a removal (SI Table 8). The higher outlet concentration for these  
467 persistent compounds could also be due to the issues previously presented regarding sampling  
468 and modification of matrix effect within the process. This confirms the necessity to deeply  
469 assess those questions prior to consistently analyze their fate in anaerobic digestion at full-  
470 scale. However, usually the difference between outlet and inlet concentrations was lower than  
471 30%. Considering measurement and propagation errors, the mass balance could be considered  
472 correct meaning that these compounds are not or poorly degraded under anaerobic condition..  
473 In addition, a negative mass balance could also reflect the production of molecules due to  
474 biological transformation. This is the case for NP (6 weeks/6 weeks), NP1EO (5/6) and t-OP  
475 (2/4). For these compounds, the higher output concentration may reflect the anaerobic  
476 transformation of parent compounds (NPnEO,  $n \geq 2$ ), which was already observed by Murdoch  
477 and Sanin (2016) and Janex-Habibi et al., (2009), even if these transformation products have  
478 been also observed to be removed anaerobically (Patureau et al., 2008; Paterakis et al., 2012).  
479 For PAH, the same reason could be argued for the low molecular weight PAH (fluorene,  
480 phenanthrene) which presented negative mass balances and may be produced from the  
481 anaerobic transformation of high molecular weight PAH. For these latter, we observed either  
482 low removals ( $< 30\%$ , Table 4, SI Table 9) or negative mass balances comprised between 0  
483 and  $-30\%$ . PAH are thus poorly degraded under anaerobic conditions which is contradictory  
484 to some results obtained in lab-scale studies with spiked mixed sludge (Barret et al., 2010).

485 These discrepancies in removals could be due to higher sample homogeneity (lab-scale  
486 reactors were fed with the same homogenized frosted/thawed sludge) and PAH availability  
487 (spiking of sludge) at lab-scale compared to full-scale. PCB and LAS were also poorly  
488 removed by anaerobic digestion with either negative mass balances (for respectively 2 and 4  
489 weeks) or removals lower than 40% and 50% respectively in other weeks. These results are  
490 consistent with data obtained at lab-scale by Benabdallah El-Hadj et al. (2007) for PCB and  
491 De Oliveira et al. (2010) for LAS. For phthalates, only DEP and DEHP presented negative  
492 mass balances for one or two weeks respectively. For other weeks, removals were below 70%,  
493 except for DEP and DnBP that were already shown to be easily degraded by comparison to  
494 DEHP and BBP (Fountoulakis et al., 2006; Abdel daiem et al., 2012). Several hormones  
495 ( $\alpha$ EE2,  $\alpha$ E2,  $\beta$ E2) presented negative mass balances at -30% for one ( $\alpha$ EE2) or three weeks  
496 ( $\beta$ E2) but were also removed between 9-58% ( $\alpha$ E2,  $\beta$ E2) and 17-79% ( $\alpha$ EE2) for the remaining  
497 weeks (SI Table 9). Similar results were obtained by Gonzales-Gil et al. (2016) in lab-scale  
498 digesters with production or low removal of  $\beta$ E2, and higher removal of  $\alpha$ EE2. However, E1  
499 was always removed above 30%, which was not observed by Gonzales-Gil et al. (2016) nor  
500 by Noguera-Oviedo and Aga (2016) in manure anaerobic digestion. Testosterone presented  
501 moderate removals whereas E3 low to moderate ones. Anaerobic transformation of  
502 testosterone was only reported under anoxic conditions with nitrate and iron as electron  
503 acceptors (Shih et al., 2017) whereas E3 was also reported to be poorly degraded under  
504 anaerobic conditions (Singh, 2015).

505 For the fluoroquinolones, only one mass balance is negative, the same for carbamazepine (SI  
506 Table 8). For the 5 remaining weeks, removals were calculated and varied between 1 and 78%  
507 for fluoroquinolones and 22-99% for carbamazepine (Table 4, SI Table 9). Those removals  
508 are quite surprising compared to literature (Liu et al., 2013; Alvarino et al., 2014; Gonzales-  
509 Gil et al., 2016). Indeed, fluoroquinolones are fully recognized as recalcitrant compounds and  
510 have been shown to be degraded under aerobic conditions (Dorival-Garcia et al., 2013; Rusch  
511 et al., 2019) but degradation under anaerobic conditions is not fully documented. From our  
512 data, anaerobic removal of ciprofloxacin was in average  $43 \pm 17\%$  (average on 5/6 weeks,  
513 range 28-72%) which is in accordance with the recent work of Do and Stuckey (2019) who  
514 observed 50-78% anaerobic removal of ciprofloxacin from synthetic wastewater with few  
515 detected transformation products. The removal range for carbamazepine was wide ( $66 \pm 39\%$   
516 average on 4/6 weeks) by comparison to the data in literature presenting carbamazepine as a  
517 very recalcitrant compounds under both aerobic and anaerobic conditions (Alvarino et al.,  
518 2014; Yang et al., 2016). However, several transformation products were identified by König  
519 et al. (2016) suggesting possible anaerobic reduction of this compound. Another PHP  
520 presented a wide range of removal, paracetamol, from 3 to 99% with 4 weeks in 6 being  
521 above 70%, classifying it as a highly removed compound. This compound has been shown to  
522 be well removed under aerobic conditions (Wu et al., 2012; Margot et al., 2015) and also  
523 anaerobic ones by Narumiya et al. (2013), Yang et al. (2016) and more recently Gonzales-Gil  
524 et al. (2019) who reported its degradation by enzymes extracted from anaerobic sludge. For

525 both carbamazepine and paracetamol, the presence of an amide electron withdrawing group  
526 may explain their anaerobic reduction as for atenolol and diatrizoate (Ghattas et al., 2017).

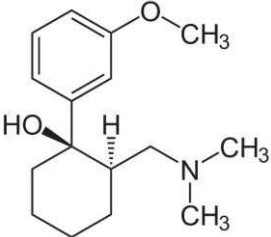
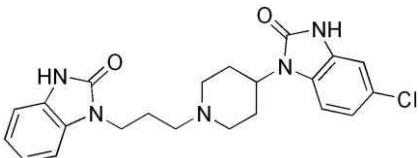
527 Among PHP with input concentration above 5 times the LQ, propranolol, escitalopram,  
528 lidocaine and verapamil presented mainly high removals (5 or 4 weeks/6) with output  
529 concentrations below the LQ. The same was observed for PFOS. Very few information on  
530 their anaerobic degradability is available in literature. Other betablockers have been shown to  
531 be moderately (metoprolol) to greatly (atenolol) removed. The removal mechanism implies  
532 amide hydrolysis (Gonzales Gil et al., 2019) for atenolol, and possibly the methoxy moiety for  
533 metoprolol like tramadol, naproxen and venlafloxin (Ghattas et al., 2017). However, none of  
534 these groups is present on the structure of propranolol (Table 6). Amide hydrolysis could  
535 explain lidocaine degradation whereas dehalogenation might be expected for escitalopram. *O*-  
536 demethylation would be possible for verapamil, which was shown to be poorly removed by  
537 Yang et al. (2016). For PFOS, it seems that the very high polarity of the C-F bond renders  
538 these compounds non-degradable by dehalogenation (Ghattas et al., 2017). The high removal  
539 observed may be due to the presence of the electron-withdrawing group sulfonyl.

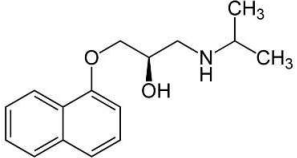
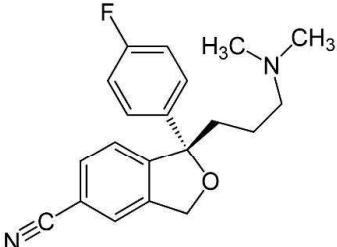
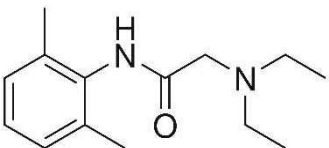
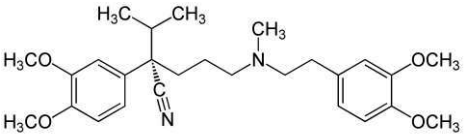
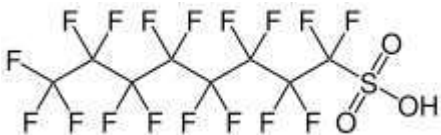

540 Sulfamethoxazole and cefoperazone presented also moderate to great removals but these  
541 results have to be confirmed, their concentrations being close to the LQ. Sulfamethoxazole  
542 has been already shown to be well removed during anaerobic digestion (Narumiya et al.,  
543 2013; Gonzales-Gil et al., 2016; Alvarino et al., 2018), may be due to the strong electron-  
544 withdrawing group sulfonyl.

545 Tramadol and domperidone were the 2 compounds presenting always high removals.  
 546 Azithromycin and loratidine behaved similarly but concentrations were very close to the LQ  
 547 making the confirmation of these results necessary. Tramadol was already shown to be  
 548 anaerobically degraded via the *O*-demethylation of the methoxy moiety (Falas et al., 2016;  
 549 Ghattas et al., 2017). No information was found for domperidone, but dehalogenation could  
 550 be hypothesized as possible reaction. The Table 5 synthetized all the confirmed and  
 551 hypothetic removal mechanisms discussed.

552

553 **Table 5** Possible reactions explaining the OC anaerobic removal (only compounds with a  
 554 high frequency of above 70% removal)

Compounds (references)	Structure	Reaction/functional group ( <i>italic</i> when hypothesis)
Tramadol (Falas et al., 2016; Ghattas et al., 2017)		<i>O</i> -demethylation
Domperidone (No reference)		<i>Reductive dehalogenation</i>

Propranolol reference)	(No		<i>Secondary amine</i>
Escitalopram reference)	(No		<i>Reductive dehalogenation</i>
Lidocaine reference)	(No		<i>Amide (EWG)</i>
Verapamil reference)	(No		<i>O-demethylation</i>
PFOS (No reference)			<i>Sulfonyl</i>
Paracetamol (Narumiya et al., 2013; Wijekoon et al., 2015 ; Yang et al., 2016)			-Amide (EWG) -Hydroxyl (EDG)

555

556

557 **CONCLUSIONS**

558 This paper dealt with organic contaminants mass balances assessment applied to

559 physicochemical sludge treatment processes from WWTP sludge treatment trains. For  
560 dewatering by centrifugation and thermal drying, the complexity to get correct mass balances  
561 for several OC was deeply shown despite prior validation of the campaign and data. Those  
562 mass balances calculations were possible as 1) the representativeness of the sampling  
563 campaigns was confirmed when analysing global performances, 2) the sampling strategy and  
564 the calculation method allowed calculating correct DM mass balances which is a prerequisite  
565 step before OC mass balance calculation, and 3) the OC quantification method used is  
566 accurately validated based on current analytical good practices. However, those verifications  
567 and insurances were not sufficient in the case of many OCs. The frequency of correct mass  
568 balances relied on three parameters: (1) the measured content compared to the analytical  
569 method limit of quantification, (2) the hydrophobicity and (3) the charge of the compounds.  
570 Thus, for centrifugation, mass balances were more frequently correct for hydrophobic and  
571 neutral compounds, and inversely for hydrophilic and charged compounds. For these latter,  
572 concentrations close to the LQ render difficult such calculation. For thermal drying, similar  
573 trends were observed, however correct mass balances were obtained frequently ( $>0.7$ ) for 47  
574 compounds, while they were frequently not correct for 8 compounds. Like centrifugation  
575 process, it seems to be mainly explained by the hydrophobicity, charge and OC content  
576 compared to LQ. This paper also highlighted negligible to limited transfer to residual water  
577 for most of the compounds. For centrifugation, only propranolol and DEP presented important  
578 mass flow that has to be considered for the overall mass balances onto WWTP. The OC

579 transfer to the residual water is even lower for thermal drying as only 11 compounds were  
580 quantified and for most of them the mass flow was really negligible (<0.5%) compared to the  
581 input mass flow, except for tramadol.

582 These differences of mass balances determination between compounds could be explained by  
583 1) the sampling practices that do not guarantee the representativeness of samples for OC and  
584 2) the analytical practices that do not fully take into account the variations of matrix effect  
585 between inlet and outlet of processes. Thus, when assessing the fate of OC in full-scale sludge  
586 treatment plants, authors would recommend increasing the number of composite samples for  
587 one campaign in order to reduce sample heterogeneity instead of increasing number of  
588 sampling campaign. The revision of the sampling practices by implementing 24h composite  
589 sampling systems adapted to sludge is also a solution that has to be investigated. This  
590 underlined that results coming from one-time punctual samples, that are mainly used in  
591 conventional sampling strategy for sludge, have to be considered with caution. The difficulty  
592 to compare results from one site to another could also be explained by this type of sampling  
593 strategy. Moreover, it is important for charged and hydrophilic compounds to measure their  
594 presence in the residual water as it may significantly contribute to the mass balance and assess  
595 the returned mass to the WWTP inlet, which could be non-negligible. Establishing and  
596 validating correct mass balances of such physicochemical processes are also a prerequisite for  
597 WWTP modelling purposes. Finally, thorough evaluation of the matrix effect in both inlet and  
598 outlet sludge from a process should be generalized to make quantification of OC more



599 reliable.

600 Regarding anaerobic digestion, even if the SRT was considered for sampling, some  
601 compounds presented high range of removals. Consequently, compounds were grouped in  
602 three classes of removal instead of giving a single value of removal. It underlined also the  
603 importance of developing more rigorous sampling strategies. Compounds like domperidone,  
604 propranolol, escitalopram, lidocaine, verapamil and cefoperazone were shown for the first  
605 time to have high removals under anaerobic conditions at full-scale, which could be explained  
606 by their physicochemical structure.

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## 609 **REFERENCES**

610

611 Abdel daiem, M.M., Rivera-Utrilla, J., Ocampo-Pérez, J.R., Méndez-Díaz, J.D., Sánchez-  
612 Polo, M., 2012. Environmental impact of phthalic acid esters and their removal from water  
613 and sediments by different technologies - A review. *Journal of Environmental Management*,  
614 109, 164-178.

615 Alvarino, T., Suarez, S., Lema, J.M., Omil, F., 2014. Understanding the removal mechanisms  
616 of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic  
617 CAS reactors. *Journal of Hazardous Materials* 278, 506-513.

618 Alvarino, T., Suarez, S., Lema, J., Omil, F., 2018. Understanding the sorption and  
619 biotransformation of organic micropollutants in innovative biological wastewater treatment  
620 technologies. *Science of the Total Environment* 615, 297-306.

621 Barret, M., Barcia, G.C., Guillon, A., Carrère, H., Patureau, D., 2010. Influence of feed  
622 characteristics on the removal of micropollutants during the anaerobic digestion of  
623 contaminated sludge. *Journal of Hazardous Materials* 181, 241–247.

624 Benabdalha El-Hadj, T., Dosta, J., Torres, R., Mata-Alvarez, J. 2007. PCB and AOX removal  
625 in mesophilic and thermophilic sewage sludge digestion. *Biochemical Engineering Journal*  
626 36(3), 281-287.

627 Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2012. Meta-  
628 analysis of environmental contamination by alkylphenols. *Environmental Science and*  
629 *Pollution Research* 19, 3798-3819.

630 Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R., 2013. Meta-  
631 analysis of environmental contamination by phthalates. *Environmental Science and Pollution*  
632 *Research*, 1-20.

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

635 Clarke, B.O., Smith, S.R., 2011. Review of 'emerging' organic contaminants in biosolids and  
636 assessment of international research priorities for the agricultural use of biosolids.

637 Environment International 37, 226-247.

638 De Oliveira, L.L., Costa, R.B., Okada, D.Y., Vich, D.V., Duarte, I.C.S., Silva, , E.L.,  
639 Varesche, M.B.A., 2010. Anaerobic degradation of linear alkylbenzene sulfonate (LAS) in  
640 fluidized bed reactor by microbial consortia in different support materials. Bioresource  
641 Technology 101, 5112–5122.

642 Do, M.T., Stuckey, D.C., 2019. Fate and removal of Ciprofloxacin in an anaerobic membrane  
643 bioreactor (AnMBR). Bioresource Technology, 289, 121683.

644 Dorival-Garcia, N., Zafra-Gomez, A., Navalon, A., Gonzalez, J., Vilchez, J., 2013. Removal  
645 of quinolone antibiotics from wastewaters by sorption and biological degradation in  
646 laboratory-scale membrane bioreactors. Science of the Total Environment 442, 317–328.

647 Falås, P., Wick, A., Castronovo, S., Habermacher, J., Ternes, T.A., Joss, A., 2016. Tracing the  
648 limits of organic micropollutant removal in biological wastewater treatment. Water Research  
649 95, 240-249.

650 Fountoulakis, M. S., Stamatelatou, K., Batstone, D. J., Lyberatos, G., 2006. Simulation of  
651 DEHP biodegradation and sorption during the anaerobic digestion of secondary sludge. Water  
652 Science and Technology 54(4), 119-128.

653 Fytily, D., Zabaniotou, A., 2008. Utilization of sewage sludge in EU application of old and  
654 new methods—A review. Renewable and Sustainable Energy Reviews 12, 116-140.

655 Ghattas, A-K., Fischer, F., Wick, A., Ternes, T.A., 2017. Anaerobic biodegradation of

656 (emerging) organic contaminants in the aquatic environment. *Water Research* 116, 268-295.

657 Gonzalez-Gil, L., Papa, M., Feretti, D., Ceretti, E., Mazzoleni, G., Steimberg, N., Pedrazzani,  
658 R., Bertanza, G., Lema, J. M., Carballa, M. 2016. Is anaerobic digestion effective for the  
659 removal of organic micropollutants and biological activities from sewage sludge? *Water*  
660 *Research* 102, 211-220.

661 Gonzalez-Gil, L., Krah, D., Ghattas, A-K., Carballa, M., Wick, A., Helmholz, L., Lema, J.M.,  
662 Ternes, T.A., 2019. Biotransformation of organic micropollutants by anaerobic sludge  
663 enzymes. *Water Research* 152, 202-214.

664 Janex-Habibi, M.-L., Huyard, A., Esperanza, M., Bruchet, A., 2009. Reduction of endocrine  
665 disruptor emissions in the environment: The benefit of wastewater treatment. *Water Research*  
666 43, 1565–1576.

667 Kelessidis, A., Stasinakis, A.S., 2012. Comparative study of the methods used for treatment  
668 and final disposal of sewage sludge in European countries. *Waste Management* 32, 1186-  
669 1195.

670 Konig, A., Weidauer, C., Seiwert, B., Reemtsma, T., Unger, T., Jekel, M., 2016. Reductive  
671 transformation of carbamazepine by abiotic and biotic processes. *Water Research* 101, 272-  
672 280.

673 Liu, Z., Sun, P., Pavlostathis, S.G., Zhou, X., Zhang, Y., 2013. Inhibitory effects and  
674 biotransformation potential of ciprofloxacin under anoxic/anaerobic conditions. *Bioresource*  
675 *Technology* 150, 28–35.

676 Mailler, R., Gasperi, J., Chebbo, G., Rocher, V., 2014a. Priority and emerging pollutants in  
677 sewage sludge and fate during sludge treatment. *Waste Management* 34, 1217-1226.

678 Mailler, R., Gasperi, J., Patureau, D., Vulliet, E., Delgenes, N., Danel, A., Deshayes, S.,  
679 Eudes, V., Guerin, S., Moilleron, R., Chebbo, G., Rocher, V., 2017. Fate of emerging and  
680 priority micropollutants during the sewage sludge treatment: case study of Paris conurbation.  
681 Part 1: Contamination of the different types of sewage sludge. *Waste Management* 59, 379-  
682 393.

683 Margo, J., Rossi, L., Barry, D.A., Holliger, C., 2015. A review of the fate of micropollutants  
684 in wastewater treatment plants. *WIREs Water*. doi: 10.1002/wat2.1090.

685 Meng, X.-Z., Venkatesan, A.K., Ni, Y.-L., Steele, J.C., Wu, L.-L., Bignert, A., Bergman, Å.,  
686 Halden, R.U., 2016. Organic Contaminants in Chinese Sewage Sludge: A Meta-Analysis of  
687 the Literature of the Past 30 Years. *Environmental Science and Technology* 50, 5454-5466.

688 Mininni, G., Blanch, A.R., Lucena, F., Berselli, S., 2015. EU policy on sewage sludge  
689 utilization and perspectives on new approaches of sludge management. *Environmental*  
690 *Science and Pollution Research* 22, 7361–7374.

691 Murdoch, F.K., Sanin, F.D., 2016. Biotransformation of Nonylphenol Diethoxylate in  
692 anaerobic digesters: Accumulation of metabolites and their effects on digester performance.  
693 *International Biodeterioration and Biodegradation* 110, 61–68.

694 Narumiya, M., Nakada, N., Yamashita, N., Tanaka, H., 2013. Phase distribution and removal

695 of pharmaceuticals and personal care products during anaerobic sludge digestion. *Journal of*  
696 *Hazardous Materials* 260, 305-312.

697 Noguera-Oviedo, K. and Aga, D. S., 2016. Chemical and biological assessment of endocrine  
698 disrupting chemicals in a full scale dairy manure anaerobic digester with thermal  
699 pretreatment. *Science of the Total Environment* 550, 827–834.

700 Paterakis, N., Chiu, T.Y., Koh, Y.K.K., Lester, J.N., McAdam, E.J., Scrimshaw, M.D.,  
701 Soares, A., Cartmell, E., 2012. The effectiveness of anaerobic digestion in removing estrogens  
702 and nonylphenol ethoxylates. *Journal of Hazardous Materials* 199–200, 88–95.

703 Patureau, D., Delgenes, N., Delgenes, J.-P., 2008. Impact of sewage sludge treatment  
704 processes on the removal of the endocrine disrupters nonylphenol ethoxylates. *Chemosphere*  
705 72, 586–591.

706 Ruel, S.M., Choubert, J.M., Budzinski, H., Miege, C., Esperanza, M., Coquery, M., 2012.  
707 Occurrence and fate of relevant substances in wastewater treatment plants regarding Water  
708 Framework Directive and future legislations. *Water Science and Technology* 65, 1179-1189.

709 Rusch, M., Spielmeyer, A., Zorn, H., Hamscher, G., 2019. Degradation and transformation of  
710 fluoroquinolones by microorganisms with special emphasis on ciprofloxacin. *Applied*  
711 *Microbiology and Biotechnology* 103, 6933–6948.

712 Singh, A.K., 2015. Aerobic and Anaerobic Transformations in Estrogens and Nutrients in  
713 Swine Manure: Environmental Consequences. *Agriculture* 5, 697-712.

714 Shih, C.J., Chen, Y.L., Wang, C.H., Wei, S.T.S., Lin, I.T., Ismail, W.A., and Yin-Ru Chiang,  
715 Y.R., 2017. Biochemical Mechanisms and Microorganisms Involved in Anaerobic  
716 Testosterone Metabolism in Estuarine Sediments. *Frontiers in Microbiology* 8:1520.

717 Verlicchi, P., Zambello, E., 2015. Pharmaceuticals and personal care products in untreated  
718 and treated sewage sludge: Occurrence and environmental risk in the case of application on  
719 soil - A critical review. *Science of the Total Environment* 538, 750–767.

720 Wijekoon, K.C., McDonald, J.A., Khan, S.J., Hai, F.I., Price, W.E., Nghiem, L.D., 2015.  
721 Development of a predictive framework to assess the removal of trace organic chemicals by  
722 anaerobic membrane bioreactor. *Bioresource Technology* 189, 391–398.

723 Wu, S., Zhang, L., Chen, J., 2012. Paracetamol in the environment and its degradation by  
724 microorganisms. *Applied Microbiology and Biotechnology* 96, 875–884.

725 Yang, S., Hai, F.I., Price, W.E., McDonald, J., Khan, S.J., Nghiem, L.D., 2016. Occurrence of  
726 trace organic contaminants in wastewater sludge and their removals by anaerobic digestion.  
727 *Bioresource Technology* 210, 153-159.

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