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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Highlights

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

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

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Abbreviations

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

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

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

LQ/LD, limit of quantification/limit of detection

OC, organic contaminants

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

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

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

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

PHP, pharmaceutical products

Qin, Qout, input and output flows of the process

SIAAP, Greater Paris sanitation authority

SRT, solid retention time

STP, sludge treatment plant

TSS, total suspended solid

WWTP, wastewater treatment plants

Abstract

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

Key-words

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

1. Introduction

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

Sludge are treated and conditioned before land application, incineration or landfilling (Fytili and Zabaniotou, 2008; Mininni et al., 2015). In France (> 70% of the DM mass), as well as in Europe in general (> 50%), the main pathway for sludge management is still land application. The sewage sludge treatment aims to reduce fermentescibility, nuisances (particularly odour), pathogens content and vector attraction potential as well as to reduce bulk and improve their physical characteristics to aid handling, dewatering and acceptability for use on agricultural land. Current practices in Europe are based on the requirements of the 1986 Directive on the

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

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

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

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

Therefore, centrifugation, anaerobic digestion, thermal drying and cooking + press filtration were considered. A total of 71 OC including Water Framework Directive priority pollutants, PHP, hormones, perfluorinated acids (PFA), linear alkylbenzene sulfonate (LAS), AP, PAE, PAH and polychlorobiphenyls (PCB) were investigated (SI Table 1). As the objective of this 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^3 of wastewater per
139 day. Its sludge treatment consists in dewatering of mixed biological and physicochemical

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

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

2.3. Mass balance assessment

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

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

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

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

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

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 ±133 and
257 729 ±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 ± 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	Concentration factor	Proportion of DM lost in residual water	Q_{out_CS}	Q_{out_CW}
Equation	DM_{out_CS}/DM_{in_RS}	TSS_{out_CW}/DM_{in_RS} × 100	Q_{in_RS}/concentration factor	$Q_{in\_RS} - Q_{out\_CS}$
Unit	-	in %	in m^3/d	in m^3/d
April, 9th, 2013	5.4	2.0	245	1067
April, 30th, 2013	5.3	3.5	317	1360
May, 14th, 2013	5.3	5.3	285	1222
May, 22th, 2013	5.9	3.1	325	1583
June, 11th, 2013	5.3	5.0	296	1281

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

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,

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

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

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

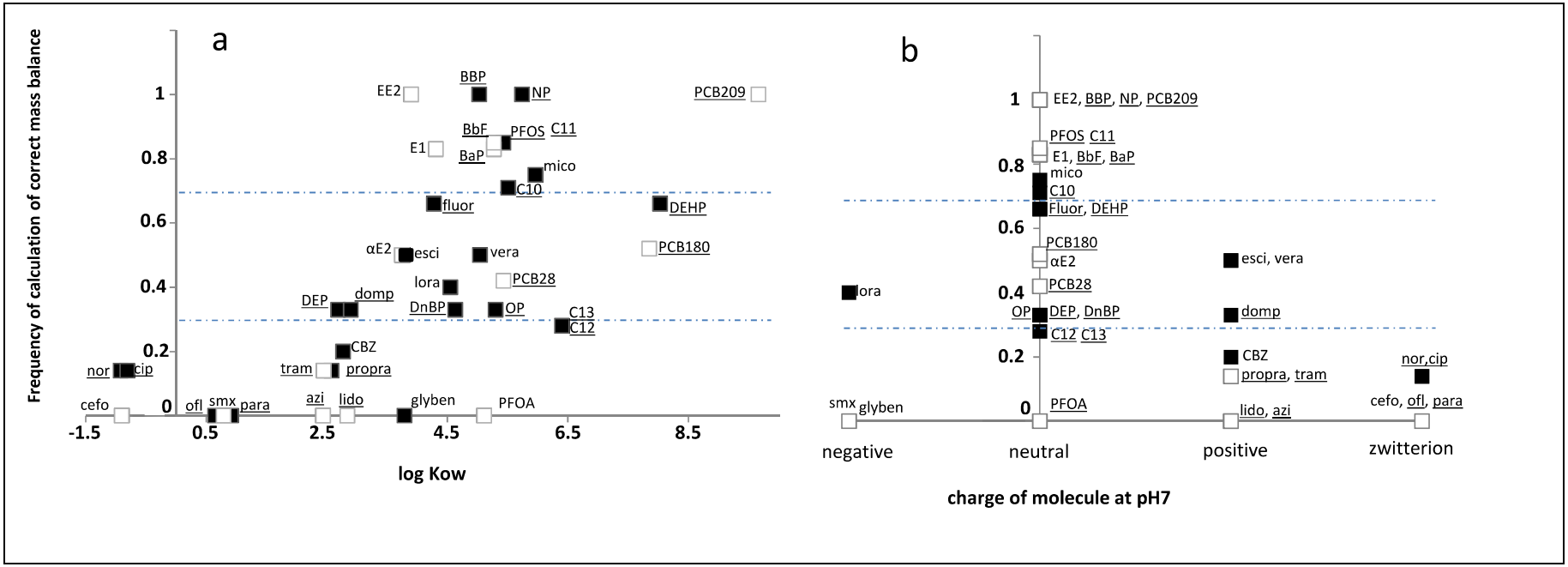
	Centrifugation	Thermal drying
Frequency > 0.7 (group 1)		
μP_{in} and $\mu P_{out} > 5 \times LQ$	<u>NP</u>, <u>BBP</u>, <u>LAS-C11</u>, <u>PFOS</u>,	<u>NP</u>, BaP, BbF, ∑PAH (13),

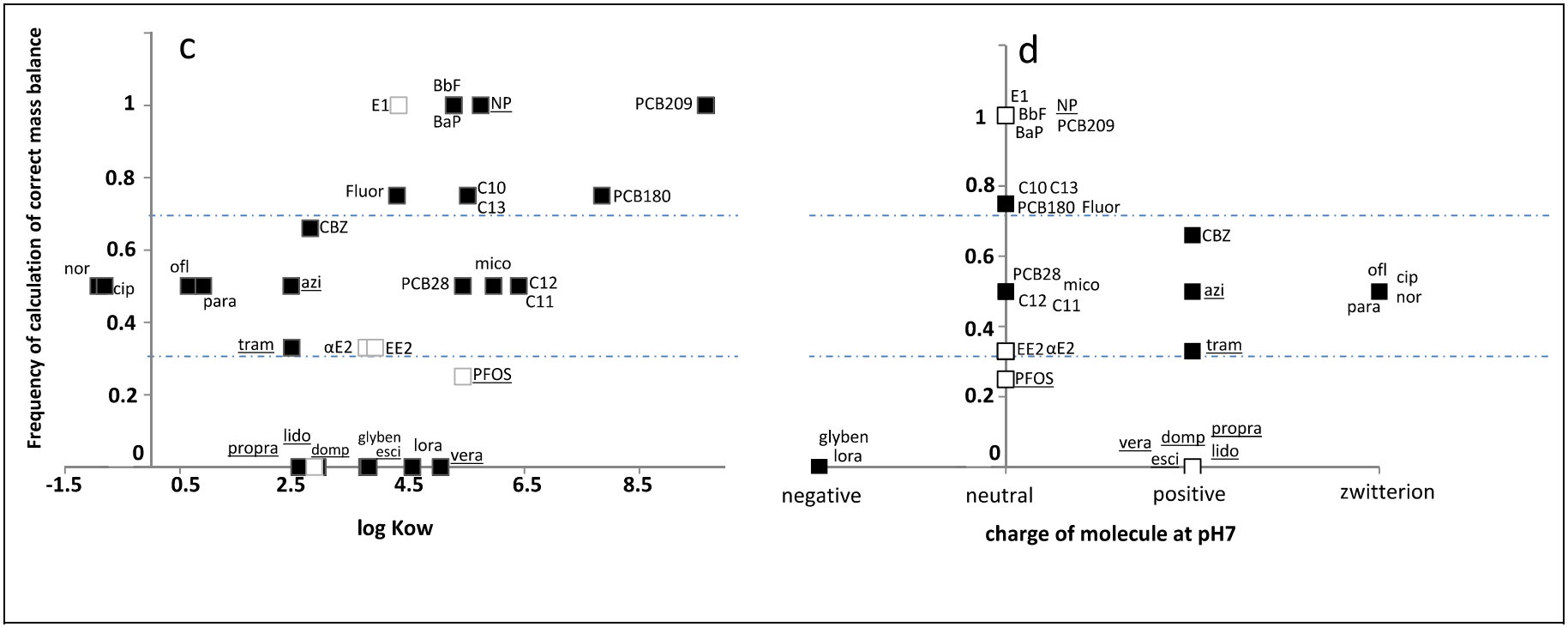
	mico, LAS-C10	Fluor, LAS-C10, LAS-C13
<5 × LQ	EE2, BbF, E1, BaP, PCB209	E1, PCB180, PCB209, ∑PCB (20)
	0.3<Frequency<0.7 (group 2)	
μP_{in} and μP_{out} > 5 × LQ	Fluor, DEHP, esci, vera, lora, t-OP, DEP, DnBP, domp	cbz, cip, nor, ofl, para, azi, mico, LAS-C11, LAS-C12, tram
<5 × LQ	αE2, PCB28, PCB180, (∑PCB (20), ∑PAH (13))	αE2, EE2, PCB28
	Frequency < 0.3 (group 3)	
μP_{in} and μP_{out} > 5 × LQ	LAS-C12, LAS-C13, cbz, propra, cip, nor, para, glyben, ofl	propra, esci, glyben, lora, vera, domp
<5 × LQ	tram, PFOA, lido, cefo, azi, smx	PFOS, lido

296

297

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 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 below 5 times LQ. Underlined compounds are those found in the residual water of centrifugation or thermal drying. For compounds abbreviation see SI Table 1.




c
Frequency of calculation of correct mass balance
1
0.8
0.6
0.4
0.2
0
-1.5
0.5
2.5
4.5
6.5
8.5
log Kow
E1
BbF
BaP
NP
PCB209
Fluor
C10
C13
PCB180
CBZ
nor
cip
ofl
para
azi
mico
PCB28
C12
C11
tram
αE2
EE2
PFOS
propra
lido
domp
glyben
esci
lora
vera
d
E1
BbF
BaP
NP
PCB209
C10 C13
PCB180 Fluor
CBZ
PCB28
mico
C12 C11
azi
ofl
cip
nor
para
EE2 αE2
tram
PFOS
glyben
lora
vera
domp
propra
esci
lido
negative
neutral
positive
zwitterion
charge of molecule at pH7

302

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

The group 2 was characterized by an intermediate frequency (between 30 and 70%) of calculation of a correct mass balance. Among the compounds, some persistent hydrophobic compounds like PCB, DEHP, fluor and t-OP, had sometimes incorrect mass balances (SI table 4) due to higher mass in the outlet. The other OCs of group 2 are 4 PHP (escitalopram, verapamil, loratidine, domperidone) with concentrations greater than 5 times the LQ and presenting positive and negative mass balances, the same was observed for αE2 whose 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 logKow<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-value < 0.05) between logKow 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.

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

3.2. Mass balance of OC in thermal drying

3.2.1. DM mass balance

The drying process was very repeatable in each sampling week of 2013 with a stable DM concentration factor of 3.5 ±0.2 and its performances were very similar to those calculated on a three months' period (Table 3, SI Table 5). The calculated DM mass balance was correct with a difference between inlet and outlet always lower than 30% (SI fig 1). The TSS concentration in the residual water, only measured in 2014, underlined a very high efficiency of separation with residual water containing extremely low concentrations of DM. The measured and calculated operation data presented a higher variability in 2014 compared to 2013. In 2014, the first campaign could not be considered due to the impossibility to obtain the volumetric flow data for the centrifuged sludge inlet. Moreover, the DM mass balance calculated for the second campaign was not correct with a difference between inlet and outlet 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^3/d	in m^3/d
April, 9th, 2013	3.4	nm	19.5	33.4
April, 30th, 2013	3.6	nm	14.6	27.1
May, 14th, 2013	3.3	nm	18.7	34.1
May, 22th, 2013	-	nm	-	-
June, 11th, 2013	3.6	nm	21.8	44.0
April, 1st, 2014	2.0	0.010	-	-
April, 8th, 2014	2.6	0.025	13.5	17.0
April, 15th, 2014	3.6	0.003	32.5	41.8
Average ± STD (5 d of sampling in 2013)	**3.5 ±0.2**	**-**	**18.6 ±3.0**	**34.6 ±7.0**

Average ± STD of daily operation data in april, may, june 2013	*3.5 ±0.3*	-	*16.2 ±6.*	*28.5 ±11.0*
Average ± STD (3 d of sampling in 2014)	**2.7 ±0.8**	**0.014 ±0.010**	**-**	**-**
Average ± STD of daily operation data in march, april, may, june 2014	*3.5 ±0.4*	-	-	-

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 (azihromycin, 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,

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

An OC mass balance is calculated for all the considered sampling weeks for 51 (2013) and 56 (2014) compounds and for 10 more compounds in 2013 for at least one week (SI Table 3). The reason for no calculation is the same as previously mentioned. Once the validation of mass balances was assessed (SI Table 6), the compounds were grouped according to the frequency of quantification of a correct mass balance (Table 3). It is important to note that only one or two mass balances were calculated for some compounds due to data lower than LQ (azithromycin, estrone, glybencyclamide, loratidine, miconazole) or lack of data (phthalates). By comparison, more compounds presented correct mass balances (Table 3) in thermal drying process than in centrifugation process but trends observed by linking it to physicochemical properties were less interpretable (Fig 1). Spearman (non-normal distributions) correlation tests were performed and indicated a significant positive correlation (p-value < 0.05) only between logKow and the compounds detected above 5 time the LQ ($r = 0.437$). Due to possible volatilization during this thermal process, other properties like volatility (expressed by means of Henry constant or vapor pressure) were considered but it did

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

Class of removal **In %**	**Compounds with low concentrations** **[OC] < 5*LQ**	**Compounds with high concentrations** **[OC] > 5*LQ**
Removal < 30	E3(3), T(1), αEE2(1), αE2(2), βE2(2)	para(1), cbz(1), ofl(1), nor(2), cip(1), LAS(2), NP2EO(2), PAH(2), PCB(3), DEHP(1), BBP(2), DEP(1)
30 < Removal < 70	PFOA(2), smx(1), cefo(1), E1(4), E3(3), T(5), αEE2(1), αE2(2), βE2(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	smx(1), azi(1), cefo(1), lora(1), αEE2(3), E1(2)	PFOS(4), para(4), cbz(2), propra(5), esci(5), lido(4), mico(3)*, trama(5), vera(4), domp(6), ofl(2), nor(2), cip(1), DEP(1), DnBP(1)

463

464 For several persistent compounds (NP, LAS, PAH, PCB, αE2, βE2), all quantified greatly

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

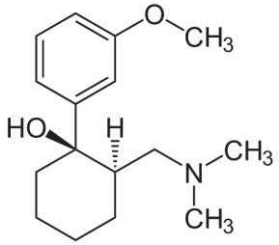
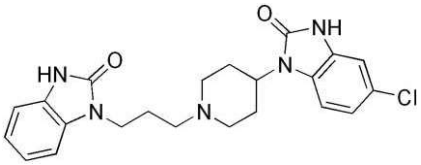
These discrepancies in removals could be due to higher sample homogeneity (lab-scale reactors were fed with the same homogenized frosted/defrosted sludge) and PAH availability (spiking of sludge) at lab-scale compared to full-scale. PCB and LAS were also poorly removed by anaerobic digestion with either negative mass balances (for respectively 2 and 4 weeks) or removals lower than 40% and 50% respectively in other weeks. These results are consistent with data obtained at lab-scale by Benabdallah El-Hadj et al. (2007) for PCB and De Oliveira et al. (2010) for LAS. For phthalates, only DEP and DEHP presented negative mass balances for one or two weeks respectively. For other weeks, removals were below 70%, except for DEP and DnBP that were already shown to be easily degraded by comparison to DEHP and BBP (Fountoulakis et al., 2006; Abdel daiem et al., 2012). Several hormones (αEE2, αE2, βE2) presented negative mass balances at -30% for one (αEE2) or three weeks (βE2) but were also removed between 9-58% (αE2, βE2) and 17-79% (αEE2) for the remaining weeks (SI Table 9). Similar results were obtained by Gonzales-Gil et al. (2016) in lab-scale digesters with production or low removal of βE2, and higher removal of αEE2. However, E1 was always removed above 30%, which was not observed by Gonzales-Gil et al. (2016) nor by Noguera-Oviedo and Aga (2016) in manure anaerobic digestion. Testosterone presented moderate removals whereas E3 low to moderate ones. Anaerobic transformation of testosterone was only reported under anoxic conditions with nitrate and iron as electron acceptors (Shih et al., 2017) whereas E3 was also reported to be poorly degraded under anaerobic conditions (Singh, 2015).

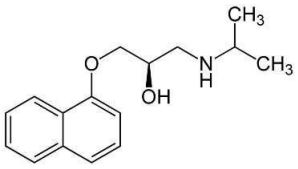
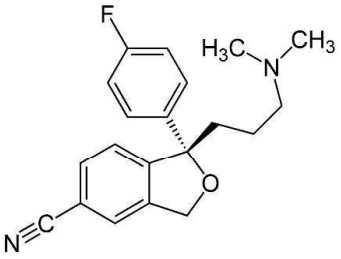
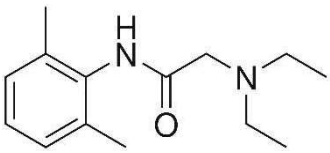
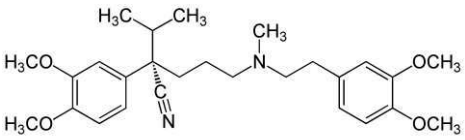
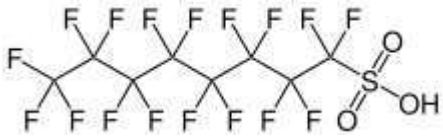
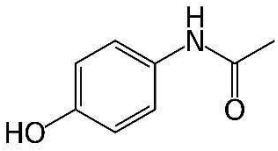
505 For the fluoroquinolones, only one mass balance is negative, the same for carbamazepine (SI
506 Table 8). For the 5 remaining weeks, removals were calculated and varied between 1 and 78%
507 for fluoroquinolones and 22-99% for carbamazepine (Table 4, SI Table 9). Those removals
508 are quite surprising 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 ±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 ±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 venlaflaxin (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 bound 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.

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

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

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

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

CONCLUSIONS

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

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

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

607

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