Priority and emerging pollutants in sewage sludge and fate during sludge treatment

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Highlights

- 117 pollutants were studied in different treated sludges from Parisian WWTPs
- The pollutant pattern is quite similar in the different sludges
- During centrifugation, no removal of pollutant is observed
- Thermal drying allows a 10 - 80% removal of alkylphenols, PAHs and MBT
- Pollutants are not, similarly or more removed than dry matter during digestion

Abstract

This paper aims at characterizing the quality of different treated sludges from Paris conurbation in terms of micropollutants and assessing their fate during different sludge treatment processes (STP). To achieve this, a large panel of priority and emerging pollutants (n=117) have been monitored in different STPs from Parisian wastewater treatment plants including anaerobic digestion, thermal drying, centrifugation and a sludge cake production unit. Considering the quality of treated sludges,

comparable micropollutant patterns are found for the different sludges investigated (in mg/kg DM - dry matter). 35 compounds were detected in treated sludges. Some compounds (metals, organotins, alkylphenols, DEHP) are found in every kinds of sludge while pesticides or VOCs are never detected. Sludge cake is the most contaminated sludge, resulting from concentration phenomenon during different treatments. As regards treatments, both centrifugation and thermal drying have broadly no important impact on sludge contamination for metals and organic compounds, even if a slight removal seems to be possible with thermal drying for several compounds by abiotic transfers. Three different behaviors can be highlighted in anaerobic digestion: i) no removal (metals), ii) removal following dry matter (DM) elimination (organotins and NP) and iii) removal higher than DM (alkylphenols - except NP -, BDE 209 and DEHP). Thus, this process allows a clear removal of biodegradable micropollutants which could be potentially significantly improved by increasing DM removal through operational parameters modifications (retention time, temperature, pre-treatment, etc.).

Keywords

Anaerobic digestion; thermal drying; centrifugation; emerging pollutants; priority pollutants; sludge

1. Introduction

Wastewater treatment plants (WWTP) produce an important quantity of sludge resulting from total suspended solids (TSS) removal and growth of microorganisms within biological treatments. Actually, about 1 million tons dry matter (DM) of sludge are produced every year by French WWTPs, while Germany and UK produce respectively 2.2 and 1.8 million tons (Kelessidis and Stasinakis, 2012), for a total of 11 million tons DM of sludge in all Europe (EU-27). The management of these sludges is achieved through three principal pathways: agricultural uses (land farming), incineration and disposal/landfilling (Fytili and Zabaniotou, 2008). In 2008, land farming was the main pathway both in France (> 60%) and in the European Union (> 50%) (Kelessidis and

Stasinakis, 2012).

Contamination of WWTP sludges by micropollutants has been reported for several years (Clarke and Smith, 2011; Harrison et al., 2006; Scancar et al., 2000). This results from pollutant sorption during primary and biological treatments because of their hydrophobicity or propensity to be adsorbed on particles (Byrns, 2001). As sludges are mainly land farmed, this contamination is worrying especially considering accumulation of some micropollutants in sludge and their transfer to the environment, like polybromodiphenyl ethers (PBDE) (Eljarrat et al., 2008), metals (Chipasa, 2003), organotins (Craig, 2003) or polychlorobiphenyls (PCB) (Stevens et al., 2002). To limit contamination of the environment by micropollutants, European and national regulations have been established to progressively forbid sludge disposal and regulate land farming. Such regulations concern principally heavy metals, PAHs and PCBs (Table 1). In particular, the Urban Wastewater Treatment Directive (EC, 1986), amended by (91/271/EEC) (EC, 1991), states maximum thresholds and maximum annual flux to land farm for metals.

Table 1 - French (order of 8th of January 1998) and European (EC, 1986) thresholds for PCBs, PAHs and metals in sludges to landfarm

	Threshold value in sludge (mg/kg DM)		**Maximal flux from sludges in last 10 years (g/m^2)**	
	General case	Pasture case	General case	Pasture case
Σ7 PCBs*	0.8	0.8	1.2	1.2
Fluoranthene	5	4	7.5	6
Benzo(b)fluoranthene	2.5	2.5	4	4
Benzo(a)pyrene	2	1.5	3	2
Cadmium	10 *(20 - 40)*		0.015	
Chrome	1 000		1.5	
Copper	1 000 *(1 000 - 1 750)*		1.5	
Mercury	10 *(16 - 25)*		0.015	
Nickel	200 *(300 - 400)*		0.3	
Lead	800 *(750 - 1200)*		1.5	
Zinc	3 000 *(2 500 - 4 000)*		4.5	
Chrome + Zinc + Copper + Nickel	4 000		6	

* PCBs 28, 52, 101, 118, 138, 153 and 180.
Figures presented are from French regulation (order of 8th of January 1998), while European thresholds from Wastewater Treatment Directive (EC, 1986) are given in brackets.

Despite that, data and knowledge are still missing concerning i) the quality of treated sludges and ii)

the efficiency of the sludge treatment processes (STP) for micropollutant removal as well as the mechanisms involved. This paper aims at improving and completing knowledge about Parisian sludges contamination by micropollutants and their fate during four different STPs, i.e. anaerobic digestion, centrifugation, thermal drying and sludge cake production.

As no typical sludge treatment layout can be identified, and different configurations exist depending on the capacity of the treatment plant or the quality of treated sludge expected (regulations), the characterization of each process individually seems to be a relevant strategy.

To achieve that, a large number of micropollutants (n=117) were monitored in these STPs. Contents were measured in raw, digested, centrifuged, thermally dried sludges and sludge cake (cooked then press filtered). Micropollutant removals were calculated, to better understand the behaviors of these compounds and to determine the potential of these processes for controlling the micropollutant contamination of sludge.

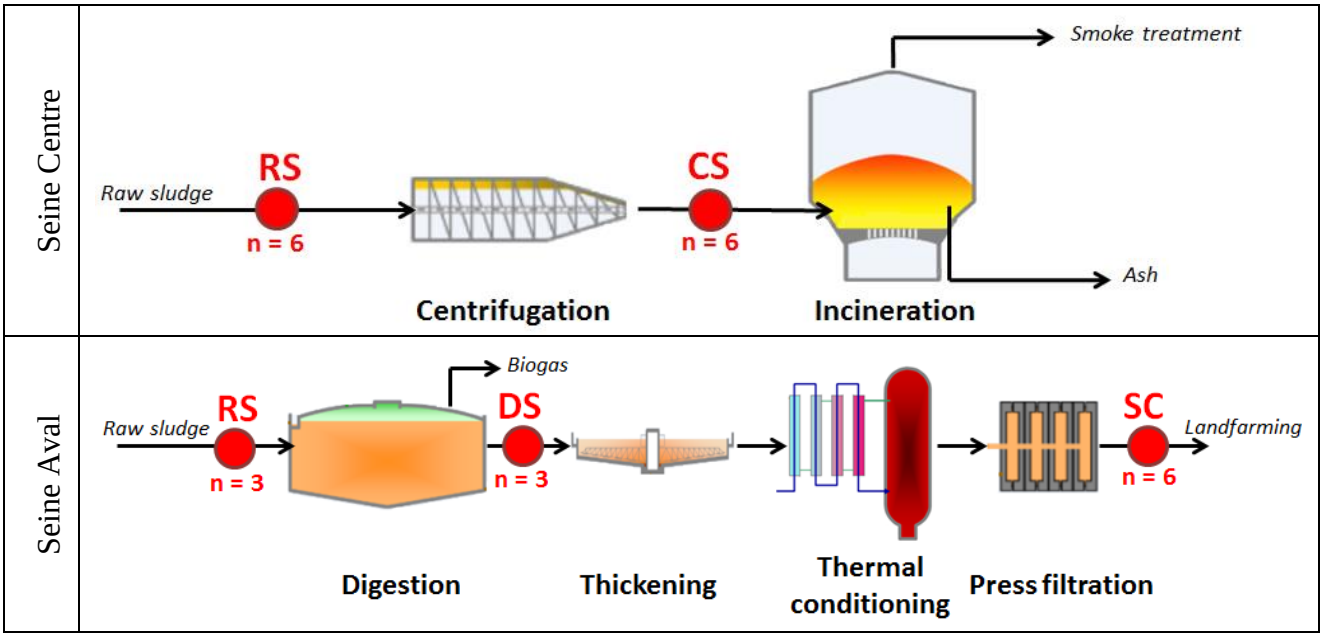
2. Material and methods

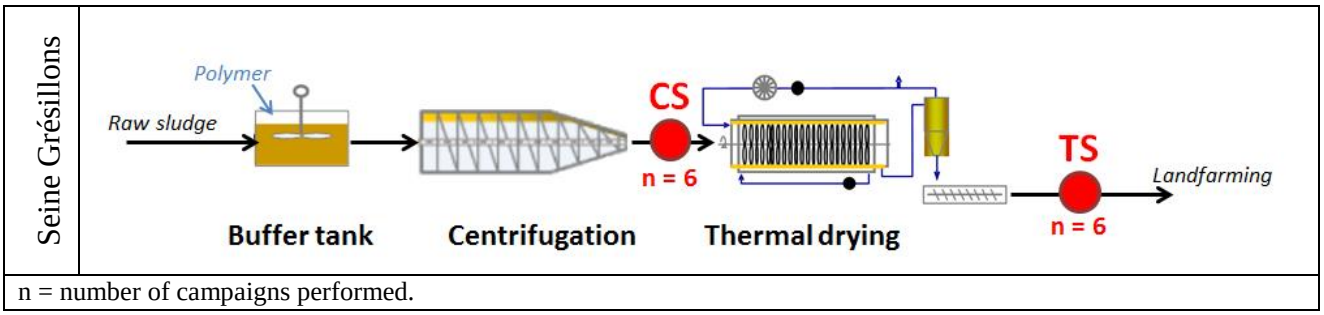
2.1. Sludge treatment processes (STP) description and sampling procedure

Three STPs from three WWTPs in Paris were studied (Figure 1). It should be noted that these WWTPs, run by the Parisian public sanitation service (SIAAP), treat wastewater from the same catchment (downstream Paris conurbation) and the comparison of processes and treated sludges (digested sludge - DS, centrifuged sludge - CS, sludge cake - SC and thermally dried sludge - TS, Figure 1) is then relevant to underline the differences in micropollutants fate.

The Seine Centre plant treats 240 000 m^3 of wastewater per day. Sludge produced is first centrifuged to achieve a volume reduction, resulting in a production of almost 21 000 tons DM of centrifuged sludge per year (SIAAP source). Then, sludge is incinerated producing ash and smoke, which is specifically treated to minimize odors. The Seine Aval plant receives 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). The first STP consists in a mesophilic (37°C) anaerobic digestion to transform an important part of organic matter into biogas and eliminating pathogens and parasites. Digested sludge is then dewatered by thickening, thermal conditioning (heat exchange and cooking at 195°C and 20 bars) and press filtration. These successive treatments allow reducing sludge volume by more than a factor 10 (i.e. DM, Table 2) and producing a dewatered cake called sludge cake which is reused as agricultural fertilizer. The Seine Grésillons plant treats 100 000 m^3 of wastewater per day. Sludge treatment is performed by centrifugation and thermal drying. The thermal drying process can operate at a wide range of temperature, but the facility used in this plant operates at a high temperature (260°C) compared to conventional dryers (generally 105°C (Voulvoulis and Lester, 2006)). This allows reducing the water content drastically (i.e. DM content, Table 2) to obtain, after compacting, almost 8 000 tons DM of solid pellets per year (SIAAP source) which are stocked in big bags or silos before to be reused in agriculture. More information about WWTPs and treatment processes are presented in supporting material - Table 1 and on SIAAP website (www.siaap.fr - in French).





n = number of campaigns performed.

Figure 1 - Layouts of the three studied plants

Different sampling points have been defined to study both the quality of treated sludges and the fate of micropollutants during treatments: raw sludge (RS), CS, DS, TS and SC – Figure 1. Thus, inlet and outlet of digestion, centrifugation and thermal drying were sampled, as well as SC.

While six independent campaigns (between October and December 2011) were performed for thermal drying and sludge cake, consecutive day sampling was considered for centrifugation and digestion to throw off the possible lack of homogeneity. Thus, one sample per day was collected within three consecutive days for digestion (October 2011). Similarly, six samples were collected within two periods of three consecutive days (one in October and one in December) for centrifugation. Each sludge sample was manually collected (2 L for TS and SC - 3 L for RS, CS and DS) respecting all guidelines to avoid sample contamination. SC samples are a mix of sludge produced within a week (7 days) while other samples were punctual due to technical issues. For digestion, a period of 16 days has been applied between inlet and outlet samples to take the solid retention time into account.

2.2. General sludge quality parameters

Table 2 displays the general quality parameters for each sample, i.e. dry matter (DM, in % - 1% = 10 g/L) and volatile matter (VM, in % DM). Both criteria are commonly used in sludge management. Minimum, maximum and mean (in italics below) values are given.

Table 2 - Dry matter and volatile matter contents (min - max - *mean*) of sludges studied

	Digestion		Thermal drying		Centrifugation		Sludge cake
	RS	DS	CS	TS	RS	CS	TS
Dry matter - DM (% - 10 g/L)	3.0 - 3.3 *3.2*	1.8 - 1.9 *1.8*	24.9 - 27.7 *26.2*	92.9 - 95.6 *94.1*	3.6 - 4.4 *3.9*	22.3 - 24.9 *23.8*	34.2 - 52.7 *48.2*

Volatile matter - VM (% DM)	78.8 - 80.1 *79.3*	62.0 - 62.1 *62.0*	66.1 - 72.9 *70.5*	65.4 - 74.4 *70.4*	74.2 - 78.3 *77.1*	75.9 - 80.0 *79.0*	39.1 - 48.0 *41.9*

Overall, removals of dry matter and volatile matter during anaerobic digestion are about 42% and 56% respectively. This removal is in good agreement with conventional anaerobic digestion removal (Moletta, 2008). VM content in sludge cake is low (42 % DM) compared to the other sludges highlighting a removal during the sludge cake production process (thermal conditioning + press filtration, Figure 1). This is most likely due to the solubilization of a fraction of the organic matter (Neyens and Baeyens, 2003; Valo et al., 2004) during thermal conditioning (195°C and 20 bars). This fraction is then removed with water during press filtration. In contrary, VM is rather constant in both thermal drying and centrifugation, highlighting that VM is whether not or similarly removed (no change in percentage) as DM during these treatments.

2.3. Pollutants and analytical procedures

A total of 117 pollutants were monitored and depending on the compound, two accredited laboratories (COFRAC - French official accreditation committee) were involved: Eurofins and SIAAP laboratory. Table 3 gives the different groups of pollutants monitored, their analytical procedures and quantification limits. The complete list of studied compounds is given in supporting material - Table 2.

Table 3 - Groups of pollutants and analytical methods

Groups[a]	Total[b]	n[c]	Standards	Methods[d]	LOQ[e]
Organotins	4	3 - 6	Eurofins Internal Method	GC-PFPD	0.005
Organochlorine pesticides	22	3 - 6	XP X 33-012	GC-MSMS	0.005 to 0.800
Organophoshorus pesticides	2	3 - 6	XP X 33-012	GC-MSMS	0.02
Nitrogenous herbicides	2	3 - 6	XP X 33-012	GC-MSMS	0.02
Urea pesticides	4	3 - 6	XP X 33-012	GC-MSMS	0.02 to 0.05
Various herbicides	3	3 - 6	XP X 33-012	GC-MSMS	0.02 to 0.05
Benzene based products	12 2	3 - 6	NF ISO 15009 XP X 33-012	GC-FID GC-MSMS	0.02
Nitrobenzenes	3	3 - 6	XP X 33-012	GC-MSMS	0.05
VOCs	17	3 - 6	NF ISO 15009	GC-ECD	0.02
Phenolic compounds	8	3 - 6	XP X 33-012	GC-MSMS	0.04 to 0.05
DEHP	1	3 - 6	XP X 33-012	GC-MSMS	0.05
Alkylphenols	6	3 - 6	XP X 33-012	GC-MSMS	0.01
PBDEs	9	3 - 6	XP X 33-012/Isotopic Dilution	GC-MSMS	0.05
Other organic compounds[f]	3	3 - 6	XP X 33-012	GC-MSMS	0.01 to 0.02
Eurofins screening	*98*				
PAHs	6	3 - 6	NF ISO 17993	GC-MSMS	0.04 to 0.2

PCBs	7	3 - 6	XP X 33-012	GC-MSMS	0.01
Metals	6	3 - 6	NF EN ISO 11885 (T90-136)	ICP-AES	5 to 20
SIAAP laboratory screening	*19*				

a Groups of molecules: DEHP = di(2-ethylhexyl) phthalate ; PBDE = polybromodiphenyl ethers; VOC = volatile organic compounds; PAH = polycyclic aromatic hydrocarbons; PCB = polychlorobiphenyls.
b Number of molecules.
c Number of measuring campaigns.
d Analytical methods: GC = gas chromatography; GC-PFPD = GC with pulsed flame photometric detector; GC-MSMS = GC with tandem mass spectrometry; GC-ECD = GC with electron capture detector; GC-FID = GC with flame ionization detector; ICP-AES = inductively coupled plasma with atomic emission spectrometry.
e Quantification limit in mg/kg DM.
f Chloroalkanes C10-C13, tributylphosphate and hexachlorocyclopentadiene.

2.4. Methodology of result exploitation and efficiency evaluation

Only contents above the quantification limits were considered. Then, removals have been calculated only when the compound is quantified both in inlet and outlet of the treatment. Removals could be also evaluated when the compound is quantified only in inlet or outlet, but this case was not encountered here.

For the second part of this paper dealing with pollutant fate during sludge treatment, thermal drying and centrifugation are differently examined from anaerobic digestion. In fact, dry matter is not removed and only water quantity is reduced (volume reduction) during dewatering treatments such as thermal drying and centrifugation. Given this, removals of micropollutant content (in mg/kg DM) have been considered for these treatments since it is not linked to the volumetric flow, which varies between inlet and outlet resulting from water removal.

In contrary, since the matrix is reduced as regards digestion, removal calculations were not based on content removals but on the removal of micropollutant loads. Therefore, the micropollutant loads ($L_{\mu p}$) have been calculated according to Equation 1.

$$\boldsymbol{L_{\mu p}\left[{}^{\boldsymbol{mg_{\mu p}}}/_{\boldsymbol{day}}\right] = C_{\mu p} \times DM \times Q_v;}$$

With $C_{\mu p}$: micropolluant content (mg/kg DM), DM: dry matter content (kg/L) and Q_v: sludge feed rate (L/day).

Equation 1

A conservation of volumetric flow during anaerobic digestion has been considered. The removal of

load (R_{load}) is then given by Equation 2, calculated from the removal of the micropollutant content (R_C) and the removal of the dry matter content (R_{DM}).

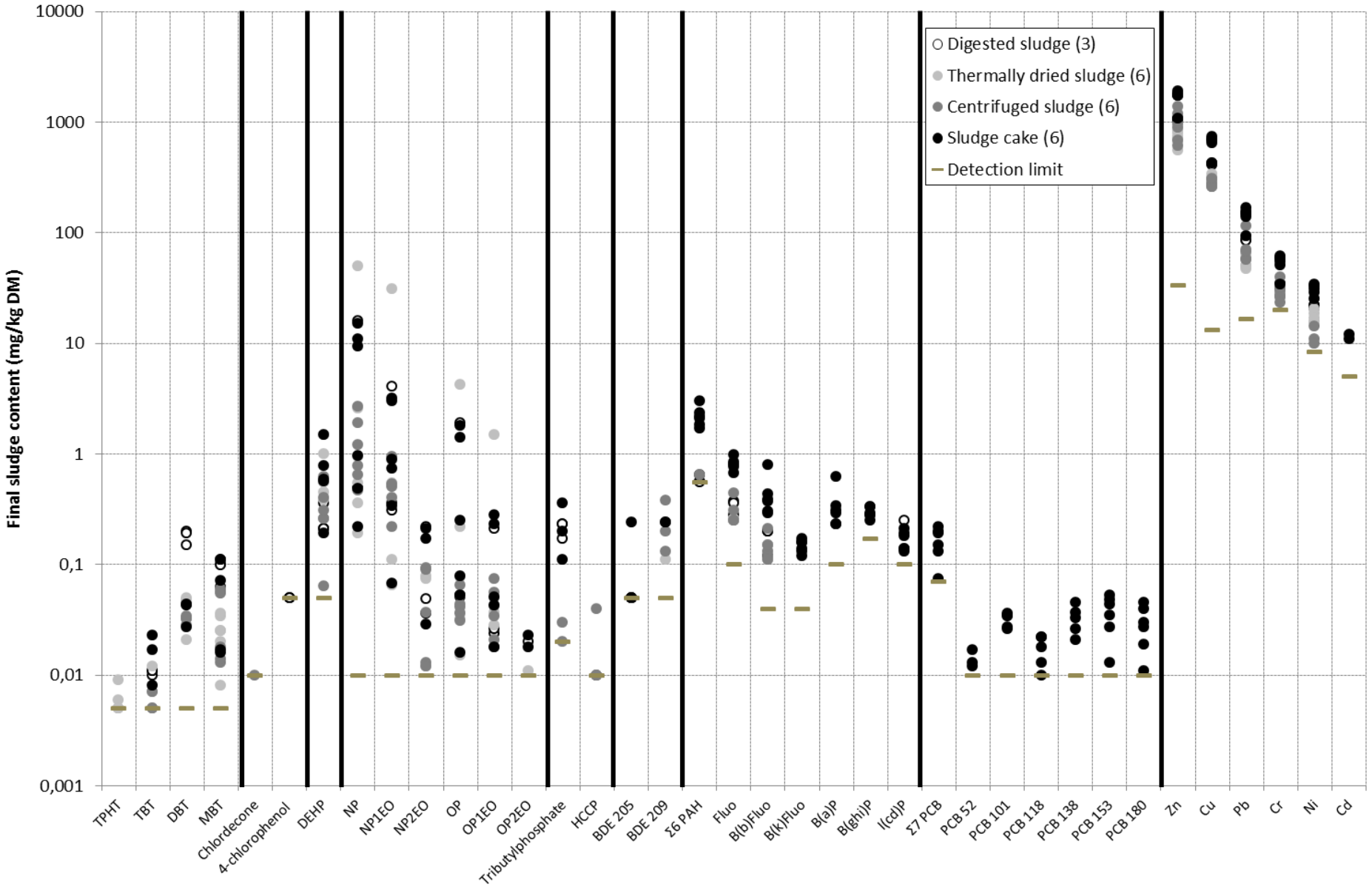
$$R_{load} = {(L_{in} - L_{out})}/{L_{in}} = 1 - {C_{out}}/{C_{in}} \times {DM_{out}}/{DM_{in}} = 1 - (1 - R_C) \times (1 - R_{DM});$$

Equation 2

3. Results and discussion

3.1. Micropollutant contamination of treated sludges

Figure 2 displays the quality of treated sludges regarding micropollutants. Each type of sludge (number of samples in brackets) and quantification limits for each compound detected are illustrated. A table with contents of all compounds found in treated sludges is given in supporting material - Table 3. In order to enable comparison of results, Table 4 provides a literature synthesis concerning micropollutant sludge contents.



With TPHT: triphenyltin, TBT: tributyltin, DBT: dibutyltin, MBT: monobutyltin, DEHP: di(2-ethylhexyl)phthalate, NP: nonylphenols, NP1EO: nonylphenol monoethoxylate, NP2EO: nonylphenol diethoxylate, OP: octylphenol, OP1EO: octylphenol monoethoxylate, OP2EO: octylphenol diethoxylate, HCCP: hexachlorocyclopentadiene, BDE 209: decabromodiphenyl ether ; Fluo: fluoranthene, B(b)Fluo: benzo(b)fluoranthene, B(k)Fluo: benzo(k)fluoranthen, B(a)P: benzo(a)pyrene, B(ghi)P: benzo(ghi)perylene, I(cd)P: indeno(1,2,3-cd)pyrene, Zn: zinc, Cu: copper, Pb: lead, Cr: chromium, Ni: nickel, Cd: cadmium.

Figure 2 - Micropollutant contents of treated sludges studied

Table 4 - Literature review of studied micropollutants in sludge

Molecules	Location	Type of sludge	n[1]	Mean[2]	Min[2]	Max[2]	Reference
Organotins							
TPHT	World	Various	5	0.63	<0.02	9	(Clarke and Smith, 2011)
TBT	Sweden	Digested	1	0.004	*	*	(Olofsson et al., 2012)
	Switzerland	Digested	1	1.1 ± 0.4	*	*	(Fent, 1996)
	World	Various	7	0.86	0.02	6	(Clarke and Smith, 2011)
DBT	Sweden	Digested	1	0.075	*	*	(Olofsson et al., 2012)
	Switzerland	Digested	1	1.5 ± 0.5	*	*	(Fent, 1996)
	World	Various	6	1.28	0.41	7.5	(Clarke and Smith, 2011)
MBT	Sweden	Digested	1	0.074	*	*	(Olofsson et al., 2012)
	Switzerland	Digested	1	0.5 ± 0.2	*	*	(Fent, 1996)
	World	Various	6	0.93	0.1	6	(Clarke and Smith, 2011)
Phtalates							
DEHP	Finland	Digested	1	126	91	179	(Marttinen et al., 2003)
	Spain	Digested	1	159	13	345	(Aparicio et al., 2009)
	Spain	Thermally dried	1	148.8	1.5	3 514	(Abad et al., 2005)
	World	Various	13	58	<0.02	3 514	(Clarke and Smith, 2011)
Alkylphenols							
NP	Greece	Digested	1	0.17	<0.04	0.45	(Stasinakis et al., 2008)
	Spain	Digested	1	102.1	<0.19	358.2	(González et al., 2010)
	France	Thermally dried	1	61.7	16.5	124.9	(Ghanem et al., 2007)
	World	Various	24	128	0.02	2530	(Bergé et al., 2012a)
NP1EO	Greece	Digested	1	12.3	1.01	41.3	(Stasinakis et al., 2008)
	Spain	Digested	1	53.2	<0.75	287.8	(González et al., 2010)
	World	Various	18	40.2	0.15	850	(Bergé et al., 2012a)
Various							
Tributylphosphate	Denmark	Various	1	*	<0.020	2.400	(Tørsløv et al., 1997)
	Sweden	Digested	1	0.011	*	*	(Olofsson et al., 2012)
PBDEs							
BDE 209	Sweden	Various	1	0.120	0.006	1.000	(Law et al., 2006)
	Germany	Digested	1	0.443	0.133	1.339	(Knoth et al., 2007)
	World	Various	14	1.039	0.003	18.632	(Clarke and Smith, 2011)
Σ6 PBDEs [3]	Sweden	Various	1	0.250	0.024	1.260	(Law et al., 2006)
	Germany	Digested	1	0.577	0.186	1.627	(Knoth et al., 2007)
Σ8 PBDEs [4]	World	Various	7	1.360	0.005	4.690	(Clarke and Smith, 2011)
PAHs							
Σ6 PAHs [5]	UK	Digested	1	14.8	4.75	28.1	(Stevens et al., 2002)
	France	Dewatered	1	1.68	0.52	3.36	(Blanchard et al., 2004)
Σ11 PAHs [6]	Spain	Thermally dried	1	1.89	0.13	7.35	(Abad et al., 2005)
PCBs							
Σ7 PCBs [7]	UK	Digested	1	0.080	0.033	0.221	(Stevens et al., 2002)
	Spain	Thermally dried	1	0.041	<0.006	0.131	(Abad et al., 2005)
	France	Dewatered	1	0.617	0.12	1.93	(Blanchard et al., 2004)
Metals							
Zn	China	Dewatered	1	557.4	361.0	1 105.9	(Chen et al., 2008)
	Greece	Digested	1	4 500 ± 450	*	*	(Karvelas et al., 2003)
	France	Treated	1	875 ± 1005	*	*	(Martin et al., 2008)
Cu	China	Dewatered	1	557.4	361.0	1 105.9	(Chen et al., 2008)
	Poland	Digested	1	240.4 ± 1.2	*	*	(Sprynskyy et al., 2007)
	Greece	Digested	1	1 200 ± 220	*	*	(Karvelas et al., 2003)
	France	Treated	1	335 ± 338	*	*	(Martin et al., 2008)
Pb	China	Dewatered	1	225.4	67.0	659.0	(Chen et al., 2008)
	Poland	Digested	1	38.12 ± 1.2	*	*	(Sprynskyy et al., 2007)
	Greece	Digested	1	330 ± 84	*	*	(Karvelas et al., 2003)

France	Treated	1	71 ± 70	*	*	(Martin et al., 2008)

[1] n = number of publications.
[2] in mg/kg DM.
[3] BDE 47, 99, 100, 153, 154 and 209.
[4] BDE 28, 47, 99, 100, 153, 154, 183 and 209.
[5] Fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene.
[6] See [5] + acenaphtene, phenanthrene, fluorene, pyrene and benzo(j)fluoranthene.
[7] PCB 28, 52, 101, 118, 138, 153 and 180.

Out of the 117 molecules monitored (Table 3), 35 are detected in treated sludges but pesticides, VOCs, hepta-, hexa-, penta-, tetra- and octa- PBDEs and benzene based products (BBP) were never detected. Concerning pesticides, it is consistent as they are mainly hydrophilic (log K_{ow} < 3-4) and their presence in water are both variable and weak (Gasperi et al., 2010). Moreover, a lot of them are now forbidden (i.e. endosulfan or atrazine). Similarly, VOCs and BBPs are volatile and mainly removed by volatilization during wastewater treatment (Byrns, 2001; Joss et al., 2008). Finally, BDE 209 is the main PBDE congener used and found in water by far and other congeners are generally quantified in sludge in lower contents than the detection limit in this study (50 µg/kg DM), as showed by (Knoth et al., 2007). Contrariwise, metals (Zn, Pb, Cu and Cr), organotins, DEHP and alkylphenols are always detected in all samples. In addition, tributylphosphate, a hydrophobic compound principally used as extractant and plasticizer but also employed as anti-foaming or herbicide agent in detergents or paints, was detected in several samples. PCBs and PAHs are classically found in sludges (Table 4), but they are only detected in sludge cake in this study due to analytical performances (detection and quantification limits).

The pollutant content variability is broadly weak (less than one order of magnitude) for one type of sludge except for alkylphenols. For this family, a variability of two orders of magnitude is observed within a type of sludge, as observed for DS and TS comparatively to others sludges. This high variability of NP was also observed for wastewater by (Bergé et al., 2012b). Contents from sludge to sludge vary in a range of about one order of magnitude due to treatments but overall all sludges have a similar micropollutant pattern. This is consistent as they are produced by WWTPs treating water from the same catchment. Sludge cake and digested sludge are the most contaminated,

particularly for PAHs, PCBs and metals, with contents found in the upper part of the range. This results from a dry matter removal of more than 40% allowed by digestion and further treatments (sludge cooking) in Seine Aval (Figure 1). In contrary, contents in centrifuged and thermally dried sludges are found in the lower part of the range for most of the compounds.

Contents found are in accordance with the literature (Table 4), particularly for organotins (0.005 - 0.2 mg/kg DM), alkylphenols (NP 0.22 - 50 and NP1EO 0.067 - 31 mg/kg DM), BDE 209 (0.11 - 0.38 mg/kg DM), individual PAHs (0.11 - 0.99 mg/kg DM), PCBs (0.010 - 0.053 mg/kg DM) and metals (10-3 000 mg/kg DM). In particular, high contents of metals, NP and NP1EO are observed while other compounds are all found below 1 mg/kg dm. Tributylphosphate is poorly documented in sludge and is found between 0.02 and 0.36 mg/kg DM. Surprisingly, DEHP is found in the very lower part of the range displayed in the literature (0.1 - 1 mg/kg DM), especially in digested sludge. Nevertheless, (Blanchard et al., 2012) observed similar DEHP levels in sludge coming from the same plants.

Comparing to regulations (Table 1), treated sludges respect European standards (EC, 1986) for metals overall, except Cd for which two sludge cake samples slightly exceeded the actual threshold value (10 mg/kg DM). Similarly, French standards (Table 1) are respected as contents of Σ7 PCBs (< 0.8 mg/kg DM) and both individual and sum of PAHs (< 2 and < 5 mg/kg DM) are always below the threshold values for agricultural reuse (EC, 2001). In addition and as shown by Figure 3 illustrating the historical evolution of heavy metals and PAH yearly average contents in sludge cake, no exceedances of threshold values were observed in the past, except the first years after the application of the Urban Wastewater Treatment Directive (EC, 1986) for Zn, Pb and Cd. Zn content respects regulation since 1988, Pb since 1987 and Cd since 1993, while Cu, Ni and Cr ones have always been below threshold values on a yearly average basis. Similarly, PAH contents were

always in accordance with French standards since they are measured (2001). All data presented in Figure 3 were provided by SIAAP from their routine quality controls which are accredited and subject to European norms. They are published for the first time (PAHs) or represent an update of former works (metals - (Meybeck et al., 2007)).

Moreover, contents obtained in this study (mean values in the box on the right - Figure 3) are totally consistent as they are in the continuity of the time-trends from Seine Aval sludge, both for PAHs and metals.

An important decrease of metal contents in sludge cake is observed since the 80s. In particular, contents have decreased from 1980 to 2012 with a factor 3 for Zn (-70%), a factor 7 for Cr (-89%) and a factor 3 to 5 for Ni (-88%), Cu (-65%), Pb (-80%) and Cd (-95%). This tendency results from a decrease of emissions like atmospheric fallout, roof runoff, street runoff, domestic sewage and industrial sewage (Thevenot et al., 2007), which was driven by different regulatory standards adopted over past decades and by global de-industrialization of Parisian catchment (Meybeck et al., 2007), inducing changes in metal uses and decrease of both industrial and domestic metal discharges. However, this decrease is not linear and three phases can be observed: until 1994 contamination of sludge decreased significantly (i.e. -76% for Zn), then between 1994 and 1996 a short period of increase is observed before another phase of decrease which is slight and tends to stabilize in the 2000s. Finally, all metals seem to undergo the same evolutions. PAH data are available since 2001 and it is not possible to establish a clear trend as contents vary with a factor 2 from year to year. In fact, the evolutions of the three PAH contents in sludge seem linked as they have all the same historical pattern. Even if contents seem overall stable over the years, periodic evolutions seem to occur when looking at weekly data (not represented), with contamination peaks observed regularly.

Actually, time-trends of sludge contamination significantly follow time-trends of quantity used in the society, generally decreasing due to regulatory actions, as shown by (Olofsson et al., 2012). Even if no time-trend is available for PBDEs in Parisian sludge, (Ricklund et al., 2009) observed a factor 10 increase in Swedish treated sludge content of BDE 209 between 2000 and 2009, showing the increasing use of this compound during this period. Thus largely used compounds can have a tendency to contaminate more and more sewage sludge if limitation is not stronger enough.

3.2. Removal of micropollutants by sewage sludge treatments

3.2.1. Thermal drying and centrifugation

Figure 4 displays the content removals of studied compounds within dewatering processes (thermal drying and centrifugation).

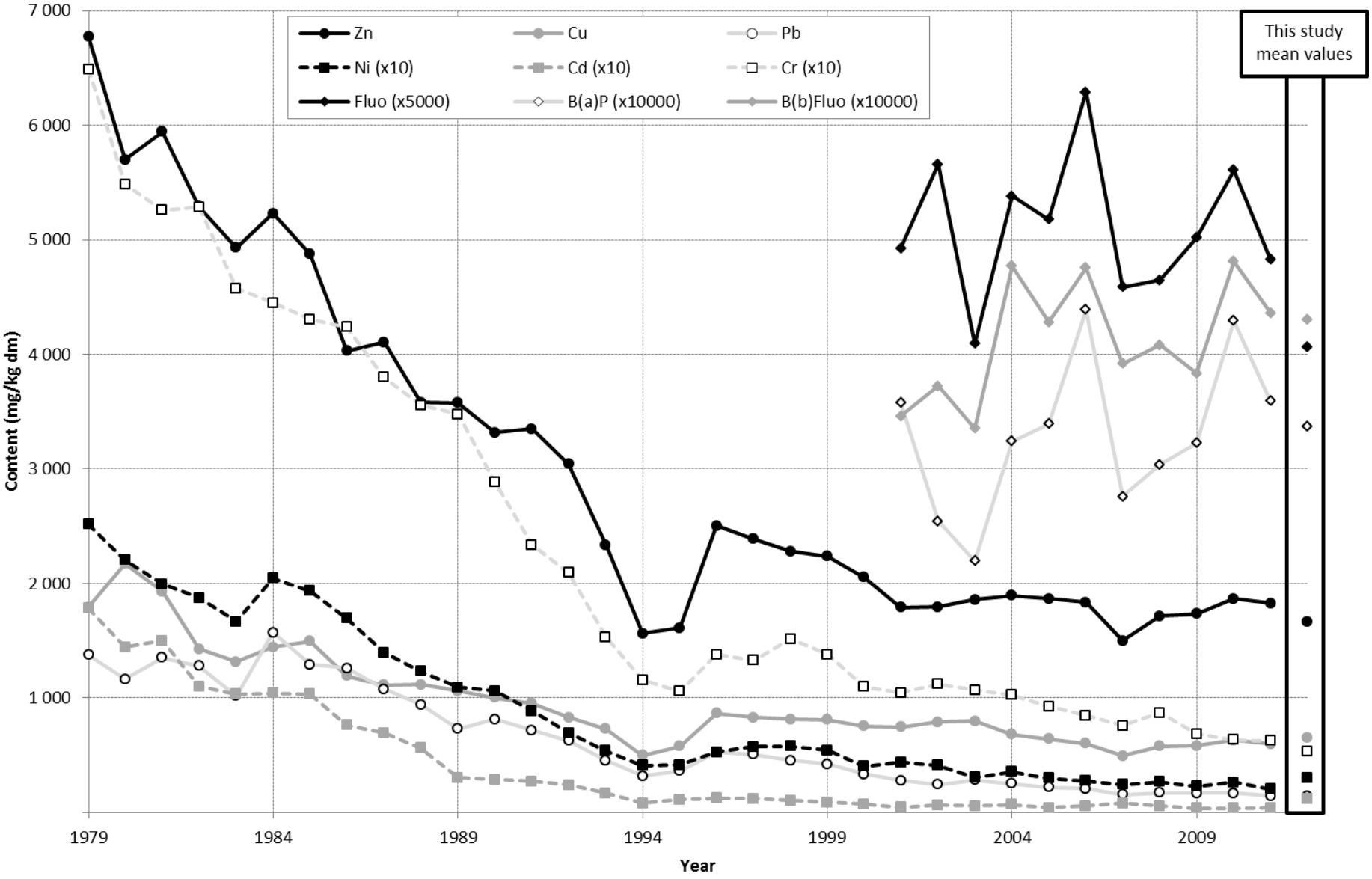


Figure 3 - Historical evolution of metal and PAH contamination of sludge cake from SIAAP routine quality controls at Seine Aval WWTP

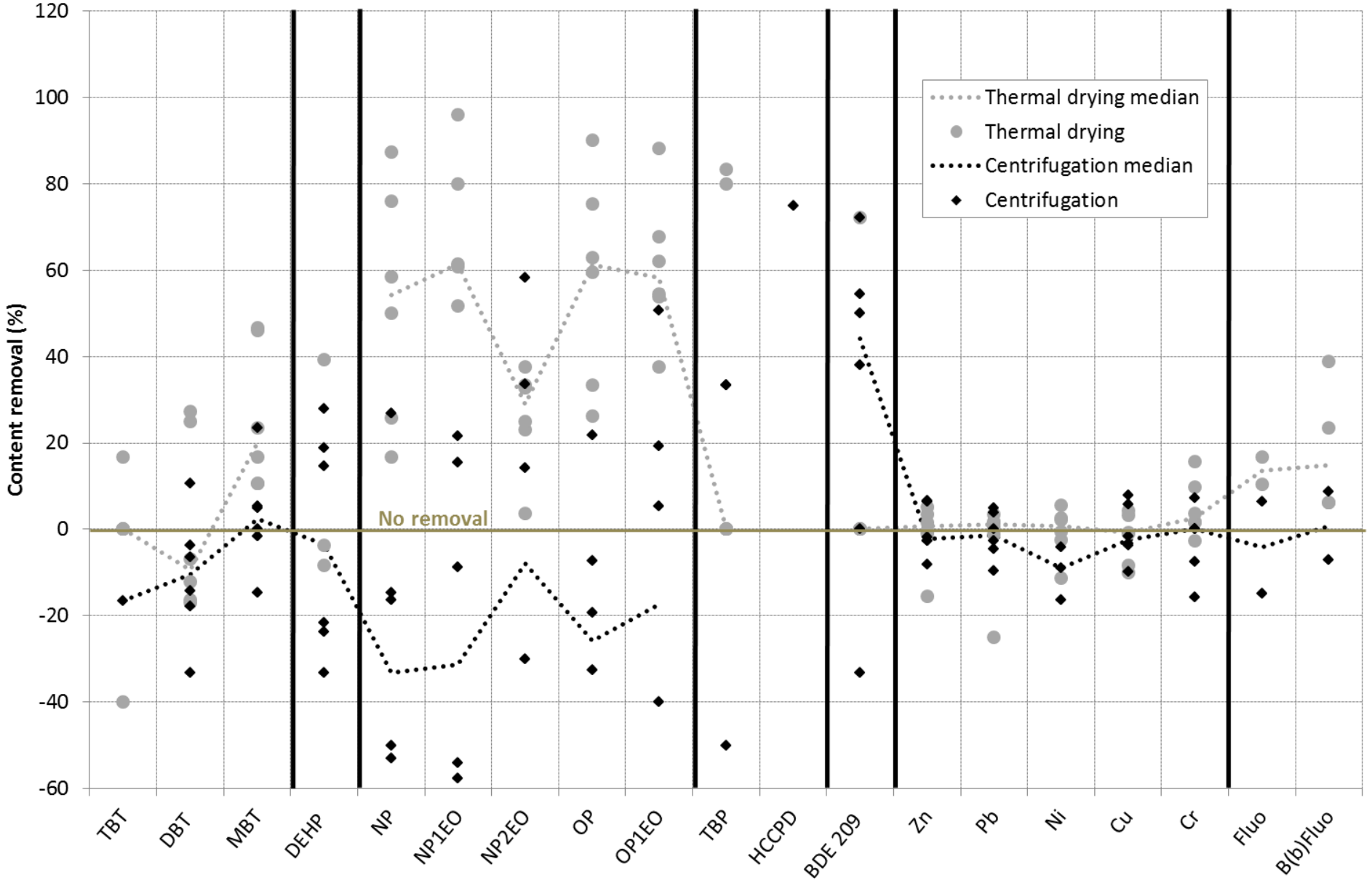


Figure 4 - Fate of micropollutants during dewatering processes

Results obtained for both dewatering processes show a high variability of content removals, except for metals and PAHs. The higher variability of removal for organic pollutants, particularly for alkylphenols, compared to metals, probably results from both the significantly lower contents of these compounds (higher analytical uncertainty) and the variability of the mechanisms involved in their removal. For metals, the low variability can be explained by both the lower analytical uncertainty and their fate during sludge treatment, since no removal mechanism is occurring for them.

Values calculated for hexachlorocyclopentadiene and tributylphosphate have to be considered with caution as these molecules were always detected very close from their detection limits or not detected.

Most of pollutants are broadly not removed during dewatering treatments, whatever the process used. This is particularly significant for metals as they are known to be highly persistent (not biodegradable and volatile) during sludge treatment (Chipasa, 2003; Dong et al., 2013). Contents of metals, TBT, DBT, tributylphosphate and DEHP are not affected by both treatments.

Only alkylphenols, MBT, PAHs and BDE 209 seem to have a different behavior in both treatments. Contrary to centrifugation, thermal drying seems to allow a quite stable removal of about 10 - 40% for PAHs and MBT, and a very variable removal of 20 - 90% for alkylphenols. As temperature inside the dryer reaches 260°C, transfers to atmosphere by desorption and volatilization could be significantly enhanced as depicted by (Tuncal et al., 2011) in spite of a short solid retention time (3 min). Similarly, abiotic degradation of these compounds, such as hydrolysis, may occur at this temperature (Kepp et al., 2000; Veeken and Hamelers, 1999). More specific measurements should be performed to highlight these pathways. In contrary, a removal of about 50% of BDE 209 is

observed in centrifugation despite a high variability, while content is rather stable during thermal drying. As this molecule is strongly hydrophobic (log K_{ow} = 12.8, (Langford et al., 2005)), so strongly linked to the particulate phase, further specific measurements are needed to explain this astonishing result.

3.2.2. Anaerobic digestion

Anaerobic digestion is widely used all over the world to stabilize sludge and reduce the quantity of dry matter. Results obtained during campaigns performed are represented in Figure 5 separated by behavior by dotted lines.

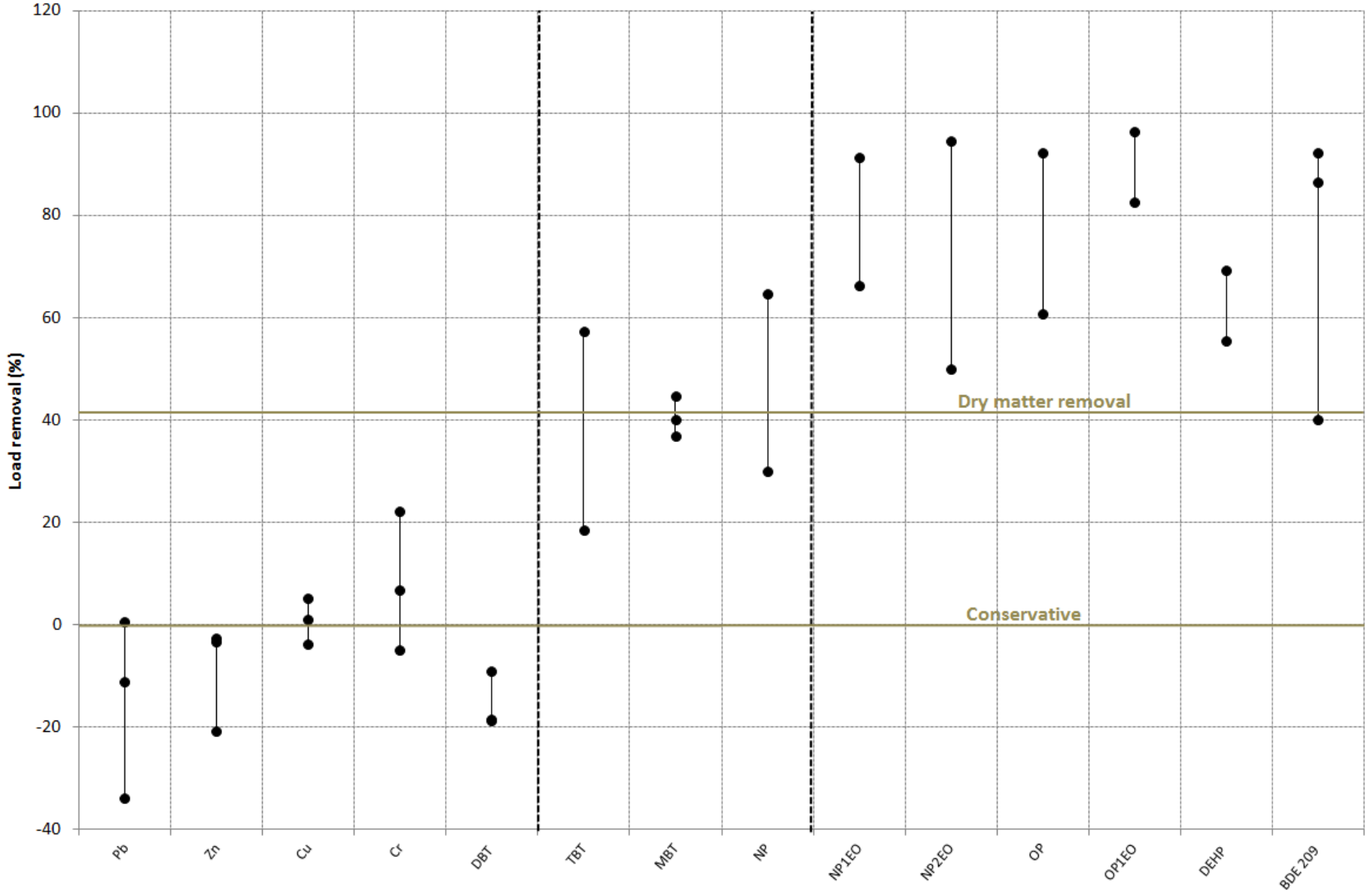


Figure 5 - Fate of micropollutants during mesophilic anaerobic digestion

As regards the three campaigns performed and similarly to dewatering processes, a higher variability of removal is observed for organic pollutants (20-50%) than for metals like Pb or Cr (max 30%), probably due to lower contents and a variability of degradation. However, three different behaviors can be observed depending on the compound: i) conservation of load, ii) removal in the same extent to dry matter removal and iii) removal higher than dry matter removal. Conservative species are those which are not removed resulting in an increase of their contents (mg/kg DM) in digested sludge, as matrix is partially removed (DM - 42%, Table 2). In contrary, compounds with removal of load higher than dry matter have their content decreasing in sludge. Finally, a load removal comparable to dry matter removal is linked with stability in sludge content. Thus, even if every positive load removal corresponds to a real elimination of the compound, it doesn't reflect automatically a decrease of content in sludge.

Loads of metals are conservative during digestion which is consistent as they are not biodegradable and volatile. Thus, this confirms the validity of the data treatment strategy applied in this study. This conservation results in an increase of metal contents in sludge within treatments. In the context of land farming, limitation of emissions (contamination of water) seems to be the easiest strategy to reduce metals contamination of sludge. As it was previously shown (Meybeck et al., 2007), this strategy clearly leads to a decrease of contents in treated sludge.

Organotins are degraded similarly to dry matter except DBT which is not removed and even slightly produced (-15%). This is confirmed by Figure 2 where it is clear that DBT content in digested sludge is significantly higher than in other sludges. Biodegradation of TBT in DBT through dealkylation mechanism has been observed at laboratory scale and in surface water and sediment under both aerobic and anaerobic conditions (Craig, 2003; Maguire and Tkacz, 1985; Stasinakis et al., 2005). This reaction in anaerobic digestion of sludge could counteract DBT biodegradation and

explain this result.

Alkylphenols are more removed than dry matter, except NP. Anaerobic biodegradation of carboxylate and ethoxylate species to NP has been observed in the literature (Ejlertsson et al., 1998; Lu et al., 2008) as well as NP biotransformation (Patureau et al., 2008; Salanitro and Diaz, 1995). Thus, the lesser load removal observed for NP compared to other alkylphenols could actually highlight that NP anaerobic biodegradation is slower than its formation from other alkylphenols with longer chains, as proposed by (Chang et al., 2005; Stasinakis, 2012). However, biodegradation kinetic measurements should be performed to validate this assumption. DEHP (50 - 70%) and BDE 209 (40 - 90%) are also removed in a higher proportion than matrix. For DEHP, such high removal has already been observed at pilot scale by (Parker et al., 1994). Biodegradation of phthalate esters such as DEHP has been reported under methanogenic conditions (El-Hadj et al., 2006; Gavala et al., 2003; Marttinen et al., 2003) and results from hydrolysis of the two ester side chains to phthalic acid and alkyl alcohols which can then be degraded to methane and carbon dioxide (Shelton et al., 1984; Stasinakis, 2012). Concerning BDE 209, anaerobic debromination of this congener to less brominated congeners could explain this removal as this mechanism has been highlighted by several papers (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008).

Overall, alkylphenols, DEHP and BDE 209 are significantly removed (> 50%) while organotins and NP are moderately removed (40%) and metals and DBT are not removed. These results show that anaerobic digestion allows a significant removal of some micropollutants despite not being designed for that.

4. Conclusions

This study has investigated the fate of a large panel of micropollutants (n=117) during sludge

treatment and the quality of treated sludges obtained. While some data are available for anaerobic digestion, centrifugation and thermal drying are still not documented. In addition, the content of a lot of micropollutants in French and Parisian sludges in particular is not well documented.

Overall, treated sludges have a similar micropollutant pattern despite different treatments. Some compounds are always detected (metals, organotins, alkylphenols, DEHP) while others are never detected (pesticides, BBPs and VOCs). Contents found in the different sludges are rather similar and in accordance with previous works. In treated sludges, micropollutant contents are always in compliance with regulations except two sludge cake samples for which Cd exceeds the threshold value. Historical evolution of micropollutants in sludge cake allows showing that contamination is directly linked to compounds uses and establishment of regulations on uses seems to be an efficient strategy to decrease the sludge content of micropollutants, as it is the case for metals.

Regarding dewatering processes, centrifugation and thermal drying seem to have no significant impact on micropollutant content of sludge overall. A slight removal of alkylphenols, MBT and PAHs by abiotic transfers (volatilization, hydrolysis) seems however to be possible by thermal drying thanks to the high temperature inside the reactor. In contrary, digestion enables the removal of a lot of organics. DEHP, BDE 209, organotins and alkylphenols are similarly or better removed than dry matter which is the designing parameter of the process, while metals are persistent. This result confirms that among the existing and largely used sludge treatments, digestion is the only one with composting to really allow a reduction of the biodegradable micropollutants load.

Specific studies on mechanisms involved in thermal drying and on the fate of micropollutants during composting should be held to complete this work. In addition, a similar work will be soon performed on pharmaceuticals, to enrich the data base obtained and improve the understanding of

the micropollutant fate during sludge treatments. An optimization of digestion operational parameters (temperature, hydraulic retention time, pre-treatment) in order to improve matrix elimination could lead to a significant improvement of treated sludge quality in terms of organic micropollutants, as they influence the biodegradation of a lot of compounds such as DEHP or alkylphenols (El-Hadj et al., 2007; Stasinakis, 2012). However, some specific processes such as bioleaching treatments (Pathak et al., 2009) could be implemented in parallel of regulations reinforcement to decrease the metal contents of sewage sludge, as they are currently persistent in almost all the treatments including digestion.

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