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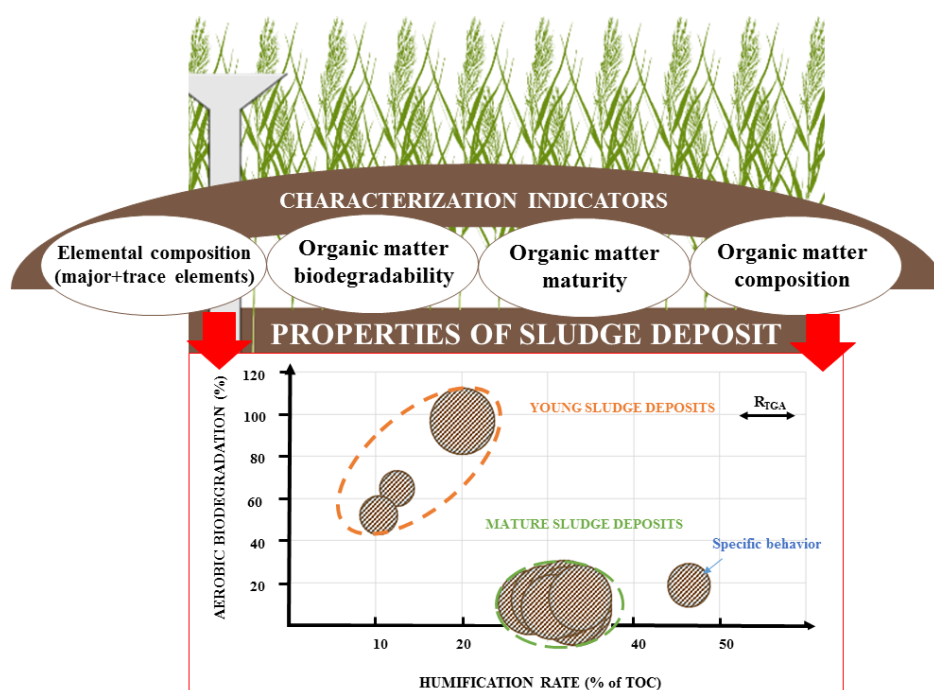
# Comparative characterization of surface sludge deposits from fourteen French vertical flow constructed wetlands sewage treatment plants using biological, chemical and thermal indices

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## Graphical abstract



## Highlights

- Particulate organic matter (POM) in sludge deposits (SD) exhibits specific properties.
- Young deposits ( $\leq 1$  y) and mature de-positions ( $>3$  y) identified as 2 distinct groups.
- Additional pretreatments affected young-age sludge deposits characteristics.
- State of maturation of POM in SD inter-mediate between peat and wet meadows

## **Abstract**

Due to their design and mode of operation, French Vertical Flow Constructed Wetlands (VFCWs) accumulate suspended solids from the inflow wastewater in the form of a sludge layer at the surface of the first filter. In order to maintain the treatment performance over the long term, the characteristics of the sludge deposits and their evolution have to be well described. In this objective, a panel of sludge deposit samples taken from 14 French VFCW sewage treatment plants was investigated. Elemental composition and organic matter content, nature and reactivity were analyzed. Results clearly revealed two categories of sludge deposits, namely the “young-age plants” type (1 year of operation and less) and the “mature plants” type (3 years of operation and more). Sludge deposits from the “mature plants” exhibited same biological, physical and chemical properties. Their organic matter was globally less abundant, more humified and less biodegradable than in the young-age plants type. Their overall contents in trace metals were also higher, although in a limited manner. The effect of additional treatments, particularly  $\text{FeCl}_3$  injection for phosphorus precipitation, was observable in the “young-age plants” group. Finally, the sludge deposits sampled from one particular plant with specific operating conditions were found to exhibit very different characteristics from those of either groups identified. This observation underlined the influence of local conditions on the typology of the sludge deposits.

## **Keywords**

Sludge deposits; Constructed wetland; indices; Characterization; Organic matter; Ageing

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## 1. Introduction

French Vertical Flow Constructed Wetlands (VFCWs) have become in the recent years in France the sewage treatment system most widely used in rural communities of  $\leq 2000$  Population Equivalent (Bellin, 2016). This rapid development may be explained by the high level of performance of these systems, their good social acceptability and landscape integration, their low energy requirements, easy operation, and low maintenance (Liu et al., 2015a; Semeraro et al., 2015; Wu et al., 2014).

The so-called “French VFCW system” comprises two stages of filters where the first stage is fed with unsettled raw wastewater. This design results in the formation of a sludge layer at the surface of the first filter which has mainly been considered until recently through its hydraulic aspects and its negative consequences with regards to the potential risk of clogging (Hua et al., 2018; Knowles et al., 2011; Nivala et al., 2012; Yang et al., 2018). Yet, the sludge layer may contribute positively to the treatment efficiency. For example, suspended solids removal, water retention and the biodegradation or retention of pollutants may be improved (Chazarenc & Merlin, 2005; Kim et al., 2013; Molle, 2014). On the other hand; the retention of most of feed organic matter within the sludge layer may limit the efficiency of subsequent denitrification (Lee et al., 2009; Van Oostrom & Russell, 1994). The effective roles of the sludge layer in the system may depend on its structural, compositional and reactional properties which are controlled by numerous factors, such as the composition of the influent wastewater, the operating conditions of the plant, or other local environmental factors (Fu et al., 2015). Although extensive work has already been published on similar issues in the fields of natural wetlands (Grasset et al., 2017; Rouwane et al., 2017), anthropic sediment (Badin, 2009; Huot, 2013), activated sludge (Alvarenga et al., 2015; Lachassagne, 2015), or sludge drying reed beds (SDRB) (Collard et al., 2017; Nielsen, 2011; Nielsen & Bruun, 2015; Nielsen & Larsen, 2016; Nielsen & Willoughby, 2005; Vincent et al., 2012), very few studies have focused on VFCWs’

surface sludge deposits (Bois et al., 2015; Chazarenc & Merlin, 2005; Kim et al., 2013; Kim et al., 2015). Molle (2014) and Perron et al. (2007) reported the influence of the VFCW plant design and operating conditions, such as organic and hydraulic loads or feed and rest periodicity. Kim et al. (2013), reported that although mainly organic, sludge deposits contained significant amounts of inorganic constituents originating from the local geological background or generated by possible operations of pretreatment of the influent such as phosphate precipitation by  $\text{FeCl}_3$  addition. Kim et al. (2013) and Kania et al. (2018, 2018a) investigated the extent of organic matter evolution within the sludge deposits, such as mineralization. Finally, the authors of this study reported structural properties data of surface sludge deposits in a recent article (Kania et al., 2018b). In the specific context of sludge drying reed bed systems, few studies investigated the mineralization of the sludge and the organic matter stabilization (Masciandaro et al., 2017; Nielsen, 2005; Nielsen et al., 2014; Peruzzi et al., 2017; Peruzzi et al., 2013).

The objective of the present study was to contribute to a better description of the properties of sludge deposits using chemical, biological and thermochemical methods. Samples from fourteen VFCW sewage treatment plants in operation in France were analyzed to assess whether specific typologies would be observed and, if so, identify the dominant factors of influence, especially with regards to the particulate organic matter (POM).

## **2. Materials and methods**

### **2.1. Sites of investigation**

Fourteen French VFCW sewage treatment plants located in the south-eastern part of France, were selected for the study. The treatment plants were all equipped with a preliminary gridding stage set between 3 and 30 mm to remove coarse solids and debris. Four of them were also equipped with a sand trap (Table 1). Three typical types of VFCW process designs were represented in the selected plants:

- Process type I, usually referred to as the “classical French system”, where gridded, unsettled raw wastewater was percolated through two successive stages of vertical flow filters.
- Process type II, where an additional stage of aerobic biological trickling filter was used to treat gridded wastewater prior to the two successive stages of vertical flow filters,
- Process type III, comprising the same operations as in type II plus the introduction of a  $\text{FeCl}_3$  solution into the outlet of the aerobic trickling filter in order to precipitate phosphorus prior to infiltration through the two successive stages of filters.

1

**Table 1** Characteristics of the 14 French VFCW sewage treatment plants selected for the study.

VFCW plants	Process type	Process line stages					Number of years of operation at sampling date	Nominal capacity (Population Equivalent)	Average hydraulic load (m <sup>3</sup> /y)
		Gridding / sieving	Sand trap	Trickling filter	FeCl <sub>3</sub> injection	Saturation of 1 <sup>st</sup> stage filter			
BAG1	<i>Classical French VFCW</i>	Yes	Yes	No	No	Unsaturated	11	1100	56940
BAG2			No				8	500	23725
SABAG			No				7	800	81030
VIL			No				7	350	11315
BAG3			No				4	290	6935
PRE			No				1	700	51830
RAM			No				0.5	350	13505
BAY	<i>AZOE</i> <sup>®</sup>	No	Yes	No	Partially saturated	7	1200	32850	
MIN		No				6	1000	25185	
NEU	<i>AZOE-N</i> <sup>®</sup>	Yes	Yes	Yes	Partially saturated	4	1600	75555	
VER	<i>AZOE-NP</i> <sup>®</sup>	No				11	1100	44165	
ORB		Yes				5	1500	126290	
COR		No				0.5	1000	51830	
MAT		<i>AZOE-P</i> <sup>®</sup>				Yes	5	1600	68620

2



3           These processes were further divided into two sub-categories according to the level of  
4 saturation of the first-stage filter as shown in Table 1. Full drainage (unsaturated conditions)  
5 was implemented to ensure good aeration in all process type I plants (“classical French system”)  
6 and in some plants of process types II and III patented as AZOE<sup>®</sup> and AZOE-P<sup>®</sup> respectively.  
7 Partially saturated conditions were implemented in the other plants of types II and III (patented  
8 as AZOE-N<sup>®</sup> and AZOE-NP<sup>®</sup>) in the objective to allow aeration of the upper unsaturated zone  
9 for nitrification, and anoxic conditions in the lower flooded zone for denitrification. More  
10 details were given in a previous article (Kania et al., 2018b; Kim et al., 2014).

## 11 **2.2. Sampling and preparation of the sludge deposits samples**

12           Sludge deposits were sampled in winter time between January and March 2015 from  
13 most wetlands, COR was sampled in November 2015 and RAM and PRE in February 2017 due  
14 to their more recent dates of implementation of these wetlands. The annual load of dry solids  
15 varied from one constructed wetland to another depending on its nominal design and its actual  
16 operating conditions. It was estimated between 20 and 35 kg of dry solids per year and m<sup>2</sup> of  
17 first stage filter cells. At the time of the field sampling operations, the sludge layer had not yet  
18 been removed from any of the wetlands and it has not been removed since. The lower part of  
19 the layer therefore contained deposits from the very beginning of the plant operation, whereas  
20 the upper part contained fresh deposits. The entire depth of the sludge layer was sampled on  
21 each site in order to obtain average samples representative of the mean composition of the  
22 sludge deposits over the whole period of operation of the VFCW plants.

23           All samples were taken following the same protocol from the stage filters. A few  
24 kilograms of deposits were taken by shoveling the entire depth of the sludge layer from 5 to 10  
25 spots (depending on the filter size) at the surface of the cell under resting period for 0-1 week.  
26 The sampling spots were randomly located at a distance of at least 5 m one from each other and  
27 at least 2 m from the feed pipes. The samples taken from each spot were treated on site to extract

28 manually reeds rhizomes, and possible traces of gravels. They were then carefully homogenized  
29 by quartering and mixing together with shovels. The representative samples from each plant  
30 thereby constituted were then taken to the laboratory within a maximum of 4 h. They were  
31 transported to the lab by car placed in a non-heated trunk at a maximal temperature of 10°C due  
32 to the winter season. There, an aliquot fraction of each sample was used to determine water  
33 content and the organic content of the dry solids. The rest was dried in thin layers at 35°C for  
34 one day, finely grinded and stored at 4°C.

## 35 **2.3. Analytical methods**

### 36 *2.3.1. General analytical parameters*

37 Upon reception in the laboratory, a few grams of fresh samples from each plant were  
38 dried in triplicates in an oven at 105°C until they reached a constant mass in order to determine  
39 their humidity. Dry solids were then burnt in an oven at 550°C for four hours to determine their  
40 organic matter contents. The rest of each sample was spread in thin layers of 1-2 cm on a  
41 laboratory bench and air-dried for 1 day at 35°C, then grinded down to less than 1 mm to obtain  
42 “dry powdered samples” which were stored at 4°C and used for all the other analyses.

43 Elemental analyses were done by alkaline fusion ( $\text{LiBO}_2$ ) followed by acid digestion  
44 ( $\text{HNO}_3$ ) and subsequent analyses of the solutions by inductively coupled plasma atomic  
45 emission spectrometry (ICP-AES) (IRIS Advantage ERS, Thermo Scientific). The following  
46 elements were analyzed : silicon (Si), aluminum (Al), iron (Fe), manganese (Mn), magnesium  
47 (Mg), calcium (Ca), sodium (Na), potassium (K), titanium (Ti) and phosphorus (P). Trace  
48 metals chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd) and lead (Pb) were  
49 analyzed using a Sciex Perkin Elmer ELAN 5000a. ICP-mass spectrometer.

50 Organic carbon contents were determined by burning at 1400°C 1g of dry powdered  
51 samples, previously de-carbonated with acid and under high temperature, and by infrared

52 absorption with a Carbon - Sulfur EMIA 320V2 (HORIBA). Total nitrogen contents were  
53 measured by burning 1g of powdered samples at 1050°C under a flow of helium and oxygen  
54 mixture in microanalyzer designed and developed at UMR 5280 Institute of Analytical Sciences  
55 which operates according to the Dumas method.

### 56 **2.3.2. Thermogravimetric and differential thermal analysis (TGA/DSC)**

57 Thermogravimetric analyses (TGA) were carried out using a METTLER TOLEDO  
58 TGA analyzer whose temperature precision was  $\pm 0.5^\circ\text{C}$  and microbalance sensitivity less than  
59  $\pm 0.1\text{mg}$ . A dry mass of  $\pm 20\text{ mg}$  of each sample was heated from  $35^\circ\text{C}$  to  $900^\circ\text{C}$  at a rate of  
60  $10^\circ\text{C}/\text{min}$ , under a flow of air of 50 mL per minute. The analyses were done in duplicates and  
61 blank experiments were carried under the same conditions as the assays but without any sample.  
62 The mass loss due to thermal degradation of the sample was recorded as a function of the  
63 temperature. Heat fluxes were also recorded during the process by differential scanning  
64 calorimetry (DSC).

65  $R_{\text{TGA}}$  index was calculated from experimental data as the ratio of the mass loss recorded  
66 between  $200$  and  $400^\circ\text{C}$  ( $\Delta m_1$ ) to that recorded between  $400$  and  $600^\circ\text{C}$  ( $\Delta m_2$ ), as proposed  
67 by several authors (Stevenson, 1982 ; Fernandez et al., 2012). In each given range of  
68 temperature, the unit mass heat release, also called “energy density”  $E$  (in  $\text{J}\cdot\text{mg}^{-1}$ ), was also  
69 calculated from the ratio between the surface area of the corresponding peak in DSC profiles  
70 over the mass loss recorded in the same range of temperatures ( $E_1$  and  $E_2$ ). The  $R_{\text{DSC}}$  index was  
71 finally calculated as the ratio of  $E_2/E_1$  (Achour, 2008).

### 72 **2.3.3. Determination of humification rate**

73 The contents in humic-like and fulvic-like substances (referred to as HULIS and FULIS,  
74 respectively) were analyzed to evaluate the humification degree of the organic matter in the  
75 sludge deposits (Albrecht, 2007). The protocol for the HULIS and FULIS extraction was

76 adapted from Serra-Wittling et al. (1996). HULIS and FULIS were extracted by suspending for  
77 2 h under constant agitation 1 g of powdered samples in 50 mL of a 0.1 M sodium hydroxide  
78 aqueous solution. The suspensions were then centrifuged at 10 000 g for 15 min and vacuum  
79 filtered at 0.45 µm using Sartorius cellulose acetate filters. The solutions, containing HULIS  
80 and FULIS fractions were analyzed for total organic carbon (TOC) using a Shimadzu TOC-L  
81 analyzer, then acidified to pH 1.5 with 1 M sulfuric acid aqueous solution and left at rest  
82 overnight at +4°C to allow precipitation of HULIS fraction. FULIS fraction was collected in  
83 solution by centrifugation at 6000 g for 15 min followed by filtration at 0.45µm. The solution  
84 was analyzed for TOC using the same protocol as for the HULIS + FULIS extracts.

85 The proportion of HULIS + FULIS in the organic matter was taken as an indicator of  
86 the degree of humification of the sludge organic matter and calculated as follows:

$$87 \text{ Humification rate} = 100 \times \frac{[\text{HULIS}] + [\text{FULIS}]}{\text{TOC}} \quad (1)$$

#### 88 **2.3.4. Biodegradation under aerobic conditions**

89 Respirometric assays were conducted to evaluate the biodegradability of the sludge  
90 deposits considered here as an indicator of stability of their organic matter. A given mass of  
91 each powdered sample, calculated to contain 75.5 mg of organic matter, was introduced into  
92 500 mL BOD flasks containing 10 mL of a mineral medium made of an aqueous solution of  
93 28.25 g.L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub> ; 146.08 g.L<sup>-1</sup> K<sub>2</sub>HPO<sub>4</sub>; ; 3.66 g.L<sup>-1</sup> CaCl<sub>2</sub> ; 28.64 g.L<sup>-1</sup> NH<sub>4</sub>Cl ; 3.06 g.L<sup>-1</sup>  
94 MgSO<sub>4</sub>, 0.7 g.L<sup>-1</sup> FeSO<sub>4</sub> and 0.4 g.L<sup>-1</sup> ZnSO<sub>4</sub> (Liu et al., 2015b). The flasks were then inoculated  
95 with 10 mL of a seed suspension prepared from biological sludge obtained from a municipal  
96 wastewater activated sludge treatment plant located in Villeurbanne (France) and cultivated in  
97 the laboratory prior to the beginning of the assays. They were finally spiked with ca. 0.2 mL of  
98 a 5 g.L<sup>-1</sup> allylthio-urea aqueous solution used as a nitrification inhibitor, hermetically closed by  
99 manometric caps to monitor pressure variations, and incubated at 30±1°C in the dark. Carbon

100 dioxide formed from biodegradation was trapped by sodium hydroxide pellets placed in a  
101 specific compartment in the headspace of the test flasks. The recorded pressure therefore  
102 decreased proportionally to the oxygen consumed and was subsequently converted into BOD  
103 values expressed in mg O<sub>2</sub> per g of sludge TOC.

104 Biodegradability was finally calculated according to eqn. (2) from the ratio between the  
105 cumulated consumption of O<sub>2</sub> (g) over 14 days of incubation (BOD<sub>14</sub>) and the theoretical  
106 oxygen demand (ThBOD) of 2667 mg O<sub>2</sub> per g of TOC (corresponding to a consumption of 32  
107 g O<sub>2</sub> for a complete bio-oxidation of 12 g C based on a stoichiometry of 1 mole of O<sub>2</sub> for 1 mole  
108 of C assuming that carbon in the sludge organic constituents was at an average degree of  
109 oxidation of zero).

$$110 \text{ Biodegradability (\%)} = \frac{\text{BOD}_{14} \text{ (gO}_2 \text{ per g TOC)}}{2.667} \times 100 \quad (2)$$

### 111 **3. Results and discussion**

#### 112 **3.1. Organic content and elemental composition**

##### 113 ***3.1.1. Organic content***

114 Table 2 shows the average contents in organic matter and organic carbon analyzed in  
115 the surface deposits samples. Organic matter (OM) contents ranged between 50.3 and 86.2% of  
116 total dry weight (% w/ w). Regardless of their wetland of origin, the surface deposits were  
117 therefore in all cases mostly organic material.

**Table 2** General composition of sludge deposits samples.

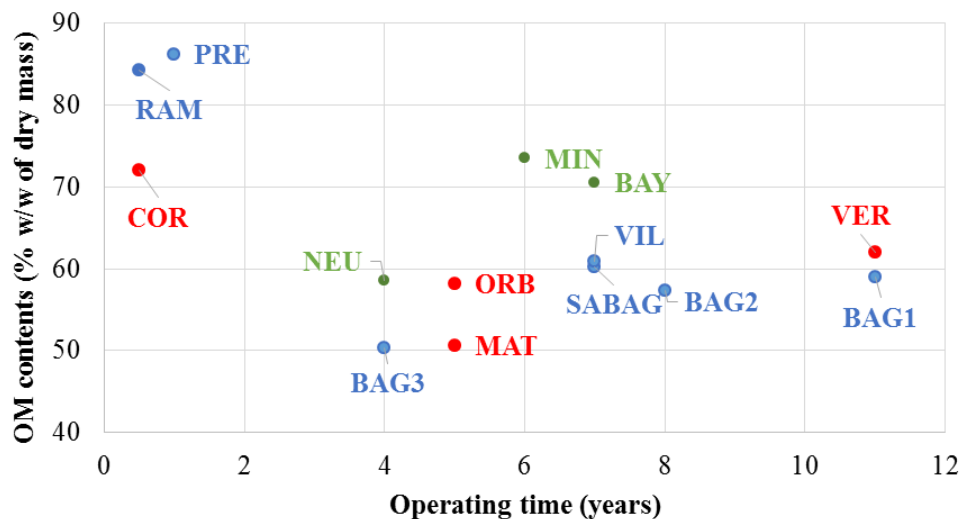
VFCW labels <sup>a</sup>	OM <sup>b</sup>	TOC <sup>c</sup>	Si <sup>d</sup>	Ca <sup>d</sup>	Al <sup>e</sup>	Fe <sup>d</sup>	Mg <sup>e</sup>	Na <sup>f</sup>	K <sup>d</sup>	Mn <sup>e</sup>	Ti <sup>e</sup>	P <sup>d</sup>	TN <sup>g</sup>	TOC/TN	Cr <sup>e</sup>	Cu <sup>d</sup>	Ni <sup>d</sup>	Zn <sup>e</sup>	Cd <sup>f</sup>	Pb <sup>d</sup>	∑metals <sub>h</sub>
	% w/w of DM		% w/w of DM											mg.kg DM <sup>-1</sup>							
BAG1	59.0	24.7	7.7	2.6	2.1	1.0	0.3	0.2	0.5	0.02	0.2	1.2	4.0	6.2	49.8	338.0	23.2	615.6	1.0	43.7	1071
BAG2	57.4	24.2	13.3	2.9	2.0	0.9	0.3	0.2	0.7	0.01	0.2	0.8	3.3	7.2	41.4	363.8	21.7	810.2	1.2	37.2	1276
SABAG	60.3	21.0	11.6	2.6	1.8	1.4	0.3	0.2	0.6	0.04	0.2	1.1	3.6	5.8	46.3	1162.0	23.1	557.4	1.0	33.4	1823
VIL	60.9	22.7	10.5	2.4	2.4	1.2	0.3	0.1	0.5	0.01	0.3	1.2	3.4	6.7	46.5	425.2	18.0	430.0	0.6	31.9	952
BAG3	50.3	18.4	13.2	3.5	2.4	1.4	0.3	0.3	0.7	0.02	0.2	1.0	3.1	5.9	59.3	282.3	25.1	481.4	1.0	34.7	884
PRE	86.2	36.4	2.1	2.5	0.4	0.2	0.1	0.1	0.2	<D.L.	0.1	0.5	1.5	24.7	19.3	216.9	7.7	463.1	0.4	13.6	721
RAM	84.3	32.3	3.4	3.2	0.6	0.3	0.2	0.1	0.2	<D.L.	0.1	0.7	2.1	15.6	18.4	304.7	10.0	481.0	0.6	18.1	833
BAY	70.5	28.5	3.3	4.7	1.5	0.5	0.3	0.1	0.3	0.01	0.2	1.9	4.5	6.4	34.5	232.9	20.3	968.9	1.5	121.5	1380
MIN	73.5	28.2	5.0	3.5	1.3	0.6	0.4	0.2	0.4	0.02	0.3	1.4	4.8	5.9	51.9	195.9	30.3	731.6	0.9	32.2	1043
NEU	58.6	21.7	9.6	3.7	2.3	1.2	0.4	0.3	0.7	0.04	0.2	1.1	3.6	6.0	51.8	223.9	26.9	573.9	1.2	45.4	923
VER	62.0	23.0	5.7	3.8	2.1	3.5	0.3	0.1	0.4	0.02	0.2	2.0	3.8	6.1	57.4	622.5	30.5	1218.5	1.6	64.2	1995
ORB	58.2	22.7	7.3	3.8	2.0	3.5	0.3	0.1	0.5	0.03	0.2	1.6	3.6	6.2	74.0	379.6	36.7	952.9	1.3	48.9	1493
COR	72.0	24.7	2.8	4.6	0.8	5.2	0.3	0.2	0.5	0.02	0.2	2.5	4.1	5.9	51.4	691.4	21.0	908.8	1.0	37.2	1711
MAT	50.6	14.0	11.2	1.6	3.2	5.9	0.4	0.4	1.2	0.5	0.3	2.0	2.5	5.5	57.6	201.7	23.4	744.7	1.1	68.7	1097

119 OM: Organic Matter; DM: Dry Matter; DL = Detection Limit

120 <sup>a</sup> See Table 1121 <sup>b</sup> Analytical results from the replicates of each sample did not exceed  $\pm 2.5\%$ 122 <sup>c</sup> Relative uncertainty of 1-2%123 <sup>d</sup> Relative uncertainty of 5%

- 124 <sup>e</sup> Relative uncertainty of 10%  
125 <sup>f</sup> Relative uncertainty of 15%  
126 <sup>g</sup> Relative uncertainty of 0.3%  
127 <sup>h</sup>  $\sum \text{metals} = [\text{Cr}] + [\text{Cu}] + [\text{Ni}] + [\text{Zn}] + [\text{Cd}] + [\text{Pb}]$ .

128 Fig. 1 illustrates the plot of organic matter contents of the surface deposits vs. the  
 129 number of years of operation of the VFCW sewage treatment plants of origin. The graph  
 130 showed that deposits from young systems with newly established thin sludge layers of about 1-  
 131 3 cm contained larger concentrations of organic matter than those from older systems of  $\geq 3$   
 132 years with a sludge layer of about 10-25 cm thick. This observation suggested that hydrolysis  
 133 and /or mineralization of POM progressively reduced the organic matter content of the deposits  
 134 within the sludge layer. However, although COR, RAM and PRE samples were all taken from  
 135 young plants (1 year and less), COR sample was less organic than those from RAM and PRE.  
 136 Time was therefore not the only factor of influence. Other analytical results discussed below  
 137 have to be considered to explain this observation.



138  
 139 **Fig. 1.** Organic matter contents of the surface deposits versus operating time of their VFCW plants of  
 140 origin. Blue dots: Classical French system with no additional treatment. Green dots: additional treatment  
 141 on trickling filter only. Red dots: trickling filter and FeCl<sub>3</sub> addition.

142  
 143 **3.1.2. Elemental compositions**

144 The contents in major elements were quite similar in all the samples, except for MAT  
 145 which exhibited high Mg, Na, K and Mn concentrations (Table 2), probably due to atypical  
 146 local conditions as discussed in the sections below. Phosphorus (P) contents in the sludge  
 147 deposits from plants with FeCl<sub>3</sub> injection (2.0; 1.6; 2.5 and 2.0% w/w in VER, ORB, COR and



148 MAT, respectively), were two-fold higher than in the plants without any additional treatment  
149 where P concentrations ranged between 0.5 and 1.2% w/w of dry matter. This result confirmed  
150 the good efficiency of FeCl<sub>3</sub> injection to precipitate phosphorus. The samples from plants with  
151 a trickling filter also revealed slightly higher P contents (1.2%; 1.9% and 1.5% in NEU, BAY  
152 and MIN samples respectively) than those with no additional treatment at all. This observation  
153 could be attributed to the assimilation of phosphorus within the biofilm in the trickling filter,  
154 which after detachment would be subsequently retained within the surface sludge layer and  
155 induce a relative increase in P contents (Andersson, 2009). Total Nitrogen (TN) contents ranged  
156 between 1.5 and 4.8% w/w of dry mass in all the samples. These results were close to those  
157 reported in sludges from lagoons sewage treatment plants, but lower than those found in  
158 suspended solids from activated sludge systems (Vincent, 2011). COR sample exhibited a TN  
159 concentration of 4.1% w/w of dry mass, which was about double of the concentrations measured  
160 in the samples of similar age RAM and PRE (1.5 and 2.1% w/w of dry mass, respectively). This  
161 observation may be explained by the interactions (complexation, coagulation, precipitation) of  
162 soluble N species with FeCl<sub>3</sub> used in COR plant. Other authors (Boucher et al., 1999; Hamdani  
163 et al., 2004; Poon & Chu, 1999) reported the effect of FeCl<sub>3</sub> on the removal of TN from dairy  
164 effluents. This effect was observable here in young-age plants but not in older plants (Table 2),  
165 showing that other ageing effects became predominant over the years of operation.

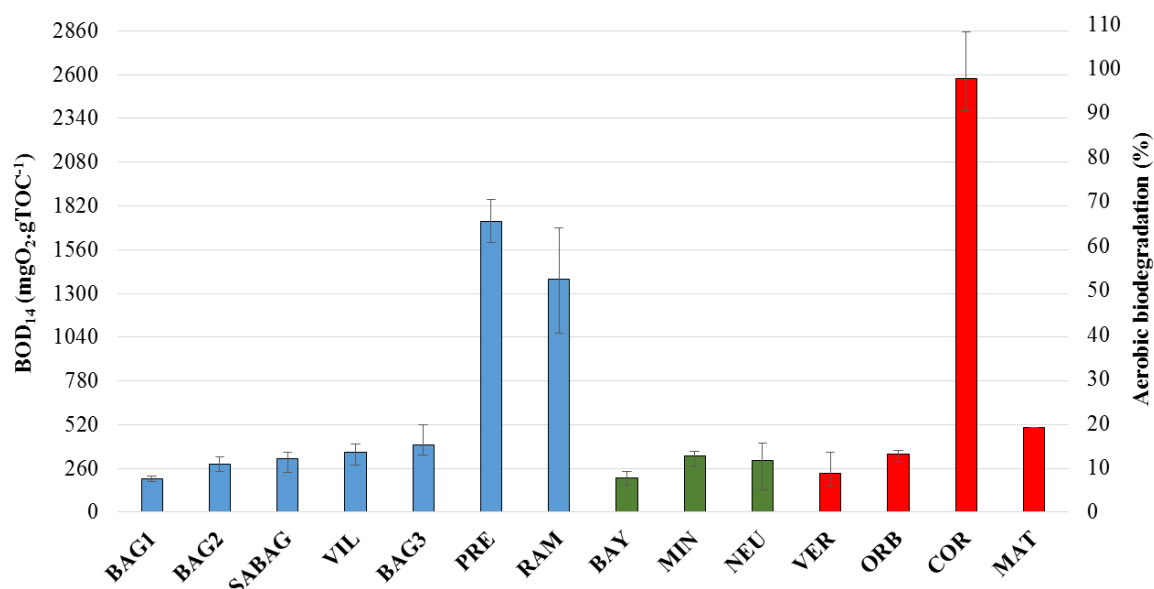
166 Table 2 showed that the contents in trace metals were in the same order of magnitude in  
167 all the samples. The accumulation of trace metals and other micropollutants is a potential  
168 environmental concern when considering land application or nutrients recovery from the  
169 dredged sludge (Fang et al., 2016; Gautier et al., 2017; Kim et al., 2016; Peccia & Westerhoff,  
170 2015; Peysson et al., 2013). Total contents in Cd, Cr, Ni, Pb, Cu and Zn in the sludge deposits  
171 analyzed here ranged in most cases between ca. 0.9 and 1.6, 35 and 74, 18 and 37, 32 and 69,  
172 196 and 425, 430 and 953 mg.kg DM<sup>-1</sup> respectively. These concentrations were in the ranges

173 classically reported in activated sludge, respectively 1-10 for Cd, 10-100 for Cr, Ni and Pb and  
174 100-1000 mg.kg DM<sup>-1</sup> for Zn and Cu (Lachassagne, 2015). A few samples revealed however  
175 relatively high contents in some elements. Sludge deposits from SABAG plant exhibited a high  
176 copper concentration (1162 mg.kg DM<sup>-1</sup>), samples from VER a high zinc concentration (1218.5  
177 mg.kg DM<sup>-1</sup>) and samples from BAY a high lead contents (121.5 mg.kg DM<sup>-1</sup>). These  
178 observations may be related to the specific nature of anthropic discharges (domestic, industrial  
179 or both) to the sewage water in the water catchments of the respective constructed wetlands  
180 (Chipasa, 2003; Ustun, 2009; Vriens et al., 2017). Table 2 showed the concentrations of trace  
181 metals analyzed in the 14 sludge deposit samples. As an informative reference, these  
182 concentrations may be compared to the upper limit concentrations of a series of trace metals  
183 considered in French regulation for land application of sludge (decree N° 97-1133 of 8/01/1998),  
184 expressed in mg of element per kg of DM: Cd and Hg 10 DM; Cr and Cu 1000, Ni 200; Pb 800;  
185 Zn 3000; Cr+Cu+Ni+Zn 4000. It was observed that the concentrations increased in time from  
186 around 780 mg.kg<sup>-1</sup> of DM in young plants RAM and PRE to  $\geq 1200$  in the older “classical”  
187 VFCW plants, suggesting a progressive accumulation of trace metals in the sludge deposits  
188 over the years of operation, which may be explained in part by their sorption onto POM and/or  
189 mineral fractions of the sludge deposits. The implementation of additional treatment did not  
190 induce observable differences of total metal concentration in the samples from mature plants.  
191 The average concentrations were 1201±386 mg.kg DM<sup>-1</sup> in samples from classical VFCW (no  
192 additional treatments), 1115±237 mg.kg DM<sup>-1</sup> in samples from AZOE<sup>®</sup> treatment plants, and  
193 1529±450 mg.kg DM<sup>-1</sup> in AZOE-NP<sup>®</sup> treatment plants. Regarding sludge deposits from the  
194 young plants, the effect of FeCl<sub>3</sub> addition (co-precipitation with and/or sorption onto flocculated  
195 mineral and organic phases) may explain here again the observed difference between the  
196 samples from COR (ca 1711 mg.kg DM<sup>-1</sup>) and RAM and PRE (721 and 833 mg.kg DM<sup>-1</sup>  
197 respectively) as already discussed by El Samrani et al. (2008) and Fu & Wang (2011). The

198 situation in the sludge layer in the VFCW seems in many aspects comparable with the sludge  
199 layer building up in SDRB systems. In sludges from reed bed systems, very similar contents  
200 were indeed reported for TOC and TN (Masciandaro et al., 2017; Nielsen et al., 2014 ; Peruzzi  
201 et al., 2013), and trace metals (Caicedo et al., 2015; Matamoros et al., 2012; Nielsen & Bruun,  
202 2015).

### 203 **3.2. Biodegradability of sludge deposits' organic matter**

204 Fig. 2 shows the results of cumulated O<sub>2</sub> consumption measured over 14 days of  
205 incubation at 30°C of the sludge deposits samples. It can be seen that the samples from the  
206 mature plants exhibited respiration levels ranging between 200 and 500 mgO<sub>2</sub>.TOC<sup>-1</sup> in 14 days  
207 of incubation, which may be considered as low values according to the scale used for compost  
208 (Wood et al., 2009) and with respect to the theoretical maximum of 2667 mg O<sub>2</sub> per g of TOC.  
209 These results therefore revealed the poor biodegradability and/or bioavailability of the organic  
210 matter in these samples. The samples from the youngest three plants PRE, RAM and COR  
211 exhibited drastically higher respiration levels (1729, 1387 and 2577 mg O<sub>2</sub> per g of TOC  
212 respectively), indicating that their organic matter was readily biodegradable and bioavailable in  
213 the conditions of the assays. Vincent (2011) reported that fresh organic matter from raw  
214 wastewater was responsible for the major part of O<sub>2</sub> consumption in “classical French” VFCWs.



215  
 216 **Fig. 2.** Aerobic biodegradation measured over 14 days of incubation at 30°C on the surface sludge  
 217 deposits sampled from French VFCW sewage treatment plants of different types. Classical system with  
 218 no additional treatment (blue bars); additional treatment on trickling filter only (green); trickling filter  
 219 and FeCl<sub>3</sub> addition (red).

220 Results obtained from the analysis of sludge deposits from VFCW sewage treatment  
 221 plants of increasing ages therefore showed that both the organic contents of the sludge deposits  
 222 and the biodegradability of their organic matter decreased over time, suggesting the occurrence  
 223 of both mineralization and humification processes. Similar phenomena were reported in other  
 224 environmental media (Albrecht, 2007; Francou, 2003).

### 225 3.3. Indicators of maturation of particulate organic matter

#### 226 3.3.1. TOC/TN ratio

227 TOC/TN ratio is a parameter classically used to monitor the progress of biodegradation  
 228 in the processes of organic waste composting (Iglesias Jiménez & Perez Garcia, 1989; Zahra El  
 229 Ouaquoudi et al., 2015). The ratio normally decreases over time since biodegradation releases  
 230 carbon (in the form of CO<sub>2</sub>) whereas nitrogen remains within the waste material during  
 231 composting operations. Compost is considered mature when the ratio falls below 15 (Zahra El  
 232 Ouaquoudi et al., 2015). Grimaud (1996) also reported that secondary sludge from conventional

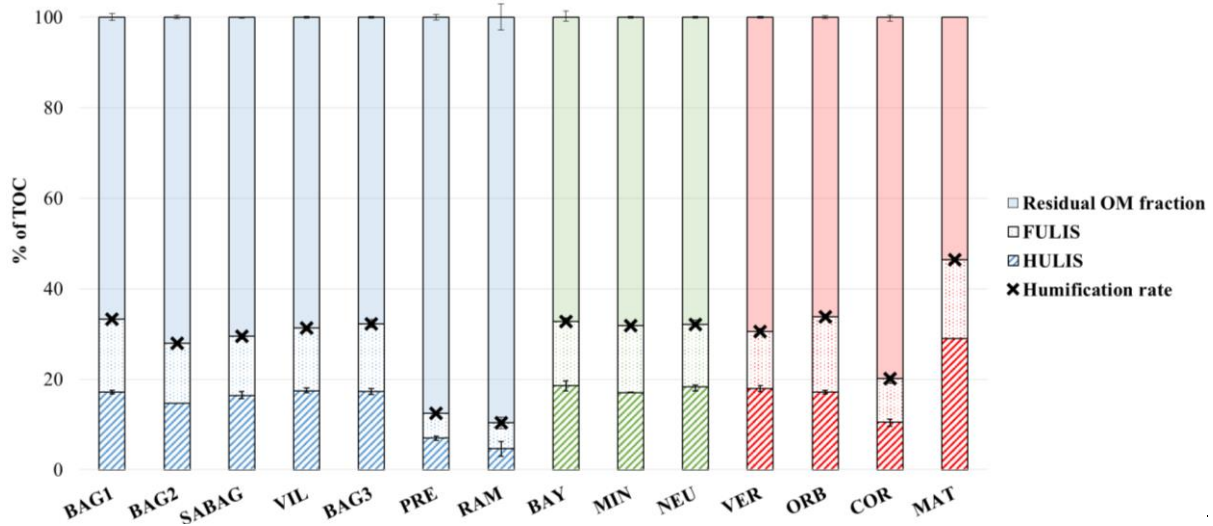
233 domestic wastewater treatment would exhibit a TOC/TN ratio between 6 and 12, whereas  
234 primary sludge would be above 12.

235         Based on these studies, the ratio was tentatively used here as an indicator of the  
236 evolution of organic matter in the sludge deposits. Table 2 showed that low values between 5.5  
237 and 7.2 were measured in sludge deposits taken from VFCW plants of three years and more,  
238 whereas samples from the young plants RAM and PRE exhibited much higher values of 24.7  
239 and 15.6 respectively. COR sample however, although also originating from a young plant,  
240 revealed a low TOC/TN value of 5.9. The ratio TOC/TN ratio was however considered non-  
241 relevant as an indicator of POM evolution in VFCW. As a matter of fact, unlike composting  
242 where N is not exported from waste material, the conditions of evolution of surface sludge  
243 deposits in VFCW allowed both the release of N in the form of soluble and leachable species  
244 and/or the accumulation of N species from wastewater via complexation and/or adsorption.  
245 Other authors (Brewer & Sullivan, 2003; Huang et al., 2006) also reported that TOC/TN ratio  
246 was not sufficient or not always relevant to discriminate the level of maturity of OM. Other  
247 indicators widely used in published studies, such as the humification rate, were therefore  
248 considered.

### 249 **3.3.2. Humification rate**

250         The contents in HULIS and FULIS fractions analyzed in the different samples,  
251 expressed as % w/w of organic carbon, and the calculated humification rate are shown in Fig.  
252 3. The humification rate of almost all the samples from mature plants were found to be relatively  
253 high and very similar, ranging from  $27.9\pm 0.5$  to  $33.8\pm 0.9\%$  w/w of sludge TOC. This indicator  
254 was therefore consistent with the results discussed above relative to the biostability of their  
255 organic matter. Masciandaro et al. (2017) obtained very similar values (humification rate  
256 between 23.7 and 30.4%) in sludge treatment reed bed systems and concluded to the  
257 effectiveness in stabilizing sludge organic matter. One sample however, also collected from a

258 mature plant, MAT, exhibited on this indicator a much higher value than all other samples, as  
 259 high as ca.  $46.4 \pm 2.8\%$ , suggesting that the organic matter in this sample was particularly  
 260 humified, although it did not exhibit the smallest biodegradability in Fig. 2. The particular  
 261 properties of this sample are discussed below.



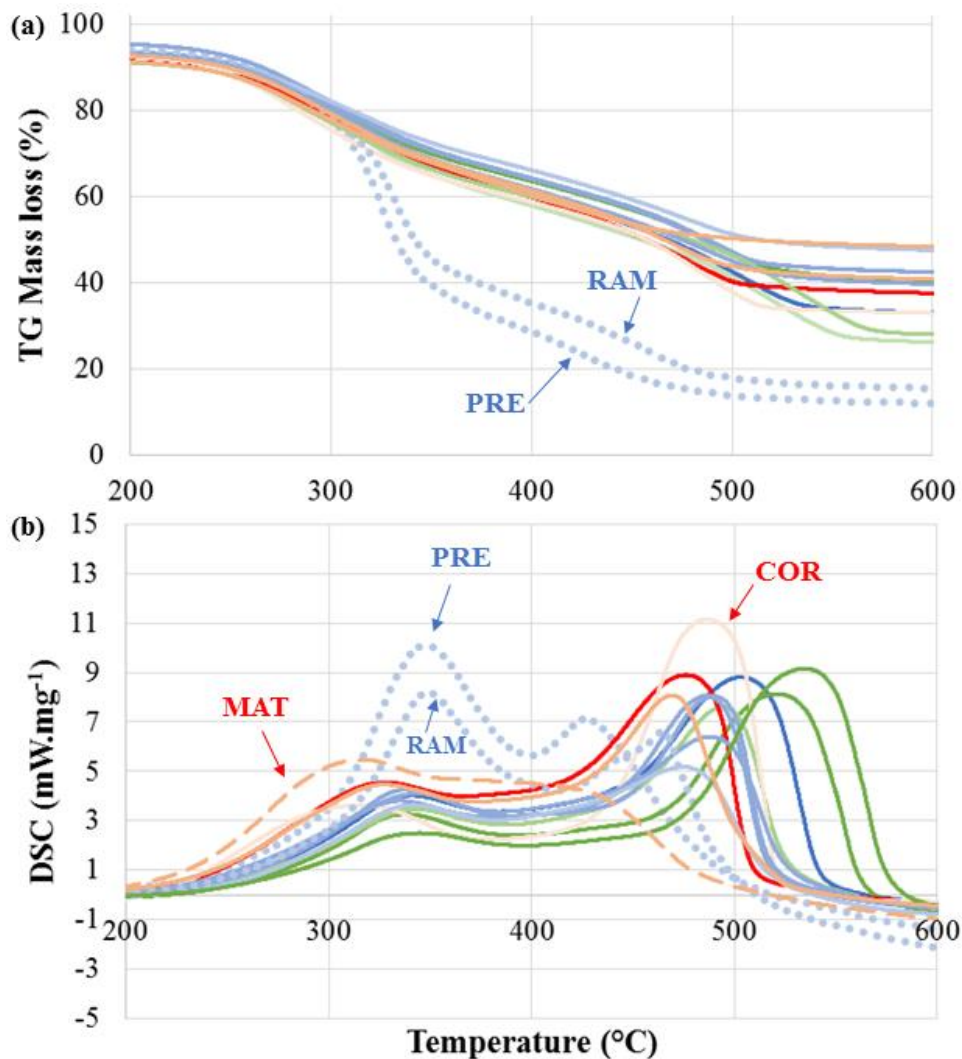
262 **Fig. 3.** Distribution of organic carbon in sludge deposits (SD) organic fractions, and humification rate  
 263 measured in the 14 VFCWs sludge deposits. Classical system with no additional treatment (blue);  
 264 additional treatment on trickling filter only (green); trickling filter and  $\text{FeCl}_3$  addition (red).  
 265

266 Samples from the young plants RAM and PRE showed lower values of humification  
 267 rates,  $12.5 \pm 0.6$  and  $10.3 \pm 2.9\%$  respectively, which were relatively close to level reported for  
 268 activated sludge ( $16.5\%$  in Riffaldi (1982) and  $10.9\%$  in Li et al. (2011)). COR sample however  
 269 exhibited a humification rate of ca  $20.1 \pm 1.6\%$  w/w of TOC which was comprised between the  
 270 levels measured in the other two young plants RAM and PRE and in mature plants. This  
 271 observation was attributed to the transformation of the organic matter through the trickling filter  
 272 and the detachment of biofilm fragments which may favor the formation of humic-like  
 273 substances as reported by other authors (Maeng et al., 2015; Zhao et al., 2013).

### 274 3.4. Thermal analyses

275 TGA and DSC profiles obtained from thermal analyses of the sludge deposits samples  
 276 are shown in Fig. 4 in the range of temperatures between  $200^\circ$  and  $600^\circ\text{C}$  known to induce

277 thermal degradation of organic compounds of natural origins (Torres-Climent et al., 2015). The  
 278 first part of the graphs, from 200°C to 400°C, was considered to correspond to the degradation  
 279 of relatively labile organic compounds, such as hemicelluloses, cellulose and some aliphatic  
 280 compounds (Chen et al., 2015; Gomez et al., 2007; Som et al., 2009; Zahra El Ouaqoudi et al.,  
 281 2015). The second part between 400 and 600°C was considered associated to more complex  
 282 and stable organic compounds such as lignin and other high molecular weight poly-aromatic  
 283 structures such as humic and fulvic substances (Chen et al., 2015; Cuypers et al., 2002; Melis  
 284 & Castaldi, 2004; Zahra El Ouaqoudi et al., 2015).



285  
 286 **Fig. 4.** Mass loss (a) and differential scanning calorimetry (b) profiles recorded from surface sludge  
 287 deposits from 14 French VFCW sewage treatment plants. Classical system with no additional treatment  
 288 (blue); additional treatment on trickling filter only (green); trickling filter and FeCl<sub>3</sub> addition (red).  
 289

290 For all samples, except RAM and PRE, TGA profiles showed that around 1/4 to 1/3 of  
291 the initial dry mass (26.2 to 35.1% w/w of dry mass) was degraded between 200 and 400°C.  
292 The mass losses between 400 and 600°C were in the same order of magnitude as from 200 to  
293 400°C, ranging between 19.8 and 32.4% w/w of dry mass. RAM and PRE samples, taken from  
294 the youngest VFCW plants, exhibited different patterns, with about 2/3 of initial dry mass  
295 degraded between 200 and 400°C (66.4 and 66.1% w/w of dry mass respectively), and only  
296 around 16% w/w of initial dry mass degraded between 400 and 600°C. Similar results were  
297 reported for activated sludge by Magdziarz et al. (2013), with around 50% degradation of initial  
298 dry mass between 200 and 400°C and 20% w/w of dry mass above 400°C. MAT sample  
299 exhibited an atypical profile. Although between 200 and 400°C the mass loss was 32.0% w/w  
300 of dry mass as in almost all samples, above 400°C the mass loss was the lowest of all samples  
301 (11.1%).

302 The thermal degradation processes were logically exothermic since the analyses were  
303 made in the presence of air (DSC profiles in Fig. 4). The heat released per unit mass of organic  
304 matter oxidized in the assays was related to the energy of inter-atomic bounds and the degree  
305 of oxidation of carbon in the organic constituents. It can be observed that the ratio  $E_1$  between  
306 200 and 400°C was much smaller than  $E_2$  between 400 and 600°C (Table 3). The thermal  
307 degradation was therefore much less exothermic per unit mass of organic constituents below  
308 400°C than above 400°C. It was therefore concluded that the POM constituents degraded below  
309 400°C were composed of molecules such as carbohydrates with relatively weak inter-atomic  
310 bounds such as C–O, C–C and C–N (activation energy of 350–412 kJ.mol<sup>-1</sup>) (Leinweber &  
311 Schulten, 1992), and a relatively high degree of oxidation of carbon indicative of the  
312 oxygenation index of the molecules (Barré et al., 2016; Soucémarianadin et al., 2018). The  
313 organic constituents degraded above 400°C were considered to contain more C=C bounds of  
314 higher energy (activation energy of 520-840 kJ.mol<sup>-1</sup>) such as in humic-like substances, lignin



315 and lignocellulosic complexes (Magdziarz & Wilk, 2013), with carbon at a lower degree of  
 316 oxidation, such as in (poly)-aromatic compounds (Leinweber & Schulten, 1992).

317 **Table 3**  $R_{TGA}$ ,  $E_1$ ,  $E_2$  and  $R_{DSC}$  values for 14 VFCW sludge deposits.

	$R_{TGA}$	$E_1$	$E_2$	$R_{DSC}$
		J.mg <sup>-1</sup>		
<b>BAG1</b>	0.95	8.6	20.7	2.4
<b>BAG2</b>	0.75	10.5	16.7	1.6
<b>SABAG</b>	0.83	9.2	15.4	1.7
<b>VIL</b>	0.77	8.9	19.1	.2
<b>BAG3</b>	0.76	10.2	21.2	2.1
<b>PRE</b>	0.24	8.9	24.1	2.9
<b>RAM</b>	0.28	7.9	24.6	3.2
<b>BAY</b>	0.92	6.6	16.3	2.5
<b>MIN</b>	1.05	6.0	17.3	2.4
<b>NEU</b>	0.85	8.0	17.7	2.2
<b>VER</b>	0.76	11.7	22.0	1.9
<b>ORB</b>	0.76	9.5	15.6	1.7
<b>COR</b>	0.79	8.5	18.7	2.2
<b>MAT</b>	0.35	13.6	18.7	1.4

318  
 319 The thermal indices  $R_{TGA}$  and  $R_{DSC}$  were calculated and the results given in Table 3. For  
 320 all samples except those from the youngest plants PRE and RAM, the  $R_{TGA}$  index was between  
 321 0.8 and 1.1, indicating the presence of relatively stable organic constituents. For comparison,  
 322 compost is considered mature for an  $R_{TGA}$  index above 0.8 (Som et al., 2009; Zahra El Ouaquoudi  
 323 et al., 2015).  $R_{TGA}$  indexes of PRE and RAM samples were 0.2 and 0.3 respectively, confirming  
 324 the previous discussions related to the predominance of labile organic compounds in these  
 325 samples and the lower humification rate.  $R_{DSC}$  values were found between 1.6 and 3.2. Samples  
 326 from the young plants RAM and PRE showed a higher index than those from the mature plants,  
 327 confirming their lower stability (Achour, 2008).

328 COR sample exhibited again a particular profile, with  $R_{TGA}$  and  $R_{DSC}$  indexes closer to  
 329 the group of mature plants than young plants. These results therefore confirmed the effects of  
 330 the additional treatments, notably the trickling filter, on the characteristics of sludge deposits in  
 331 young-age VFCW plants.

332 Finally, the TGA/DSC analysis allowed to highlight the particular behavior of MAT  
 333 sample which did not feature a clear bimodal pattern but showed instead a peak around 320°C  
 334 followed by a shoulder at 445°C. The particularities of MAT sample are further discussed below.

### 335 3.5. Multi-parameter cross-analysis of sludge deposits characteristics

#### 336 3.5.1. Inter-comparison of the 14 sludge deposits

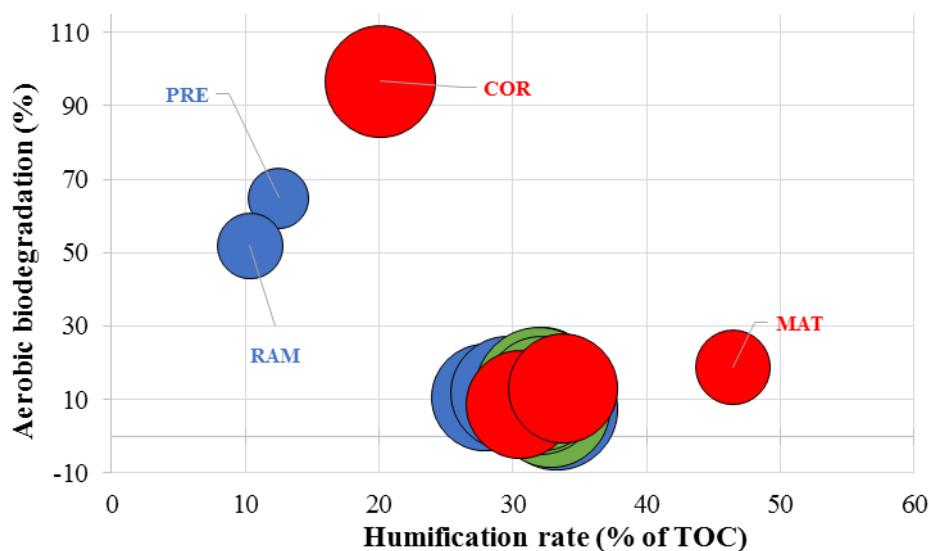
337 A correlation analysis was conducted on the different parameters of OM maturity and  
 338 stability used in this study. Results gathered in Table 4 showed that OM content was relatively  
 339 correlated with aerobic biodegradation and  $R_{DSC}$ , and anti-correlated with the humification rate.  
 340 A high organic content was typical of young-age VFCW plants, where fresh organic matter was  
 341 readily biodegradable and poorly humified.  $R_{DSC}$  index was anti-correlated with the  
 342 humification rate and  $R_{TGA}$  was not significantly correlated to any other indexes.

343 **Table 4** Correlation coefficients (and P-value) between the parameters of biological, chemical and  
 344 thermal characterization. Correlation coefficients shown in bold were considered statistically significant,  
 345 with  $P < 0.05$ .

	OM	Humification rate	Aerobic biodegradation	$R_{TGA}$	$R_{DSC}$
OM	1	<b>-0.834 (2.10<sup>-4</sup>)</b>	<b>0.623 (0.02)</b>	-0.363	<b>0.828 (3.10<sup>-4</sup>)</b>
Humification rate		1	<b>-0.702 (0.01)</b>	0.427	<b>-0.750 (2.10<sup>-3</sup>)</b>
Aerobic biodegradation			1	-0.467	0.436
$R_{TGA}$				1	-0.253
$R_{DSC}$					1

346 To allow a relevant and discriminant graphical representation of the different SD  
 347 samples with respect to their characteristics, the most discriminant parameter within each type  
 348 of analyses was selected (namely biological, thermochemical, and chemical analyses). Based  
 349 on the results shown in the previous sections, biodegradability and humification were selected  
 350 as the biological and chemical parameters. Based on the statistical correlation assessment,  $R_{TGA}$   
 351 index was selected as the thermochemical parameter because it did not show significant  
 352

353 correlations with the first two parameters according to Table 4, and was therefore considered  
354 to provide independent additional information. The corresponding 3-D representation shown in  
355 Fig. 5 clearly revealed distinct typologies of samples. A first group was identified with the  
356 samples from the young-age VFCW plants RAM, PRE and COR. COR sample was positioned  
357 slightly apart from RAM and PRE samples, underlining the influence of the additional  
358 treatments on the characteristics of the sludge deposits within the young-age of the VFCW  
359 plants. A second group was clearly formed with the samples from the mature plants. This group  
360 was very homogeneous, revealing the very strong similarities in the characteristics of the sludge  
361 deposits of the VFCW plants of three years of operation and more, regardless of the  
362 implementation or not of additional treatments and other local conditions. Sludge samples from  
363 mature VFCW plants exhibited a humification rate between 20 and 40%, an OM biodegradation  
364 rate between 0 and 35%, and a  $R_{TGA}$  between 0.75 and 1. Finally, MAT sample was excluded  
365 from both previous groups in the graphical representation of Fig. 5. Its overall characteristics  
366 were therefore distinct from either groups of young-age and mature VFCW plants. MAT plant  
367 was actually an atypical VFCW plant as compared to the others. For example, a predominance  
368 of baby's wipes was observed at the surface of the first filter when the sludge deposits were  
369 sampled. These wipes are made of about 60% polyester and 40% cellulose for most of them  
370 and affect the composition of the sludge deposits. Fig. 5 therefore allowed to clearly identify a  
371 third group of samples whose characteristics revealed a particular situation.



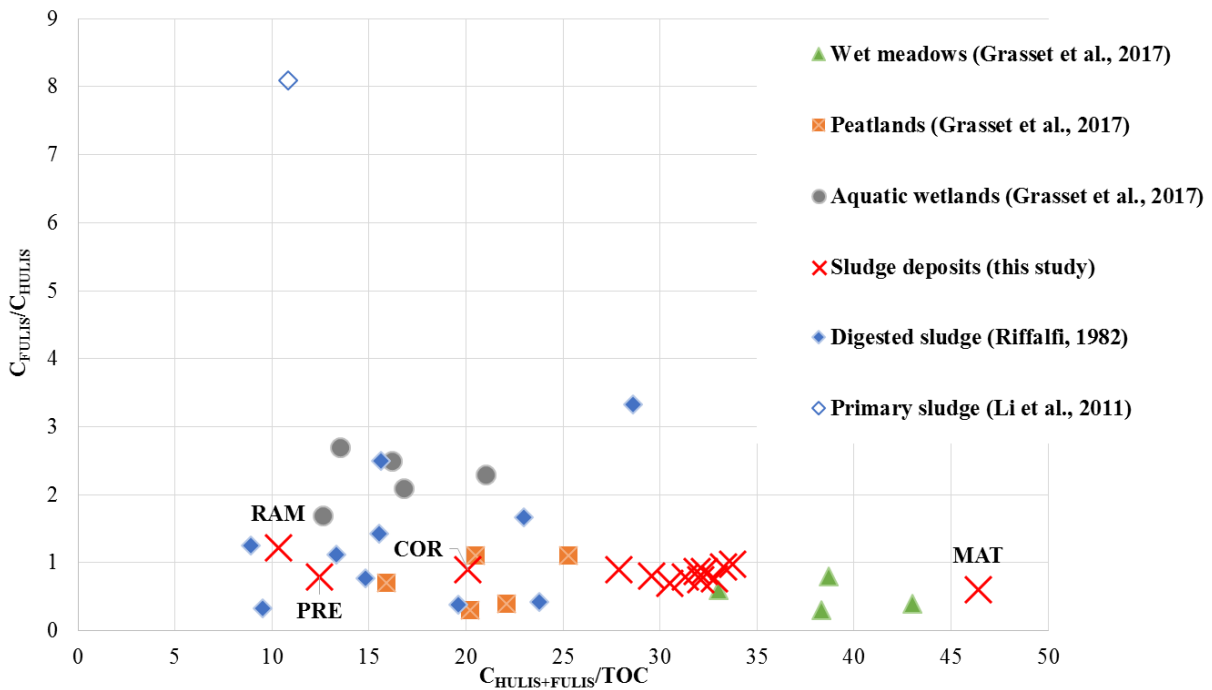
372

373 **Fig. 5.** Differentiation of sludge samples according to their indices related to the stability and maturity  
 374 of the OM. Each sample is represented with a circle whose center is positioned according to the  
 375 biodegradation rate and humification rate of the samples, and diameter is proportional to their  $R_{TGA}$   
 376 indices. Classical system with no additional treatment (blue); additional treatment on trickling filter only  
 377 (green); trickling filter and  $FeCl_3$  addition (red).

### 378 3.5.2. Comparison to other samples at different levels of POM evolution

379 Although some debates still remain on the subject, it is usually considered in the  
 380 literature that ageing of natural particulate organic matter (POM) occurs via (i) the hydrolysis  
 381 and mineralization of at least part of the most readily biodegradable constituents and (ii) the  
 382 rearrangement of the remaining constituents into complex supra-structures usually called  
 383 humus and usually considered as made of humic-like and fulvic-like substances. These  
 384 phenomena are considered to increase (i) the proportion of HULIS+FULIS within the  
 385 particulate organic matter and (ii) the proportion of HULIS vs. FULVIC within humus fraction.  
 386 To assess the extents to which these processes occurred in the sludge deposits, Fig. 6 illustrates  
 387 the plot of the ratio FULIS concentration/HULIS concentration of the samples as a function of  
 388 the overall proportion of HULIS+FULIS within the total organic carbon of the samples. Data  
 389 reported by Grasset et al. (2017) for different types of samples from natural systems were  
 390 included in Fig. 6, along with other data calculated for activated sludges using the results of  
 391 other studies (Li et al., 2011; Riffaldi, 1982). Fig. 6 illustrated the maturation pattern of natural  
 392 organic matter from the early stages of evolution (fresh OM) in the top left part to the mature

393 state in the bottom right of the graph. The VFCW sludge deposits samples appeared as two  
 394 major groups in Fig. 6. The samples from young VFCW plants (RAM, PRE and to a lesser  
 395 extent COR) constituted a first group situated at an earlier stage of maturation from the second  
 396 group made of the samples from the mature VFCW plants. COR sample was actually positioned  
 397 between the young and mature groups, revealing the effects of the additional treatments  
 398 discussed previously.



399  
 400 **Fig. 6.**  $C_{FULIS}/C_{HULIS}$  against  $C_{HULIS+FULIS}/TOC$  for natural wetlands (aquatic wetlands, peatlands and wet  
 401 meadows), activated sludges and the 14 sludge deposits of this study.

402 Altogether, the spots showing the VFCW sludge deposits exhibited a specific state of  
 403 evolution of the organic matter as compared to the other samples. Their position in the graph  
 404 revealed a specific typology of samples, despite the differences existing amongst them. Most  
 405 sludge deposits samples were positioned between the spot of digested sludge samples and  
 406 peatlands and the spot of wet meadows. On the contrary, RAM, PRE and COR samples were  
 407 positioned close to the area of peatlands and digested sludge samples.

408 **4. Conclusions**

409 Biological, chemical and thermochemical methods were applied to characterize surface  
410 sludge deposits sampled from 14 French VFCW sewage treatment plants. Results clearly  
411 revealed the existences of two groups of samples. The dominant factor of distinction between  
412 the two groups was the age of the VFCW plant of origin. The first group corresponded to sludge  
413 deposits taken from VFCW plants which were still in their first year of operation at the time the  
414 samples were collected. These samples exhibited a high content of organic matter of high  
415 biodegradability, high thermal lability, and low humification. Although the number of samples  
416 in this category (3) was low to permit a straightforward generalization, it was observed that the  
417 implementation of additional treatments in one of the three VFCW plants of this group modified  
418 the characteristics of its sludge deposits in terms of humification rate and thermal behavior.  
419 This observation showed that the presence of additional treatments modified the characteristics  
420 of the sludge deposits into a signature close to that of samples from mature systems. The second  
421 group gathered samples from 10 distinct French VFCW plants in a remarkably homogenous  
422 manner. The plants of origin were three years of age or more. Their sludge deposits were  
423 characterized by a lower organic content, lower biodegradability and thermal lability, and  
424 higher humification than those of the first group. This common set of properties was favorable  
425 to a relative accumulation of trace metals, which were analyzed at higher concentrations in this  
426 group of samples. However, the concentrations measured were found compatible with a land  
427 application practice should the sludge have to be dredged out from the filters for maintenance.  
428 One last sample, although originating from a mature VFCW plant, revealed quite different  
429 properties as compared to the other ten samples of the group. This observation could not be  
430 explained by the implementation of additional treatments. Rather, it revealed that the sample  
431 was identified as “atypical”, suggesting a particular situation in the VFCW plant of origin.

432 This study therefore showed that the organic matter captured within the surface sludge  
433 layer in French VFCW sewage treatment plants was submitted to a relatively rapid evolution

434 process over the very first year of operation of the plants. After one to three years of operation,  
435 a certain equilibrium was established, resulting from the balance between the flow of fresh  
436 POM continuously brought to the surface and the evolution of the rest of the deposits within  
437 the depth of the layer. This equilibrium state was found to be remarkably similar in all the plants  
438 of 3 years and more, regardless of the implementation of additional treatments, local conditions,  
439 and time. Surface sludge deposits therefore appeared as integrative tracers of the evolution of  
440 the system.

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