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Influence of pH on the release of colloidal and dissolved organic matter from Vertical Flow Constructed Wetland surface sludge deposits.

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Abstract

The very rapid development of vertical flow constructed wetlands (VFCW) in Europe and throughout the world has induced a growing concern on the conditions of management of their surface sludge deposits (SD). The leaching of organic components from SD was explored in this study with respect to their potential impact on biochemical oxygen demand (BOD) and their role as complexing agents in the release of trace contaminants. The aromaticity and molecular size of leached organic compounds was investigated over a large range of pHs. Experimental results showed that the pH of the leaching aqueous solution influenced the concentration and characteristics of leached OC. Around the natural pH of SD aqueous suspensions (6 to 8), truly dissolved organics (<3 kDa) exhibited high aromatic content. Under alkaline conditions (pH >8), large organic colloids (>30 kDa) were found predominant, exhibiting a low aromaticity growing with pH. Under acidic conditions (pH<6), hydrophilic truly dissolved organics were leached. Comparison of concentration, aromaticity and molecular size of OC leached from 14-year and 7-year SD suggested that ageing of SD reduced their sensitivity to pH conditions and may improve their agronomic properties.

Keywords

Lixiviation; Organic carbon; Molecular weight; Ultrafiltration; Aromaticity; pH variations.

Abbreviations

BOD: Biochemical Oxygen Demand

LOC: Large Organic Colloids

MW: Molecular Weight

OC: Organic Carbon

SD: Sludge Deposit

SOC: Small Organic Colloids

SOM: Solid Organic Matter

SUVA: Specific Ultra Violet Absorbance

tDOC: Truly Dissolved Organic Carbons

TOC: Total Organic Carbon

VFCW: Vertical Flow Constructed Wetlands

1. Introduction

In porous media such as soil, sediment and sludge, the partition of organic molecules between solid and dissolved states controls the fate of many trace contaminants [1–3]. The presence of complexing groups in solid organic matter (SOM) contributes to the retention of trace metals within the solid fraction. The solubilization of organic molecules through SOM hydrolysis thereby induces the release and transport of associated pollutants [4,5] which may alter the quality of the receiving water bodies.

A large variety of organic molecules may be leached in the dissolved form. Depending of the SOM of origin, these molecules may exhibit different molecular sizes and chemical compositions, particularly with regards to their functional groups (aromatic rings, carboxylic acids, N-containing groups, etc.). Molecular fractionation using ultrafiltration [6,7] and UV-visible spectroscopy [8,9] have been used

extensively to characterize the molecular weight (MW) and aromaticity of DOM. $SUVA_{254}$, defined as the ratio between absorbance at a wavelength of 254 nm and dissolved organic carbon concentration, is a well-known indicator of DOM aromaticity. It has also been reported to be a good indicator of DOM capacity to sorb trace metals in organic rich water [4,10] or organic-rich soil solutions [11]. Moreover, the chemical speciation of associated trace metals has been shown to be largely affected by the molecular weight of organic ligands in natural water samples [7,12]. Finally, the aromaticity of DOM, estimated by $SUVA_{254}$ or other parameters, has also been shown to play a role in biodegradabily as shown by the anti-correlation observed between the biological oxygen demand BOD and the aromaticity of dissolved organic compounds [13].

The release of DOM from SOM may occur by different mechanisms, such as the hydrolysis of macromolecular structures [14,15] or the desorption of organic molecules attached to solid mineral phases [16,17]. The extent to which each mechanism may contribute to the overall leaching phenomenon is dictated by the physico-chemical characteristics of the solid matter of origin [18] and the environmental conditions of the medium. pH conditions appears to be a key factor of influence [1,19]. Several studies have reported that dissolved organics with high MW and aromaticity were preferentially aggregated by solid mineral phases [18,20], resulting in a poor solubilization of these molecules. Alkaline pHs were reported to destabilize organo-mineral associations via the deprotonation of the ligands in both phases inducing anionic electrostatic repulsion [21,22]. Pédrot et al. [23] reported that low pHs could also induces the disaggregation of supramolecular assemblies of humic substances, leading to the release of low molecular weight organic molecules.

Constructed wetlands are engineered nature-based systems designed to treat domestic wastewaters and similar effluents [24]. So-called “Classical French” vertical flow constructed wetlands (VFCWs) are based on the percolation of unsettled wastewaters through 2 successive stages of filters filled with gravels or sand and planted with reeds. This process induces the formation of a sludge deposit (SD) layer at the surface of the first-stage filter which has been shown to play a major role in the retention and degradation of a large variety of contaminants during regular conditions of operation [25,26].

Organic matter in SD is mostly present in the solid form and its concentration ranges between 40% and 90% of dry mass [25]. It originates predominantly from anthropic sources (wastewaters), but may also be autochtonous (*e.g.* biofilms, plants and microbial cells fractions; [27]) or allochtonous (*e.g.* terrestrial organic residues from the catchment area). The surface sludge layer is the siege of numerous reactions which induce the evolution of organic matter [26,28] that could in turn influence the quantity and the chemical nature of the DOM.

Some studies have already monitored the concentration of DOM in VFCW systems, from inflow to outflow [29–31]. Kania et al.[25] showed that SDs were sources of DOM and reported a pH-dependent leaching pattern. However, despite the significant scientific and operational implications this observation may have during the operation of VFCW systems or for the use of the sludge outside the system, little is known on the influence of pH on the fluxes, molecular weight and other characteristics of DOM leached from the SDs. Yet, by controlling the quantities, nature, and molecular size of DOM, the pH conditions could strongly influence the associated release of contaminants from the SDs [1,25]. During the operation of a wastewater treatment plant unit, the SD layer is usually submitted to pHs ranging between 6 and 9 [31,32]; However, more acidic conditions (pH below 6) can be observed with winery effluents for example [33]. A better description of the leaching of organic compounds from the SDs may also provide useful information regarding the final use of the sludge material in land applications where it would be submitted to pHs ranging from 5 to 9 [34].

The general objective of this study was thus to generate scientific knowledge on the release of organic colloids from the SOM of VFCW surface sludge deposits, and more specifically on the effects of pH on the quantities and physical–chemical characteristics of the leached organic compounds. Previous work from our group compared the characteristics of 14 SDs samples from different origins and identified 2 typologies of samples according to their age, namely the older SDs group beyond 3 years of age, and the younger SDs group of 1 year or less [26]. The present study focused on sludge deposits of the older SDs group (beyond 3 years of age) which was considered as representative of a steady state mode of operation of the VFCW unit. The work was therefore done using SD samples taken from a same plant

at different ages above 3 years, respectively 7 and 14 years, in order to investigate the influence of ageing on the leaching properties. SD samples were leached under controlled conditions over a wide pH range to generate information which would not be accessible in field studies. The aqueous extracts were fractionated by ultrafiltration and then analyzed for DOC concentration. Each ultrafiltrate was then further analyzed to evaluate the chemical nature of the organic compounds.

2. Materials and methods

2.1. Sampling

SD were sampled from the Vertical Flow Constructed Wetland (VFCW) treatment plant of Vercia (FRANCE) already described in details by Kim et al.[35]. This plant is designed according to the AZOE-NP patented process (EP1857419A1). It is considered as a "French system" because it receives unsettled wastewater. It differs from the so-called "classical French system" by some additional operations, in particular the implementation of a trickling filter before the first filter stage and the presence of a water-saturated zone in the lower part of the first stage filter, providing anoxic conditions to allow partial denitrification. SD samples were taken from the surface sludge layer of the first-stage filter which had been left in place since the first day of operation of the treatment plant following the protocol reported by Kania et al.[25]. The 7-year samples were taken by Kania et al.[25], freeze-dried for conservation and stored at 4 °C The 14-year samples were taken specifically for the present study following the same protocol. All samplings were done in winter time for the good accessibility to the sludge layer due to the absence of the reeds. Several kg of SD were collected over the whole depth of the sludge layer (>15 cm) from 8 different spots at the surface of the first-stage filter. All samples were sorted manually on site to remove reeds rhizomes and gravels, and subsequently mixed together by shoveling. A representative sample of a few kg was then prepared by quartering, refrigerated and transported to the laboratory within a maximum of 4 hours. Then, aliquot fractions were prepared, crushed and sieved at 1 mm, freeze-dried and stored at 4 °C for further analyses and assays.

2.2. Analysis of particulate matter

Organic carbon contents of the two SD samples were determined by a carbon sulfur analyzer (EMIA-320V2, Horiba Scientific Co., Ltd) previously decarbonized by hot digestion with diluted HCl. The precision of the analysis for carbon is ±2 mg/kg.

The freeze-dried SD samples were analyzed in duplicates for humic-like, fulvic-like and humin-like components, following a protocol adapted from Serra-Wittling et *al.* [36]. To obtain humic and fulvic-like content, a dry mass of 1g of SD was suspended and mixed for 2 hours in 50 mL of a 0.1 M sodium hydroxide aqueous solution. The suspension was then centrifuged at 10 000 g for 15 min and filtered at 0.45 µm using Sartorius acetate cellulose filters. The solutions, containing humic- and fulvic-like substances, were analyzed for OC using a Shimadzu TOC-L analyzer with an uncertainty of ± 5%. The residual solids contained all the SD constituents which were not extracted under the alkaline conditions used. Their OC content, representing the humin-like fraction, was calculated as the difference between the total organic carbon (TOC) content of the initial SD sample and the OC content of the filtered solution. To obtain fulvic-like content, SD solutions were acidified to pH 1.5 with 1 M sulfuric acid aqueous solution and kept overnight at +4°C to allow precipitation of humic-like substances. Fulvic-like substances were collected in the solutions by centrifugation at 6000 g for 15 min followed by filtration at 0.45µm. The filtered solutions were analyzed for OC concentration.

The SD samples were also analyzed by thermogravimetry (TGA) coupled to differential scanning calorimetry (DSC) using a METTLER TOLEDO TGA /DSC analyzer. Analyses were done in duplicates. Aliquote sub-samples of 20 mg dry mass (DM) were heated from 35 to 900 °C at a rate of 10 °C.min^{-1} under an airflow of 50 NmL.min^{-1}. Blanks were run under the same conditions without any samples. Mass losses obtained from TGA and heat fluxes obtained from DSC were monitored as a function of the temperature. The data were used to calculate R_{TGA} and R_{DSC} indexes as indicators of the stability of the organic matter as described previously [26]. These indexes were respectively calculated as the ratios between the mass loss (R_{TGA}) and the heat release (R_{DSC}) recorded between 400 and 600°C to those recorded between 200 and 400 °C. They were shown to increase with the contents in complex organic

compounds such as lignin, poly aromatic structures of high MW and O-containing functional groups in the solid organic matter SOM [25].

2.2. pH-dependent leaching test

A batch leaching test, based on the CENTS/TS 14429 European standard, was used to evaluate the effect of pH on the release of organic components from the sludge deposits (SD) samples. The assays were performed in Nalgene® polypropylene centrifuge tubes, at a solid-to-liquid ratio of 100 g of SD dry matter per liter of leaching solution. Prior to the tests, all tubes were soaked in 1M HCl aqueous solution overnight and then rinsed with deionized water. All assays were duplicated.

The SD samples were contacted with: (i) deionized water for natural pH conditions (blank), (ii) 0.022, 0.08, 0.13, 0.25, 0.35 M nitric acid aqueous solutions for acidic conditions and (iii) 0.02, 0.03, 0.06, 0.1, 0.15, 0.20 M potassium hydroxide aqueous solution for alkaline conditions. The number of moles of protons (acidic solutions) or hydroxide ions (alkaline solutions) in each leaching solution was calculated as the product of HNO_3 or KOH concentrations by the volumes of solution used in each assay**.** Altogether, 5 acidic and 6 alkaline leaching solutions were used, in addition to the blank at natural pH. All assays and blank were stirred at room temperature in a rotary shaker set at 9 rpm until an apparent steady state was reached, which was observed within 48 hours in preliminary experiments.

2.3. Fractionation of leached compounds

The suspensions obtained from the batch leaching experiments described above with the two SD samples at the different pHs tested were centrifuged at 4000 rpm (2400 g) and the supernatants were filtered at 0.45 µm using Sartorius cellulose acetate filters to separate SOM from truly dissolved or colloidal forms. The solutions filtered at 0.45µm were analyzed for OC concentration and the results expressed as $[OC]_{0.45\ \mu m}$ corresponding to the colloidal and truly dissolved compounds leached. They were then further filtered at 0.22 µm on Sartorius microporous cellulose acetate.

Then, ultracentrifugation tubes equipped with Sartorius Vivaspin cellulose acetate ultrafiltration membranes of 30 kDa, 10 kDa and 3 kDa were used to fractionate the soluble components according to their MW. Centrifuge ultrafiltrations were performed at 3000g for 30 min using a swinging bucket rotor. Ultracentrifugation cells were previously rinsed with a 0.1M NaOH solution followed by de-ionized ultrapure water to guarantee initial concentrations of dissolved organic carbon (DOC) below 0.1 $mg.L^{-1}$ in the ultrafiltrate.

2.4. Analyses of suspensions and solutions

The suspensions obtained from the leaching experiments were analyzed for pH and conductivity before being filtered. A Consort C3020 meter equipped with Bioblock 11706358 and Consort SK10T electrodes was used for pH and conductivity.

Organic carbon (OC) concentrations were measured in solid, colloidal and truly dissolved fractions using a Shimadzu TOC-V CSH analyzer previously calibrated with a standard solution of potassium hydrogen phthalate. The uncertainty of the analysis was estimated to ± 5%. OC concentrations in blanks at natural pH (leaching in de-ionized ultrapure water) were found to be systematically below 0.2 $mgC.L^{-1}$. The colloidal and truly dissolved fractions were further analyzed for UV-visible absorbance using a Perkin-Elmer Lambda 25 spectrophotometer to record UV-visible spectra from 800 to 220 nm with 0.5 nm increments. Analyses were done in duplicates at room temperature in 1-cm light-path quartz cells. The ratio of the absorbances measured at 250 and 365 nm (referred to as E_2:E_3) was calculated as an indicator of the size of the UV-absorbing organic molecules present in the solutions [8]. It was considered that an increase of the ratio revealed a decrease of the average molecular size of the UV-absorbing molecules in solution [37]. The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$, $L.mgOC^{-1}.m^{-1}$), defined as the ratio of the absorbance at 254 nm to the organic carbon concentration was used as an indicator of the degree of aromaticity of the molecules [37,38]. Values of $SUVA_{254}$ above 4 and below 2 were considered to reveal highly aromatic and poorly aromatic molecules, respectively [31].

3. Results and discussion

3.1. Comparison of the SDs physicochemical properties

3.1.1. General characteristics of the SDs

Table 1- Analyses of surface sludge deposits (SD) from Vercia VFCW wastewater treatment plant sampled after 7 and 14 years of operation

Sample	TOC [(1)] (g TOC/g DM)	Humic-like[(2)] (% of TOC)	Fulvic-like[(2)] (% of TOC)	Humin-like[(2)] (% of TOC)	R_{DSC}	R_{TGA}	N_{tot}[(2)] (% of DM)	P_{tot}[(2)] (% of DM)
14-year SD	0.17	13.0	12.7	74.3	2.14	0.84	2.45	2.11
7-year SD	0.23	18.0	12.6	69.5	1.90	0.76	3.78	2.04

TOC: total organic carbon (in dry solids); DM: dry matter; R_{DSC}: calorimetric index; R_{TGA}: thermogravimetric index.

[(1)] Uncertainty of ± 2%; [(2)] Uncertainty of ± 5%

The results of the characterization tests of our samples including the total amount of organic carbon (TOC), the extractions of humic and fulvic-like compounds and thermogravimetric indexes are shown in Table 1. TOC contents in both SD samples (0.17 and 0.23 g TOC/g DM, for 14-years and 7-years SD respectively) were far above the concentrations reported in literature for natural systems like natural wetlands sediments in which TOC rarely exceeds 10% [39,40]. TOC content in SD samples are closer to the 30-45% of TOC content generally observed in the first peatland soil profiles of temperate climate [16,41]. The rest of the sludge deposits' matter is composed of inorganic matter such as Fe-oxyhydroxydes, carbonates, silica and clays [35]. The lower TOC content in 14-year, compared to 7-year SD, was assigned to the mineralization of organic matter which was reported in several studies [35,42].

About 70 to 75% of the TOC was present in the humin-like fraction in both samples (Table 1). Fulvic- and humic-like compounds were found to account for approximately 31% and 25% of the TOC content

in the 7-year and 14-year samples, respectively. Previous studies from literature showed that the humin fraction's OC exhibited a higher concentration in aromatic and polyhydroxy aromatic compounds than the humic and fulvic-like fraction [38,43]. This observation was confirmed here by TGA-DSC analyses that revealed higher values of R_{TGA} and R_{DSC} indexes for the 14 years old sludge deposit (Table 1). These results indicate that with aging, the sludge deposits' concentrates more and more aromatic and O-containing functional groups despite the continuous input of low aromatic organic matter from wastewater [25].

3.1.2 Acid-base buffering capacity of SDs

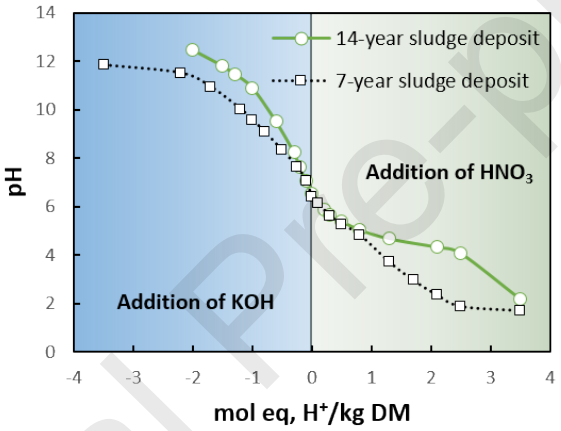

Figure 1. Acid and basic titration curves of the 14-year and 7-year SD. The error bars, comprised within the symbols, represent the standard deviation of two measurements.

Fig 1a shows the acid-base buffering capacity of the two SD samples over the whole pH range tested. The x-axis shows the number of moles of protons (positive values, acidic solutions) or hydroxide ions (negative values, alkaline solutions) in each leaching solution, expressed per g of SD dry matter. The pH buffering capacity of solid samples such as soils, sediments or composts is largely influenced by the density of functional groups of OM [44,45]. Plaza et *al.* [45] evidenced that OM enrichment in carboxyl and phenolic groups, occurring with composting process of various sludge residue, increase their acid buffering capacity. The buffer capacity of the two SDs were similar over most of the pH range but, with respect to 7-year SD, the 14-year SD shows a greater buffering capacity for acidic conditions (pH~5).

Thus, this was probably due to the enrichment of the 14-year SD in aromatic and O-containing functional groups as observed in the previous section. This change in acid-base proprieties occurring with aging could improve the SD's resistance to acidic rain or acidic agricultural soils.

3.2. Characterization of the conventionally dissolved fraction (<0.45µm)

3.2.1. Evolution of the OC concentration

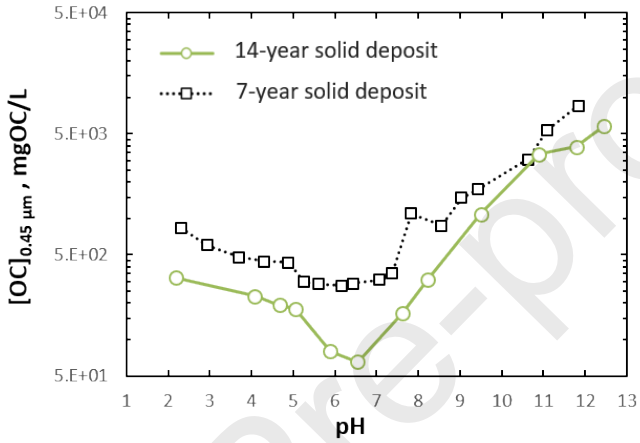

Figure 2. Effect of pH on the leaching of OC from 7-year and 14-year solid deposits sampled from the same wastewater treatment plant. The size of the dots includes the 5% experimental uncertainty.

Fig. 2 shows the concentration of organic carbon measured at equilibrium in the 7-year and 14-year SD leachates after filtration at 0.45 µm ($[OC]_{0.45\,\mu m}$). The lowest extraction was observed at neutral pH (*i.e* pH 6.5), where only 0.4% and 1.6% of the TOC content was leached for 14-year and 7-year SD, respectively. These leaching values are similar to those reported in literature for agricultural soils with pH close to 7 and much lower TOC contents [46,47]. Under these circum-neutral pH conditions, the conformational structures of the organic matter and organo-mineral aggregates are less impacted than under more acidic conditions [23] resulting in a lower leaching.

For both samples, leaching of organic compounds increased below pH 5 and above pH 7. Leaching at neutral to acidic pH affected only a very small proportion (less than 5%) of TOC present in the samples: the highest release under acidic conditions was obtained at pH 2.2 with 323 mg/L for the 14-year and 830

mg/L of OC for the 7-year SD, corresponding to 1.8% and 4.8% of the TOC respectively. The increased release of OC observed, for both SD samples, under acidic conditions is the net effect of several phenomena [18]. For example, under acidic conditions, protonation of hydroxyl groups and the development of a positive surface charge at mineral surfaces favored the adsorption of negatively charged organic molecules, thereby limiting the transfer of OC into the aqueous solution [18,48]. But, the increase of protons competition under acidic conditions reduce cation bridging of organic molecules and could induce the release of OC [18,49]. The sum of these phenomenon produces a net increase of the OC leached concentration observed under acidic conditions as compared to circum-neutral pH conditions.

The effect of pH on the leaching of soluble compounds was much stronger over the alkaline range (Fig. 2). For the 14-year SD, leaching was increased by a factor 4 from pH 6.5 to 8.0 (from 65 mg/L to more than 300 mg/L of OC), and by a factor 20 from pH 8 to 12 (6000 mg/L of OC at pH 12, Fig. 2). At pH 12, more than 33% of the overall TOC content of the sludge deposits was leached into the solution. For the 7-year SD, the maximum release, obtained at pH 12, was around 8000 mg/L, corresponding to 48% of the overall TOC content. The increasing solubilization of organic molecules with increasing pH could be attributed to the deprotonation of SD's mineral surfaces (e.g. Fe-oxyhydroxydes, clays…) occurring with increasing pH conditions which would disrupt organo-mineral association [21,50] and lead to the solubilization of organic molecules associated to these mineral surfaces.

The chemical structure of organic functional groups was also reported as a factor controlling the solubilization of organic molecules [51]. This factor may explain the differences observed in the leaching behavior of the 7-year and 14-year samples (Fig.2), which cannot be attributed only to their different TOC contents. Over the entire pH range, released OC concentrations were higher for the 7-year SD but the largest gap was observed close to neutral pH (*i.e* pH 6.5) where 14-year SD released about 4 times less OC than the 7-year SD. This result emphasized that the 7-year SD contained more easily leachable organic molecules than the 14-year sample. This observation was attributed to the higher aromaticity of the 14-year sample and its higher content in oxygenated functional groups (Table

1), which increased the proportion of OC trapped in organo-mineral aggregates [52] and thus OC stability.

3.2.2. pH-dependent characteristics of soluble organic compounds

Figure *3a* shows the $SUVA_{254}$ values of the soluble organic compounds leached over the tested pH range for the 7-year and 14-year after filtration at 0.45 µm. At neutral pH (*i.e.* pH 6.5), SUVA values around 1 $L.mgOC^{-1}.m^{-1}$ were recorded for both 7-year and 14-year SD, suggesting a low aromaticity and high proportion of proteins, lipids and carbohydrates. Aromatic compounds were reported to have a higher affinity with mineral phases [17,53] and were therefore probably sorbed under these pH conditions. The SUVA measured here were similar to those obtained by other authors on natural wetlands [54], sediments [55] and various agricultural soils with pH varying from pH 8 to pH 5 [34].

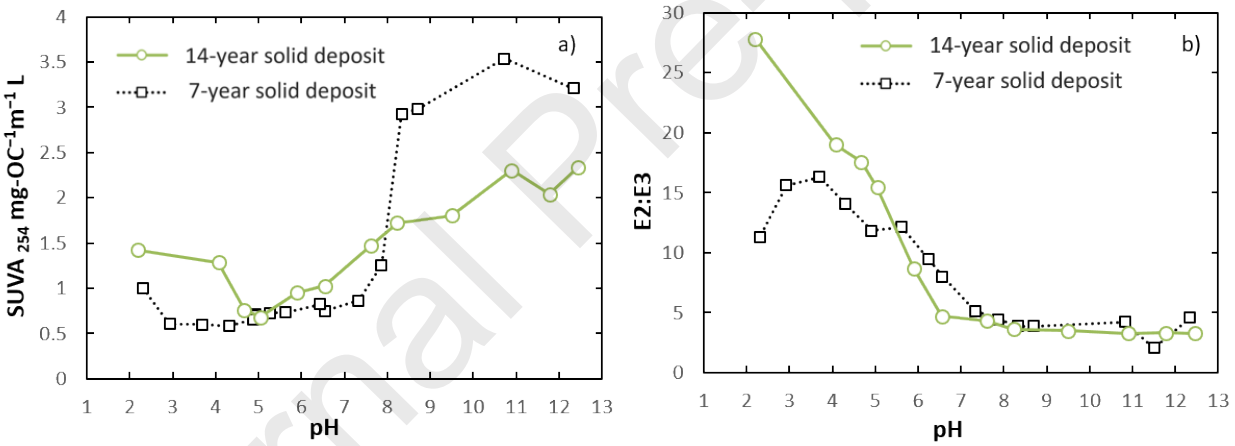

Figure 3. Effect of pH on a) the SUVA and b) E2:E3 ratio of the soluble organic compounds leached at equilibrium from each sludge deposit. The size of the dots includes the 5% experimental uncertainty.

Under alkaline conditions, an increase of $SUVA_{254}$ values was observed, up to 2.5 $L.mgOC^{-1}.m^{-1}$ (14-years SD) and 3.5 $L.mgOC^{-1}.m^{-1}$ (7-years SD) at pH 12, suggesting the release of more aromatic organic compounds. The higher aromaticity of the compounds leached at increasingly alkaline pHs was attributed to the desorption of fulvic and humic-like compounds. Above pH 8 or so, $SUVA_{254}$ values were higher for the 7-year SD than the 14-year sample (Fig. 3a) despite the aromatic content deduced from table 1, which were lower in the 7-year SD. This observation could be attributed to a stronger

stability in the 14-year SD as compared to the 7-year sample of the complexes between organic compounds and clay [6] or metal-oxyhydroxides [56] within the SD particles. Under very acidic conditions, the SUVA of the leached compounds was slightly higher than under natural pH conditions (around 1.5 and 0.5-1.0 respectively). This result may be explained by the possible dissolution of carrier mineral phases [57] at very acidic pH leading to the release of associated organic compounds.

Figure 3b shows the evolution of E2:E3 values of the soluble organic compounds leached over the tested pH range for the 7-year and 14-year after filtration at 0.45 µm. For both samples, higher E2:E3 are observed below pH 7 compared to pH above 7. This result suggests that the SD release smaller UV-absorbing organic compounds at acidic pHs. In addition, the constant increase in E2:E3 values from pH 7 to pH 2 suggests a gradual decrease in the size of the UV-absorbing released molecules as the solutions become more acidic. At pH values below 5, the 14-year SD soluble organic compounds induced a higher proportion of small size organic components assimilated to fulvic acids. Between pH 7 and pH 12, for both samples, E2:E3 remains stable in the range of 4.5 to 3.5. These values were similar to those obtained for pore water of peatland that fluctuate around 4 [8,58] and for agricultural soil solution [59]. Finally, the evolution of SD characteristics with ageing seemed to affect only partially the molecular size of UV-absorbing leached organic molecules as shown by the similar E2:E3 between the two SDs.

3.3. Ultrafiltration of the leached organic compounds from the 14-year SD

3.3.1. Assessment of the molecular size of emitted organics compound at various pH from SD

The OC concentration measured in each filtrates (0.45 and 0.22 µm) and ultrafiltrates (30, 10 and 3 kDa) depending on pH conditions is presented in Figure 4a. The OC concentrations were very similar in the 0.45 µm and 0.22 µm filtrates regardless of pH conditions, indicating that only a very small quantity of compounds were leached in the size range comprised between 0.22 and 0.45 µm. The same was observed for 30 kDa and 10 kDa filtrates over the whole pH range, indicating that very few molecules are comprised between 10 and 30 kDa. At acidic pH, the comparison of the different curves indicated that a large proportion of organic molecules exhibited a molecular size below 3 kDa. At neutral and alkaline

pH's, it was observed that the $OC_{<0.45\mu m}$ curve differed from the others indicating a large proportion of molecules with a molecular size higher than 30 kDa.

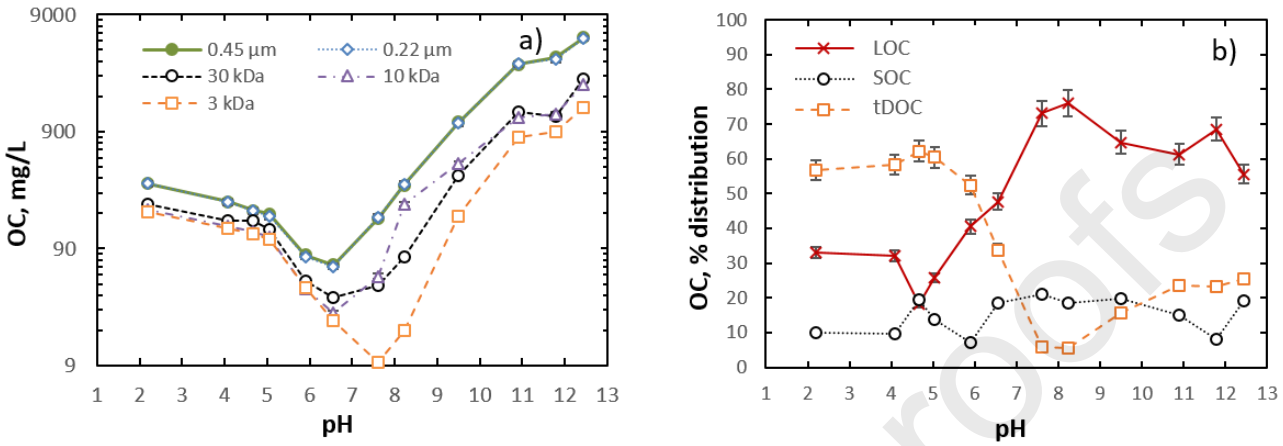

Figure 4: Effect of pH on a) the size distribution of the leached organic compounds and b) the distribution of OC in 3 different MW fractions previously defined. The size of the dots includes the 5% experimental uncertainty.

The pH-dependent molecular size of organic compounds released from the 14-year SD can be simplified by grouping the results within different molecular size classes [14,60]. The size of the leached organic compounds was therefore described here in a simplified manner according to the following classes: (i) Large Organic Colloid (LOC) between 30 kDa and 0.45 µm, (ii) Small Organic Colloid (SOC) between 3 kDa and 10 kDa and (iii) "truly" Dissolved Organic Carbon (tDOC), smaller than 3 kDa. All designations and acronyms, along with the equations used for the calculations, are gathered in supplementary data in Table S1.

The relative abundance of leached organic compounds in each molecular-size fraction, expressed in % of total released OC concentration, is shown in Figure 4b. Over the whole pH range, the percentage of small colloids remained relatively constant (between 5 and 20%), but the proportions of LOC and truly dissolved compounds varied considerably with the pH. Under acidic conditions, truly dissolved compounds were predominantly leached (about 60% of overall leached OC), whereas large colloids were predominant above pH 7. This observation was in agreement with the increase of E_2:E_3 measured on the $OC_{<0.45\mu m}$, observed from pH 6.5 to 2 (Fig.3 b.) confirmed that the size of the leached organic

compounds was smaller as the pH was decreased. The size distribution of leached organic compounds remained relatively stable below pH 6 (tDOC predominant) and above pH 8 (LOC predominant). However, the E2:E3 suggests a progressive decrease in the MW of leached organic compounds with acidification, which cannot be detected with the 3 kDa cut-off. Thus, the proportion of molecules <3 kDa remains constant but within this class, the released molecules are increasingly smaller with acidification. The strongest variations in the size distributions were observed between pH 6 and 8 that is, naturally occurring pH conditions. An increase of one pH unit (from pH 6 to pH 7) was found to divide by 2.5 the proportion of truly dissolved compounds (from more than 50% to less than 20% of overall of leached OC).

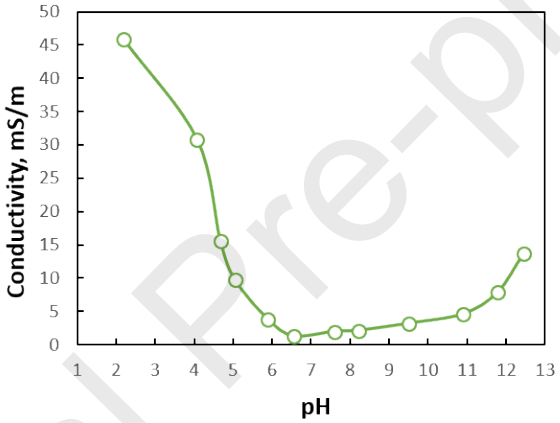

Figure 5: Conductivity of the 14-year SD sample recorded at equilibrium in the batch leaching assays.

Mineral phases preferentially sorb high MW OC with higher content in aromatic and O-containing polar groups [20,61], thus the desorption of OC from these phases occurring with alkalization of the solution conditions could both explain the increasing of OC MW and the relative aromaticity of released OC described in further details in the following paragraph. The preferential solubilization of small MW organic matter under acidic conditions have been previously observed on soils batch experiments [1] and in acidic soil solutions [2]. This phenomenon could be explained by both pH and conductivity of the SD solutions. Under acidic pH conditions, organic molecules with higher net surface charge are preferentially solubilized [62]. Fulvic acids, which MW is smaller than humic acids, have stronger total charge per gram of carbon and higher proportion in weak proton affinity sites compare to humic acids

[63]. These proprieties of small organic molecules assimilated to fulvic acids could explain the release of tDOC from the SD submitted to acidic conditions. Besides pH conditions, the size of the released OC could be affected by the conductivity of the solution which is described in Figure 5. The dissociation of metal oxides and the important release of multivalent cation showed via ICP-MS analysis by Kania et *al.* [25] on the 7-year SD sample could explain the significant increase in conductivity observed under acidic conditions for the 14-year SD. This phenomenon occurring with the acidification of the solutions may promote the aggregation of large macromolecules (>20 kDa) into solid OM >0.45 µm [14,64]. Smaller molecules were not affected resulting in an increase of the proportion of dissolved compounds with the acidification.

3.3.2. Aromaticity of the leached organic compounds in the different size ranges and effect of pH

Figure 6 shows the $SUVA_{254}$ values of the leached compounds in each size range at the different pHs of equilibrium. Over the entire pH range, the SUVA of large and small colloids (LOC and SOC) were very similar, increasing with the pH from 0.4 at pH 6.5 to 3 $L.mgOC^{-1}.m^{-1}$ at pH 12. The $SUVA_{254}$ was however always below 3, suggesting a high proportion in hydrophilic molecules. Several factors may explain the relative low aromaticity measured for large and small colloidal fractions, such as the preferential sequestration of aromatic compounds by minerals [61] present in the solid phases. Moreover, it has been shown that weak acids groups and aliphatic structure can be linked via hydrogen, hydrophobic or cation bonding to aromatics rings of the large and small colloidal fraction [15,65] thus decreasing the aromaticity of the supramolecular assemblies observed in these size fraction.

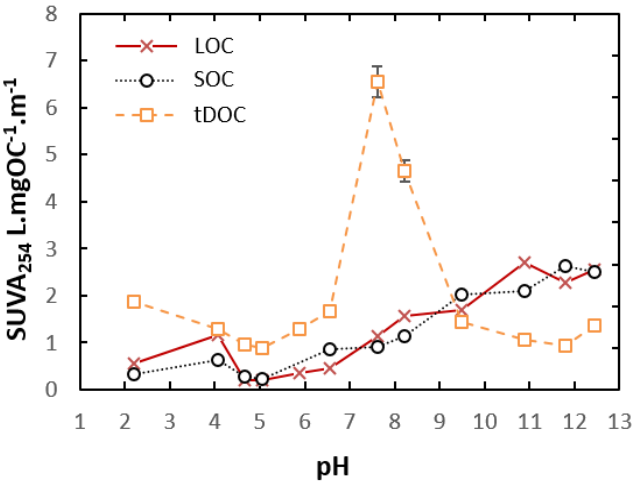

Figure 6. $SUVA_{254}$ values of leached organic compounds as a function of pH and MW fractions. (Bars represent the analytical uncertainty).

The $SUVA_{254}$ of the tDOC fraction remained close to 1 $L.mgOC^{-1}.m^{-1}$ over the acidic and alkaline pH ranges, but fluctuated greatly around the neutral pH (6.5) from 1.4 $L.mgOC^{-1}.m^{-1}$ at pH 6 to 7 $L.mgOC^{-1}.m^{-1}$ at pH 8. These high $SUVA_{254}$ values suggested that truly dissolved organic matter contained a high proportion of aromatic molecules like phenols, phenolic acids and flavonoids [66]. This near-neutral pH range is also the range with the lowest conductivity (Fig. 5) and the smallest amount of tDOC released (Fig. 6). The important tDOC aromaticity could be reasonably explained by the low conductivity suggesting low cations release and thus low quantity of cationic bridging between low MW aromatic structure and other low MW hydrophilic compounds decreasing the aromaticity such as polysaccharides. The major results of this section (*i.e* transition between a release of LOC versus a release of tDOC and the release of highly aromatic truly dissolved molecules) are obtained in a pH range ranging from 5.5 to 8. These results were even more important as the sensitivity of SD is manifested in a critical pH range that SD may encounter during regular conditions of operation with environmental implications described in the following section.

4. Environmental significance

The results presented in this study contribute to a better description of the mechanisms of retention and release of organic compounds during the contact between aqueous solutions and sludge deposits solid organic matter. The experimental conditions used allow potential applications to various conditions that the sludge may encounter either in the VCFW during its operation or outside during its reuse in agriculture for example. The pH range tested in this study by far encompasses the possible situations that may be encountered in practice. Results show the effects of pH on the quantities, nature and

molecular size of leached organics, and provide indications on the retention or co-transport of pollutants with organic carriers and the potential associated environmental impacts.

SD layer play a major role in the performance of VFCW systems [67]. By reducing the release and transfer of OC and associated contaminants from the SD solid organic matter, ageing may improve the performance in carbon removal. However, for the same reason, SD ageing may be unfavorable to denitrification which requires sufficient quantities of bioavailable OM [68].

At the end of their operational life, SD may be reused as soil applications to increase or restore organic matter content of the receiving soils [69]. This study suggests the importance of the SD ageing process to improve the environmental safety and agronomic performance of this practice. The main benefits of soil application of organic amendments such as compost [51,54] or related materials is in the formation of soil organo-mineral aggregates which reduce the erosion phenomena and contribute to the improvement of the agronomic properties of the soil such as its porous structure and water retention capacity. However, application of readily biodegradable matter (as in younger SDs) would cause a series of undesired phenomena such as oxygen depletion due to its rapid aerobic mineralization. Improving the agronomic properties of the soil while reducing the potential environmental impacts is achievable by applying stable forms of organic matter [69] such as in older SDs. 14-year sludge deposits were also shown in this study to reduce the release of soluble organic compounds regardless of pH conditions, thereby limiting carbon loss in the receiving soil and increasing the residence time of solid organic matter.

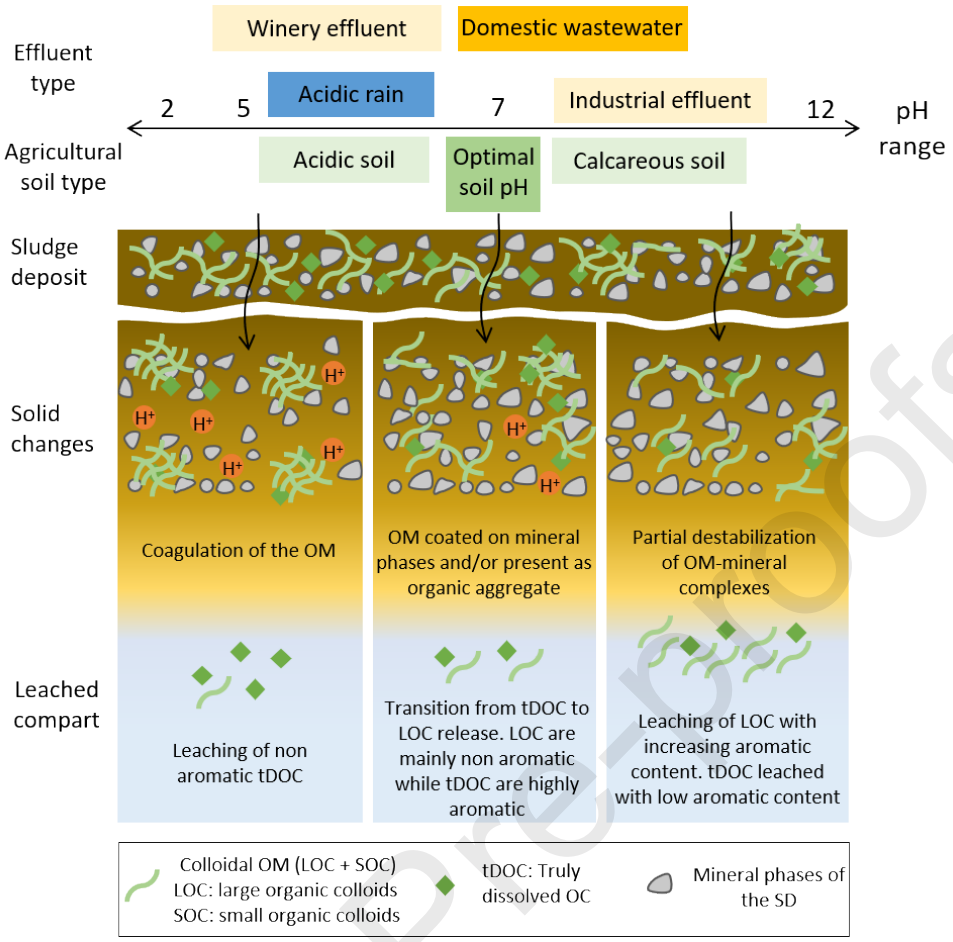

Figure 7. Conceptual solid-solution partition of organic matter and evolution of the quality of the released organic molecules from SD under various pH conditions corresponding to different operational and reuse conditions SD might undergo.

Under regular operating conditions, the deposits in the surface sludge layer of VFCWs would be in contact with close to neutral to slightly alkaline solution (Fig.7). This study showed that small pH variations in this range would strongly affect the leaching of organic matter, both quantitatively and qualitatively (size and aromaticity). In this pH range, the colloidal fraction was found to contain mostly hydrophilic compounds. The low $SUVA_{254}$ values [70] as well as, in a less extent, the molecular weight [71] of this colloidal pool are indicators of a high biodegradability of these molecules. Indeed, molecular weight and $SUVA_{254}$ are positively and negatively, correlated to the biodegradability of natural organic molecules, respectively. Thus, the leaching of this colloidal fraction could negatively influence water

quality indicator such as the Biochemical Oxygen Demand (BOD) of the treated water. The "truly" dissolved fractions containing a high proportion of aromatic compounds could have strong interactions with the micropollutants possibly present in the SD. However, the high aromaticity, and consequently the probable low biodegradability of these molecules, limits their contribution to the BOD of the leachates.

Under alkaline conditions, the leached organics were predominantly in the form of large colloids, containing aromatic compounds. These pH conditions would increase the interactions between the leached organic molecules and trace metals thus enhancing the mobility of such pollutants from the SD to the receiving environment.

Under conditions of flooding for example, anoxic to anaerobic conditions may cause the installation of reductive conditions associated with possible acidification due to the formation of volatile fatty acids [72]. SD would then leach poorly aromatics molecules of small molecular size (<3 kDa), probably composed by low-molecular weight organic acids, carbohydrates and small amino-acids, having the capacities to sorb heavy metals contaminants [2] and would be more bio-available [13].

5. Conclusion

The nature of the organic compounds leached from the SD under a wide range of pH was approached here through their size distribution using (ultra)filtration and their aromaticity using UV-visible spectroscopy indicators. Under acidic conditions, leached organics were predominantly (more than 50%) in the form of truly dissolved compounds tDOC made of poorly aromatic molecules. Under alkaline conditions however, tDOC was less than 20% of leached organics which were associated to large colloids for more than 70%. The release of OC trapped in solid organo-mineral association increased the overall aromaticity and molecular size of the leachates. This study clearly demonstrated important changes in the nature of the leaching molecules in the natural range of pH (*i.e.* pH 5 to pH 8). These results showed that a small variation in pH could induce strong effects on the characteristics of the

released organic matter. The organic components in the large colloids were mostly carbohydrates, proteins, and aliphatic molecules, whereas the truly dissolved components were predominantly aromatic molecules.

The transformation of the SD occurring with ageing increased their acid-base buffering capacity, reduced the amount and aromaticity of the leached organic molecules without changing the molecular size of UV-absorbing molecules. These effects of ageing may be seen as improving the capacity of the SD surface layer to retain pollutants during the operation of a VFCW unit, and also the suitability for land applications of sludge deposits dredged from French VFCW.

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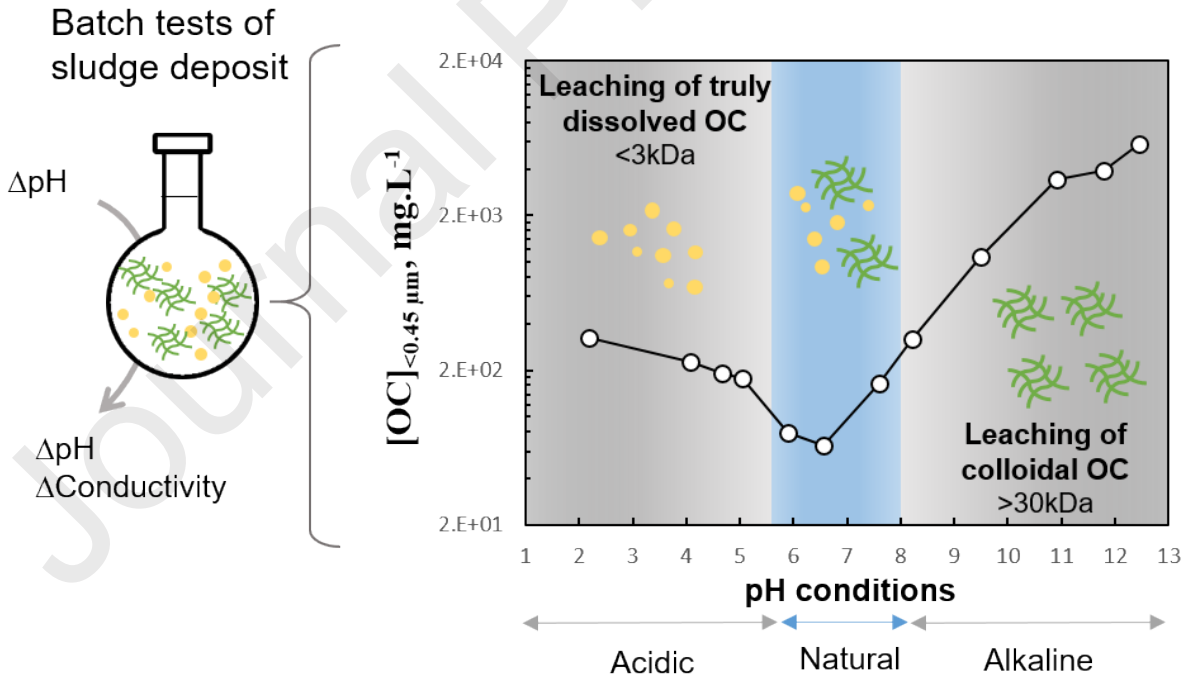

Highlights :

1. Organic matter from VFCW's sludge deposits is less soluble after aging.

2. Truly dissolved organics (< 3kDa) are leached under acidic conditions.
3. Larger colloids (> 3 kDa) are leached under alkaline conditions.
4. Truly dissolved organics leached around neutrality are very aromatic.
5. Leached colloids are all poorly aromatic regardless of pH and molecular size.