



**HAL**  
open science

# Exploration of changes in the chemical composition of sedimentary organic matter and the underlying processes during biodegradation through advanced analytical techniques

Morgane Derrien, Laurent Jeanneau, Emilie Jardé, Jin Hur, Sunghwan Kim

## ► To cite this version:

Morgane Derrien, Laurent Jeanneau, Emilie Jardé, Jin Hur, Sunghwan Kim. Exploration of changes in the chemical composition of sedimentary organic matter and the underlying processes during biodegradation through advanced analytical techniques. *Environmental Chemistry*, 2023, 20 (5), pp.212-225. <10.1071/EN23083>. <hal-04300346>

**HAL Id: hal-04300346**

**<https://hal.science/hal-04300346v1>**

Submitted on 22 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

1           **Exploration of changes in the chemical composition of**  
2           **sedimentary organic matter and the underlying processes during**  
3           **biodegradation through advanced analytical techniques**

4  
5  
6           Morgane Derrien<sup>1,2,\*</sup>, Laurent Jeanneau<sup>3</sup>, Emilie Jardé<sup>3</sup>, Jin Hur<sup>1</sup>, and Sunghwan Kim<sup>4,5</sup>

7           <sup>1</sup>*Department of Environment and Energy, Sejong University, Seoul 05006, South Korea*

8           <sup>2</sup>*Instituto de Ciencias Agroalimentarias, Animales y Ambientales, Universidad de O'Higgins,*  
9           *San Fernando, Chile*

10           <sup>3</sup>*Centre National de la Recherche Scientifique (CNRS), Géosciences Rennes – UMR 6118,*  
11           *Université de Rennes 1, 35042 Rennes, France*

12           <sup>4</sup>*Department of Chemistry, Kyungpook National University, Daegu 41566, South Korea*

13           <sup>5</sup>*Mass Spectrometry Based Convergence Research Center, Daegu 41566, South Korea*

14  
15  
16  
17  
18  
19  
20  
21  
22           \* Corresponding author

23           E-Mail: [morgane.derrien@uoh.cl](mailto:morgane.derrien@uoh.cl)

25 **Abstract**

26 **Rationale.** Although the scientific community widely investigated the organic matter  
27 biodegradation processes, only a limited number of studies have explored the molecular  
28 changes of this material while its structure, composition, and origin play a key in these  
29 processes. **Methodology.** In this context, we decided to examine the effects of the  
30 biodegradation on the chemical composition of sedimentary organic matter and to explore the  
31 underlying mechanisms. We conceived a laboratory-based degradation experiment utilizing  
32 organic-rich sediments artificially composed of two contrasting organic matter end-members  
33 (i.e., soil and algae) under two oxygen conditions. The sediment samples before and after  
34 incubation were then analyzed via laser desorption/ionization Fourier transform ion cyclotron  
35 resonance mass spectrometry for molecular characterization and via thermally assisted  
36 hydrolysis and methylation gas chromatography–mass spectrometry in order to offer insights  
37 into the mechanisms driving biodegradation processes. **Results.** Our results from molecular  
38 characterization unveiled distinct pathways of biodegradation contingent upon the source  
39 material. Moreover, they hinted at a predilection for altering high molecular weight compounds  
40 like lignin/CRAM and CAS compounds, manifesting as a conversion into lower molecular  
41 weight counterparts. Furthermore, the complementary findings from biomarker analyses  
42 underscored the influence of environmental factors - specifically oxygen conditions and  
43 microbial communities - on organic matter decomposition. **Discussion.** Although this study is  
44 a controlled laboratory experiment and more studies are needed, it demonstrated the intricate  
45 interplay among chemical, biological, and environmental factors, profoundly shaping the  
46 reactivity of organic matter. This study underscores the critical need for persistent inquiry,  
47 aimed at unraveling the factors and conditions governing the diverse pathways of  
48 biodegradation.

49 **Keywords:** Sedimentary organic matter; Biodegradation; Molecular characterization; LDI FT–  
50 ICR MS; Biomarkers.

51

## 52 **1. Introduction**

53 Sediments operate as sources and sinks of nutrients and pollutants in aquatic systems.  
54 They also represent a large reservoir of organic matter (OM) from diverse sources (e.g.,  
55 terrestrial, aquatic, estuarine, marine, etc.) and in various proportions according to the  
56 environment, region, and hydrology. Indeed, sedimentary OM is derived from aquatic material  
57 such as algae, bacteria, plankton, macrophytes, and nekton formed in situ, but also receives  
58 terrestrial OM such as soil, vascular plants, leaves, root exudates and anthropogenic OM such  
59 as soil OM, which is easily transported from the upstream catchment into rivers through  
60 hydrological processes, finally ending up in sediments (Briand et al. 2015; Jeanneau et al. 2018;  
61 van der Meij et al. 2018). Sediments are also a reactive compartment where diagenetic  
62 processes occur, inducing physical, chemical, and/or biological changes to the sedimentary OM  
63 (Henrichs 1992; Kuznetsova et al. 2019; Milliken 2003). Among the diagenetic processes,  
64 biodegradation plays a key role in OM biogeochemistry as it is one of the main processes  
65 causing changes in its amount, composition, and properties in aquatic systems (Moran et al.,  
66 2000; Arndt et al., 2013; Sankar et al., 2019; Derrien et al., 2019a).

67 OM biodegradation is based on the common preconception that OM is represented as a  
68 mix of recalcitrant materials usually associated with terrestrial origin and labile materials  
69 associated with aquatic OM (Hansell 2013). OM biodegradation is often oversimplified and/or  
70 restricted to preferential degradation of labile and/or low molecular weight (LMW) organic  
71 compounds leading to the rapid loss of them rather than the recalcitrant material like lignin and  
72 high molecular weight (HMW) organic compounds (Curtis-Jackson et al. 2009; Hach et al.  
73 2020; Hansen et al. 2016; Moran and Zepp 1997; Ward et al. 2019). However, since the early

74 2000s, new paradigms on the stability of terrestrial OM and more specifically on soil OM have  
75 been proposed (Wershaw 2004). They conceptualized soil OM stabilization as the result of a  
76 combination of physical factors controlling its accessibility (Lützow et al. 2006) as well as  
77 chemical factors such as its oxidizing degree controlling the energy available for  
78 microorganisms (LaRowe and Van Cappellen 2011). Even recalcitrance as an intrinsic property  
79 of molecules has been questioned arguing that under favorable environmental conditions, all  
80 organic molecules would be biodegradable (Kleber 2010). These paradigms are in line with  
81 what was observed in several studies where a preferential conversion of high molecular weight  
82 (HMW) compounds into reactive and bioavailable LMW compounds were observed  
83 (Kellerman et al. 2015; Kothawala et al. 2020; Liu et al. 2019). In the literature, biodegradation  
84 processes have also been associated with the production of HMW aromatic material through  
85 alteration and recombination of existing compounds (e.g., large organic biomolecules or  
86 humification processes) (Hach et al. 2020; Kleber and Lehmann 2019; Lee et al. 2016). These  
87 various scenarios of biodegradation processes and our difficulties in finding a consensus on the  
88 biodegradation mechanisms and pathways are related not only to the characteristics of OM  
89 itself such as composition and sources but also to the characteristics and properties of the  
90 ecosystem (i.e., physiochemical conditions and biological communities) (D'Andrilli et al.  
91 2019; Kothawala et al. 2020; McCallister et al. 2018). Furthermore, priming effects represent  
92 a potentially important mechanism underlying the biodegradation of OM in aquatic systems  
93 complexifying our understanding (Bianchi 2011; Bianchi and Ward 2019; Zhuang et al. 2021).  
94 Priming effects refer to quantitative and qualitative changes in the microbial decomposition of  
95 recalcitrant OM upon the addition of labile OM (Guenet et al. 2014, 2010a). They are  
96 delineated as negative, neutral, or positive effects depending on the consequences in the ways  
97 that they may reduce or exert no effect on or stimulate OM biodegradation (B Guenet et al.,  
98 2010; Gontikaki et al., 2013; Ward et al., 2016, 2019; Bengtsson et al., 2018; Derrien et al.,

99 2019c). All these discrepancies in the observed biodegradation mechanisms coupled with the  
100 no consensus on the occurrence and role of priming effects result in a critical need for more  
101 studies focused on the biodegradation processes and mechanisms through approaches  
102 combining analyses providing quantitative and qualitative information (D'Andrilli et al. 2019).  
103 Most of the biodegradation studies in the literature aim at quantifying the OM degradation and  
104 mineralization, and its kinetic through microbial biomass measurement, dissolved organic  
105 carbon or CO<sub>2</sub> concentrations/fluxes (Bowen et al. 2009; Kalbitz et al. 2003; Moran et al. 2000;  
106 Sankar et al. 2019; Vähätalo et al. 2010). Only a few studies target the qualitative aspect of the  
107 biodegradation processes (i.e., exploration of the molecular changes) while the structure and  
108 composition of OM play a key in these processes (Arndt et al. 2013; Herzprung et al. 2017;  
109 Kellerman et al. 2015; Kothawala et al. 2020). Yet, investigating these molecular changes in  
110 similar conditions will not only allow us to lighten our knowledge of biodegradation concepts  
111 but also provide a chemical fingerprint that helps the understanding of OM reactivity and  
112 metabolism. Additionally, the few studies exploring the molecular composition during  
113 biodegradation are limited to the dissolved fraction while two fractions exist (i.e., particulate  
114 and dissolved) and both are intimately linked to each other (Derrien et al. 2019a). Hence, we  
115 decided to tackle this knowledge gap by investigating the compositional changes of  
116 sedimentary OM during biodegradation in this study.

117         Due to the high heterogeneity and complexity of the OM composition related to its  
118 dynamics, involvement in a large number of biogeochemical processes, and the type of  
119 environment, we have decided to head toward a laboratory experiment for this study. Indeed,  
120 controlled laboratory experiments offer the benefits of providing in-depth insight into the  
121 effects of selected parameters have on OM composition, in contrast with field samples that  
122 only represent a snapshot in space and time. The controlled laboratory degradation experiment  
123 was conducted using organic-rich sediments artificially composed of two contrasting OM end-

124 members (i.e., soil and algae) at known mixing ratios and under two oxygen conditions (oxic  
125 and anoxic). The molecular changes induced by biodegradation in sediments and the  
126 mechanisms behind them were investigated through two advanced analytical tools: laser  
127 desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry (LDI FT–  
128 ICR MS) and thermally assisted hydrolysis and methylation gas chromatography-mass  
129 spectrometry (THM–GC–MS). Currently, high-resolution mass spectrometry techniques such  
130 as FT–ICR MS are likely considered as the most powerful tool used to characterize the OM  
131 molecular properties (Kellerman et al. 2015; Valle et al. 2018). The LDI FT–ICR MS technique  
132 was chosen as it represents a direct and highly sensitive analysis at the molecular level to  
133 explore the biodegradation-induced changes in chemical composition in sedimentary OM. The  
134 second technique was selected to explore the biomarker fingerprints to obtain clues to  
135 understand the underlying processes during biodegradation (Meyers and Ishiwatari 1993;  
136 Wakeham and Ertel 1988). Both techniques were also selected as they present the advantage  
137 of being able to directly analyze artificial sediments without any pre-treatment step such as  
138 chemical extraction and thus limiting modifications of the sample (Aubriet and Carré 2019).  
139 The main goal of this study was to provide a detailed exploration of the molecular composition  
140 changes of sedimentary OM induced by biodegradation and evaluate the role of factors such as  
141 type of sources and oxygen on it. The study specifically aimed at answering the following  
142 questions: (i) what molecules or groups of molecules are the most affected by biodegradation  
143 processes, (ii) what is the potential effect of OM source or oxygen conditions (i.e., oxic versus  
144 anoxic) on biodegradation processes? and (iii) what are the underlying processes behind  
145 biodegradation?

146

## 147 **2. Material and methods**

### 148 *2.1. Experimental design of the incubation experiment*

149 Two contrasted end-members (i.e., soil and algae) were mixed at soil-to-algae ratios  
150 (S:A) of 100:0, 75:25, 50:50, 25:75, and 0:100, based on the organic carbon (OC)  
151 concentrations (Derrien et al. 2019b). In natural aquatic systems, ratios between both OM  
152 sources greatly vary according to the season and the hydrology. Therefore, we decided to  
153 perform the study at several ratios. The soil end-member (topsoil, 0-10cm) was collected at  
154 Bukhansan National Park, South Korea (37°43'37.0" N 127°00'50.9"), a fully forested area  
155 composed of broadleaved trees such as *Quercus mongolica*, *Q. serrata*, the coniferous tree,  
156 *Pinus densiflora*, and the *Robinia pseudoacacia* plantation (Choi and Yang 2012). A  
157 commercial unicellular green alga (*Chlorella vulgaris*), which is commonly found in  
158 freshwaters and marine environments, was purchased from Aquanet Co., Ltd. in  
159 Gyeongsangnam-do, South Korea, and used as the algae end-member. Further details regarding  
160 the end-members and the experiment can be found in Derrien et al. 2019c. Briefly, incubation  
161 experiments in oxic and anoxic conditions were performed in pre-washed and pre-combusted  
162 (450 °C for 4 hours) 125 ml Wheaton® amber glass bottles with Teflon screwcaps. Samples  
163 for anoxic incubation were prepared and sampled using a sterile Aldrich® AtmosBag two-hand  
164 glove bag under nitrogen atmosphere. A mass (12 g) of end-member mixed samples were  
165 mixed with ultrapure water (Barnstead™ Easypure™ RoDi, Thermo Scientific) at a solid-to-  
166 solution ratio of 1:4 and equilibrated for 48 h in the dark at room temperature after shaking at  
167 100 rpm for one hour. River water from the Jungnang River, a tributary of Seoul's Han River  
168 (37°40'16"N, 127°04' 47"E), was used as inoculum for microbial incubation. Before  
169 incubation, all artificial sediment samples were spiked with 3% (v/v) of the prepared inoculum,  
170 and a sufficient amount (1%, v/v) of nutrients (NH<sub>4</sub>NO<sub>3</sub> and K<sub>2</sub>HPO<sub>4</sub> at 10 mM) was added to  
171 each sample to avoid nutrient limitations during the incubation. The low inoculum-to-sample  
172 ratio had a negligible effect on the final OC concentrations of the end member mixtures (<1%)  
173 and on the molecular signature. Therefore, we concluded that the concentration and signature

174 of the inoculum could be safely ignored. Finally, the samples in oxic and anoxic conditions  
175 were incubated in the dark at 25 °C for 60 days (Guenet et al. 2014; Navel et al. 2012). Samples  
176 were collected for sampling on day 0 and day 60, with “day 0” corresponding to the day when  
177 the samples were inoculated. Degradation experiments were carried out in duplicate.

178         The sampling was performed as follows. First, samples were taken from the incubator,  
179 and the overlying water was carefully removed so as not to disturb the sediment. The artificial  
180 sediment samples were then centrifuged at 5000 rpm for 20 min to remove the porewater.  
181 Finally, the porewater-free sediment samples were freeze-dried, ground, and homogenized for  
182 further analyses. All the analyses were performed on both replicates except for the LDI FT-  
183 ICR MS where both replicates were carefully mixed in order to obtain a representative sample  
184 for the different modalities. Total organic carbon (TOC) contents of sediments were measured  
185 using an elemental analyzer coupled with an isotope ratio mass spectrometer (EA-IRMS;  
186 EuroEA-Isoprime IRMS, GV instruments, UK) for all samples in order to estimate the  
187 percentage of removal or production of OC after the 60 days of incubation (Supplementary  
188 Material, Table A.1).

## 189 *2.2. Laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry* 190 *(LDI FT-ICR MS)*

191         Molecular analyses were performed with a (-) LDI solariX 2XR FT ICR mass  
192 spectrometer (Bruker Daltonic, Bremen, Germany) in Mass Spectrometry Based Convergence  
193 Research Center at Kyungpook National University. The instrument was equipped with a 7 T  
194 refrigerated actively shielded superconducted magnet and a dual-mode ESI/matrix-assisted  
195 laser desorption/ionization ion source with a frequency-tripled Nd:YAG (neodymium-doped  
196 yttrium aluminum garnet) laser emitting at 355 nm. Briefly, between 2 and 5 µg of freeze-dried  
197 artificial sediment samples were directly loaded onto preplaced double-sided tape on a MALDI  
198 (matrix-assisted laser desorption/ionization) plate. Before analysis, the plate was dried under

199 vacuum for 2 hours. The broadband spectra were acquired between  $m/z$  100 and 1000, with a  
200 4MW free induction decays ( $2 \Omega$ ), and 300 spectra were averaged to improve the signal-to-  
201 noise ratio. For data processing, only peaks with an S/N ratio of  $\geq 4$  were considered. A detailed  
202 description of the analytical method is given in Solihat et al. (2019).

203 Molecular formulae were assigned to peaks in the mass range of  $m/z$  200-600 with a  
204 mass error range of  $\pm 1$  ppm. Molecular formulae were identified considering the following  
205 elemental combinations:  $^{12}\text{C}_{0-\infty}^{1}\text{H}_{0-\infty}^{16}\text{O}_{0-\infty}^{14}\text{N}_{0-5}^{32}\text{S}_{0-2}$ . Only the formulae presented the  
206 following elemental ratio criteria,  $0.3 \leq \text{H/C} \leq 2.25$ ,  $\text{O/C} < 1.2$ ,  $\text{N/C} < 0.5$ , and  $\text{S/C} < 0.2$ , and  
207 the double bond equivalent rule (i.e.,  $\text{DBE} = 1/2(2\text{C}-\text{H}+\text{N}) \geq 0$ ) was considered (Koch et al.  
208 2007). Several selected indices, including intensity-weighted average (wa) molecular masses,  
209 elemental ratios, DBE,  $\text{AI}_{\text{mod}}$  (modified aromatic index), and  $\text{MLB}_L$  (molecular lability  
210 boundary for labile contributions) were also calculated (D'Andrilli et al. 2015; Koch and  
211 Dittmar 2006). Finally, the assigned molecular formulae were examined using the van  
212 Krevelen diagram and were categorized into eight different compound classes (Supplementary  
213 Material, Table A.2) (Derrien et al. 2017; Kim et al. 2003).

### 214 2.3. Thermally assisted hydrolysis and methylation (THM) gas chromatography-mass 215 spectrometry (THM-GC-MS)

216 THM-GC-MS analyses were performed according to Jeanneau et al. (2014). Briefly,  
217 we introduced between 0.3 mg (algae) and 5 mg (soil) of freeze-dried solid residue into an 80  
218  $\mu\text{L}$  aluminum reactor with an excess of solid tetramethylammonium hydroxide (ca. 10 mg).  
219 The THM reaction was performed on-line using a vertical micro-furnace pyrolyzer PZ-2020D  
220 (Frontier Laboratories, Japan) operating at  $400^\circ\text{C}$ . The products of this reaction were injected  
221 into a gas chromatograph GC-2010 (Shimadzu, Japan) equipped with a SLB 5MS capillary  
222 column in the split mode ( $60 \text{ m} \times 0.25 \text{ mm ID}$ ,  $0.25 \mu\text{m}$  film thickness). The temperature of  
223 the transfer line was  $321^\circ\text{C}$ , and the temperature of the injection port was  $310^\circ\text{C}$ . The oven

224 was programmed to maintain an initial temperature of 50 °C for 2 minutes, then rise to 150 °C  
225 at 15 °C min<sup>-1</sup>, and then rise to 310 °C at 3 °C min<sup>-1</sup> where it stayed for 14 minutes. Helium  
226 was used as the carrier gas at a flow rate of 1.0 ml/min. Compounds were detected using a  
227 QP2010+ mass spectrometer (Shimadzu, Japan) operating in full scan mode. The temperature  
228 of the transfer line was set at 280 °C, the ionization source at 200 °C, and molecules were  
229 ionized by electron impact using an energy of 70 eV. The list of analyzed compounds and *m/z*  
230 ratios used for their integration are given in the Supplementary Material (Table A.2).  
231 Compounds were identified based on their full-scan mass spectra by comparison with the NIST  
232 library and with published data (Nierop and Verstraten 2004; Nierop et al. 2005).

233 The target compounds (i.e., 136 biomarkers) were classified into eight chemical  
234 families: small organic acids (SOAc), phenolic compounds (PHE) including lignin and tannin  
235 markers, carbohydrates (Car), low molecular weight fatty acids (LMWFA), high molecular  
236 weight fatty acids (HMWFA), fatty alcohols (F Alcohol), chlorophyll markers (Phytol)  
237 including phytol and neophytadiene, and N-containing compounds (Ncompound). The peak  
238 area of the selected *m/z* (mass/charge) for each compound was integrated and corrected by a  
239 mass spectra factor calculated as the reciprocal of the proportion of the fragment used for the  
240 integration and the entire fragmentogram provided by the NIST library (Supplementary  
241 Material, Table A.3) (Denis et al. 2017; Jeanneau et al. 2018). The proportion of each  
242 compound class was calculated by dividing the sum of the areas of the compounds in this class  
243 by the sum of the peak areas of all analyzed compounds expressed as a percentage.

#### 244 *2.4. Statistical analyses*

245 All the statistical analyses were performed with R (version 3.4.3) using the packages  
246 Vegan (Vegan 2.4-1) and FactoMineR.

##### 247 *2.4.1. LDI FT-ICR MS data*

248 The Bray-Curtis dissimilarity matrix was computed for the whole set of the LDI FT-  
249 ICR MS data (Supplementary Material, Table A.4 and A.5) to quantify the intra- and inter-  
250 variability of the samples (Bray and Curtis 1957). Principal coordinates analysis (PCoA) was  
251 then performed based on this dissimilarity matrix.

#### 252 2.4.2. THM-GC-MS data

253 A first principal component analysis (PCA) was performed using the relative  
254 proportions of the 136 biomarkers as variables, which allows the direct comparison of the  
255 different samples without the concentration effect (Supplementary Material, Table A.6 and  
256 A.7). This PCA allows identification of the correlated variables based on a modulus of the  
257 Pearson coefficient  $> 0.8$ . When the two variables were correlated, the least abundant was  
258 removed. Then a second PCA was performed. The variables with a correlation lower than 0.5  
259 with the two first factors were removed, resulting in a new set of 67 variables. A third PCA  
260 and the associated hierarchical ascendant classification (HAC) were calculated. A last PCA  
261 and HAC were performed using specific microbial biomarkers (i.e., microbial FA:  $nC_{12:0}$ ,  
262  $nC_{13:0}$ ,  $nC_{14:0}$ ,  $aC_{15:0}$ ,  $nC_{15:0}$ ,  $brC_{16:0}$ ,  $nC_{16:1}$ ,  $nC_{17:0}$ ,  $nC_{18:1}$  (2 isomers), and  $nC_{19:1}$ ) in order to  
263 explore the role of the microbial activity during biodegradation.  $nC_{16:0}$  and  $nC_{18:0}$  were not  
264 considered since these biomarkers are produced by the THM of algae and derive from higher  
265 plant inputs, respectively.

266

267 **3. Results and discussion**

268 All the detailed results of LDI FT-ICR MS and THM-GC-MS are presented in Supplementary  
269 Material (Tables A.4-7),

270 *3.1. Identification of the biodegradation-induced changes in the pure end-member artificial*  
271 *sediments*

272 At day 0, no differences were observed based on the H/C and O/C ratios, but a clear  
273 distinction was observed for the distribution between the CHO, CHON, CHOS, and CHONS  
274 elemental formulae, common indices, and compound classes between both pure artificial  
275 sediments (S:A, 100:0 and S:A, 0:100) (Table A4-5). S:A, 100:0 mainly contained carbon-rich  
276 and heavily carboxylated compounds with a part of them rich in nitrogen (e.g., CHO of 55.2%  
277 and 39.3% and CHON of 33.6% and 38.4% in oxic and anoxic conditions respectively). By  
278 contrast, S:A, 0:100 exclusively consisted of CHO compounds (e.g., 98.9% and 96.5% in oxic  
279 and anoxic conditions respectively). Higher values of DBE and  $AI_{mod}$  and a much lower value  
280 for the  $MLB_L$  for S:A, 0:100 than for S:A, 100:0 indicated the presence of highly aromatic and  
281 unsaturated compounds in the composition of the algae and the near absence of labile  
282 compounds. This was supported by the identification and distribution of the compounds classes  
283 as the S:A, 0:100 mainly consisted of unsaturated hydrocarbons (e.g., 36.3% and 37.5% for  
284 oxic and anoxic conditions, respectively), lignins/CRAM (e.g., 30.7% and 30.4% for oxic and  
285 anoxic conditions, respectively) and condensed aromatic structures (CAS, e.g., 30.1% and  
286 27.2% for oxic and anoxic conditions, respectively) (Fig. 1). Algae material is commonly  
287 associated with labile material, however, it was also demonstrated that this kind of material can  
288 be characterized by a high amount of hydrocarbons (Youngblood et al. 1971), lignins (Alzate-  
289 Gaviria et al. 2020; Martone et al. 2009) and by biopolymers such as the algaenans, which  
290 represent the major constituent of the cell walls of green algae, for instance (Derenne et al.  
291 1992; Gelin et al. 1996). S:A, 100:0 also presented a distribution in compounds class rich in

292 CAS (e.g., 51.2% and 37.2% for oxic and anoxic conditions, respectively) and lignins/CRAM  
293 (e.g., 31.1% and 38.2% for oxic and anoxic conditions, respectively). However, the rest of the  
294 distribution consisted of lipids (e.g., 7.1% and 7.3% for oxic and anoxic conditions,  
295 respectively), unsaturated hydrocarbons and/or tannins (e.g., ~5%), and a small amount of  
296 labile material such as proteins (e.g., ~3%) and carbohydrates and amino sugars (e.g., ~2%)  
297 (Fig. 1).

298         After 60 days of incubation, the main observed differences were related to the  
299 distribution in compound classes. A decrease of the highest molecular weight compounds (i.e.,  
300 CAS and Lignins/CRAM) in S:A, 0:100 was observed in favor of an increase of the percentage  
301 of unsaturated hydrocarbons of 10.8 and 21.7 points with values reaching 47.1% and 59.2%  
302 for oxic and anoxic conditions, respectively (Fig. 1). A slight increase in labile compounds was  
303 also observed. Regarding the S:A, 100:0, the few changes were mainly observed in oxic  
304 conditions, with a decrease in the observed percentage of the CAS (e.g., from 51.2% to 38.9%  
305 at day 0 and day 60, respectively). In parallel, a slight increase in the percentage of the  
306 lignins/CRAM and labile compounds was also noted for both oxygen conditions. Classically,  
307 biodegradation is associated with a rapid loss of low molecular weight (LMW) compounds  
308 (Hansen et al. 2016; Wetzel 2001). However, in the present study, the results suggest  
309 preferential biodegradation of the high molecular weight (HMW) compounds associated with  
310 conversion into lower molecular weight compounds (Curtis-Jackson et al. 2009; Hach et al.  
311 2020; Liu et al. 2019; Moran and Zepp 1997). These observations agree with the paradigm in  
312 which all organic molecules could be biodegradable irrespective of their recalcitrance if  
313 favorable physical, chemical, and biological factors are present (Kleber 2010). This  
314 observation can be also the result of two-step processes. As it was previously observed in the  
315 literature, LMW compounds could have been consumed primarily generating a rapid loss of  
316 labile and LMW materials followed by the consumption of HMW compounds (e.g., CAS and

317 lignins/CRAM) and their transformations in LMW compounds (D'Andrilli et al. 2019; Hansen  
318 et al. 2016). Unfortunately, the sampling design does not allow us to identify which processes  
319 (one or two steps processes) occurred.

320 Regarding the biomarker distributions, two distinctive fingerprints were identified between the  
321 2 pure end-member artificial sediments but closely the same irrespective of the oxygen  
322 condition (Fig. 2). In S:A, 100:0, the most abundant chemical family was HMWFA with  
323 aliphatic side chain containing 20 and more C atoms ( $60.6 \pm 3.3\%$  and  $60.0 \pm 7.4\%$  for oxic  
324 and anoxic conditions, respectively). These HMWFA included linear n-alkanoic acids from n-  
325 C<sub>20:0</sub> to n-C<sub>30:0</sub> with an even-over-odd predominance characteristic of plant-derived inputs  
326 (Eglinton and Hamilton 1967), linear  $\omega$ -hydroxyacids and  $\alpha,\omega$ -diacids from n-C<sub>16</sub> to n-C<sub>26</sub>,  
327 10,16-dihydroxyC<sub>16:0</sub> and 9,10,18-trihydroxy C<sub>18:0</sub> characteristic of plant-derived aliphatic  
328 biopolymers cutin and suberin (Armas-Herrera et al. 2016; Kolattukudy 2001). The main  
329 molecules were 9,10,18-trihydroxyC<sub>18:0</sub> ( $21.4 \pm 0.9\%$  and  $14.5 \pm 7.6\%$  for oxic and anoxic  
330 conditions, respectively) and  $\omega$ OH-C22 ( $7.9 \pm 0.7\%$  and  $10.7 \pm 0.7\%$  for oxic and anoxic  
331 conditions, respectively), which indicated a higher proportion of suberin from roots than cutin  
332 from leaves (Mueller et al. 2012) (Table A6-7). The second most abundant chemical family  
333 was PHE produced by the THM of lignins and tannins ( $11.5 \pm 0.0\%$  and  $11.7 \pm 3.2\%$  for oxic  
334 and anoxic conditions, respectively). This chemical family was dominated by 3,4-  
335 dimethoxybenzoic acid methyl ester and 3,4,5-trimethoxybenzoic acid methyl ester, which are  
336 typical of the THM of woody plants (Challinor 1995) and applied to investigate the transfer  
337 and reactivity of OM (Denis et al. 2017; Williams et al. 2016). The third chemical family was  
338 LMWFA with  $8.9 \pm 0.4\%$  and  $11.4 \pm 3.1\%$  for oxic and anoxic conditions, respectively. This  
339 chemical family includes n-alkanoic acids from n-C<sub>8:0</sub> to n-C<sub>19:1</sub>, iso and anteiso C<sub>15:0</sub> and C<sub>17:0</sub>,  
340 iso C<sub>14:0</sub> and C<sub>16:0</sub> and n-alkenoic acids n-C<sub>16:1</sub>, n-C<sub>18:1</sub> and n-C<sub>19:1</sub>. The LMWFA with less than  
341 13 C atoms can be derived from microbial or plant-derived inputs, while the LMWFA with

342 more than 13 C atoms are known as phospholipid fatty acids and are microbial biomarkers  
343 (Frostegård et al. 1993) except for *n*-C<sub>16:0</sub> and *n*-C<sub>18:0</sub>, which can derive from plant-derived  
344 inputs. In S:A, 0:100, the most abundant chemical family was LMWFA with  $67.8 \pm 3.1\%$  and  
345  $61.3 \pm 3.8\%$  for oxic and anoxic conditions, respectively. The distribution of the compounds  
346 was different from that analyzed in S:A, 100:0, with a large predominance of *n*-C<sub>16:0</sub> ( $19.3 \pm$   
347  $0.2\%$  and  $22.3 \pm 0.3\%$  for oxic and anoxic conditions, respectively) and a large proportion of  
348 *n*-C<sub>16:2</sub> ( $12.1 \pm 2.3\%$  and  $9.5 \pm 0.7\%$  for oxic and anoxic conditions, respectively) and *n*-C<sub>18:2</sub>  
349 ( $32.9 \pm 2.3\%$  and  $25.7 \pm 2.8\%$  for oxic and anoxic conditions, respectively). The second most  
350 abundant chemical family was the chlorophyll biomarkers with two compounds: phytol and  
351 neophytadiene. They represented  $18.3 \pm 3.2\%$  and  $21.5 \pm 7.8\%$  of oxic and anoxic conditions,  
352 respectively. Finally, the third chemical family was composed of N-containing compounds,  
353 which represented  $10.6 \pm 0.1\%$  and  $13.6 \pm 3.2\%$  (i.e., for oxic and anoxic conditions,  
354 respectively). Among this family, 1,3-dimethyluracil was the dominant compound ( $4.3 \pm 0.6\%$   
355 and  $7.3 \pm 1.1\%$  for oxic and anoxic conditions, respectively).

356 After 60 days of incubation, the characteristic chemical fingerprints of each pure end-  
357 member artificial sediments remained the same, and no significant differences were observed  
358 (Fig. 2).

### 359 3.2. Identification of the biodegradation-induced changes in mixed samples

360 The mixed artificial sediments (e.g., S:A, 75:25; S:A, 50:50 and S:A, 25:75) did not  
361 show notable differences in their molecular profile at day 0 (Table A.4- 5). A slight increase  
362 for the  $H/C_{wa}$  was observed compared to the end members with values of  $\sim 1.1$  instead of 0.8  
363 or 0.9, suggesting a lower unsaturation for these samples that was confirmed by the values of  
364 DBE, which are much lower than for both pure end-member artificial sediments (e.g., values  
365 ranged from 10.8 to 12.6 irrespective of the oxygen conditions). Likewise, the values of  $AI_{mod}$   
366 0.5 and inferior to both pure end-member artificial sediments demonstrated the occurrence also

367 of less aromatic compounds. The elemental formula distributions of CHO and CHON are also  
368 quite close to each other, whatever the proportions of algae; even so, a slightly higher  
369 proportion of CHON formula compounds is observed in anoxic conditions for the S:A, 25/75  
370 mixed sediment which reaches 49.2% for instance. The percentages of formulae with sulfur  
371 (i.e., CHOS and CHONS) were higher than for either end members with values ranging from  
372 ~10% to ~17% for CHOS and ~7% to 14.3% for CHONS. Regarding the distribution in  
373 compound classes, similarities in values were also observed (Fig. 1). The two main groups of  
374 compound classes were lignins/CRAM and CAS with percentages ranging from 38.6% to  
375 44.2% and 22.2% to 30.2% respectively, followed by lipids and unsaturated hydrocarbons with  
376 percentages ranged between 9% and 17.9%. Proteins and carbohydrates and aminosugars  
377 occurred at less than 5%, respectively. This distribution was also reflected in the  $MLB_L$  index  
378 (percentage of labile material), which reaches values 1.5- to 7-fold those observed for the soil  
379 or pure algae artificial sediment, respectively (Table A.4 and A.5).

380 After 60 days of incubation, each mixed artificial sediment displayed a unique  
381 molecular profile compared to the initial according to its ratio of end-members and/or its  
382 oxygen condition. S:A, 50:50, irrespective of the oxygen conditions, strictly showed the same  
383 distribution in compounds class, suggesting a homogeneous effect of the biodegradation on the  
384 whole pool of OM an. A similar observation was made for S:A, 75:25 in oxic conditions. By  
385 contrast, molecular changes were observed in S:A, 25:75 for both oxygen conditions and  
386 specifically for S:A, 75:25 in anoxic conditions (Fig. 1). In S:A, 75:25, a decrease of the CAS  
387 and lignin/CRAM was noted in favor of the unsaturated hydrocarbons becoming, thus, the main  
388 compound class (i.e., 33.7%). For S:A, 25:75, similar changes were also observed, however,  
389 the lignin/CRAM compound class remained the main one (i.e., values of 39% and 33% for oxic  
390 and anoxic conditions, respectively). Similar changes to the changes observed for the end-  
391 member in higher proportion would have been expected, however, results displayed different

392 trends as 3 different scenarios of biodegradation according to the mixing ratios were observed  
393 (e.g., no changes or homogeneous changes for all types of compounds, consumption of LMW  
394 compounds associated to production of LMW compounds and preferential degradation of one  
395 type of HMW compounds). These differences and similarities in the compound distribution for  
396 the mixed samples suggest the occurrence of underlying mechanisms.

397 At day 0, the biomarker distribution of biomarkers into chemical families illustrated a  
398 gradual modification of the biomarker distribution induced by the mixing of end-members (Fig.  
399 2). This gradual modification was characterized by the progressive increase in the proportion  
400 of LMWFA from  $24.0 \pm 5.2\%$  (S:A,75:25;  $26.3 \pm 6.0\%$  and  $21.6 \pm 4.7\%$  in oxic and anoxic  
401 conditions, respectively) to  $55.4 \pm 3.8\%$  (S:A, 25:75;  $57.8 \pm 4.6\%$  and  $53.0 \pm 0.2\%$  in oxic and  
402 anoxic conditions, respectively). An increase in the proportion of chlorophyll biomarkers was  
403 also observed with the increase of algae proportions with values from  $3.0 \pm 1.3\%$  (S:A, 75:25,  
404  $3.8 \pm 1.4\%$  and  $2.2 \pm 0.9\%$  in oxic and anoxic conditions, respectively) to  $11.0 \pm 3.5\%$  (S:A,  
405 25:75,  $11.0 \pm 1.4\%$  and  $11.0 \pm 5.8\%$  in oxic and anoxic conditions, respectively). At the same  
406 time, the proportion of HMWFA decreased from  $45.0 \pm 6.4\%$  (S:A, 75:25;  $41.6 \pm 7.5\%$  and  
407  $48.3 \pm 4.6\%$  in oxic and anoxic conditions, respectively) to  $19.6 \pm 3.9\%$  (S:A, 25:75;  $18.5 \pm$   
408  $4.1\%$  and  $20.6 \pm 4.8\%$  in oxic and anoxic conditions, respectively). The PHE proportion also  
409 decreased regularly from  $9.5 \pm 1.1\%$  (S:A, 75:25;  $8.8 \pm 0.2\%$  and  $10.2 \pm 1.0\%$  in oxic and  
410 anoxic conditions, respectively) to  $2.3 \pm 0.4\%$  (S:A, 75:25;  $2.0 \pm 0.2\%$  and  $2.6 \pm 0.3\%$  in oxic  
411 and anoxic conditions, respectively).

412 At day 60, various changes were observed in the distribution of biomarkers. The most  
413 significant changes were observed for S:A, 75,25, and S:A, 50:50, and specifically in anoxic  
414 conditions, where a significant (p-value < 0.05) diminution was observed for almost all the  
415 types of chemical families. By contrast, an increase in the proportion of LMWFA was observed  
416 for all mixing ratios and oxygen conditions, but this increase was significant only for S:A,

417 75:25 and S:A, 50:50 in anoxic conditions. Regarding S:A, 25:75 only the diminution of SOAc  
418 and Ncompound were significant.

### 419 3.3. Factors controlling the biodegradation

#### 420 3.3.1. Source mixing factor

421 In order to understand the role and the weight of the factor “source”, a PCoA was  
422 performed based on the Bray-Curtis dissimilarity matrix computed all the FT-ICR MS  
423 parameters (Fig. 3). Unfortunately, the ordination did not show any clear distinction either  
424 according to the sources or mixing of sources and/or the incubation time. Although FT-ICR  
425 MS analysis has emerged as a reliable tool for the in-depth molecular characterization of  
426 complex mixtures as OM with the capacity of identifying thousands of molecules per sample  
427 and assigning associated elemental formulae with a high level of confidence (Repeta 2015;  
428 Stubbins and Dittmar 2014), this technique can also present some inherent limitations. The  
429 main limitations of the FT-ICR MS tool relate to the inconsistent ionization efficiency for  
430 different sample matrices, potentially leading to a bias of detection toward certain groups of  
431 compounds or even to un-characterization of material (Blackburn et al. 2017; D’Andrilli et al.  
432 2020; Dittmar et al. 2008; Hawkes et al. 2019; Mopper et al. 2007; Patriarca et al. 2020). In the  
433 present study, it is noticed the number of assigned formulae decreased gradually with the  
434 increase of the algae end-member, which could be assimilated to lower efficiency of the  
435 ionization for this kind of matrix (Table A.4 and A.5) (Blackburn et al. 2017; Kew et al. 2018).  
436 A lower ionization efficiency and preferential ionization for some group of compounds might  
437 constrain the data interpretation and make it harder for disentangling the complexity of the OM  
438 molecular composition (Derrien et al. 2019a; Hawkes et al. 2018). This could be one of the  
439 reasons for the failure of the ordination to identify sub-groups according to the sources, oxygen  
440 conditions, and/or time of incubations. Another reason could be related to the non-  
441 discriminatory character of the data. FT-ICR MS is a technique able to identify with high

442 accuracy hundreds to several thousands of ions with an  $m/z$  range typically from 200 to 1000  
443 Da. However, this level of sensitivity is not that discriminant for observing an ordination  
444 between our set of samples.

445 By contrast, we clearly identified an effect of the factor “source” through the use of the  
446 biomarkers. The PCA based on the distribution of the 67 variables displayed a clear separation  
447 on axis-PC1 according to the proportion of algae (Fig. 4). The HAC performed on the results  
448 of this latter PCA identified 4 groups. The 2 pure artificial sediments at day 0 and day 60 were  
449 grouped with their respective endmember sample in two different groups (Groups 1 and 3).  
450 The biomarker fingerprint modifications induced by the mixing of end-members were fairly  
451 well illustrated by the projection of the samples at day 0 on PC1, representing 62.7% of the  
452 variance of the dataset. They corresponded almost exactly to the theoretical points calculated  
453 via the end-member mixing approach (Fig. 4). The HAC grouped S:A, 75:25 at day 0 samples  
454 with the S:A, 100:0 (Group 3) and the rest of the mixed samples (S:A, 50:50 and 25:75) from  
455 day 0 as a distinct group (Group 2). The last group identified by the HAC consisted of all three  
456 S:A mixed samples from day 60 (Group 4). This group was characterized by proportions of  $n$ -  
457  $C_{14:0}$ ,  $n$ - $C_{15:0}$ ,  $n$ - $C_{16:0}$ ,  $aC_{15:0}$ , and  $n$ - $C_{18:0}$  FA higher than the mean of the samples and by  
458 proportions of N-containing compounds, succinic and fumaric acids,  $n$ - $C_{18:1}$ ,  $n$ - $C_{18:2}$ ,  $n$ - $C_{16:2}$   
459 FA, and  $\alpha,\omega$ -diacid  $n$ - $C_{9:0}$  lower than the mean of the samples. 60 days’ incubation resulted in  
460 a specific decrease in the proportion of compounds that were specific to algae namely N-  
461 containing compounds and di-unsaturated FA. However, this decrease was not associated with  
462 an increase in soil-specific markers such as HMWFA or PHE whose proportions tend to  
463 decrease or to remain stable during the incubation (Fig. 2). This decrease was significant  
464 (Wilcoxon test) only for PHE for S:A, 75:25, and 50:50. In the same time, the proportion of  
465 microbial FA increased, which could be interpreted as stimulation of microbial biomass and  
466 therefore the occurrence of positive priming effects (Guenet et al. 2014).

### 467 3.3.2. Oxygen factor

468 Oxygen is one of the most important reactants in biogeochemical cycles as it impacts  
469 the redox potential of the environment as well as the energetic situation of the microorganisms  
470 (Brune et al. 2000). Therefore, its occurrence or absence may affect the biodegradation  
471 processes and pathways. In the molecular profiles obtained by LDI FT-ICR MS, the main  
472 differences were observed in S:A, 25:75, S:A, 75:25, and S:A, 0:100. The absence of oxygen  
473 led to a higher production of unsaturated hydrocarbons of 1.5 to ~3 times higher at day 60 than  
474 at day 0 with values from 12.0% to 33.7% and from 17.9% to 28.3% for the S:A, 25:75 and  
475 S:A, 75:25 samples, respectively (Fig. 1 and Table A.5). In parallel, for the same samples, a  
476 higher distribution was noticed in labile compounds after biodegradation than in oxic  
477 conditions. These observations suggest a preferential biodegradation through the conversion of  
478 HMW molecules into smaller compounds. By contrast, no differences were observed for the  
479 distribution in biomarkers (Fig. 2). This was also confirmed with the PCA as the oxic and  
480 anoxic samples are gathered together with no exceptions (Fig. 4). From our results, it seems  
481 difficult to state on the effect of the oxygen condition on the observed biodegradation pathways.

### 482 3.4. Behind the chemical mechanisms of biodegradation

483 In order to further investigate the potential stimulation of the microbial biomass and  
484 determine if there was a modification of the composition of the microbial community, the  
485 distribution of microbial FA (e.g., FA with a low molecular weight ( $< C_{19:0}$ ) except for  $C_{16:0}$   
486 and  $C_{18:0}$ ) was investigated using a PCA and a HAC, resulting in four groups depicted by grey  
487 areas in Fig. 5. At day 0, the distribution of microbial FA in soil was modified by the addition  
488 of algae. The evolution of this distribution was almost regular along the segment formed by the  
489 end members. For algae, samples from days 0 and 60 remained in the same group (Group 1),  
490 which highlighted that the distribution of FA remained almost stable during the incubation. On  
491 the contrary for the soil, samples from day 60 were plotted in a distinct group (Group 3). This

492 indicates a modification of the distribution of microbial FA during the experiment, which could  
493 be interpreted as a modification of the composition of the microbial community (Frostegård et  
494 al. 1993). The S:A mixed samples at day 60 were also classified as a specific group (Group 4).  
495 The direction of the modifications of the distribution of microbial FA was almost orthogonal  
496 (i) to the segment formed by the end members and (ii) to the direction of the modifications in  
497 the soil during the experiment. Consequently, these changes in the distribution of FA were not  
498 only the result of the mixture but were also due to the adaptation of the composition of  
499 microbial communities to the mixture of soil and algae.

500 A second point is that the Euclidean distance between day 0 and 60 for the different  
501 S:A ratios seems to increase with the proportion of algae from  $2.9 \pm 0.9$  (S:A, 75:25) to  $3.9 \pm$   
502  $0.3$  (S:A, 50:50) and  $4.7 \pm 0.3$  (S:A, 25:75). The number of experimental replicates was not  
503 sufficient to test the significance of this increase. However, it could suggest that the magnitude  
504 of the modification of the composition of microbial communities increased with the proportion  
505 of algae added to the soil. Moreover, S:A mixed samples at day 60 were grouped without clear  
506 differentiations of mixture ratios, which could indicate that the modification of the microbial  
507 communities was independent of the S:A ratio. Finally, this group of S:A mixed samples from  
508 day 60 were characterized by proportions of *n*-C<sub>12:0</sub> and *n*-C<sub>14:0</sub> higher than the average and  
509 proportion of *n*-C<sub>18:1</sub> (isomer 1), *n*-C<sub>17:0</sub> and *n*-C<sub>19:1</sub> lower than the average. Moreover, *n*-C<sub>18:1</sub>  
510 (isomer 1) correlated with *i*C<sub>17:0</sub>. The differences between the average proportion in group 4  
511 and the average proportion in the entire dataset were significant for *i*C<sub>17:0</sub> (*p*-value < 0.001).  
512 This group may then be associated with a decrease in the proportion of terminally branched FA  
513 (*i*C<sub>17:0</sub>) that has been proposed as a marker of Gram-positive bacteria (Willers et al. 2015).  
514 These results could signify that this microbial group was disadvantaged by the mixing of soil  
515 with algae.

516

#### 517 **4. Conclusion**

518           This study aimed at gaining insights into the biodegradation pathways and molecular  
519 modifications of sedimentary organic matter, as well as to fathom the underlying mechanisms  
520 via a laboratory experiment. The FT-ICR MS analysis allowed us to identify the group of  
521 compounds preferentially degraded during early microbial diagenesis. In both pure end-  
522 members, CAS and lignins/CRAM were identified as the molecules the most affected by  
523 biodegradation. For the mixed artificial sediments (i.e., S:A, 75:25, S:A, 50:50, and S:A,  
524 25:75), distinct biodegradation alterations emerged for each ratio, underscoring the potent  
525 influence of the "source" factor. The divergent shifts in compositional changes for different  
526 mixing ratios post-incubation also hint at the potential involvement of underlying mechanisms,  
527 such as priming effects. Notably, with the present study design, no discernible correlation was  
528 established between the proportions of labile material and the intensity of priming effects.  
529 Furthermore, the combination of the biomarker and molecular analyses allowed us to suggest  
530 the capability of the microbial communities to adapt or shift in response to the varying types  
531 and proportions of organic matter sources, facilitating the biodegradation of diverse materials.  
532 However, additional studies and complementary qualitative analyses are imperative to test this  
533 hypothesis conclusively. Nevertheless, this latter observation underscores the compelling need  
534 to delve into and elucidate the intricate interplay between microbial communities and organic  
535 matter. Addressing this challenge necessitates a holistic analytical approach, one that combines  
536 organic geochemistry and meta-omic methods. This holistic approach, as underlined by  
537 Bianchi and Ward (2019), would enable the identification of both the composition and function  
538 of microbial communities. While this study indeed stems from a controlled laboratory  
539 experiment, resulting in the formulation of questions and hypotheses for future testing, it  
540 fundamentally demonstrates the intrinsic significance of chemical, biological, and  
541 environmental factors in shaping the reactivity of OM.

542

543 **Acknowledgments**

544 This work was supported by a National Research Foundation of Korea (NRF) grant [No.  
545 2017R1D1A1B033546, 2017] funded by the Korean government (MSIP). The authors thank  
546 Dr. Yunju Cho for handling the LDI FT–ICR MS analyses. THM-GCMS analyses were  
547 performed through the support of the Condate Eau - OSUR analytical platform of Rennes  
548 University.

549

550 **Data Availability Statement**

551 The data that support this study are available in the article and accompanying online  
552 supplementary material.

553

554 **Conflict of Interest statement**

555 The authors declare no conflicts of interest.

556

557 **Declaration of Funding**

558 The funding of this work was the National Research Foundation of Korea (NRF) grant [No.  
559 2017R1D1A1B033546, 2017] from the Korean government (MSIP).

560

561 **Figure' captions**

562 **Fig. 1** Distribution in compounds classes and elemental formulas of all the artificial sediments  
563 for both oxygen conditions (i.e., oxic and anoxic). Characteristics of compound classes are  
564 presented in Table A.2.

565 **Fig. 2** Relative proportions of the chemical families identified by the THM–GC–MS analysis  
566 of the end members at t = 0 day and t = 60 days in all the artificial sediments for both oxygen  
567 conditions (i.e., oxic and anoxic). Uncertainties are the standard deviation of two experimental  
568 replicates. Asterisks was added on data where a significant difference (p-value < 0.05) is  
569 observed between day 0 and day 60.

570 **Fig. 3** Principal coordinate analysis ordination of the Bray-Curtis dissimilarity matrix  
571 computed for the LDI FT–ICR MS data.

572 **Fig. 4** Principal component analysis performed with the distribution of biomarker (67). Purple  
573 pentagons are the theoretical points of the S:A mixed samples calculated using an end-member  
574 mixing approach. Grey shapes highlight the groups identified by the hierarchical analysis  
575 classification.

576 **Fig. 5** Principal component analysis performed with the distribution of microbial fatty acids  
577 biomarker (11). Grey shapes highlight the groups identified by the hierarchical analysis  
578 classification.

579

## 580 **References**

- 581 Alzate-Gaviria, L., Domínguez-Maldonado, J., Chablé-Villacís, R., Olguin-Maciel, E., Leal-  
582 Bautista, R.M., Canché-Escamilla, G., Caballero-Vázquez, A., Hernández-Zepeda, C.,  
583 Barredo-Pool, F.A., Tapia-Tussell, R., 2020. Presence of polyphenols complex aromatic  
584 “lignin” in *Sargassum* spp. from Mexican Caribbean. *J Mar Sci Eng* **9**, 6.  
585 Armas-Herrera, C.M., Dignac, M., Rumpel, C., Arbelo, C.D., Chabbi, A., 2016. Management  
586 effects on composition and dynamics of cutin and suberin in topsoil under agricultural  
587 use. *Eur J Soil Sci* **67**, 360–373.  
588 Arndt, S., Jørgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., Regnier, P., 2013.  
589 Quantifying the degradation of organic matter in marine sediments: A review and

590 synthesis. *Earth Sci Rev* **123**, 53–86.  
591 <https://doi.org/10.1016/J.EARSCIREV.2013.02.008>  
592 Aubriet, F., Carré, V., 2019. Fourier transform ion cyclotron resonance mass spectrometry  
593 and laser: A versatile tool. *Fundamentals and Applications of Fourier Transform Mass*  
594 *Spectrometry* 281–322. <https://doi.org/10.1016/B978-0-12-814013-0.00010-7>  
595 Bengtsson, M.M., Attermeyer, K., Catalán, N., 2018. Interactive effects on organic matter  
596 processing from soils to the ocean: are priming effects relevant in aquatic ecosystems?  
597 *Hydrobiologia*. <https://doi.org/10.1007/s10750-018-3672-2>  
598 Bianchi, T.S., 2011. The role of terrestrially derived organic carbon in the coastal ocean: a  
599 changing paradigm and the priming effect. *Proc Natl Acad Sci U S A* **108**, 19473–19481.  
600 <https://doi.org/10.1073/pnas.1017982108>  
601 Bianchi, T.S., Ward, N.D., 2019. Editorial: The Role of Priming in Terrestrial and Aquatic  
602 Ecosystems. *Front Earth Sci (Lausanne)* **7**. <https://doi.org/10.3389/feart.2019.00321>  
603 Blackburn, J.W.T., Kew, W., Graham, M.C., Uhrin, D., 2017. Laser desorption/ionization  
604 coupled to FTICR mass spectrometry for studies of natural organic matter. *Anal Chem*  
605 **89**, 4382–4386.  
606 Bowen, S.R., Gregorich, E.G., Hopkins, D.W., 2009. Biochemical properties and  
607 biodegradation of dissolved organic matter from soils. *Biol Fertil Soils* **45**, 733–742.  
608 Bray, J.R., Curtis, J.T., 1957. An Ordination of the Upland Forest Communities of Southern  
609 Wisconsin. *Ecol Monogr* **27**, 325–349. <https://doi.org/10.2307/1942268>  
610 Briand, M.J., Bonnet, X., Goiran, C., Guillou, G., Letourneur, Y., 2015. Major Sources of  
611 Organic Matter in a Complex Coral Reef Lagoon: Identification from Isotopic  
612 Signatures ( $\delta(13)C$  and  $\delta(15)N$ ). *PLoS One* **10**, e0131555.  
613 <https://doi.org/10.1371/journal.pone.0131555>  
614 Brune, A., Frenzel, P., Cypionka, H., 2000. Life at the oxic–anoxic interface: microbial  
615 activities and adaptations. *FEMS Microbiol Rev* **24**, 691–710.  
616 <https://doi.org/doi:10.1111/j.1574-6976.2000.tb00567.x>  
617 Challinor, J.M., 1995. Characterisation of wood by pyrolysis derivatisation—gas  
618 chromatography/mass spectrometry. *J Anal Appl Pyrolysis* **35**, 93–107.  
619 Choi, H.-M., Yang, K.-C., 2012. Classification of tree species using high-resolution  
620 QuickBird-2 satellite images in the valley of Ui-dong in Bukhansan National Park. *J*  
621 *Ecol Environ* **35**, 91–98.  
622 Curtis-Jackson, P.K., Massé, G., Gledhill, M., Fitzsimons, M.F., 2009. Characterization of  
623 low molecular weight dissolved organic nitrogen by liquid chromatography-electrospray  
624 ionization-mass spectrometry. *Limnol Oceanogr Methods* **7**, 52–63.  
625 <https://doi.org/doi:10.4319/lom.2009.7.52>  
626 D’Andrilli, J., Cooper, W.T., Foreman, C.M., Marshall, A.G., 2015. An ultrahigh-resolution  
627 mass spectrometry index to estimate natural organic matter lability. *Rapid*  
628 *Communications in Mass Spectrometry* **29**, 2385–2401.  
629 <https://doi.org/10.1002/rcm.7400>  
630 D’Andrilli, J., Fischer, S.J., Rosario-Ortiz, F.L., 2020. Advancing Critical Applications of  
631 High Resolution Mass Spectrometry for DOM Assessments: Re-Engaging with Mass  
632 Spectral Principles, Limitations, and Data Analysis. *Environ Sci Technol* **54**, 2020.  
633 <https://doi.org/10.1021/acs.est.0c04557>  
634 D’Andrilli, J., Junker, J.R., Smith, H.J., Scholl, E.A., Foreman, C.M., 2019. DOM  
635 composition alters ecosystem function during microbial processing of isolated sources.  
636 *Biogeochemistry*. <https://doi.org/10.1007/s10533-018-00534-5>  
637 Denis, M., Jeanneau, L., Petitjean, P., Murzeau, A., Liotaud, M., Yonnet, L., Gruau, G., 2017.  
638 New molecular evidence for surface and sub-surface soil erosion controls on the

639 composition of stream DOM during storm events. *Biogeosciences* **14**, 5039–5051.  
640 <https://doi.org/10.5194/bg-14-5039-2017>

641 Derenne, S., Largeau, C., Berkaloff, C., Rousseau, B., Wilhelm, C., Hatcher, P.G., 1992.  
642 Non-hydrolysable macromolecular constituents from outer walls of *Chlorella fusca* and  
643 *Nanochlorum eucaryotum*. *Phytochemistry* **31**, 1923–1929.  
644 [https://doi.org/10.1016/0031-9422\(92\)80335-C](https://doi.org/10.1016/0031-9422(92)80335-C)

645 Derrien, M., Lee, Y.K., Park, J.E., Li, P., Chen, M., Lee, S.H., Lee, S.H., Lee, J.B., Hur, J.,  
646 2017. Spectroscopic and molecular characterization of humic substances (HS) from soils  
647 and sediments in a watershed: comparative study of HS chemical fractions and the  
648 origins. *Environmental Science and Pollution Research* **24**, 16933–16945.  
649 <https://doi.org/10.1007/s11356-017-9225-9>

650 Derrien, M., Retelletti Brogi, S., Gonçalves-Araujo, R., 2019a. Characterization of aquatic  
651 organic matter: Assessment, perspectives and research priorities. *Water Res* **163**,  
652 114908. <https://doi.org/10.1016/J.WATRES.2019.114908>

653 Derrien, M., Shin, K.H., Hur, J., 2019b. Assessment on applicability of common source  
654 tracking tools for particulate organic matter in controlled end member mixing  
655 experiments. *Science of The Total Environment* **666**, 187–196.  
656 <https://doi.org/10.1016/j.scitotenv.2019.02.258>

657 Derrien, M., Shin, K.-H.H., Hur, J., 2019c. Biodegradation-induced signatures in sediment  
658 pore water dissolved organic matter: Implications from artificial sediments composed of  
659 two contrasting sources. *Science of The Total Environment* **694**, 133714.  
660 <https://doi.org/10.1016/j.scitotenv.2019.133714>

661 Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. A simple and efficient method for the  
662 solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnol*  
663 *Oceanogr Methods* **6**, 230–235. <https://doi.org/10.4319/lom.2008.6.230>

664 Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science (1979)* **156**, 1322–1335.

665 Frostegård, Å., Tunlid, A., Bååth, E., 1993. Phospholipid fatty acid composition, biomass,  
666 and activity of microbial communities from two soil types experimentally exposed to  
667 different heavy metals. *Appl Environ Microbiol* **59**, 3605–3617.

668 Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Hatcher, P.G., De  
669 Leeuw, J.W., 1996. Novel, resistant microalgal polyethers: An important sink of organic  
670 carbon in the marine environment? *Geochim Cosmochim Acta*.  
671 [https://doi.org/10.1016/0016-7037\(96\)00038-5](https://doi.org/10.1016/0016-7037(96)00038-5)

672 Gontikaki, E., Thornton, B., Huvenne, V.A.I., Witte, U., 2013. Negative priming effect on  
673 organic matter mineralisation in NE Atlantic slope sediments. *PLoS One* **8**, e67722.

674 Guenet, B., Danger, M., Abbadie, L., Lacroix, G., 2010a. Priming effect: bridging the gap  
675 between terrestrial and aquatic ecology. *Ecology* **91**, 2850–2861.  
676 <https://doi.org/doi:10.1890/09-1968.1>

677 Guenet, B., Danger, M., Harrault, L., Allard, B., Jauset-Alcala, M., Bardoux, G., Benest, D.,  
678 Abbadie, L., Lacroix, G., 2014. Fast mineralization of land-born C in inland waters: first  
679 experimental evidences of aquatic priming effect. *Hydrobiologia* **721**, 35–44.  
680 <https://doi.org/10.1007/s10750-013-1635-1>

681 Guenet, B., Leloup, J., Raynaud, X., Bardoux, G., Abbadie, L., 2010b. Negative priming  
682 effect on mineralization in a soil free of vegetation for 80 years. *Eur J Soil Sci* **61**, 384–  
683 391.

684 Hach, P.F., Marchant, H.K., Krupke, A., Riedel, T., Meier, D. V., Lavik, G., Holtappels, M.,  
685 Dittmar, T., Kuypers, M.M.M., 2020. Rapid microbial diversification of dissolved  
686 organic matter in oceanic surface waters leads to carbon sequestration. *Sci Rep* **10**,  
687 13025. <https://doi.org/10.1038/s41598-020-69930-y>

688 Hansell, D.A., 2013. Recalcitrant dissolved organic carbon fractions.

689 Hansen, A.M., Kraus, T.E.C., Pellerin, B.A., Fleck, J.A., Downing, B.D., Bergamaschi, B.A.,  
690 2016. Optical properties of dissolved organic matter (DOM): Effects of biological and  
691 photolytic degradation. *Limnol Oceanogr* **61**, 1015–1032.  
692 <https://doi.org/10.1002/lno.10270>

693 Hawkes, J., Sjöberg, P.J.R., Bergquist, J., Tranvik, L., 2019. Complexity of dissolved organic  
694 matter in the molecular size dimension: insights from coupled size exclusion  
695 chromatography electrospray ionisation mass spectrometry. *Faraday Discuss.*  
696 <https://doi.org/10.1039/C8FD00222C>

697 Hawkes, J.A., Patriarca, C., Sjöberg, P.J.R., Tranvik, L.J., Bergquist, J., 2018. Extreme  
698 isomeric complexity of dissolved organic matter found across aquatic environments.  
699 *Limnol Oceanogr Lett* **3**, 21–30. <https://doi.org/doi:10.1002/lol2.10064>

700 Henrichs, S.M., 1992. Early diagenesis of organic matter in marine sediments: progress and  
701 perplexity. *Mar Chem* **39**, 119–149. [https://doi.org/10.1016/0304-4203\(92\)90098-U](https://doi.org/10.1016/0304-4203(92)90098-U)

702 Herzsprung, P., von Tümpling, W., Wendt-Potthoff, K., Hertkorn, N., Harir, M., Schmitt-  
703 Kopplin, P., Friese, K., 2017. High field FT-ICR mass spectrometry data sets enlighten  
704 qualitative DOM alteration in lake sediment porewater profiles. *Org Geochem* **108**, 51–  
705 60. <https://doi.org/https://doi.org/10.1016/j.orggeochem.2017.03.010>

706 Jeanneau, L., Jaffrézic, A., Pierson-Wickmann, A.-C., Gruau, G., Lambert, T., Petitjean, P.,  
707 2014. Constraints on the sources and production mechanisms of dissolved organic  
708 matter in soils from molecular biomarkers. *Vadose Zone Journal* **13**.

709 Jeanneau, L., Rowland, R., Inamdar, S., 2018. Molecular fingerprinting of particulate organic  
710 matter as a new tool for its source apportionment: changes along a headwater drainage in  
711 coarse, medium and fine particles as a function of rainfalls. *Biogeosciences* **15**, 973–985.  
712 <https://doi.org/10.5194/bg-15-973-2018>

713 Kalbitz, K., Schmerwitz, J., Schwesig, D., Matzner, E., 2003. Biodegradation of soil-derived  
714 dissolved organic matter as related to its properties. *Geoderma* **113**, 273–291.

715 Kellerman, A.M., Kothawala, D.N., Dittmar, T., Tranvik, L.J., 2015. Persistence of dissolved  
716 organic matter in lakes related to its molecular characteristics. *Nature Geosci* **8**, 454–  
717 457. <https://doi.org/10.1038/ngeo2440>  
718 [http://www.nature.com/ngeo/journal/v8/n6/abs/ngeo2440.html#supplementary-](http://www.nature.com/ngeo/journal/v8/n6/abs/ngeo2440.html#supplementary-information)  
719 [information](http://www.nature.com/ngeo/journal/v8/n6/abs/ngeo2440.html#supplementary-information)

720 Kew, W., Blackburn, J.W.T., Uhrin, D., 2018. Response to comment on “laser  
721 desorption/ionization coupled to FTICR mass spectrometry for studies of natural organic  
722 matter”. *Anal Chem* **90**, 5968–5971.

723 Kim, S., Kramer, R.W., Hatcher, P.G., 2003. Graphical Method for Analysis of Ultrahigh-  
724 Resolution Broadband Mass Spectra of Natural Organic Matter, the Van Krevelen  
725 Diagram. *Anal Chem* **75**, 5336–5344. <https://doi.org/10.1021/ac034415p>

726 Klaas G. J. Nierop, \*, Caroline M. Preston, ‡ and, Joeri Kaal†, §, 2005. Thermally Assisted  
727 Hydrolysis and Methylation of Purified Tannins from Plants.  
728 <https://doi.org/10.1021/AC050564R>

729 Kleber, M., 2010. What is recalcitrant soil organic matter? *Environmental Chemistry* **7**, 320–  
730 332.

731 Kleber, M., Lehmann, J., 2019. Humic Substances Extracted by Alkali Are Invalid Proxies  
732 for the Dynamics and Functions of Organic Matter in Terrestrial and Aquatic  
733 Ecosystems. *J Environ Qual* **48**, 207–216. <https://doi.org/10.2134/jeq2019.01.0036>

734 Koch, B.P., Dittmar, T., 2006. From mass to structure: an aromaticity index for high-  
735 resolution mass data of natural organic matter. *Rapid Communications in Mass*  
736 *Spectrometry* **20**, 926–932. <https://doi.org/10.1002/rcm.2386>

737 Koch, B.P., Dittmar, T., Witt, M., Kattner, G., 2007. Fundamentals of Molecular Formula  
738 Assignment to Ultrahigh Resolution Mass Data of Natural Organic Matter. *Anal Chem*  
739 **79**, 1758–1763. <https://doi.org/10.1021/ac061949s>

740 Kolattukudy, P.E., 2001. Polyesters in higher plants. In 'Biopolyesters'. Springer, pp. 1–49.

741 Kothawala, D.N., Kellerman, A.M., Catalán, N., Tranvik, L.J., 2020. Organic Matter  
742 Degradation across Ecosystem Boundaries: The Need for a Unified Conceptualization.  
743 *Trends Ecol Evol*.

744 Kuznetsova, O. V, Sevastyanov, V.S., Timerbaev, A.R., 2019. What are the current analytical  
745 approaches for sediment analysis related to the study of diagenesis? Highlights from  
746 2010 to 2018. *Talanta* **191**, 435–442.  
747 <https://doi.org/https://doi.org/10.1016/j.talanta.2018.08.080>

748 LaRowe, D.E., Van Cappellen, P., 2011. Degradation of natural organic matter: a  
749 thermodynamic analysis. *Geochim Cosmochim Acta* **75**, 2030–2042.

750 Lee, Y., Lee, B., Hur, J., Min, J.O., Ha, S.Y., Ra, K., Kim, K.T., Shin, K.H., 2016.  
751 Biodegradability of algal-derived organic matter in a large artificial lake by using stable  
752 isotope tracers. *Environ Sci Pollut Res Int* **23**, 8358–8366.  
753 <https://doi.org/10.1007/s11356-016-6046-1>

754 Liu, S., Feng, W., Song, F., Li, T., Guo, W., Wang, B., Wang, H., Wu, F., 2019.  
755 Photodegradation of algae and macrophyte-derived dissolved organic matter: A multi-  
756 method assessment of DOM transformation. *Limnologica* **77**, 125683.  
757 <https://doi.org/10.1016/J.LIMNO.2019.125683>

758 Lützow, M. v, Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner,  
759 B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and  
760 their relevance under different soil conditions—a review. *Eur J Soil Sci* **57**, 426–445.

761 Martone, P.T., Estevez, J.M., Lu, F., Ruel, K., Denny, M.W., Somerville, C., Ralph, J., 2009.  
762 Discovery of Lignin in Seaweed Reveals Convergent Evolution of Cell-Wall  
763 Architecture. *Current Biology* **19**, 169–175. <https://doi.org/10.1016/J.CUB.2008.12.031>

764 McCallister, S.L., Ishikawa, N.F., Kothawala, D.N., 2018. Biogeochemical tools for  
765 characterizing organic carbon in inland aquatic ecosystems. *Limnol Oceanogr Lett* **3**,  
766 444–457. <https://doi.org/doi:10.1002/lo12.10097>

767 van der Meij, W.M., Temme, A.J.A.M., Lin, H.S., Gerke, H.H., Sommer, M., 2018. On the  
768 role of hydrologic processes in soil and landscape evolution modeling: concepts,  
769 complications and partial solutions. *Earth Sci Rev*.  
770 <https://doi.org/10.1016/j.earscirev.2018.09.001>

771 Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry—an overview of  
772 indicators of organic matter sources and diagenesis in lake sediments. *Org Geochem* **20**,  
773 867–900. [https://doi.org/http://dx.doi.org/10.1016/0146-6380\(93\)90100-P](https://doi.org/http://dx.doi.org/10.1016/0146-6380(93)90100-P)

774 Milliken, K.L., 2003. Late Diagenesis and Mass Transfer in Sandstone–Shale Sequences.  
775 *Treatise on Geochemistry* 159–190. <https://doi.org/10.1016/B0-08-043751-6/07091-2>

776 Mopper, K., Stubbins, A., Ritchie, J.D., Bialk, H.M., Hatcher, P.G., 2007. Advanced  
777 Instrumental Approaches for Characterization of Marine Dissolved Organic  
778 Matter: Extraction Techniques, Mass Spectrometry, and Nuclear Magnetic Resonance  
779 Spectroscopy. *Chem Rev* **107**, 419–442. <https://doi.org/10.1021/cr050359b>

780 Moran, M.A., Sheldon Jr., W.M., Zepp, R.G., 2000. Carbon loss and optical property changes  
781 during long-term photochemical and biological degradation of estuarine dissolved  
782 organic matter. *Limnol Oceanogr* **45**, 1254–1264.  
783 <https://doi.org/doi:10.4319/lo.2000.45.6.1254>

- 784 Moran, M.A., Zepp, R.G., 1997. Role of photoreactions in the formation of biologically labile  
785 compounds from dissolved organic matter. *Limnol Oceanogr.*  
786 <https://doi.org/10.4319/lo.1997.42.6.1307>
- 787 Mueller, K.E., Polissar, P.J., Oleksyn, J., Freeman, K.H., 2012. Differentiating temperate tree  
788 species and their organs using lipid biomarkers in leaves, roots and soil. *Org Geochem*  
789 **52**, 130–141.
- 790 Navel, S., Mermillod-Blondin, F., Montuelle, B., Chauvet, E., Marmonier, P., 2012.  
791 Sedimentary context controls the influence of ecosystem engineering by bioturbators on  
792 microbial processes in river sediments. *Oikos* **121**, 1134–1144.  
793 <https://doi.org/doi:10.1111/j.1600-0706.2011.19742.x>
- 794 Nierop, K.G.J., Verstraten, J.M., 2004. Rapid molecular assessment of the bioturbation extent  
795 in sandy soil horizons under pine using ester-bound lipids by on-line thermally assisted  
796 hydrolysis and methylation-gas chromatography/mass spectrometry. *Rapid*  
797 *Communications in Mass Spectrometry* **18**, 1081–1088.  
798 <https://doi.org/10.1002/rcm.1449>
- 799 Patriarca, C., Balderrama, A., Može, M., Sjöberg, P.J.R., Bergquist, J., Tranvik, L.J.,  
800 Hawkes, J.A., 2020. Investigating the ionization of dissolved organic matter by  
801 electrospray ionization. *Anal Chem* [acs.analchem.0c03438](https://doi.org/10.1021/acs.analchem.0c03438).  
802 <https://doi.org/10.1021/acs.analchem.0c03438>
- 803 Repeta, D.J., 2015. Chapter 2 - Chemical Characterization and Cycling of Dissolved Organic  
804 Matter A2 - Hansell, Dennis A. In 'Biogeochemistry of Marine Dissolved Organic  
805 Matter (Second Edition)' (Ed. Carlson, C.A.). Academic Press, Boston, pp. 21–63.  
806 <https://doi.org/https://doi.org/10.1016/B978-0-12-405940-5.00002-9>
- 807 Sankar, M.S., Dash, P., Singh, S., Lu, Y., Mercer, A.E., Chen, S., 2019. Effect of photo-  
808 biodegradation and biodegradation on the biogeochemical cycling of dissolved organic  
809 matter across diverse surface water bodies. *Journal of Environmental Sciences*.  
810 <https://doi.org/https://doi.org/10.1016/j.jes.2018.06.021>
- 811 Solihat, N.N., Acter, T., Kim, D., Plante, A.F., Kim, S., 2019. Analyzing Solid-Phase Natural  
812 Organic Matter Using Laser Desorption Ionization Ultrahigh Resolution Mass  
813 Spectrometry. *Anal Chem* **91**, 951–957. <https://doi.org/10.1021/acs.analchem.8b04032>
- 814 Stubbins, A., Dittmar, T., 2014. Dissolved Organic Matter in Aquatic Systems.  
815 <https://doi.org/10.1016/B978-0-08-095975-7.01010-X>
- 816 Vähätalo, A. V, Aarnos, H., Mäntyniemi, S., 2010. Biodegradability continuum and  
817 biodegradation kinetics of natural organic matter described by the beta distribution.  
818 *Biogeochemistry* **100**, 227–240.
- 819 Valle, J., Gonsior, M., Harir, M., Enrich-Prast, A., Schmitt-Kopplin, P., Bastviken, D.,  
820 Conrad, R., Hertkorn, N., 2018. Extensive processing of sediment pore water dissolved  
821 organic matter during anoxic incubation as observed by high-field mass spectrometry  
822 (FTICR-MS). *Water Res* **129**, 252–263.  
823 <https://doi.org/https://doi.org/10.1016/j.watres.2017.11.015>
- 824 Wakeham, S.G., Ertel, J.R., 1988. Diagenesis of organic matter in suspended particles and  
825 sediments in the Cariaco Trench. *Org Geochem* **13**, 815–822.
- 826 Ward, N.D., Bianchi, T.S., Sawakuchi, H.O., Gagne-Maynard, W., Cunha, A.C., Brito, D.C.,  
827 Neu, V., de Matos Valerio, A., da Silva, R., Krusche, A. V, 2016. The reactivity of  
828 plant-derived organic matter and the potential importance of priming effects along the  
829 lower Amazon River. *J Geophys Res Biogeosci* **121**, 1522–1539.
- 830 Ward, N.D., Morrison, E.S., Liu, Y., Rivas-Ubach, A., Osborne, T.Z., Ogram, A. V., Bianchi,  
831 T.S., 2019. Marine microbial community responses related to wetland carbon

832 mobilization in the coastal zone. *Limnol Oceanogr Lett* **4**, 25–33.  
833 <https://doi.org/10.1002/lol2.10101>

834 Wershaw, R.L., 2004. Evaluation of conceptual models of natural organic matter (humus)  
835 from a consideration of the chemical and biochemical processes of humification.

836 Wetzel, R.G., 2001. Limnology: Lake and River Ecosystems, 3rd. *Academic press, AQn*  
837 *Elsevier imprint, Sanfrancisco, New York, London*.

838 Willers, C., Jansen van Rensburg, P.J., Claassens, S., 2015. Phospholipid fatty acid profiling  
839 of microbial communities—a review of interpretations and recent applications. *J Appl*  
840 *Microbiol* **119**, 1207–1218.

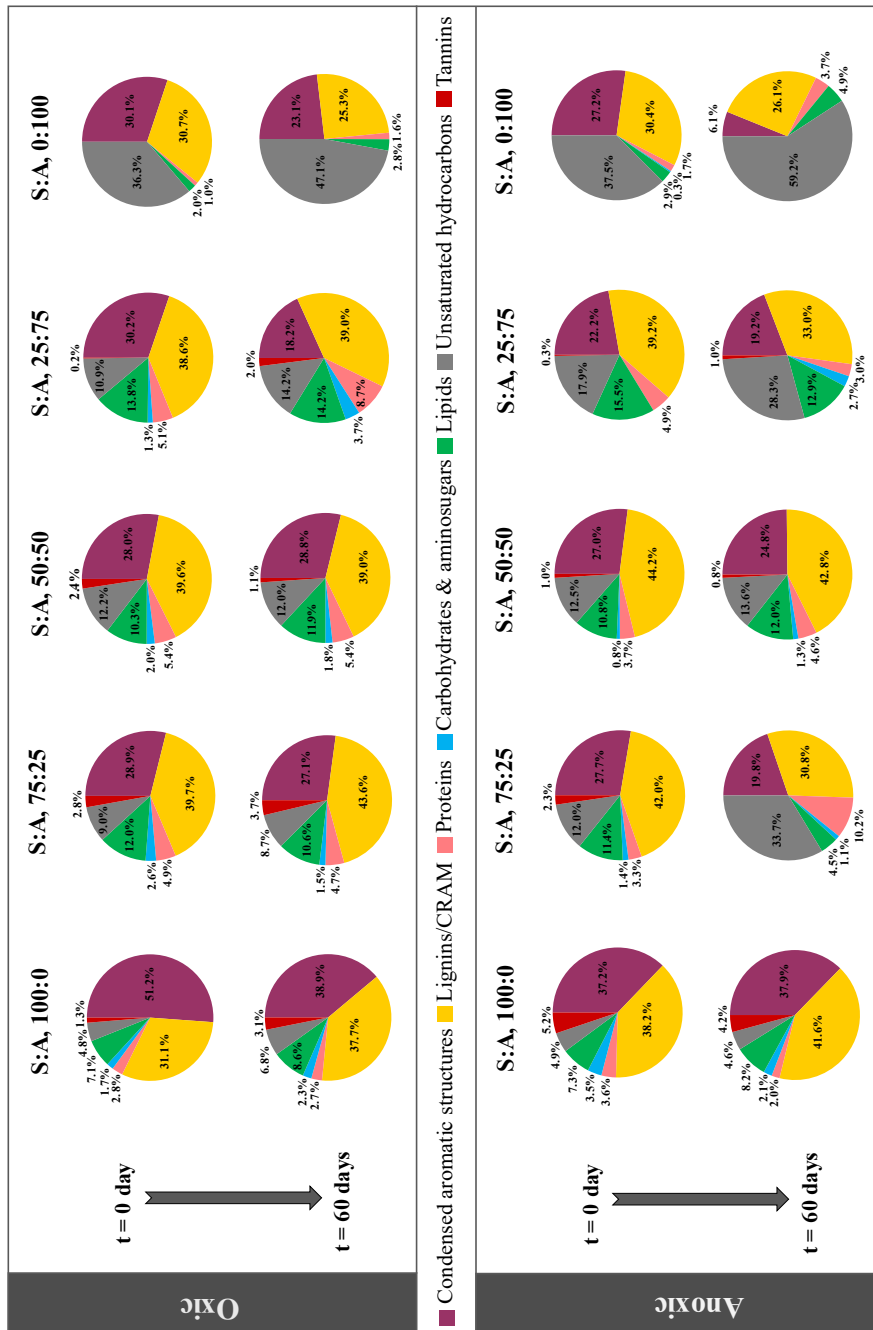
841 Williams, J.S., Dungait, J.A.J., Bol, R., Abbott, G.D., 2016. Contrasting temperature  
842 responses of dissolved organic carbon and phenols leached from soils. *Plant Soil* **399**,  
843 13–27.

844 Youngblood, W.W., Blumer, M., Guillard, R.L., Fiore, F., 1971. Saturated and unsaturated  
845 hydrocarbons in marine benthic algae. *Mar Biol* **8**, 190–201.  
846 <https://doi.org/10.1007/BF00355215>

847 Zhuang, W.-E., Chen, W., Cheng, Q., Yang, L., 2021. Assessing the priming effect of  
848 dissolved organic matter from typical sources using fluorescence EEMs-PARAFAC.  
849 *Chemosphere* **264**, 128600. <https://doi.org/10.1016/j.chemosphere.2020.128600>

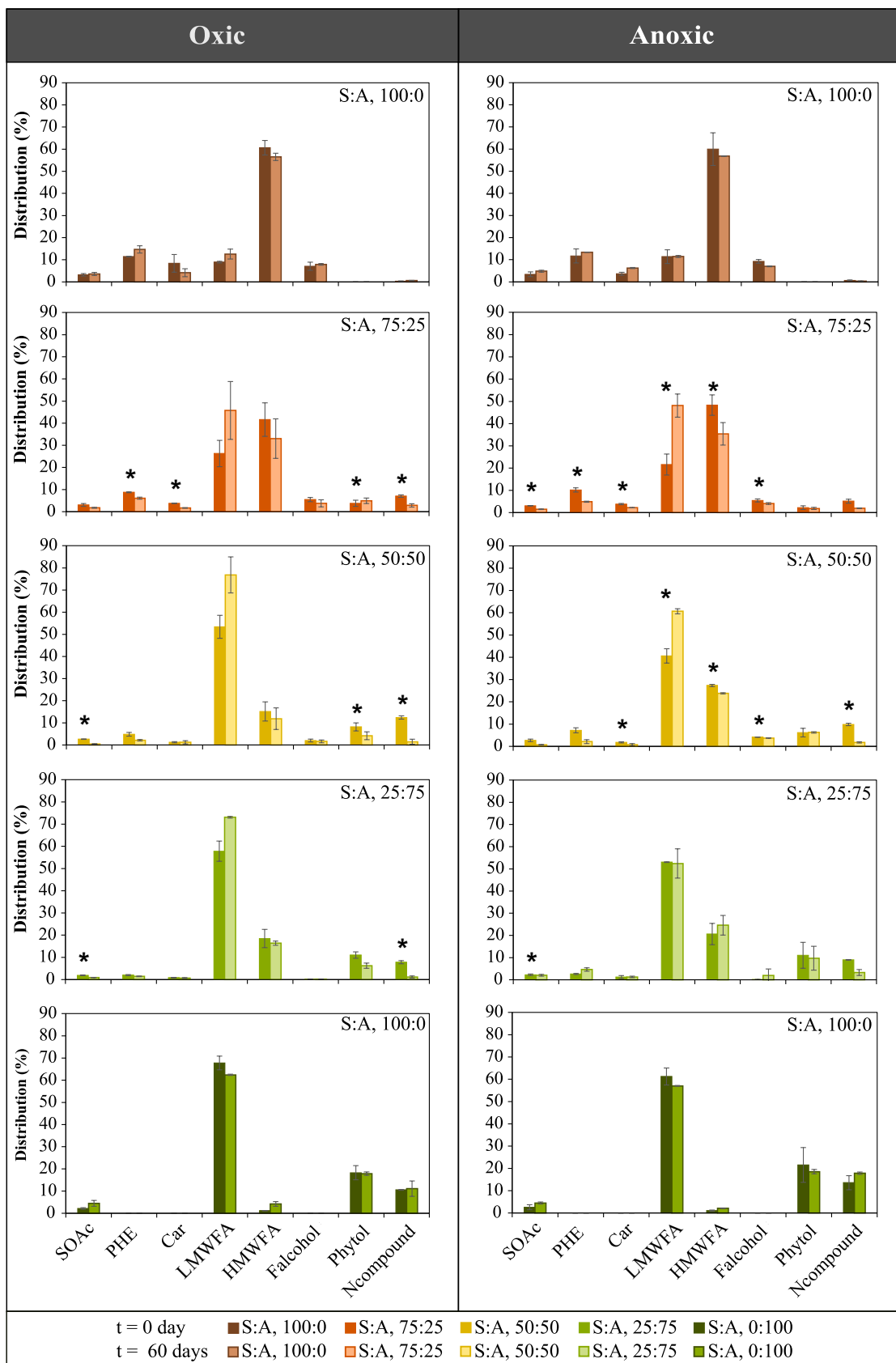
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880

881 **Fig. 1** Distribution in compounds classes of all the artificial sediments for both oxygen conditions  
 882 (i.e., oxic and anoxic). Characteristics of compound classes are presented in Table A.2.



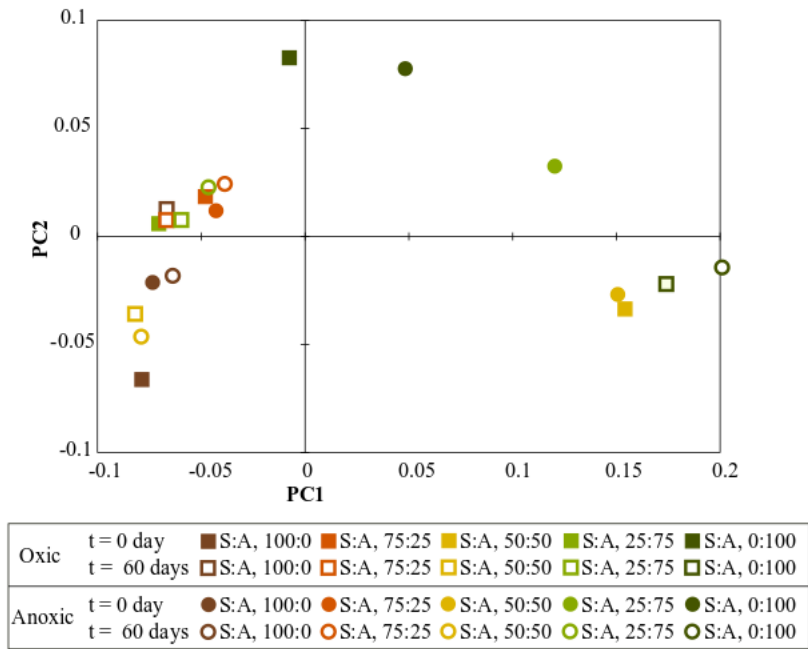
884 **Fig. 2** Relative proportions of the chemical families identified by the THM–GC–MS analysis of the  
885 end members at t = 0 day and t = 60 days in all the artificial sediments for both oxygen conditions  
886 (i.e., oxic and anoxic). Uncertainties are the standard deviation of two experimental replicates.  
887 Asterisks was added on data where a significant difference ( $p$ -value < 0.05) is observed between day 0  
888 and day 60.

889



890  
891  
892  
893

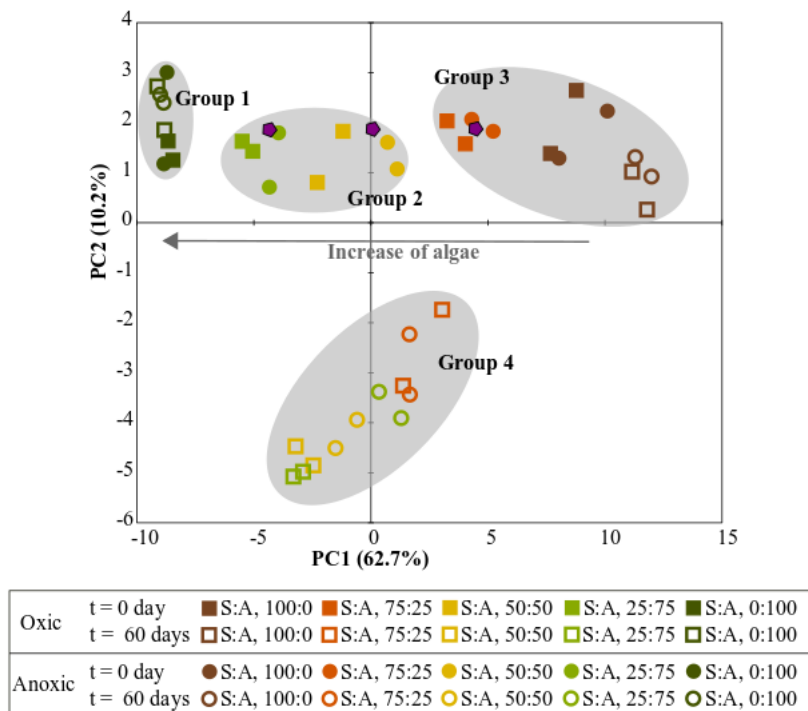
894 **Fig. 3** Principal coordinate analysis ordination of the Bray-Curtis dissimilarity matrix computed for  
 895 the LDI FT-ICR MS data.



896  
 897  
 898  
 899  
 900  
 901  
 902

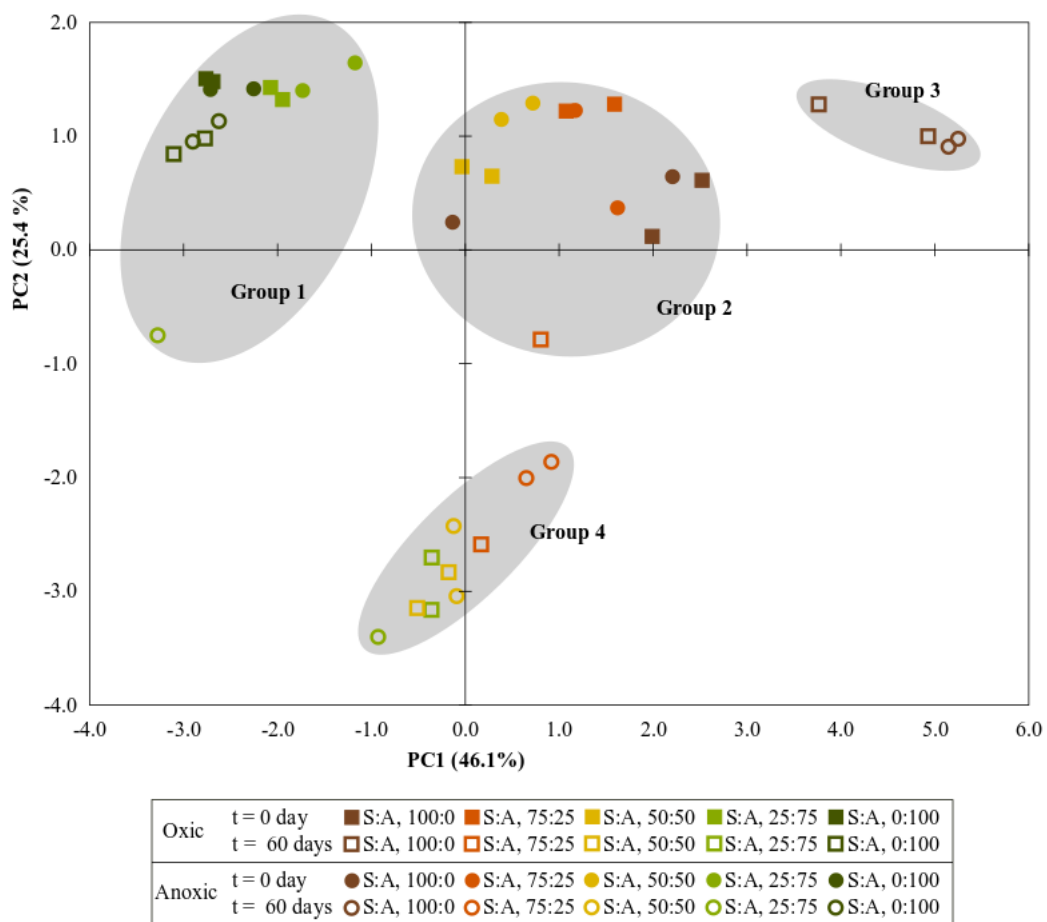
903 **Fig. 4** Principal component analysis performed with the distribution of biomarker (67). Purple  
 904 pentagons are the theoretical points of the S:A mixed samples calculated using an end-member  
 905 mixing approach. Grey shapes highlight the groups identified by the hierarchical analysis  
 906 classification.

907 <sup>43</sup>



908  
 909  
 910

911 **Fig. 5** Principal component analysis performed with the distribution of microbial fatty acids  
 912 biomarker (11). Grey shapes highlight the groups identified by the hierarchical analysis classification.



913