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# Impact of polyethylene and polypropylene geomembranes in sensitive aquatic environment

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## **Highlights :**

- Geomembranes widely used in hydraulic works located in sensitive ecological areas can represent hazard for human health and environment.
- This study quantifies the impact of additives extracted from geomembranes in aqueous solutions.
- Molecules extracted from geomembranes may affect the aquatic environment.
- Immersion of geomembranes in aqueous solutions leads to the extraction of additives and derived molecules first inhibiting, then activating the behavior of the microorganisms.

**Keywords** : geomembranes, , hydraulic works, additives, Daphnia, ecotoxicity

## **Abstract**

Geomembranes (GMs) are widely used in hydraulic applications. Unfortunately, some additives contained in GMs are extracted upon prolonged contact with water or soil. Depending on their chemical nature, additives contained within GMs or degradation products thereof may affect natural ecosystems. To better understand this effect, the present study evaluates the

29 potential impact of additives extracted from GMs that are commonly used in hydraulic  
30 applications. The approach consists of identifying additives contained in both unaged and aged  
31 high-density polyethylene and polypropylene GMs. Next, these GMs are immersed for various  
32 time intervals at 80, 55, and 25 °C in aqueous solutions (pH 4 and 7), and the chemical  
33 composition of the resulting solution is analyzed by ultraviolet absorbance spectroscopy. In  
34 addition, the effect of these solutions containing the GM extracts on the growth of *Chlorella*  
35 *vulgaris* and on the swimming of *Daphnia sp.* is studied. The first few days of exposure to the  
36 extracted molecules negatively impact *C. vulgaris* growth and *Daphnia sp.* swimming  
37 behaviour. However, after prolonged exposure, the impact is reversed and microalgae growth  
38 is stimulated instead. This result may be related to the change of the nature of the molecules  
39 detected by UV spectroscopy.

40

41

## 42 1 INTRODUCTION

43 France is home to thousands of small dams made of soil and mainly built in rural areas. Since  
44 the early nineties, farmers from the plains in the west of France have increasingly built water  
45 storage ponds for irrigation and lined them with geomembranes (GMs). Various polymers are  
46 used to manufacture the GMs used in such hydraulic applications: high-density polyethylene  
47 (HDPE), polypropylene (PP), polyvinyl chloride (PVC), ethylene propylene diene terpolymer  
48 (EPDM), and bituminous GMs (Touze-Foltz, 2010). In addition, a number of additives (i.e.,  
49 chemical compounds) are used in the manufacturing process to ensure the durability of the  
50 polymeric materials. Despite the low solubility of these additives in water, various studies  
51 provide evidence that prolonged contact between GMs and the surrounding aqueous medium  
52 extracts such additives from GMs. Then, the extracted additives may decompose themselves  
53 and form hydrolysis products. This situation occurs, for example, with plasticizers in PVC GMs  
54 (Blanco et al., 2012) and with antioxidants (AOs) in PP geotextiles (Farcas et al., 2012) and in  
55 polyethylene (PE) GMs (Pons et al., 2012). . Moreover, anti-oxidants receive special attention  
56 because they are extracted in aqueous media (Moisan, 1982; Begley, 2005; Farcas, 2012).

57 Constitutive molecules from geomembrane additives and their degradation products represent  
58 potential sources of pollution that may impact surrounding ecosystems (Grosclaude, 1999,  
59 Lacaze 1993). If hydraulic works are located in sensitive areas such as mountains (e.g., for  
60 snowmaking ponds) or protected ecological zones (e.g., close to sources of drinking water or  
61 areas of organic agriculture), the ecotoxicological impact of additives released by the various  
62 types of geomembranes becomes a serious environmental concern (Grosclaude, 1999,  
63 Lacaze 1993, Lahimer 2017).

64 Because synthetic polymers are increasingly used in modern industry, it is vital that their  
65 impact on the environment and on public health be well understand. Synthetic polymers have  
66 a high molecular weight, from 5000 to  $10^6 \text{ g mol}^{-1}$ , which prevents them from being used by  
67 living organisms. However, the various plastics used in GMs are obtained from synthetic

68 polymers and additives with a much lower molecular weight ( $<1000 \text{ g mol}^{-1}$ ), which makes  
69 them more bio-available (Jakubowicz 2003, Koutny 2006). The molecules able to impact the  
70 environment include monomers, catalysts, solvents, pigments, and additives such as anti-  
71 oxidants, anti-statics, anti-foggers, and stabilizers (Fátima and Hogg, 2007).

72 The main research on the toxicity of plastic additives has been done in the medical and agro-  
73 food sectors (Lau and Wong, 2000; Brocca et al., 2002; Piotrowska, 2005; Lahimer et al.,  
74 2013). However, although civil engineering emphasizes the ageing of GMs, very few studies  
75 have evaluated the ecotoxicity of additives and degradation products from the different types  
76 of GMs used in hydraulic applications.

77 Therefore, the present study investigates the toxicity of chemical products extracted from  
78 HDPE and PP GMs, which are widely used in sensitive ecological areas. This study was done  
79 in three stages: First, the presence of anti-oxidants most commonly added to GMs was  
80 monitored. To do this, the various additives extracted in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), such as  
81 phosphite and phenol anti-oxidants (El Mansouri et al., 1998), were characterized. In the  
82 second stage, to accelerate the desorption of additives, GMs were immersed in aqueous  
83 solutions at various temperatures and at two pH values (4 and 7) according to soil in France  
84 (Sangam & Rowe, 2002). Finally, the potential toxicity of HDPE and PP additives extracted by  
85 aqueous media was evaluated by testing the effect on the growth of microalgae *Chlorella*  
86 *vulgaris* and on microcrustacean *Daphnia sp.* swimming.

87

## 88 2 MATERIALS AND METHODS

89

### 90 2.1 Materials

91

#### 92 2.1.1 Geomembrane samples

93

94 A HDPE GM and a PP GM, are widely used in hydraulic works, were used for all tests because  
95 no reports exist on the ecotoxicology of the AOs contained in these types of GM. The HDPE  
96 and PP GMs were 2 and 1.5 mm thick, respectively. The oxidation-induction time (OIT) was  
97 measured by using the standard NF-EN 728 (1997) at 190°C was  $320 \pm 2$  min for HDPE and  
98  $140 \pm 2$  min for PP.

99

#### 100 2.1.2 Chemicals

101 The AO references are Irganox 1010 [pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-  
102 hydroxyphenyl)propionate] (ACS 6683-19-18, Sigma Aldrich), Irganox 1076 [octadecyl-3-(3,5-  
103 di-tert.butyl-4-hydroxyphenyl)-propionate] (CAS 2082-79-3 sigma Aldrich), and Irgafos 168  
104 [Tris(2,4-ditert-butylphenyl)phosphite] (CAS 31570-04, sigma Aldrich).

105 Ultraviolet (UV) spectrometric analysis of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (Sigma Aldrich  
106 CHROMASOLV® CAS 45-09-2) solutions of Irganox 1010 and 1076 and Irgafos 168 does not  
107 distinguish between the two phenolic stabilizers (Bart, 2005). Both have absorption bands at  
108 275 and 280 nm. The UV absorbance spectrum of phosphite stabilizer reveals a maximum UV  
109 absorption at 270 nm (Stuart, 2008; Djouani et al., 2011).

110 Each AO extracted in  $\text{CH}_2\text{Cl}_2$  was identified by gas chromatography coupled with mass  
111 spectrometry (GC-MS). The Irganox 1010 GC-MS chromatogram contains a peak at 18.05  
112 min, which corresponds to 3-(3,5-di-tert-butyl-4-hydroxyphenyl)methylpropanoate acid (CAS  
113 number 6386-38-5) in the mass spectrum. According to the literature, this compound is a

114 degradation product of Irganox 1010 (Brocca et al., 2002; Kim et al., 2013; Lahimer et al.,  
115 2013). The peak at 18.05 min in the Irganox 1076 GC-MS spectrum, which also appears in the  
116 GC-MS spectrum of Irganox 1010, results from the cleavage of the C<sub>18</sub>H<sub>37</sub> linear chain of  
117 Irganox 1076. A second peak at 31.61 min has a mass spectrum equivalent to that of Irganox  
118 1076 (as reported in the library of the National Institute of Standards and Technology, USA).  
119 Irgafos 168 chromatograms reveal peaks at retention times of 29.58 and 31.31 min The mass  
120 spectrum for the first peak corresponds to the Irgafos 168 molecule and the second peak is  
121 attributed to its oxidized form. Both mass spectra have been observed by Simoneit et al.  
122 (2005).

## 123 **2.2 Solvent extraction of anti-oxidants from geomembranes**

124 To ensure that the method makes the best compromise between simplicity, rapidity, and  
125 efficiency, hindered phenol and phosphite AOs were extracted from GMs by immersion in  
126 boiling HPLC-grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (Sigma Aldrich CHROMASOLV® CAS Number  
127 75-09-2), *i.e.*, at a temperature of 39.8 °C (El Mansouri et al., 1998). A 5 g piece of each GM  
128 was cut into pieces of about 0.5 x 0.5 cm<sup>2</sup> and extracted for 44 h. The extraction was controlled  
129 by monitoring the OIT at 190 °C by differential scanning calorimetry (77 min for the HDPE GM  
130 and 7 min for the PP GM). Immersion conditions

## 131 **2.3 Immersion conditions**

132 The extraction of additives depends on the nature of the environment with which the GM is in  
133 contact (pH, temperature, etc.). In other words, it depends on where the GM is located. Most  
134 soils in France are humic, sandy, loamy, or clayey soils (Antoni 2011). The distribution of pH  
135 is such that most soils are either slightly acidic (5.5 < pH < 6.5) or slightly basic (7.5 < pH <  
136 8.5) (Antoni 2013). To accelerate extraction, this study considers soils with an acidic pH of 4.3  
137 ± 0.2, which are found in the southwest of France where many irrigation ponds are lined with  
138 GMs. A second pH value close to 7 is also considered; this corresponds to the soil pH in the

139 western and central areas of France (Antoni 2013). This neutral pH allowed us to obtain  
140 conclusive ecotoxicological tests.

141 An aqueous solution at a pH of  $4.3 \pm 0.2$  was obtained by adding the requisite amount of 99%  
142 formic acid (additive for LC/MS, Sigma-Aldrich, CAS Number 64-18-6) solution to ultrapure  
143 water (Merck Millipore, 18.2 M $\Omega$ ).

144 An aqueous solution at pH  $6.7 \pm 0.2$  was obtained by adding an ammonium hydroxide solution  
145 (additive for LC/MS, Sigma-Aldrich, CAS Number 1336-21-6) to ultrapure water (Merck  
146 Millipore, 18.2 M $\Omega$ ). The pH of each solution was controlled by using an MP230 pH meter  
147 (Mettler-Toledo) and an IP 67 probe (Mettler-Toledo).

148 To exploit temperature to accelerate extraction (Sangam & Rowe, 2002), the GMs were  
149 immersed in solutions maintained at 80 and 55 °C. To better approximate field conditions, an  
150 immersion temperature of 25 °C was also studied. Rectangular 10 g single-piece GM samples  
151 were inserted into square Fisher Bioblock amber wide-neck 250 mL glass bottles closed with  
152 Fisher Bioblock PBT GL45 caps equipped with polytetrafluoroethylene (PTFE) screw-tight lids.  
153 The glass bottles were then filled to the brim so that the GMs samples were fully immersed.  
154 The length of the GM specimens was adjusted as a function of the material density to obtain a  
155 10 g sample with a 7 cm width (see Table 1).

156 Table 1: Features of immersed GM specimens.

Specimen	Mass per unit area (g m <sup>-2</sup> )	Surface area for 10 g specimen (m <sup>2</sup> )
High Density Polyethylene GM (HDPE)	1 465	6.82 10 <sup>-3</sup>
Polypropylene GM (PP)	877	11.40 10 <sup>-3</sup>



157

158 Duplicate specimens were analyzed after 11, 18, 96, 150, and 300 days at 80 °C, 300 days at  
159 55 °C, and 500 days at 25 °C .

160

## 161 **2.4 Ecotoxicity**

### 162 *Algal-growth inhibition*

163

164 The purpose of this test was to determine how extraction solutions affect the growth of  
165 freshwater microalgae. Assays were done on *Chlorella vulgaris* purchased from the culture  
166 collection of the Museum of Natural History (Paris). *C. vulgaris* is a single-cell green algae  
167 belonging to the phylum chlorophyte. The axenic algal strain was grown in the culture medium  
168 and under conditions described by the International Organization for Standardization (ISO  
169 8692).The strain was transplanted weekly and kept at  $20 \pm 1$  °C with a 16:8 (light:dark)  
170 photoperiod. Two days before starting the test, the algae were inoculated ( $10^4$  cell mL<sup>-1</sup>) in the  
171 culture medium dissolved in the aqueous solutions (pH 4.3 and 6.7) described in Section 2.3  
172 to adapt the algae to the test conditions. Cultures were maintained at 20 °C to within  $\pm 0.5$  °C  
173 and exposed to a continuous daylight illumination of  $100 \mu\text{E m}^{-2} \text{s}^{-1}$ .

174 For the growth test, the algae were inoculated in aqueous solutions with culture nutrients with  
175 extraction solutions added at 90%, 50%, and 10% with three replicates at each concentration.  
176 Cell growth was monitored 72 h after inoculation by using a cell-counting chamber equipped  
177 with an optical microscope.

178

### 179 *Microcrustacean swimming inhibition test*

180

181 The ecotoxicity tests for *Daphnia sp.* were done on neonates. The microcrustaceans were  
182 cultured in an M4 medium held at  $22 \pm 2$  °C with a 16:8 (light:dark) photoperiod, as per ISO

183 6341:2013 recommendations. *Daphnia* sp. were fed with algal cells twice a week. Five  
184 neonates were put in 10 mL of immersion solutions at concentrations of 6.25%, 12.5%, and  
185 25% of HDPE and PP after 11, 96 and 150 days of immersion at a pH 6.7.  
186 Essay were not performed the HDPE and PP immersion at a pH 4. Experiments were done in  
187 triplicate including controls. Observations of *Daphnia* sp. mobility were made after 24 and 48  
188 h of exposure.

## 189 **2.5 Chemical-characterization methods**

### 190 *2.5.1 Analysis by Fourier transform infrared attenuated total reflection*

191 Fourier transform infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode was  
192 used for direct analysis of the GM surfaces and dichloromethane extraction solutions.

193 Spectra were obtained by using a Thermo Optek Impact 380 apparatus with a diamond crystal  
194 (Durascope) driven by Omnic 5.1 software (Thermo Fischer Scientific). An accumulation of 32  
195 spectra was recorded with a resolution of 4 cm<sup>-1</sup>.

### 196 *2.5.2 Ultraviolet analysis*

197 Ultraviolet absorbance spectroscopy was used to analyze the dichloromethane extraction and  
198 aqueous immersion solutions. The UV spectra were acquired in transmittance mode by using  
199 a Perkin Elmer Lambda 35 double-beam apparatus driven by Perkin Elmer UV Winlab software  
200 spectra.

201 Quartz cells with 10 mm optical length were used for all spectrophotometric measurements,  
202 which were made between 190 and 400 nm with a 2 nm bandwidth and a 400 nm min<sup>-1</sup> scan  
203 speed. To compare the spectra, the absorbance was normalized to 100 mL of solution.

### 204 *2.5.3 Analysis by differential scanning calorimetry*

205 Initial and residual stabilizer activities were determined from the OIT obtained by differential  
206 scanning calorimetry under 0.1 MPa oxygen at 190 °C by using a Q10 apparatus (TA

207 Instruments) and following the standard method NF-EN 728 (1997). Measurements were made  
208 on 5–10 mg samples placed in hermetic aluminum pans. Samples were heated from 35 to  
209 190 °C at a rate of 10 °C/min in a nitrogen environment with a gas-flow rate of 50 mL min<sup>-1</sup>.  
210 After reaching 190 °C, the gas flow was changed isothermally from nitrogen to oxygen. Tests  
211 were terminated upon detection of an exothermal peak.

#### 212 *2.5.4 Gas chromatograph mass spectrometer*

213 Extractive solutions were analyzed by using a GC-MS (Trace DSQ Thermo Fisher Scientific,  
214 Bremen, Germany) equipped with a CombiPAL autosampler and Xcalibur acquisition software.

215 The separation was done by using a 60-m-long ZB-5MS capillary column with a 0.25 mm inner  
216 diameter and 0.25 mm film thickness. The oven remained at an initial temperature of 80 °C for  
217 1 min, then increased in steps of 10 °C min<sup>-1</sup> to 330 °C where it remained for 10 min.

218 Helium carrier gas was used with a flow rate of 1.5 ml min<sup>-1</sup>. Samples of 1 µl were injected in  
219 splitless mode, with the injector temperature maintained at 280 °C and the transfer line at  
220 350 °C to avoid problems due to condensation.

221 Ionization in the mass spectrometer results from electron impact, and the ionization energy is  
222 70 eV. The mass-spectrometer source temperature was 280 °C, and the detectable mass  
223 range extended from 52 to 1050 amu.

224

#### 225 *2.5.5 Direct-infusion mass spectrometer*

226

227 Analyses of immersion solutions was done with a LTQ Orbitrap XL™ (Thermo Fisher Scientific,  
228 Bremen, Germany) controlled by Xcalibur software. An electrospray source in the positive  
229 mode was used for full-scan analysis (150 to 2000 Da). The samples were diluted in methanol  
230 (LC-MS grade, Sigma-Aldrich, CAS Number 67-56-1) and directly injected into the source at a  
231 rate of 5 µL min<sup>-1</sup>. An ion trap was used for acquisition, and the spray voltage was fixed at 4.2  
232 kV.

233 Each sample was analyzed twice. For data processing, the scans were averaged for each  
234 sample and processed by using the XCMS package (Smith et al., 2006; Tautenham et al.,  
235 2008; Benton et al., 2010) of the R software, which yielded all mass/charge (m/z) ratios with a  
236 signal-to-noise ratio greater than three and with the respective abundance for each sample.  
237 Next, identification was made by using the CAMERA software package (Kulh et al., 2012) and  
238 comparison with metabolomic databases (MZedDB). Finally, a principal component analysis  
239 (PCA) was applied to explain the variability of the mass-charge list obtained.

### 240 **3 RESULTS AND DISCUSSION**

#### 241 **3-1 Analysis of additives in initial geomembranes**

242  
243 In addition to PP characteristic bands (2800, 3000, 1460, and 1375  $\text{cm}^{-1}$ ), the FTIR-ATR  
244 spectra of PPGM includes absorption bands of alcohol groups (OH, 3390  $\text{cm}^{-1}$ ) and ester  
245 carbonyl groups (C=O, 1734  $\text{cm}^{-1}$ ) which highlight the presence of hindered phenol stabilizers  
246 in Irganox 1010 and Irganox 1076, which are widely used in GMs (Farcas et al., 2014).

247 The presence in the HDPE GM FTIR-ATR spectrum of the 2915, 2847, and 1472–1463  $\text{cm}^{-1}$   
248 absorption bands of ethyl groups, the 720  $\text{cm}^{-1}$  absorption of hydrocarbon chains with more  
249 than four ethylene groups, and the absence of the  $\text{CH}_3$  absorption at 1375  $\text{cm}^{-1}$  is consistent  
250 with polyethylene-type polymer. Band splitting is due to crystalline phases of the polymer  
251 (Nishikida and Coates, 2003). No additional bands are present to indicate additive compounds  
252 (Farcas et al., 2014).

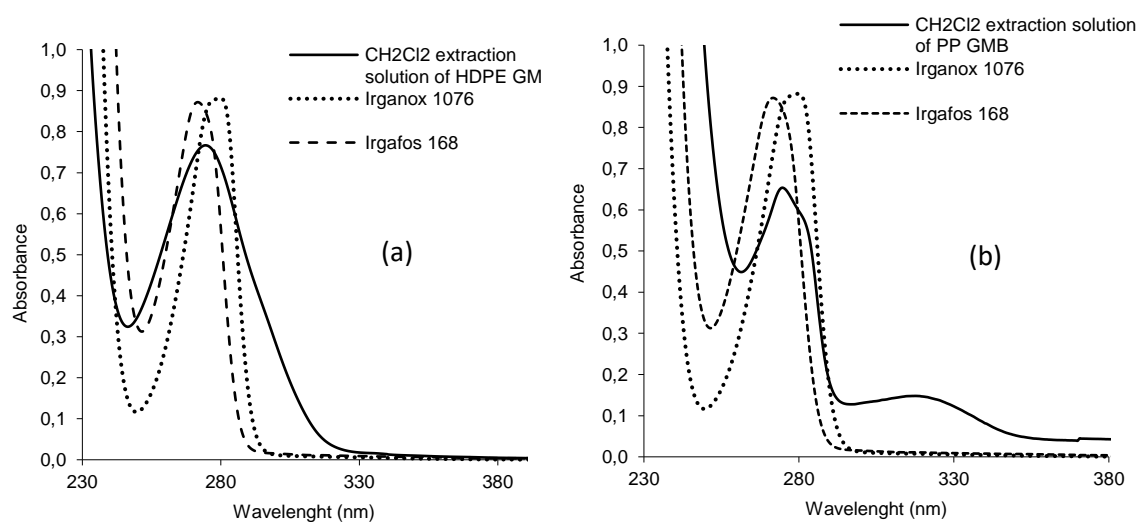
253

254 FTIR-ATR is a reproducible and easy to implement analytic technique. However, when used  
255 with GMs, such techniques do not always identify additives present in small amounts (about  
256 0.5% to 1% by mass), which explains why a preliminary extraction using solvents is often  
257 required (Marcato and Vinello, 2000; Dopico Garcia et al., 2004; Crompton 2007; ISO standard  
258 6427). The extraction efficiency depends on the polymer-solvent combination (Bart, 2003).

259 Following this, various spectroscopic (Bart, 2003; Crompton et al., 2007; Farcas et al., 2012)  
260 and chromatographic techniques (Dopico Garcia et al., 2003; Sanches Silva et al., 2006;  
261 Djouani et al., 2012) may be applied to characterize the AOs extracted from the plastics. In the  
262 FTIR-ATR spectra of CH<sub>2</sub>Cl<sub>2</sub> GM extraction solutions, absorption bands appear at 3365, 1742,  
263 and 1151 cm<sup>-1</sup>, which is characteristic of OH alcohol bonds, ester C=O bonds, and phenolic  
264 tertiary alcohol C–O bonds, thereby confirming the presence of phenolic AOs in HDPE and PP  
265 GMs (Farcas et al., 2014).

266 The UV absorbance spectra of CH<sub>2</sub>Cl<sub>2</sub> extraction solution reveals absorption from  
267 chromophore groups at 276 nm for HDPE (Fig. 1a) and 276 and 280 nm for PP (Fig. 1b).  
268 Comparing these with model AO UV absorptions indicate that the measured absorption bands  
269 correspond to phenolic and/or phosphite stabilizers, although the extraction of Irganox 1010 or  
270 1076 and Irgafos 168 from the GMs cannot be asserted with certainty. The spectrum of a  
271 solution containing a mix of compounds differs from the spectrum of the pure compounds.

272



273

274 *Figure 1: Ultraviolet absorbance spectrum of CH<sub>2</sub>Cl<sub>2</sub> extraction solutions of (a) HDPE GM,*  
275 *(b) PP GM, revealing the presence of Irganox 1010 and Irgafos 168 in CH<sub>2</sub>Cl<sub>2</sub>.*

276

277 The GC-MS chromatogram of extraction solution for the HDPE GM has a peak at 18.03 min,  
278 which also appears in the Irganox 1010 and 1076 chromatograms. However, the absence of a  
279 peak at 31.61 min excludes the presence of the Irganox 1076 AO. Instead, this peak  
280 corresponds to the cleavage of the linear chain of many Irganox compounds, so the presence  
281 of Irganox in the sample cannot be ascertained with certainty.

282 GC-MS chromatograms of the extraction solution of HDPE and PP GMs unambiguously  
283 identify Irgafos 168: chromatographic peaks appear at 29.54 and 31.29 min whose mass  
284 spectra correspond to those of Irgafos 168 and its oxidized form.

285 The presence of additional chromatographic peaks in both cases indicates that other  
286 compounds are also extracted from GMs by CH<sub>2</sub>Cl<sub>2</sub>. However, these compounds are not  
287 identified.

288

### 289 **3- 3- Analysis of extraction solutions**

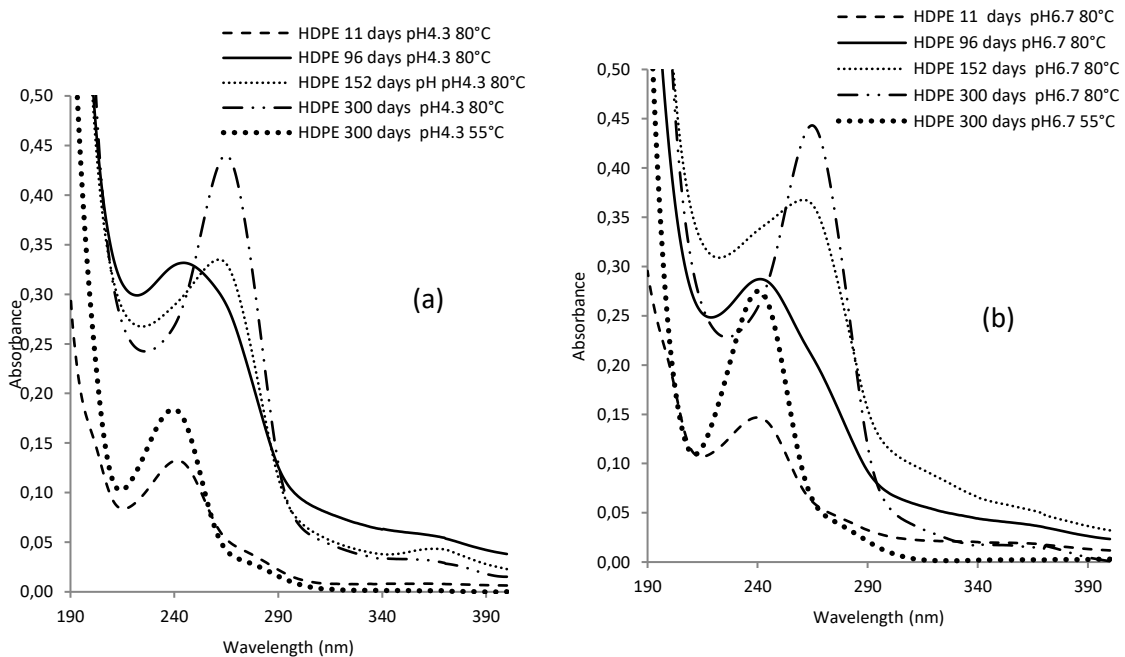
290 For both GMs, the UV absorbances of pH 4.3 and 6.7 solutions are similar, meaning that pH  
291 is not a factor in determining which compounds are extracted.

292 The UV absorbance spectra of pH 6.7 and 4.3 extraction solutions of HDPE and PP GMs  
293 (Figs. 2 and 3) indicate the extraction of organic compounds which, after 11 days of immersion  
294 at 80 °C, absorb at 240 nm for HDPE and at 230 nm for PP. These absorptions increase with  
295 immersion time. A bathochromic shift occurs from 96 days at 80 °C (240 to 262 nm for the  
296 HDPE GM and 230 to 240 nm for the PP GM), revealing a change in the solution composition  
297 due to extraction of more compounds and/or the decomposition of previously extracted  
298 compounds. Comparison with the UV spectrum of a commercial Irganox 1010 boiled 24 h in  
299 deionized water, which absorbs at 274 nm, indicates that these extracted compounds do not  
300 correspond to hindered phenolic stabilizers.

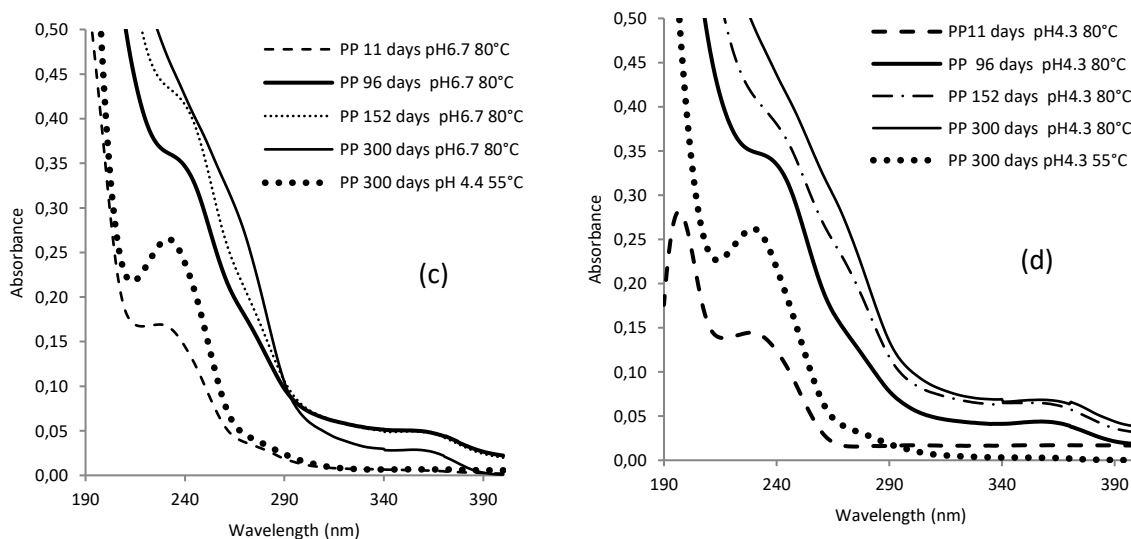
301

302 After 11 days, the appearance of a shoulder at 277 nm suggests that extraction of a phenolic  
303 stabilizer has begun. The weak absorption at 360 nm probably corresponds to quinoic

304 compounds resulting from the degradation of phenolic AOs (Pospíšil et al., 2002; Beißmann  
 305 et al., 2013). This peak grows with immersion time, appearing first after immersion for 11 days  
 306 of the HDPE GM in pH 6.7 solution, then after immersion for 96 days of PP and HDPE GMs in  
 307 pH 4.3 solutions, and finally for immersion of the PP GM in pH 6.7 solution after immersion for  
 308 96 days.  
 309



310



311

312 *Figure 2: Ultraviolet absorbance spectra of pH (a,c) 6.7 and (b,d) 4.3 extraction solution*  
 313 *containing the HDPE GM (a,b) PP GM (c,d) at 80 and 55 °C.*

314

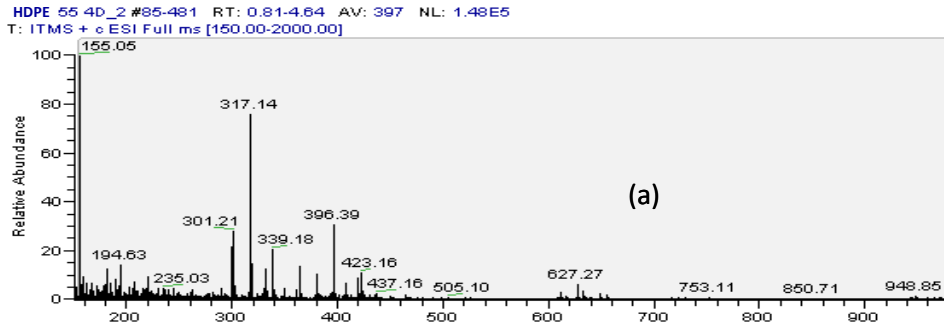
315 The UV absorbance spectra of pH 6.7 and 4.3 extraction solutions containing HDPE and PP  
316 GMs and maintained at 55 °C for 300 days (Fig. 2) show a UV absorption similar to that of the  
317 extraction solution maintained at 80 °C for 11 days for both HDPE and for PP GMs. The  
318 stronger absorption band of the solutions held at 55 °C indicates a greater extraction than for  
319 the extraction solutions maintained at 80 °C for 11 days.

320

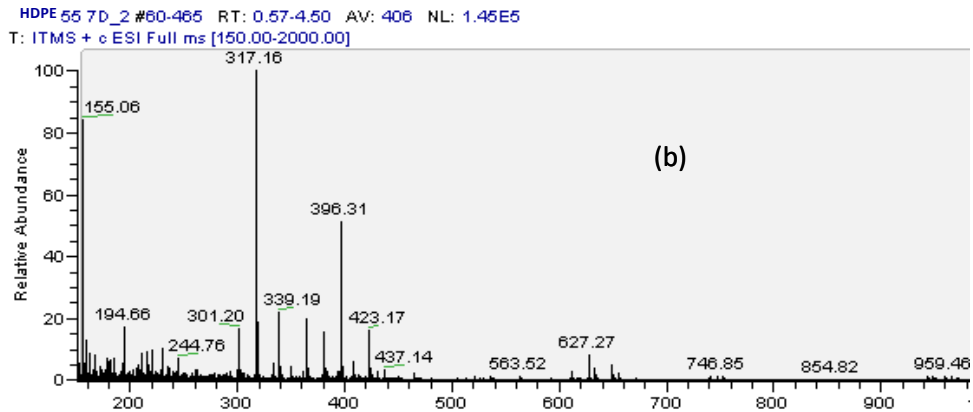
321 Analysis by direct-injection mass spectrometry of extraction solutions containing HDPE GMs  
322 maintained 300 days at 55 °C reveals mass spectra with similar patterns with respect to pH  
323 (see Fig. 3), with fairly large peaks appearing between 317 and 423 relative abundance, and  
324 a cluster of peaks near 627 relative abundance, confirming that pH does not influence the type  
325 of compound extracted.

326

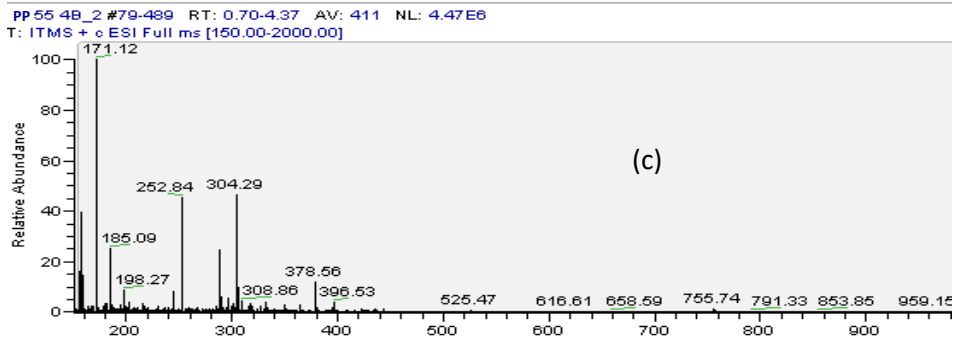




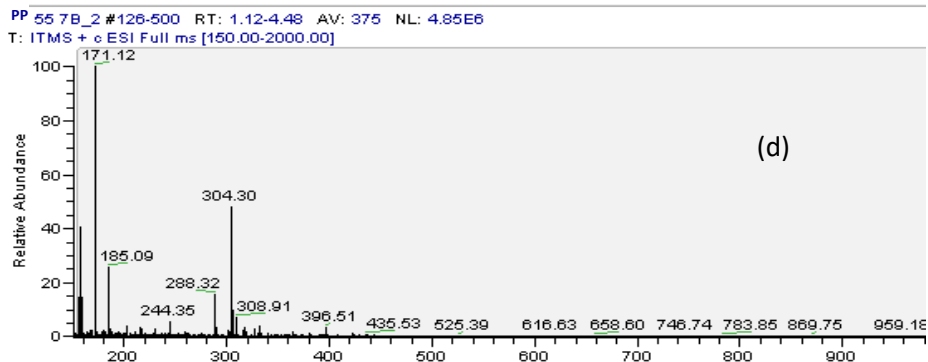
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330

331 *Figure 3: Mass spectra of extraction solution containing immersed HDPE GM (a,b) and PP*

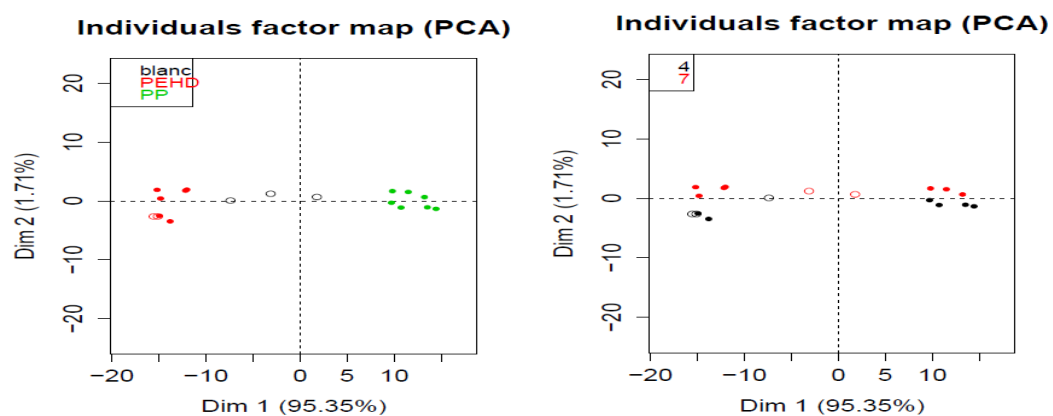
332 *GM (c,d) at pH (a,c) 4.3 and (b,d) 6.7 maintained at 55 °C for 300 days.*

333 The MS spectra obtained for the PP GM at pH 4.3 and 6.7 are similar, with fairly large peaks  
334 appearing between 171.12 and 396.51 relative abundance (Fig. 3). However, note that the  
335 peaks at 198.27 and 378.56 appear only at pH 4.3.

336 The mass spectra differ for compounds extracted from HDPE and from PP GMs maintained  
337 for 300 days in an aqueous solution at 55 °C (Fig. 3). These results show that the type of  
338 compound extracted depends on the makeup of the GM.

339 The PCA was done based on the mass-charge list obtained from the XCMS process. Figure 6  
340 shows the variability of the sample (individuals).

341 The variability is mainly explained by the nature of the geomembrane (dimension 1: 95.35%),  
342 dimension 2 differentiates between blank and samples, confirming that the compounds  
343 extracted are specific to each GM (Fig. 4). The influence of pH is visible from dimension 2: it  
344 represents only 1.71% of the total variability.



345

346

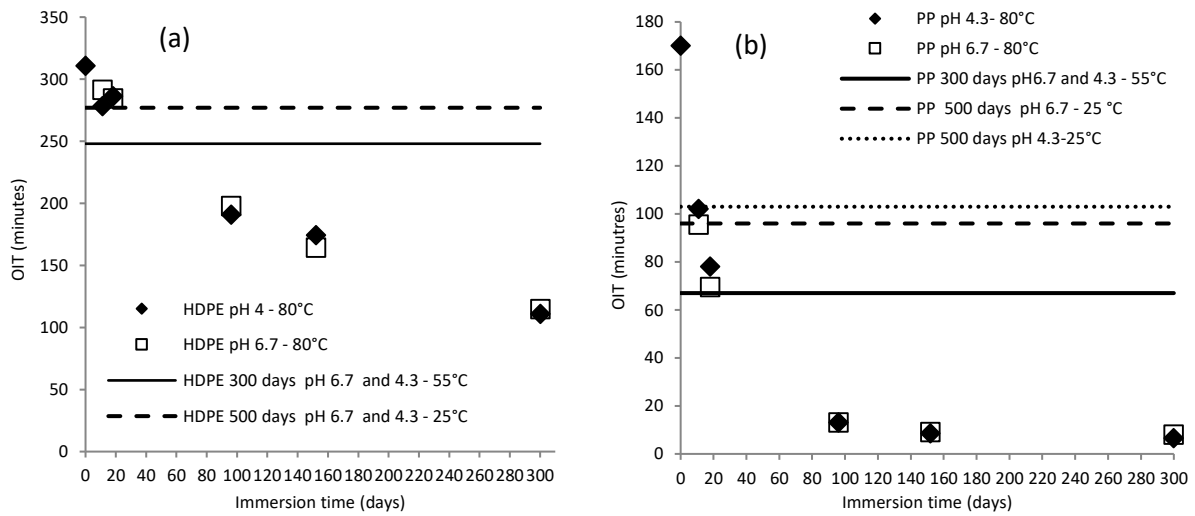
347

348 *Figure 4: Principle component analysis of direct-injection mass spectrometry results of HDPE*  
349 *and PP immersion samples maintained at 55 °C for 300 days.*

350

351 For both GMs, the decrease of OIT (Fig. 5) confirms the loss of AOs during immersion,  
352 independent of pH and temperature.

353



354

355 *Figure 5: Oxidation-induction time of (a) HDPE and (b) PP GMs after pH 4 and 6.7 at 80°C and*  
 356 *55°C.*

357

358 The decrease in OIT confirms the extraction of AOs from the GMs. After 96 days at 80 °C, a  
 359 greater percent of AO (95%) is extracted from the PP GM than from the HDPE GM (63%). This  
 360 difference is attributed in part to the nature of the AO and to the GM thickness: thinner GMs  
 361 result in shorter diffusion time for AOs from the GM core to the GM surface. The results for OIT  
 362 are stable but nonzero, meaning that stabilizers other than phenols and phosphites are not  
 363 extracted.

364

365 When GMs are immersed for 500 days at 25 °C, which is closer to the temperature actually  
 366 encountered in field conditions, the loss of AO is equivalent to the loss incurred by GMs  
 367 immersed for 11 days at 80 °C. When GMs are immersed for 300 days at 55 °C, the loss of AO  
 368 from the HDPE (PP) GM is equivalent to that of a GM immersed for 40 days at 80 °C. This  
 369 result confirms the greater extractability of AOs from PP GMs than from HDPE GMs. However,  
 370 note that extraction at a typical operating temperature (25 °C) is significantly lower than  
 371 extraction at a higher temperature (e.g., 80 and 55 °C).

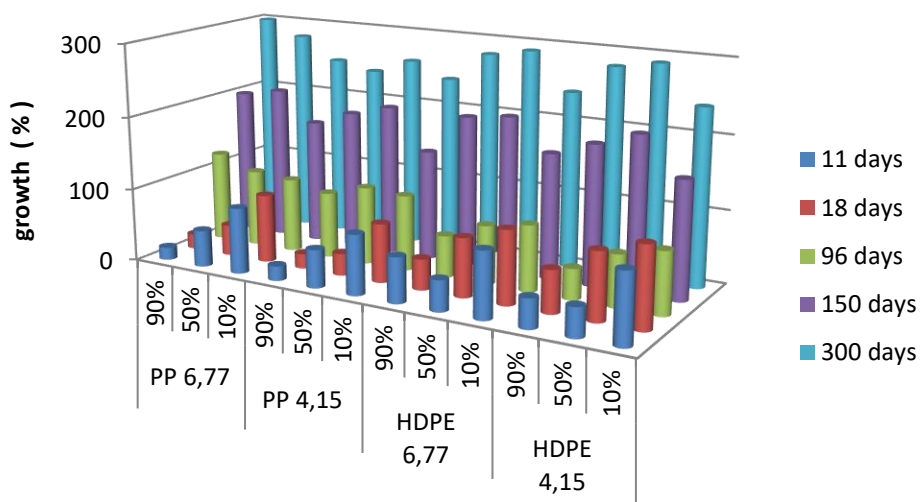
372

373 Spectroscopic and chromatographic studies highlight extraction of organic compounds from  
 374 HDPE and PP immersed in pH 4.3 and 6.7 laboratory aqueous solutions. No influence of pH  
 375 is detected. The molecules extracted differ depending on the nature of the GM. A change in  
 376 the molecular composition of the extraction solution after 11 and 96 days is detected. In the  
 377 next part of this paper we evaluate the possible impact of these molecules on aquatic systems.  
 378

### 379 3.4 Impact of immersion solutions on aquatic ecosystems

#### 380 3.4.1- Impact on micro-algae

381 The results shown in Fig. 6 indicate that pH has no impact on *C. vulgaris* growth. The extraction  
 382 solutions obtained after 11 days of immersion of the PP GM at 80 °C inhibit algal growth with  
 383 LD 50 at about 50%, and this inhibition seems to increase slightly after 18 days. Extraction  
 384 solutions of the HDPE GM after 11 and 18 days inhibit algal growth less than the extraction  
 385 solutions of the PP GM. After 96 days, the HDPE GM and PP GM extraction solutions have  
 386 different effects on algal growth. Whereas the PP GM extraction solutions produce only a slight  
 387 increase in algal growth, the HDPE GM extraction solutions inhibit algal growth. After 152 days  
 388 of immersion, an increase in algal growth occurs (200% with respect to the control HDPE GM  
 389 extraction solution). After 300 days of immersion, the increase in algal growth appears stronger  
 390 for a solution with pH 6.77.



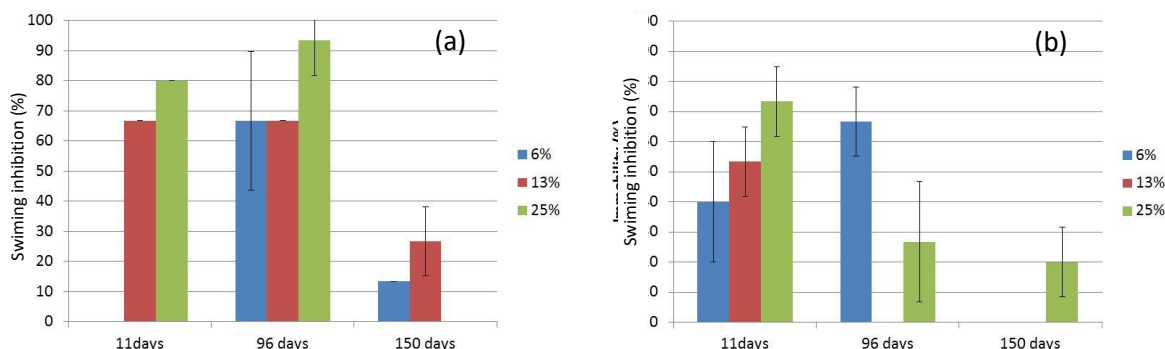
392

393 Figure 6: Growth of *Chlorella vulgaris* inoculated during 72 h in different dilutions (90%, 50%,  
 394 10%) of extraction solutions. These assays were done on pH 6.77 and 4.15 solutions in which  
 395 PP and HDPE GMs were immersed for 11, 18, 96, 150, and 300 days.

396

### 397 3.4.2- Effect on microcrustaceans

398 Solutions containing immersed HDPE GMs have the same impact on microcrustaceans as  
 399 those containing immersed PP GMs. In fact, after 11 days, the solutions containing immersed  
 400 PP and HDPE GMs both inhibit the swimming of *Daphnia sp.* (with EC<sub>50</sub> after 48 hours of 11%  
 401 for HDPE versus 16.5% for PP). After immersion of 96 days of the PP GM, the resulting solution  
 402 does not affect microcrustacean swimming, which differs from the results obtained with the  
 403 HDPE GM, for which the resulting solution immobilizes the microcrustaceans. After 150 days,  
 404 neither solution affects the swimming of *Daphnia sp.* (see Fig. 7).



405 Figure 7: Swimming inhibition on *Daphnia sp.* of PP (a) and HDPE (a) solutions maintained at  
 406 80°C for 11, 96, and 150 days.

407

### 408 3.4.3 Global impact on aquatic environment

409 After immersion of the GMs for 11 days at 80 °C, the extracted substances influence the  
 410 behavior of microalgae and microcrustaceans. For both HDPE and PP GMs, the behavior of  
 411 microalgae and microcrustaceans is modified as a function of immersion time (i.e., inhibition  
 412 the growth and swimming) after 11 days of immersion and activation microalgae growth after

413 150 days of immersion). This ecotoxicologic change is attributed to the change in the solution  
414 composition as revealed by UV absorbance spectroscopy.

415 This study was done under laboratory conditions; specifically, at temperatures much higher  
416 than those encountered in field conditions and with much less water in contact with the GMs  
417 than is the case in a retention tank. However, even at 25 °C, which is a common temperature  
418 encountered in the field, molecular extraction occurs from GMs into the surrounding water.

419

## 420 **Conclusion**

421

422 This study on the impact of HDPE and PP GMs on sensitive ecological areas focusses on the  
423 extraction of organic compounds such as the additives Irganox 1010 or Irgafos 168 after  
424 immersion of the GMs in aqueous media at pH 4.3 and 6.7 and at 80, 55, and 25 °C. The  
425 results highlight the effect of temperature on the extraction kinetics: higher temperature results  
426 in a greater extraction flux. In contrast, pH affects neither the kinetics nor the composition of  
427 the extracted molecules. Ultraviolet absorbance spectroscopy indicates that different chemical  
428 compositions develop in solutions containing HDPE and PP GMs immersed for 11 days vs 96  
429 days. These differences are attributed to new extracted molecules and/or degradation of  
430 previously extracted molecules.

431

432 Ecotoxicological tests show how microalgae growth (*C. vulgaris*) and microcrustacean  
433 swimming (*Daphnia sp.*) are impacted by exposure to the extraction solutions. Differences in  
434 the chemical composition of extraction solutions are reflected in modified behavior of these  
435 microorganisms. The molecules extracted from the PP and HDPE GMs immersed in solution  
436 for 11 days inhibit the behavior of the microorganisms (i.e., growth for microalgae and  
437 swimming for microcrustaceans). However, after 96 days of immersion this process is  
438 reversed, and at 150 days the extracted molecules activate microalgae growth and have no  
439 effect on microcrustacean swimming. This algal stimulation may be due to the extracted

440 molecules serving as fertilizer. If this process is confirmed by field studies of GMs, it may  
441 increase local eutrophication. As this study has been performed in laboratory conditions, future  
442 studies should investigate the extent to which microorganisms are sensitive to extractable  
443 compounds.

444

445

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449

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