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To cite this version:

Marielle Gueguen Minerbe, Claude Durrieu, Angéline Guenne, Lénaïck Rouillac, Dinarzed Diafi, et al.. Impact of polyethylene and polypropylene geomembranes in sensitive aquatic environment. Ecotoxicology and Environmental Safety, 2018, 148, pp. 884-891. 10.1016/j.ecoenv.2017.11.015 . hal-01702335

HAL Id: hal-01702335

https://hal.science/hal-01702335v1

Submitted on 25 May 2021

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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

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

1 INTRODUCTION

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

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

Because synthetic polymers are increasingly used in modern industry, it is vital that their impact on the environment and on public health be well understand. Synthetic polymers have a high molecular weight, from 5000 to 106 g mol^{-1}, which prevents them from being used by living organisms. However, the various plastics used in GMs are obtained from synthetic

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

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

Therefore, the present study investigates the toxicity of chemical products extracted from HDPE and PP GMs, which are widely used in sensitive ecological areas. This study was done in three stages: First, the presence of anti-oxidants most commonly added to GMs was monitored. To do this, the various additives extracted in dichloromethane (CH_2Cl_2), such as phosphite and phenol anti-oxidants (El Mansouri et al., 1998), were characterized. In the second stage, to accelerate the desorption of additives, GMs were immersed in aqueous solutions at various temperatures and at two pH values (4 and 7) according to soil in France (Sangam & Rowe, 2002). Finally, the potential toxicity of HDPE and PP additives extracted by aqueous media was evaluated by testing theieffect on the growth of microalgae *Chlorella vulgaris* and on microcrustacean *Daphnia sp.* swimming.

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Geomembrane samples

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

2.1.2 Chemicals

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

Ultraviolet (UV) spectrometric analysis of dichloromethane (CH_2Cl_2) (Sigma Aldrich CHROMASOLV® CAS 45-09-2) solutions of Irganox 1010 and 1076 and Irgafos 168 does not distinguish between the two phenolic stabilizers (Bart, 2005). Both have absorption bands at 275 and 280 nm. The UV absorbance spectrum of phosphite stabilizer reveals a maximum UV absorption at 270 nm (Stuart, 2008; Djouani et al., 2011).

Each AO extracted in CH_2Cl_2 was identified by gas chromatography coupled with mass spectrometry (GC-MS). The Irganox 1010 GC-MS chromatogram contains a peak at 18.05 min, which corresponds to 3-(3,5-di-tert-butyl-4-hydroxyphenyl)methylpropanoate acid (CAS number 6386-38-5) in the mass spectrum. According to the literature, this compound is a

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

2.2 Solvent extraction of anti-oxidants from geomembranes

To ensure that the method makes the best compromise between simplicity, rapidity, and efficiency, hindered phenol and phosphite AOs were extracted from GMs by immersion in boiling HPLC-grade dichloromethane (CH_2Cl_2) (Sigma Aldrich CHROMASOLV® CAS Number 75-09-2), *i.e.*, at a temperature of 39.8 °C (El Mansouri et al., 1998). A 5 g piece of each GM was cut into pieces of about 0.5 x 0.5 cm^2 and extracted for 44 h. The extraction was controlled by monitoring the OIT at 190 °C by differential scanning calorimetry (77 min for the HDPE GM and 7 min for the PP GM). Immersion conditions

2.3 Immersion conditions

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

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

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

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

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

Table 1: Features of immersed GM specimens.

Specimen	Mass per unit area ($g\ m^{-2}$)	Surface area for 10 g specimen (m^2)
High Densitiy Polyethylene GM (HDPE)	1 465	$6.82\ 10^{-3}$
Polypropylene GM (PP)	877	$11.40\ 10^{-3}$

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

2.4 Ecotoxicity

Algal-growth inhibition

The purpose of this test was to determine how extraction solutions affect the growth of freshwater microalgae. Assays were done on *Chlorella vulgaris* purchased from the culture collection of the Museum of Natural History (Paris). *C. vulgaris* is a single-cell green algae belonging to the phylum chlorophyte. The axenic algal strain was grown in the culture medium and under conditions described by the International Organization for Standardization (ISO 8692).The strain was transplanted weekly and kept at 20 ± 1 °C with a 16:8 (light:dark) photoperiod. Two days before starting the test, the algae were inoculated (104 cell mL^{-1}) in the culture medium dissolved in the aqueous solutions (pH 4.3 and 6.7) described in Section 2.3 to adapt the algae to the test conditions. Cultures were maintained at 20 °C to within ±0.5 °C and exposed to a continuous daylight illumination of 100 μE m^{-2} s^{-1}.

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

Microcrustacean swimming inhibition test

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

6341:2013 recommendations. Daphnia sp. were fed with algal cells twice a week. Five neonates were put in 10 mL of immersion solutions at concentrations of 6.25%,12.5%, and 25% of HDPE and PP after 11, 96 and 150 days of immersion at a pH 6.7.

Essay were not performed the HDPE and PP immersion at a pH 4. Experiments were done in triplicate including controls. Observations of *Daphnia sp.* mobility were made after 24 and 48 h of exposure.

2.5 Chemical-characterization methods

2.5.1 Analysis by Fourier transform infrared attenuated total reflection

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

Spectra were obtained by using a Thermo Optek Impact 380 apparatus with a diamond crystal (Durascope) driven by Omnic 5.1 software (Thermo Fischer Scientific). An accumulation of 32 spectra was recorded with a resolution of 4 cm^{-1}.

2.5.2 Ultraviolet analysis

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

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

2.5.3 Analysis by differential scanning calorimetry

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

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

2.5.4 Gas chromatograph mass spectrometer

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

The separation was done by using a 60-m-long ZB-5MS capillary column with a 0.25 mm inner diameter and 0.25 mm film thickness. The oven remained at an initial temperature of 80 °C for 1 min, then increased in steps of 10 °C min^{-1} to 330 °C where it remained for 10 min.
Helium carrier gas was used with a flow rate of 1.5 ml min^{-1}. Samples of 1 µl were injected in splitless mode, with the injector temperature maintained at 280 °C and the transfer line at 350 °C to avoid problems due to condensation.
Ionization in the mass spectrometer results from electron impact, and the ionization energy is 70 eV. The mass-spectrometer source temperature was 280 °C, and the detectable mass range extended from 52 to 1050 amu.

2.5.5 Direct-infusion mass spectrometer

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

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

3 RESULTS AND DISCUSSION

3-1 Analysis of additives in initial geomembranes

In addition to PP characteristic bands (2800, 3000, 1460, and 1375 cm^{-1}), the FTIR-ATR spectra of PPGM includes absorption bands of alcohol groups (OH, 3390 cm^{-1}) and ester carbonyl groups (C=O, 1734 cm^{-1}) which highlight the presence of hindered phenol stabilizers in Irganox 1010 and Irganox 1076, which are widely used in GMs (Farcas et al., 2014).
The presence in the HDPE GM FTIR-ATR spectrum of the 2915, 2847, and 1472–1463 cm^{-1} absorption bands of ethyl groups, the 720 cm^{-1} absorption of hydrocarbon chains with more than four ethylene groups, and the absence of the CH_3 absorption at 1375 cm^{-1} is consistent with polyethylene-type polymer. Band splitting is due to crystalline phases of the polymer (Nishikida and Coates, 2003). No additional bands are present to indicate additive compounds (Farcas et al., 2014).

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

Following this, various spectroscopic (Bart, 2003; Crompton et al., 2007; Farcas et al., 2012) and chromatographic techniques (Dopico Garcia et al., 2003; Sanches Silva et al., 2006; Djouani et al., 2012) may be applied to characterize the AOs extracted from the plastics. In the FTIR-ATR spectra of CH_2Cl_2 GM extraction solutions, absorption bands appear at 3365, 1742, and 1151 cm^{-1}, which is characteristic of OH alcohol bonds, ester C=O bonds, and phenolic tertiary alcohol C–O bonds, thereby confirming the presence of phenolic AOs in HDPE and PP GMs (Farcas et al., 2014).

The UV absorbance spectra of CH_2Cl_2 extraction solution reveals absorption from chromophore groups at 276 nm for HDPE (Fig. 1a) and 276 and 280 nm for PP (Fig. 1b). Comparing these with model AO UV absorptions indicate that the measured absorption bands correspond to phenolic and/or phosphite stabilizers, although the extraction of Irganox 1010 or 1076 and Irgafos 168 from the GMs cannot be asserted with certainty. The spectrum of a solution containing a mix of compounds differs from the spectrum of the pure compounds.

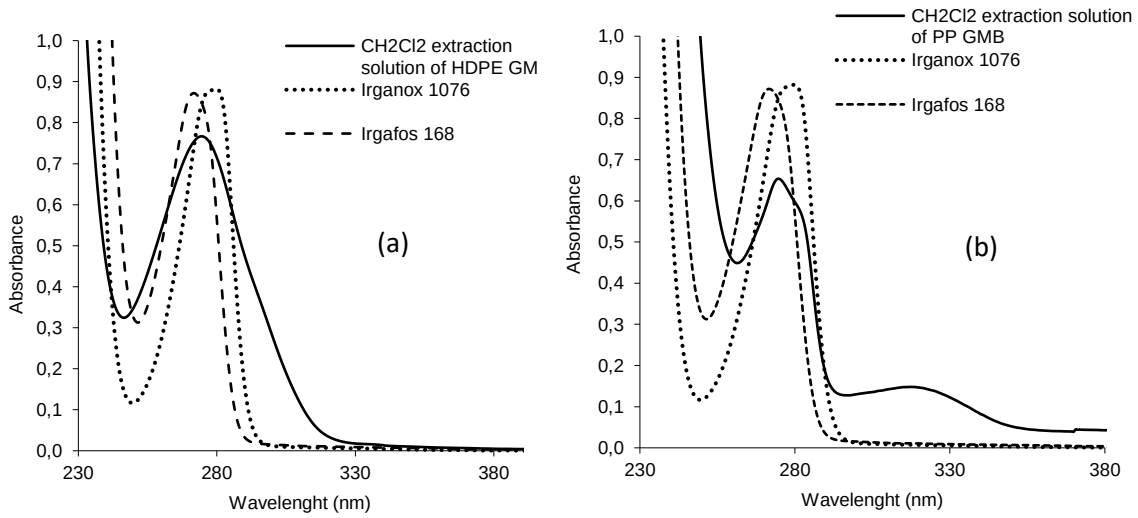

Figure 1: Ultraviolet absorbance spectrum of CH_2Cl_2 extraction solutions of (a) HDPE GM, (b) PP GM, revealing the presence of Irganox 1010 and Irgafos 168 in CH_2Cl_2.

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

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

The presence of additional chromatographic peaks in both cases indicates that other compounds are also extracted from GMs by CH_2Cl_2. However, these compounds are not identified.

3- 3- Analysis of extraction solutions

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

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

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

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

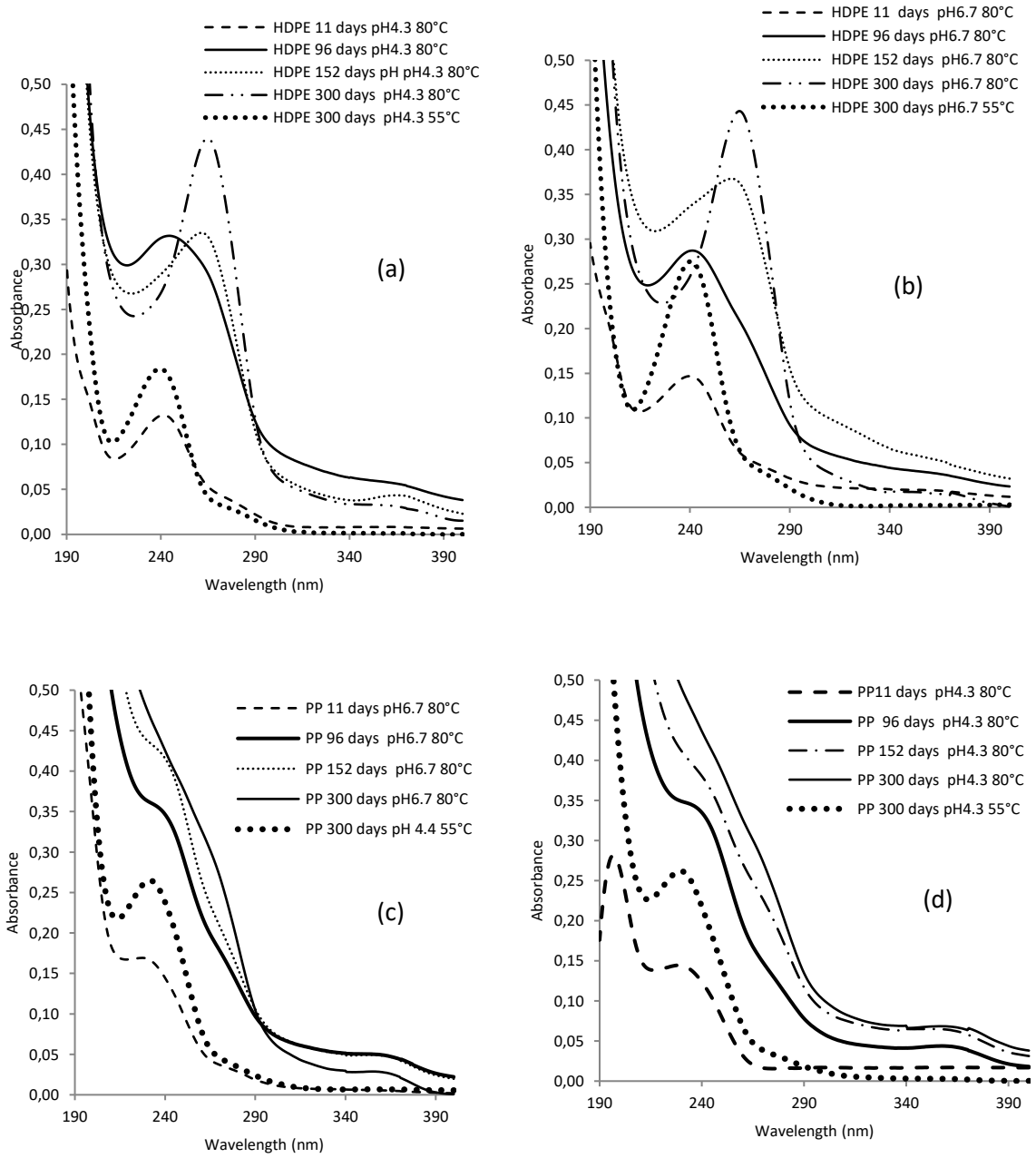

Figure 2: Ultraviolet absorbance spectra of pH (a,c) 6.7 and (b,d) 4.3 extraction *solution containing the HDPE GM (a,b) PP GM (c,d) at 80 and 55 °C.*

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

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

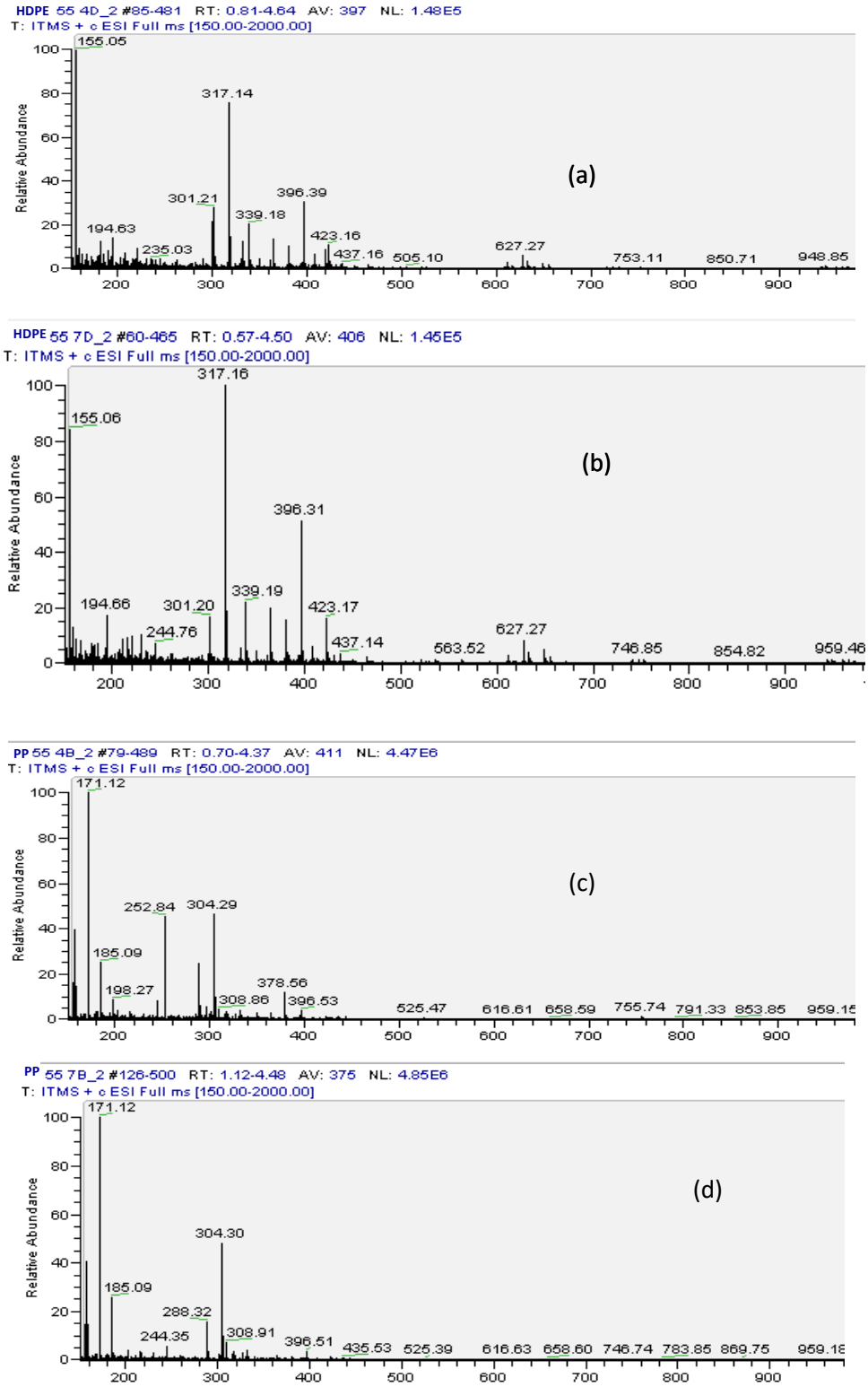

Figure 3: Mass spectra of extraction solution containing immersed HDPE GM (a,b) and PP GM (c,d) at pH (a,c) 4.3 and (b,d) 6.7 maintained at 55 °C for 300 days.

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

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

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

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

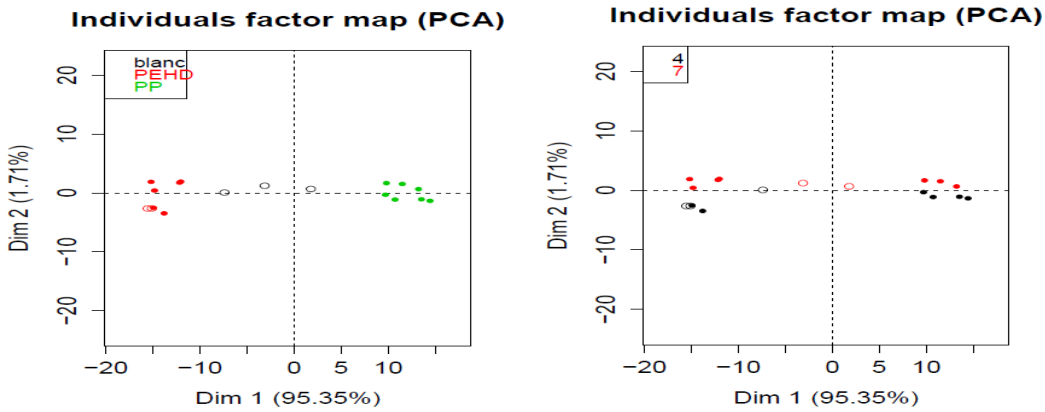

Figure 4: Principle component analysis of direct-injection mass spectrometry results of HDPE and PP immersion samples maintained at 55 °C for 300 days.

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

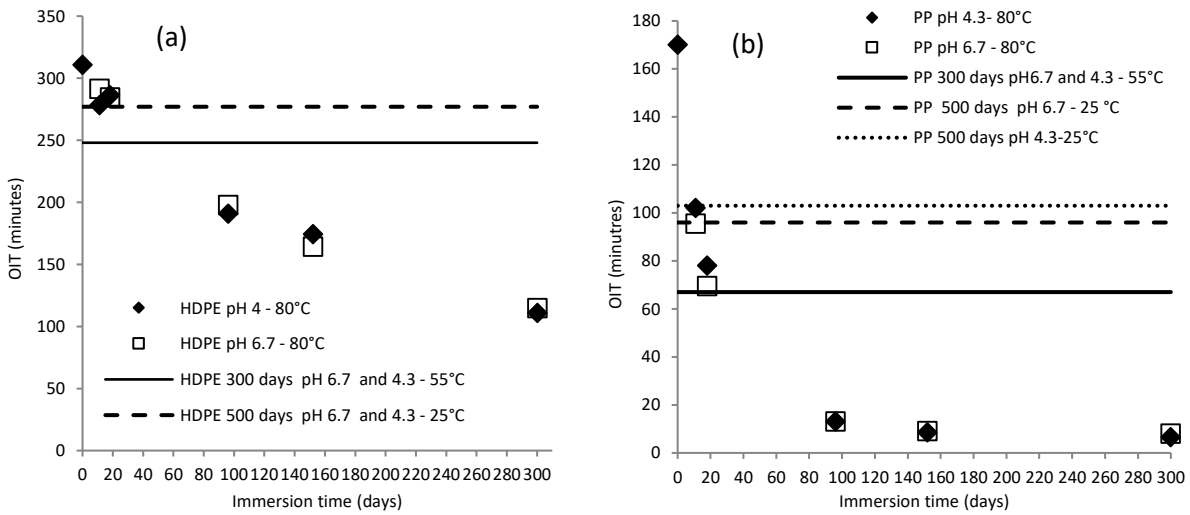

Figure 5: Oxidation-induction time of (a) HDPE and (b) PP GMs after pH 4 and 6.7at 80°C and 55°C.

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

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

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

3.4 Impact of immersion solutions on aquatic ecosystems

3.4.1- Impact on micro-algae

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

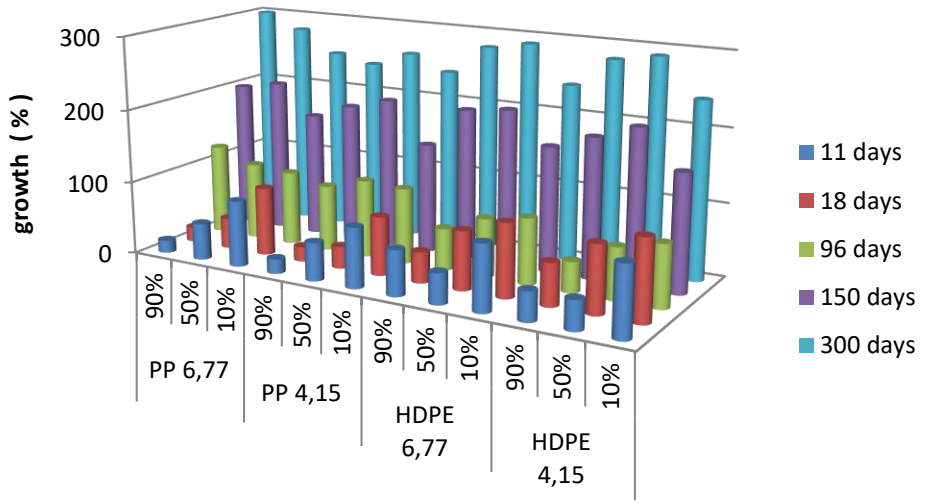

Figure 6: Growth of Chlorella vulgaris inoculated during 72 h in different dilutions (90%, 50%, 10%) of extraction solutions. These assays were done on pH 6.77 and 4.15 solutions in which PP and HDPE GMs were immersed for 11, 18, 96, 150, and 300 days.

3.4.2- Effect on microcrustaceans

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

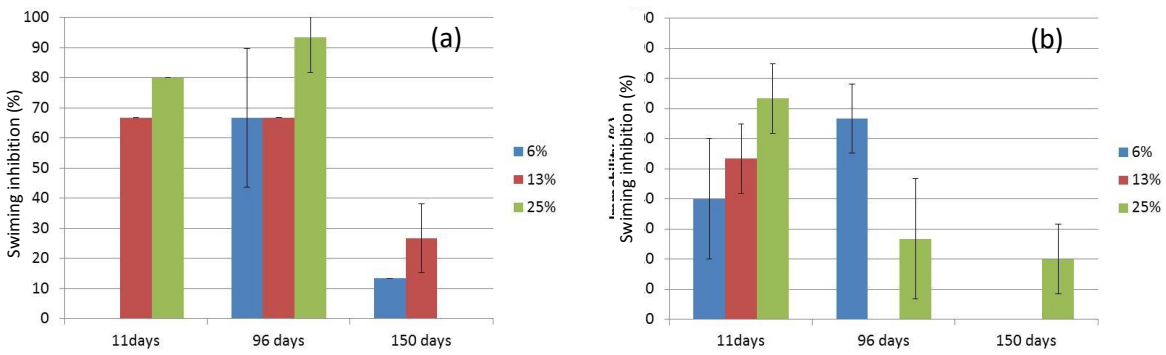

Figure 7: Swimming inhibition on Daphnia sp. of PP (a) and HDPE (a) solutions maintained at 80°C for 11, 96, and 150 days.

3.4.3 Global impact on aquatic environment

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

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

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

Conclusion

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

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

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

Acknowledgments:

This project was funded by the French national project Ecosphère Continentale et Cotière (EC2CO)

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