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1 **Identification of plastic additives: Py/TD-GC-HRMS method**
2 **development and application on food containers.**

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Highlights

- A single method for the analysis of OPAs using Py/TD-GC-HRMS has been implemented
- The developed method allowed to create a plastic additive database
- 49 additives molecules out of the selected 57 have been successfully identified
- 10 plastic additives were found in PP and PLA food packaging

13 **Abstract**

14 The interest of studying organic plastic additives (OPAs) is growing since many of them
15 are considered as toxic for human beings, marine organisms and have been found in
16 the ecosystem. The impact and the extent of this pollution is not fully understood
17 because of the lack of methods able to comprehensively analyze the wide diversity of
18 OPAs. This study aims at offering a quick and efficient way to identify specific harmful
19 plastic additives in polymer materials. For this purpose, a general method, for
20 identifying 49 OPAs, has been successfully developed using pyrolyzer/thermal
21 desorption-gas chromatography coupled to a high-resolution mass spectrometer
22 (Py/TD-GC-HRMS). The retention indices were calculated for each compound and a
23 high-resolution mass spectra database for plastic additives was implemented. This
24 method was then applied to characterize the OPAs included in food containers that are
25 frequently found in the environment. Four samples made of polypropylene (PP) and
26 polylactic acid (PLA) coming from two distinct suppliers were then selected. A total of
27 10 additives, which were plasticizers (phthalates and adipates), antioxidants
28 (bisphenol B) and phosphorous flames retardants, were found in these food packaging.
29 Generally, higher peak signals were detected in the PP samples in comparison to PLA
30 samples, except for tributyl phosphate and bisphenol B that were exclusively found in
31 PLA samples. Moreover, the experimentations pointed out additives differences
32 between suppliers, for products intended for the same use and made of the same
33 polymer, for both PP and PLA samples highlighting the complexity of identifying and
34 generalizing the additive content of plastic materials.

35 **Keywords:** Phosphorous flame-retardants, Plasticizers, antioxidants, UV stabilizers,
36 Py/TD-GC-HRMS, analytical method development.

1. Introduction

Plastic pollution is a threat for the environment and marine organisms [1]. The presence of plastics is ubiquitous in the environment. In 2020, plastic production reached 307 million metric tons worldwide [2], of which 24% were used for food and beverages packaging [3]. These items are in the top ten of the most common plastic waste found in the environment [4].

A key concern of plastic pollution is linked to the risks to both ecosystem and human health. These adverse effects classified in several categories including the “physical” effects related to the inhalation and ingestion of plastic debris and the “chemical” effects related to the harmful chemicals associated with plastics such as the organic plastic additives (OPAs) included in the polymer [5,6]. While the “physical” impacts of plastics are well described in the literature, the “chemical” impacts, partly related to the presence of OPAs, is less documented and limited information is available for the majority of them. Several categories and families of OPAs exist, sorted by decreasing total amounts in polymers: plasticizers, flame retardants, colorants, antioxidants, heat stabilizers, UV stabilizers or bio-stabilizers (biocides), lubricants, foaming agents, and antistatic agents. These chemicals are added to polymers during their formulation, without being chemically bound to polymers [7], in order to confer them specific properties and advantages. However, there are increasing concerns about their impacts on marine organisms or human health since some of them were found to be toxic [7]. Indeed some phthalates, nonylphenols (NPs), Bisphenols, as well as some brominated flames retardants (BFRs) have been identified as carcinogens, mutagens and may have detrimental impacts on the reproduction being endocrine disrupting chemicals [1,8-11]. As most of the OPAs are not chemically bound to the polymeric matrix, they can leach into the surrounding environment or can be transferred to marine organisms or humans upon plastic debris uptake [5,12-14]. Additionally, OPAs may migrate from the packaging leading to contamination of the food packed [15-18]. As a result, the use of OPAs in plastics has become controversial and the assessment of their nature and toxicity is of utmost importance.

A considerable number (more than 5300) of polymer formulations are available on the market, and more than 4000 known chemicals are used in the formulation of plastic packaging, i.e. intentionally added substances (IAS). Additionally, plastic packaging may contain non-intentionally added substances (NIAS) [19,20]. That demonstrates the chemical complexity of plastic polymers. The identity of most IAS and NIAS are unknown making difficult to assess the safety of plastic materials, especially in regards with food contact materials (FCM). In order to broaden understanding of the chemical impact of these additives, it is necessary to have a more-detailed assessment of plastic packaging associated chemicals. This involves the development of robust analytical method to identify and quantify them. The analysis of OPAs in polymers is an analytical challenge because of the wide array of their chemical compositions

73 and the diversity of the molecules mixed within a polymer. Also, the most frequently used
74 processes, e.g. solvent extraction (SE), present constraints. These methods are time
75 consuming for the sample preparation, generate wastes and involve the use of toxic solvents.
76 Besides, there is no universal solvent able to dissolve all types of polymers [21-24]. Under
77 such circumstances, the need of avoiding the complexity of analytical processes is of concern.
78 Pyrolysis coupled to a gas chromatography and a mass spectrometry (Py-GC-MS) is an
79 analytical tool that enables relatively quick and easy analyses [25]. Moreover, this technique
80 minimizes the sample preparation steps, limiting the potential contamination prior to the
81 analysis and does not require the use of toxic solvents [21,26-28]. Analytical pyrolysis also
82 offers a major advantage. It permit to successively analyze both the OPAs and the polymer
83 with a multi-step approach including an initial thermal desorption (TD) step at sub pyrolytic
84 temperatures (i.e. approximately <500 °C) to characterize the additives regardless of the
85 polymer, and a second pyrolysis step at higher temperatures (i.e. >500 °C) to analyze the
86 polymeric matrix [29-31]. Py-GC-MS has already been reported as beneficial to thermally
87 desorb and screen plastic additives in several studies using pyrolyzer/thermal desorption
88 (Py/TD) GC-MS methods [32-34] and is a recognized method for the fast identification of
89 OPAs. Akoueson et al., (2021) review, listed a wide array of OPAs studied using Py and Py/TD-
90 GC-MS [25]. However all the developed methods focused on few analytes from a type of
91 additives. No general method exists to analyze a wider diversity of additives. Thus, we aimed
92 to develop a TD method able to identify diverse harmful, emergent, or widely used OPAs.

93 The objectives of the present study are: (i) set up a high-resolution Mass spectral library which
94 includes a selection of OPAs used as plasticizers, flame retardants, antioxidants and
95 stabilizers, (ii) implement a general analytical method using Py/TD-GC-HRMS to identify and
96 detect the selected plastic additives, and (iii) apply the method to several items of food
97 packaging materials in order to characterize their OPAs content.

98 **2. Materials and methods**

99 **2.1. Implementation of a general GC-HRMS method for OPAs** 100 **detection**

101 **2.1.1. Targeted additives, reagents and preparation of the samples**

102 According to different criteria, detailed in part 3.1, 56 additives were selected. The additives
103 and their corresponding suppliers are listed in Table 1. A standard mixed solution of C₃–C₃₃ n-
104 alkanes (Cat. No. 40147-U) was purchased from RESTEK (Lisses, France). Analytical GC
105 grade solvents were used such as methanol, acetone, toluene or acetonitrile and were all
106 purchased from Sigma-Aldrich Co. (Saint-Quentin-Fallavier, France).

107 Diluted solutions of each additives stock solutions were prepared in suitable solvents at
108 concentrations ranging from 0.05 to 100 mg.L⁻¹. The diluted solutions were then transferred
109 and conserved in 2 mL GC autosampler vials with a PTFE coated seal. An aliquot of 1 µL of
110 each additive solution was injected in the GC-HRMS using a microliter syringe at increasing
111 concentrations (0.12, 0.25, 0.5, 1, 2.5 and 5 mg.L⁻¹) until visualization of the limit of detection
112 additives when the signal to noise (s/n) was > 3. For the mixed n-alkanes, 1 µL of the 10 mg.L⁻¹
113 solution was also injected.

114 **2.1.2. GC-HRMS method and parameter settings**

115 Samples were analysed using a GC Trace 1310-MS Orbitrap Q-exactive from ThermoFisher
116 Scientific (Les Ulis, France) equipped with a TriPlus RSH auto-sampler. The compounds in
117 standard solutions were separated on a 30 m × 0.25 mm × 0.25 µm RXi-5ms capillary column
118 acquired from Restek (Lisses, France). The injection volume was 1 µL.

119 Based on the literature, several methods (Supplementary data S1) were compiled in order to
120 propose a compromise, i.e. a general method suitable for the 56 selected additives, being
121 aware of its limitations regarding the analysis sensitivity for each additive.

122 Analytical conditions are detailed in Table 2.

123 Chromatograms were analyzed using Thermo Scientific Xcalibur software (4.3.73.11) and with
124 the help of an automated search for the markers by deconvolution using TraceFinder™
125 software (5.0.889.0). The identity of the additives was confirmed using target and confirming
126 ions obtained from the literature [35-40] and the National Institute of Standards and Technology
127 (NIST) Database.

128 **2.1.3. Construction of the database**

129 Following the acquisition, and after obtaining robust chromatograms signals for all the
130 analytes, a database containing mass spectra for all the detected additives was implemented
131 using TraceFinder software including quantitative and qualitative ions for each molecule, as
132 specific as possible. The HRMS files are available on Zenodo [41].

133 Following the analysis of the standard additives solutions and the mixed *n*-alkane solution, the
134 retention time (RT) of the additive analytes and the *n*-alkanes were used to calculate the
135 Kováts retention indices (RI) following equation (1). Respective RI were calculated [42] and
136 registered in the database. The RI were validated when the calculated values were in the range
137 of RI values found in the literature.

$$138 \quad RI = 100 \times (C_{n+1} - C_n) \times \left[\frac{(t_x - t_n)}{(t_{n+1} - t_n)} \right] + 100 \times C_n \quad (1)$$

139 With the carbon numbers of *n*-alkanes eluted before (C_n) and after (C_{n+1}) the corresponding
140 target molecule, retention time of the target molecule expressed in min (t_x) and retention times
141 for C_n (t_n) and C_{n+1} (t_{n+1}) for the flanking *n*-alkanes expressed in min.

142
143 The RI and the specific qualitative and quantitative ions are gathered for each additive in
144 Table 3.

145 **2.2. Thermodesorption method development for the detection of** 146 **OPAs using Py/TD-GC-HRMS**

147 A TD step using a Pyrolyser, CDS Analytical Pyroprobe 6150 from Quad Service (Oxford, PA
148 US), was added to the GC-HRMS developed method.

149 **2.2.1. Sample preparation optimization**

150 Four protocols of sample preparation (Supplementary data S2) were previously tested in order
151 to ease the analytical process and to reduce the high volatility of several low molecular weight
152 additives. Briefly, the analysis of the selected plastic additives have been done by introducing
153 1 μL of the additives stock solutions at concentrations ranging from 5 to 100 $\text{mg}\cdot\text{L}^{-1}$. The
154 solutions were either added in an empty pyrolysis quartz tube or in a pyrolysis quartz tube
155 containing three types of different materials used as “solution trapping matrix” such as a piece
156 of quartz filter, a piece of quartz wool or a small amount of diatomaceous earth (silicium
157 dioxide). These media were selected for their documented chemically inert features and their
158 thermal resistance [43,44]. In brief, considering the results (S2), the quartz filter was chosen
159 as a suitable « trapping matrix » since it permit to stabilize the compounds despite the waiting
160 time between the sample preparation and the analysis

161 **2.2.2. Implementation of a general method using Py/TD-GC-HRMS device**

162 The analyses were carried out using a Pyrolyser CDS Analytical Pyroprobe 6150 from Quad
163 Service (Oxford, PA US) coupled to a GC-HRMS device (Trace 1310-MS Orbitrap Q-exactive,
164 ThermoFisher Scientific) thanks to a heated transfer line with the method presented in part
165 2.1.2.

166 According to the preliminary results obtained following the sample preparation optimization
167 tests presented part 2.2.1., 1 μL of the additives standard solutions was introduced in a
168 pyrolysis quartz tube containing a piece of quartz filter. The pyrolysis quartz tube and the quartz
169 filter were both heated beforehand at 1000 °C during 15 seconds to get rid of any residual
170 compounds. Sample tubes were then placed in the pyrolyzer auto-sampler and analysis was
171 performed. Selection of the thermal desorption temperature was carried out on the additives
172 standard solutions by testing three desorption temperatures: 250 °C, 350 °C and 450 °C, with

173 three replicates. The TD time was fixed at 60 seconds based on the literature, being the most
174 frequently used TD time (Table S1).

175 To ensure the reliability of the results and the absence of contamination in the analytical device
176 two precautions were taken for each batch: (i) a 1000 °C auto-clean of the pyrolysis chamber
177 during 15 seconds between each analysis; (ii) and five empty pyrolysis quartz tube without
178 sample, hereafter referred as “blank”, were pyrolyzed at the beginning of each run.

179 **2.3. Application: OPAs identification in food contact materials**

180 **2.3.1. Sample selection and preparation**

181 Two types of food packaging items made of polypropylene (PP) and polylactic acid (PLA),
182 coming from two different suppliers, tagged with either A or B, have been selected. The
183 selection of PP was based on its high production and high presence in the marine environment
184 [3,19]. The PLA was selected for being the most used bio-based alternative in order to compare
185 its additive content to a petro-based polymer [45].

186 Punches, i.e. cylinders of 1 mm diameter, were cut in the food packaging items using biopsy
187 punches from Farla-Medical (Antwerpen, Belgium), in order to have a homogeneous sample
188 taking process. Thickness of the cylinders was measured using a binocular microscope
189 (Olympus SZX16) and OLYMPYS cellSens Dimension 3.2 software (n=3). The volumes and
190 the masses (μg) of each particle were calculated using the diameters and the thickness
191 measurements. The cylinders were then introduced in pyrolysis sample cups. Sample tubes
192 were placed in the pyrolyzer auto-sampler and analysis was performed (n=3).

193 **2.3.2. Py/TD-GC-HRMS analyses**

194 In order to thermally desorb the additives contained in the samples, each cylinder was
195 successively analyzed three times at a thermal desorption temperature of 350 °C to maximize
196 the extraction of the chemicals present in the samples. An approximation of the extraction
197 efficiency percentage (%) was calculated dividing the area recorded at the first step by the total
198 area over the three steps.

199 All analyses were carried out using the method previously developed and presented part 2.1.2.

200 The selected OPAs (Table 1) were identified on the basis of the RT, RI, quantitative and
201 qualitative ions and ions ratios with the help of the previously implemented database. The
202 obtained signals were corrected taking in account the procedural blanks, i.e., pyrolysis tubes
203 without sample, the calculated mass of the samples and the extraction efficiency of the method.

2.4. Statistical analysis

All statistical analyses were performed using R-Studio software (1.4.1106) [46]. For all the analysis, the normality and the homoscedasticity of the distribution were verified before carrying out ANOVA follow by Tuckey post Hoc test (adding the car package (3.0-12) [47]). Assuming that one of the hypothesis was not verified, a non-parametric Kruskal-Wallis test was performed. Kruskal Wallis tests were followed by a Nemejni's post hoc test. Post hoc tests were achieved using agricolae (1.3-5) [48] and PMCMR (4.4) [49] packages. Mean differences were considered as significant when p-value < 0.05.

3. Results and discussion

3.1. Preliminary work and implementation of a HR mass spectra database

A total of 56 additives were selected as relevant compounds. This selection was based on a bibliographic work including previous publications, the European Food Safety Authority's (EFSA) list containing their evaluation on substances for FCM and the European chemical agency's (ECHA) additives list containing 400 substances imported in the European Union that are used in plastic products with a trade volume higher than 100 ton/year (Table 1) [1,7,23,25,26,34,45,50-55]. This bibliographic work was performed based on different priority criteria such as: the use of additives in plastic and plastic packaging, a balance between their toxicity and their concentration in polymers, the environment and marine organisms, and finally, the feasibility of GC-MS analysis on these additives.

A standard solution containing all targeted compounds was prepared to set up a suitable GC-HRMS method for their simultaneous analysis. This preliminary work was carried out using GC-HRMS with the method presented part 2.1.2 and allowed the detection of all the selected additives (Figure 1). The spectra of each additives peaks in figure 1 permitted the implementation of our own plastic additives database [41].

The identification of the additives not already included in NIST database was confirmed by the presence of their respective quantitative and qualitative characteristic ions presented in table 3. An additional confirmation for this set of additives has been made using Kováts RI (Table 3).

In this work, as the analytes were partly selected on their amenability to GC-MS analysis, some additives known to be toxic and widely used in plastic materials (e.g. Tetrabromobisphenol A and the hexabromocyclododecane isomers (α , β and γ -HBCD)) were not targeted. Indeed, depending on their chemical nature, certain OPAs may be complex to analyze and are hard to mobilize [34]. These analytical limitations can be overcome with a derivatization step that will

238 modify the sample and product more volatile derivative [56]. It was not employed in the present
239 study, which consisted to implement a fast and easy method. However, using a derivatization
240 approach or leading analysis using liquid extraction could be complementary to have a more
241 complete analysis.

242 **3.2. Optimization and characterization of a Py/TD-GC-HRMS method** 243 **for the detection of OPAs**

244 Three temperatures were tested at this step: 250 °C, 350 °C and 450 °C. The pyrolyzer thermal
245 desorption temperature had a significant impact on the peaks area of several additives. Figure
246 2 illustrates the relevant temperature patterns for each additive families. The detailed results
247 for each additive are presented in supplementary data S3.

248 The areas of most flame-retardants (9 out of 14) showed no significant difference between the
249 three tested temperatures. Areas were significantly higher at 350 °C for three additives (TCEP,
250 TCPP and TDCPP), whereas the area of the 2,4,6-TBP and BTBPE were significantly higher
251 respectively at 250 °C and 450 °C. The analysis of the plasticizers additives indicates
252 significantly higher areas at 350 °C for 13 additives (BBP, DBP, DCHP, DEHP, DEP, DHP,
253 DIBP, DIDP, DIHP, DINCH, DNOP, DNP, DOA) out of 16, and at 450 °C for the ATBC. No
254 significant difference has been detected for three additives between the three tested
255 temperatures (DAP, DIHP and DMP). Concerning the antioxidants, areas were significantly
256 higher at 450 °C for six additives (NPs, 4-NP, NP10E, 4NP10E and Irganox 1081®), at 350°C
257 for the Lowinox TBM 8® and at 250 °C for the 4-t-OP. Five additives showed no significant
258 difference between the tested temperatures. Finally, no significant difference was observed for
259 the three UV stabilizers.

260 Overall, based on these results, 350 °C seems to be the more relevant thermal desorption
261 temperature for the analysis of the selected additives, either being significantly optimal or
262 because no significant differences has been observed between the three temperatures. In line
263 with our results, other studies generally used a thermal desorption temperature of 350 °C
264 [25,27,52]. Moreover, the temperature is one of the key factors for a successful extraction and
265 subsequent detection [27]. Indeed, it affects the degree of fragmentation and the generated
266 pyrolysis products, its selection must allow a suitable desorption of the additive without altering
267 it. At too high temperatures, usually above 500 °C, the polymeric matrix begins to degrade and
268 the excess of polymer fragments interfere with the identification of characteristic additive
269 fragments, which make the analysis of the results complicated [21] and may lead to
270 misinterpretation of the results.

271 The Py/TD-GC-HRMS method was used to analyze 56 additives at various concentration
272 levels (1, 5, 10, 25, 50 and 100 mg.L⁻¹). Eight additives, marked with “*” in the Table 1, were

273 not detected even when the highest concentration was injected in the pyrolyzer. Among them,
274 three phosphorous flame-retardants (TCP, TCrP and TToP), two plasticizers (bisphenol S and
275 TEHPA), two UV stabilizers (Uvinul 3049[®] and 3008[®]) and one antioxidant (NP2OE). The 49
276 additives identified have been detected at 5 ng except for the BDEs, the alkylphenols and the
277 Irganox 1081[®] at 10 ng; for DIDP, DINP, DIHP and the BTBPE at 25 ng; for Lowinox TBM 6[®]
278 at 50 ng; and for the Irganox 1076[®] with a detection threshold at 100 ng (Table 1).

279 A previous study [53] mentioned the complicated analysis of phosphorous flame-retardants.
280 Indeed, some analytes are more difficult to analyze than others using Py/TD-GC-HRMS
281 according to their physico-chemical properties [25]. For instance, TEHPA and Uvinul 3008[®]
282 start to decompose at a temperature of 250°C and 350°C respectively, unlike BPS that has a
283 low volatility and is more thermally stable than its bisphenol's analogs [57].

284 Increasing the thermal desorption temperature might help to volatilize the most stable
285 additives, such as the BPS. Nonetheless, the temperatures selected in the study did not permit
286 the desorption of the BPS. Other studies managed to analyze this molecule, for instance
287 Becerra and Odermatt (2012) conducted their analysis with a temperature of 500 °C and added
288 derivatizing agents using trimethyl ammonium hydroxide (TMAH), to increase the volatility of
289 the additive [58]. However, in the present study, it was a thoughtful choice not to derivatize the
290 samples, since the aim was to implement a quick method with minimal sample preparation
291 steps. Some polymers, such as polystyrene (PS) or polyvinyl chloride (PVC), start to
292 decompose at relatively low temperatures [21]. These limitations explain the selection of a
293 method that does not permit the analysis of all additives.

294 **3.3. Application of the method on plastic food packaging**

295 3.3.1. Integration of samples mass variability

296 The masses (μg) of each sample cylinders were calculated using their diameter and thickness
297 as well as the density of each polymer type. The average calculated mass of PP-B, i.e. 203
298 μg , is significantly different ($p\text{-value} < 0.05$) from the three other samples, i.e. 338 μg , 317 μg
299 and 276 μg respectively for PP-A, PLA-B and PLA-A. Moreover, a high standard deviation (sd)
300 is noticed especially for PLA-B sample and can be explain by thickness variations according
301 to the location where the sample was cut out on the plastic container (supplementary data S4).
302 In that respect, the respective masses of each analyzed food packaging cylinders were taken
303 into account in order to normalize the additives signal measured in each sample.

304 3.3.2. Efficiency characterization

305 The method was developed on additives standard solutions. However, once additives are
306 included in a polymeric matrix, some interactions can occur between the additives and the
307 matrix [21]. Hence, the extraction efficiency of the method was directly calculated on the

308 matrices of interest, i.e. following the analysis of PP and PLA food packaging samples, in order
309 to take into account the potential interactions.

310 Each sample were submitted to three successive heating at a thermal desorption temperature
311 of 350 °C. No additive was detected during the third analysis, indicating that the entirety of the
312 additive included in the samples has been desorbed and analyzed during the first or second
313 pyrolysis step (supplementary data S5). Consequently, the sum of the areas obtained during
314 the two first analysis steps is considered as representing 100% of the additives amount
315 included in each sample. The extraction efficiency percentage of each step was therefore
316 calculated based on this assumption.

317 The results of the extraction efficiency after a first step of desorption were more than 80% for
318 most compounds (Table 4, bold printed characters), with a few exceptions. Five additives
319 required a total of two desorption steps to be fully extracted from the samples, e.g. DMP, DEP
320 (for PP samples), DEHA (PP-A), TBP (PLA-A and PP-A) and TCPP, with average extraction
321 efficiency percentages ranging from 50 to 80% or <50% upon the first desorption step (Table
322 4). Carrying out two desorption steps doubles the time of the analysis. For this reason, the
323 developed method only includes one thermal desorption step at 350 °C. The average
324 extraction efficiency percentages of each additive for each sample were taken into account in
325 order to correct the additives signal recorded. However, care must be taken about the
326 completeness of the extraction with this TD method. Although the punch is thin and the cross-
327 section expose the core of the material. It can also be assumed that only the additives on the
328 first layers of the punch could have been desorbed.

329 3.3.3. Identification of the selected OPAs in PP and PLA food packaging samples

330 The additives amounts detected in the food packaging samples are expressed in Area
331 (Arbitrary unit (A.U)) per µg of plastic. The values were corrected with the extraction efficiency
332 percentage and the calculated mass of each particle analyzed.

333 Ten OPAs of interest have been detected in the selected food packaging samples (Figure 3),
334 mostly plasticizers (eight molecules) and flames retardants (two molecules). Two plasticizers,
335 DEP and DIBP and a phosphorous flame retardant, TCPP, have been detected in all samples
336 regardless of the supplier or polymer type. DMP and DBP plasticizers have been identified in
337 all the samples except PLA-A, and DCHP was identified in all the samples except PP-B.
338 Finally, the plasticizer DINP has only been detected in the two PP samples and Bisphenol B
339 exclusively in the two PLA samples. TBP, a phosphorous flame retardant, has been identified
340 both in PP-A and PLA-B only.

341 The area of DCHP is equivalent among all samples regardless of the supplier or polymer type.
342 Overall, peaks areas for a majority of the OPAs are higher for the PP samples than for the PLA

343 (six out of ten; Figure 3). DBP and DEP peak areas are significantly higher in PP-A samples
344 than in PLA-A and B samples. The areas of DEHA, DIBP, DINP and TCPP in both PP samples
345 are significantly higher than in PLA samples. On the other hand, the peak area of the
346 phosphorous flame retardant TBP is significantly higher in the PLA-A than in both PP samples.

347 Looking at the differences between PLA-A and B (Figure 3), the PLA-B contains more additives
348 than the PLA-A. Nine OPAs were identified in the PLA-B, including seven plasticizers (BPB,
349 DBP, DCHP, DEHA, DEP, DIBP and DMP) and two flames retardants (TBP and TCPP), while
350 only seven OPAs were identified in the PLA-A in which the DEHA and DMP have not been
351 detected. In addition, a trend appears that the areas of the OPAs peaks found in PLA-B are
352 mostly higher than those found in the PLA-A, except for the DCHP where the areas are
353 identical. This trend is significant for the Bisphenol B (15 times higher in PLA-B) and the DEHA
354 (absent in the PLA-A while detected in the PLA-B). The same pattern is observed when looking
355 at the PP-A and B samples results (Figure 3). The PP-A contains two additives more than the
356 PP-B. Nine OPAs have been detected in the PP-A, including seven plasticizers (DBP, DCHP,
357 DEHA, DEP, DIBP, DINP and DMP) and two flames retardants (TBP and TCPP), while the
358 PP-B sample only contains seven OPAs (DCHP and TBP missing). The peaks areas of the
359 OPAs identified in the PP-A samples tends to be higher than in the PP-B. It is significant for
360 the DBP (three times higher in PP-A), the DEHA (8x), the DIBP (x1.5), DMP (x2) and TCPP
361 (x4).

362 However, regarding DEP and DIBP (respectively for PLA and PP, and for PLA only), it is
363 difficult to draw conclusions. Indeed, a large spread in the data can be observed as these
364 additives show a wide 95% confidence interval (IC 95 %). This dispersion can be explained by
365 a lack of homogeneity in the distribution of additives within the same sample. This would then
366 require the multiplication of replicates to be able to take these disparities into account.

367 These results lead to a few remarks:

368 First, a petro-based vs bio-based difference. For all analyzed sample, the majority of the OPAs
369 identified were plasticizers. Indeed, during the formulation of plastic materials, OPAs are added
370 at different proportions depending on the polymer and its usage. Most of the time, plasticizers
371 are used extensively, reaching up 60% weight/weight (w/w) [59]. Here, the same number of
372 additives detected in both PLA and PP materials (10 OPAs each) confirms that “bio-based” do
373 not pledge “additives free”. Overall, lower amounts (Area (A.U)/mass (μg)) of additives were
374 noticed in PLA samples (except BPB, DCHP and TBP), while, surprisingly, bisphenol B, a toxic
375 endocrine disruptor analogue of the bisphenol A [10], has only been detected in PLA samples.
376 Zimmerman et al., [19,60] tested the *in-vitro* toxicity and the chemical content of many bio-
377 based materials (PLA items used as FCM). Their study detected priority concern compounds

378 (such as additives, oligomers, along with non-intentional added substances (NIAS)) and
379 highlighted that bio-based materials are not safer than conventional plastics regarding their
380 chemicals content.

381 Secondly, an inter-suppliers difference. This study underlined non-negligible differences on the
382 identification of OPAs in two food-packaging products manufactured with the same polymer
383 and that are intended to have the same use. That reflects the complexity to generalize and
384 estimate the potentially dangerous additives in the studied material and thus the exposition of
385 marine organisms and consumer, since the chemical composition of a material don't seem to
386 be related to the polymer type but to each individual product. This match the conclusion of
387 Zimmermann, et al. [61] that investigated the toxicity and the chemical composition of several
388 plastic leachates made of conventional in PLA sample including FCM. They ended up with that
389 same conclusion being that the contaminant content and the toxicity cannot be generalized
390 based on the polymer type and are product specific. Plastic products formulation is different
391 depending on the manufacturers, and may explain this difference in additives types and
392 additives abundances between products made with the same polymer. It underlines the need
393 of identifying the chemical content and the chemical safety of each material rather than
394 polymers types, which is not a straightforward task but is inevitable considering the disparity
395 in plastic formulation of the commercially available products. Moreover, the formulation's
396 recipes remain unknown from the scientific community and hinder the evaluation of potential
397 impacts and toxicity of plastic materials.

398 **4. Conclusion**

399 This study was conducted with the aim to set up a suitable Py/TD-GC–HRMS method for
400 simultaneous identification of various selected organic additives and to set up a high-resolution
401 spectral database. The developed method showed its ability to detect the majority of the
402 targeted additives. Nevertheless, this method may be limiting for certain OPAs harder to
403 mobilize using GC. In complement, a liquid extraction analysis would provide more
404 comprehensive results. Ten additives were detected in PP and PLA food contact materials.
405 The results indicate the presence of multiples additives, some of them being toxic, in both
406 petro-based and bio-based food packaging samples (e.g. plasticizers, phosphorous flames
407 retardants). Moreover, significant differences were pointed out depending on either the
408 polymer type or the suppliers. The present study highlights the complexity to assess and
409 generalize the additive content and their amount in plastic packaging items due the variety and
410 differences in plastic formulation.

411 **5. Declaration of competing interest**

412 Authors do not declare any competing interest.

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422 **F. Akoueson**: Conceptualization, Investigation, Methodology, Formal analysis, Software,
423 Validation, Visualization, Writing - original draft, Writing - review & editing. **C. Chbib**:
424 Methodology Investigation, Writing - review & editing. **A. Brémard**: Investigation, Formal
425 analysis. **S. Monchy**: Writing - review & editing. **I. Paul-Pont**: Writing - review & editing. **P.**
426 **Doyen**: Writing - review & editing. **A. Dehaut**: Conceptualization, Funding acquisition,
427 Supervision, Project administration, Writing - review & editing. **G. Duflos**: Resources,
428 Conceptualization, Funding acquisition, Supervision, Project administration, Writing - review &
429 editing.

430 **8. REFERENCES**

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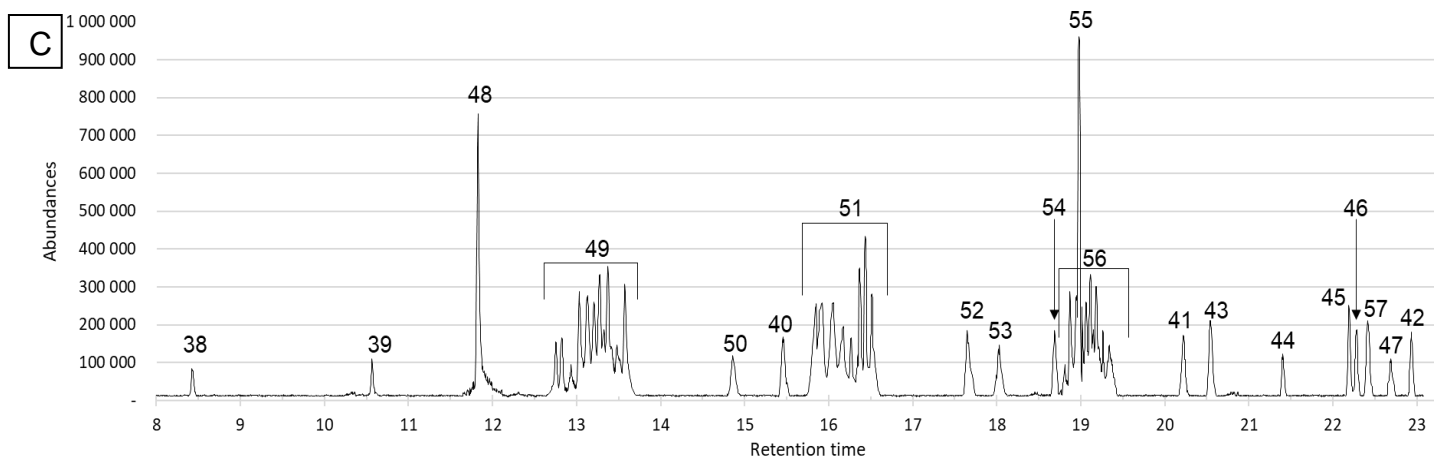
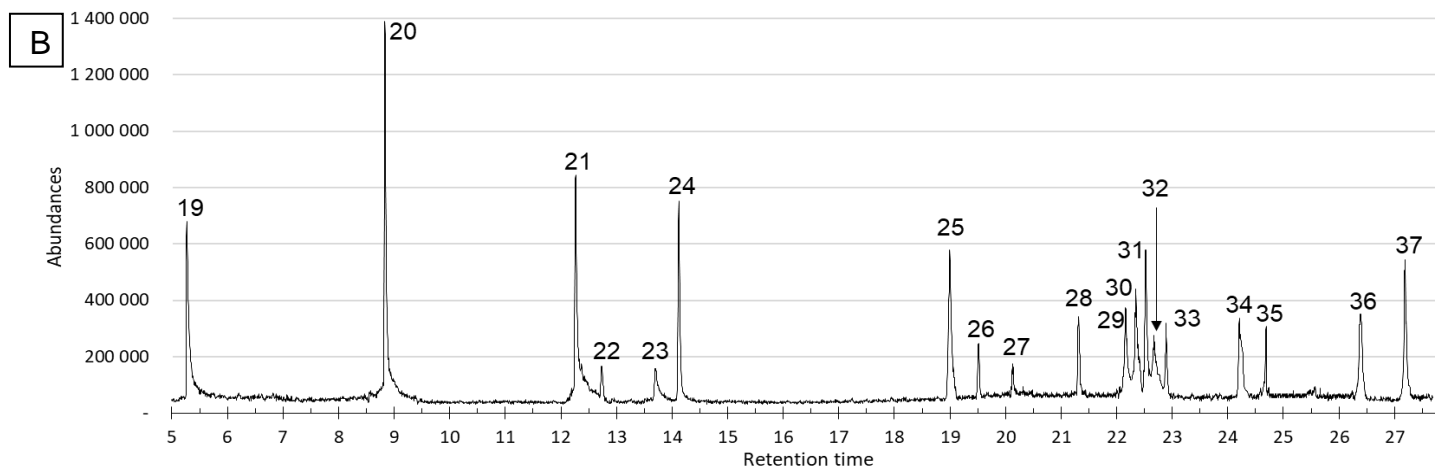
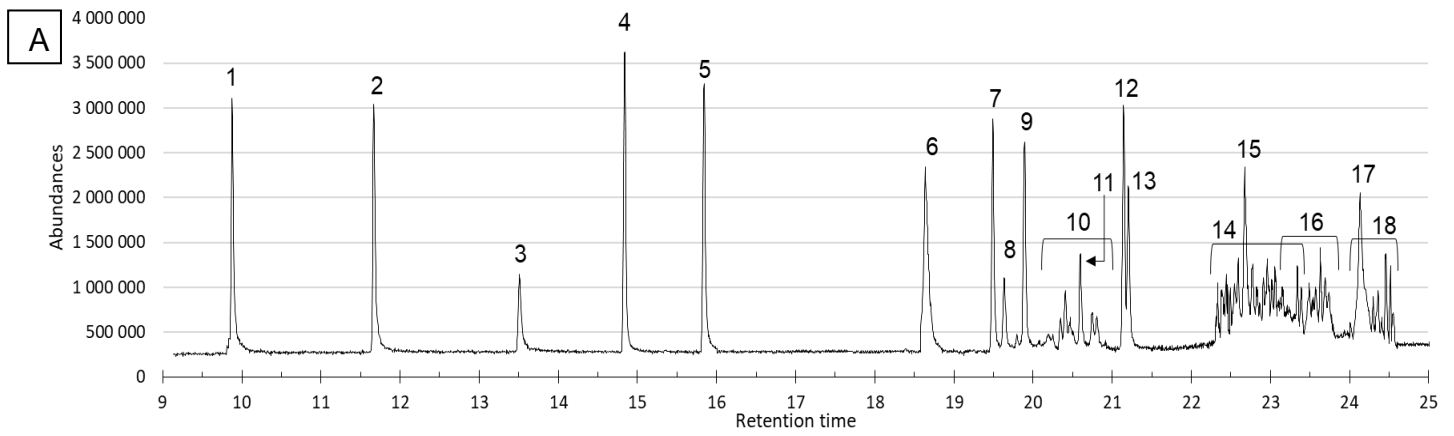
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631 **Figure captions**

632 **Figure 1:** Chromatograms of the targeted plastic additives analyzed using GC-HRMS. (A)
633 plasticizers additives; (B) flames retardants additives; and (C) antioxidants, UV stabilizers and
634 plasticizers additives. The numbers refer to the name of the molecules mentioned in Table 1.

635 **Figure 2:** Peak areas of some selected OPAs depending on the thermal desorption
636 temperature (250 °C, 350 °C and 450 °C, respectively in blue, yellow and grey). (A) plasticizers
637 and flame-retardants; (B) antioxidants; and (C) antioxidants and UV-stabilizers. Values are
638 expresses as mean± 95% confidence interval. Homogeneous groups are indicated by the
639 same letter.(n=3).

640 **Figure 3:** Corrected peak areas of the OPAs found in the 4 food plastic packaging samples in
641 polypropylene (PP) and polylactic acid (PLA). The letters A and B referred to the suppliers.
642 Homogeneous groups are indicated by the same letter. (n=3).



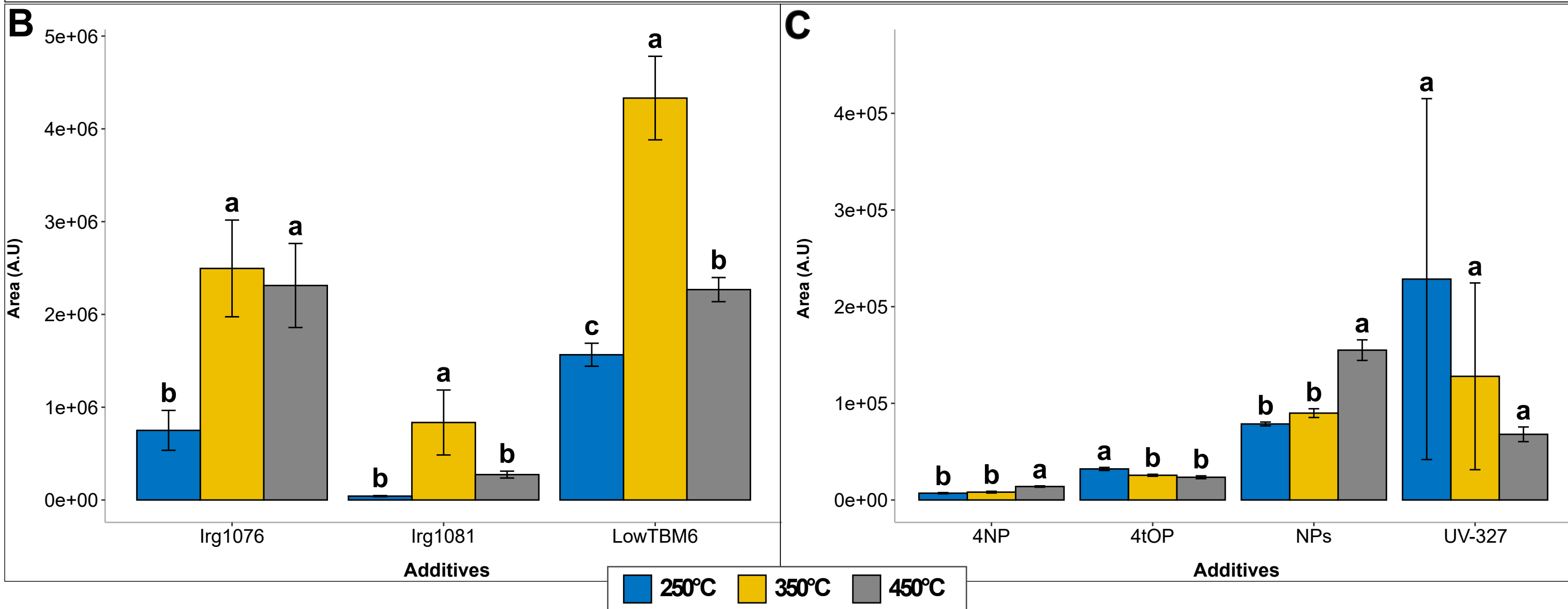
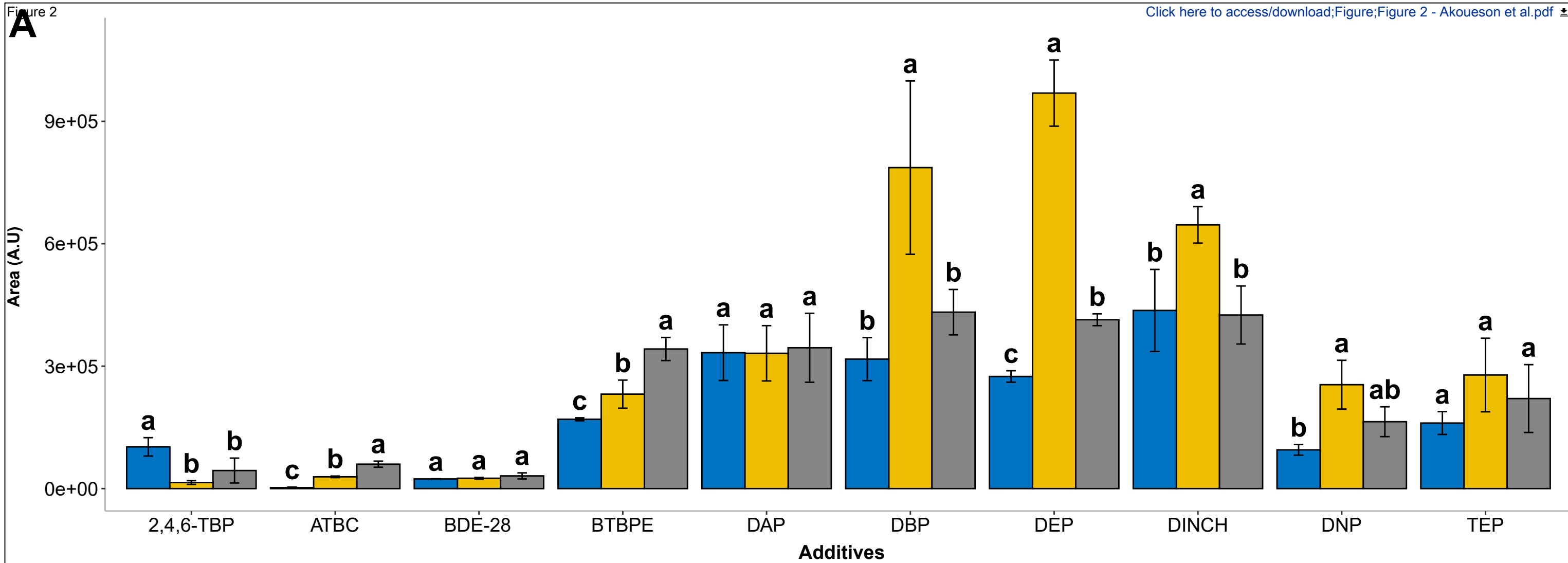
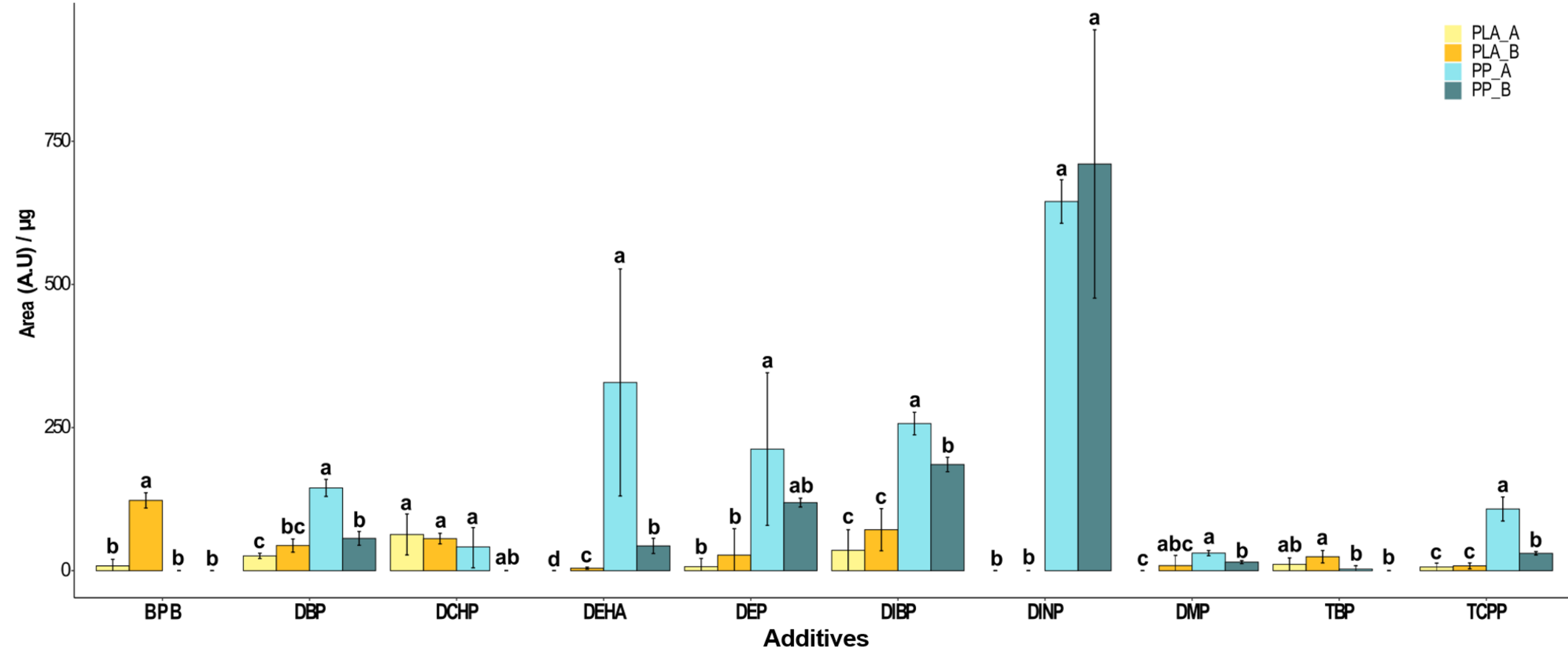


Figure 3



643 Table 1: selected organic plastic additives (OPAs) with their corresponding suppliers and the quantity that allowed peaks detection using Py-GC-
 644 HRMS analysis. The molecules tagged with “*” represent the OPAs not detected (n.d) at the highest concentration available.

Function	N°	Additive	Abbreviation	CAS	Suppliers	Limit of detection (ng) (split 5)			
Plasticizers	1	Dimethyl phthalate	DMP	131-11-3	Restek	5			
	2	Diethyl phthalate	DEP	84-66-2					
	3	Di-allyl phthalate	DAIP	131-17-9					
	4	Diisobutyl phthalate	DIBP	84-69-5					
	5	Di-n-butyl phthalate	DBP	84-74-2					
	6	Tributyl Acetyl Citrate	ATBC	77-90-7	Accustandard				
	7	Di-n-hexyl phthalate	DHP	84-75-3	Restek				
	8	Benzyl butyl phthalate	BBP	85-68-7					
	9	Bis-2-Ethylhexyl Adipate	DEHA	103-23-1	Accustandard				
	10	Diisoheptyl phthalate	DIHP	71888-89-6	Accustandard		25		
	11	Tri(2-ethylhexyl) phosphate	TEHPA *	78-42-2	Accustandard		n.d (at 100)		
	12	Dicyclohexyl phthalate	DCHP	84-61-7	Restek		5		
	13	Bis(2-Ethylhexyl) phthalate	DEHP	117-81-7					
	14	Diisononyl hexahydrophthalate	DINCH	166412-78-8	Accustandard				
	15	Di-n-octyl phthalate	DIOP	117-84-0	Restek				
	16	Diisononyl phthalate	DINP	68515-48-0	Accustandard			25	
	17	Di-nonyl phthalate	DNP	84-76-4	Restek			5	
	18	Diisodecyl phthalate	DIDP	68515-49-1	Accustandard			25	
Flames retardants	19	Triethyl Phosphate	TEP	78-40-0	LGC standard	5			
	20	Tripropyl Phosphate	TPP	115-86-6					
	21	Tributyl Phosphate	TBP	126-73-8					
	22	2,4,6-Tribromophenol	2,4,6,TBP	118-79-6	LGC standard				
	23	Tris(2-Chloroethyl)Phosphate	TCEP	115-96-8	LGC standard				
	24	Tris(2-Chloroisopropyl)Phosphate	TCPP	13674-84-5	LGC standard				
	25	2,4,4'-Tribromodiphenyl ether	BDE-28	41318-75-6	Accustandard			10	
	26	Tris(1,3-Dichloro-2-Propyl)Phosphate	TDCPP	13674-87-8	LGC standard			5	
	27	Triphenyl Phosphate	TPhP	513-08-6					
	28	2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	5436-43-1	Accustandard				10
	29	Tricresyl Phosphate	TCP *	1330-78-5	Accustandard				n.d (at 100)
	30	Tricresyl Phosphate - isomer	TCrP *	78-30-8			n.d (at 100)		
	31	2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	60348-60-9	Accustandard		5		

Function	N°	Additive	Abbreviation	CAS	Suppliers	Limit of detection (ng) (split 5)
	32	Tri-o-tolyl phosphate	TToP *	78-30-8	Accustandard	n.d (at 100)
	33	2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	189084-64-8	Accustandard	10
	34	2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	68631-49-2		
	35	2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	207122-15-4		
	36	2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE-183	207122-16-5		
	37	1,2-Bis (2,4,6 Tribromophenoxy) ethane	BTBPE	37853-59-1		
Antioxidants	38	6,6'-di-tert-butyl-2,2'-thiodi-p-cresol	Irganox® 1081	90-66-4	Accustandard	10
	39	Butylated hydroxytoluene	BHT	128-37-0	Accustandard	5
	40	3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, octadecyl ester	Irganox® 1076	2082-79-3	Accustandard	100
	41	6,6'-ditert-butyl-4,4'-thiodin-m-cresol	Lowinox® TBM-6	96-69-5		50
UV stabilizers	42	2,2-dihydroxy-4,4-dimethoxybenzophenone	Uvinul® 3049 *	131-54-4	Accustandard	n.d. (at 100)
	43	2-t-Butyl-6(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol	UV-326	3896-11-5-		5
	44	2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol	UV-328	25973-55-1		
	45	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	UV-327	3864-99-1		
	46	2-hydroxy-4-octyloxybenzophenone	Uvinul 3008 *	1843-05-6		n.d. (at 100)
Antioxidants – plasticizers - stabilizers	47	4-Tert-Octylphenol	4-t-OP	140-66-9	Accustandard	5
	48	Nonylphenol	NPs	84852-15-3	Accustandard	10
	49	4-nonylphenol	4-NP	104-40-5	Accustandard	
	50	Nonylphenol Monoethoxylate	NP1EO	27986-36-3	Accustandard	
	51	Bisphenol F	BPF	620-92-8	Accustandard	5
	52	4-Nonylphenol Monoethoxylate	4-NP1EO	104-35-8	Accustandard	10
	53	Bisphenol A	BPA	80-05-7	Accustandard	5
	54	Bisphenol B	BPB	77-40-7		
	55	Nonylphenol diethoxylate	NP2EO *	N/A	Accustandard	n.d. (at 10)
	56	Bisphenol S	BPS *	80-09-1	Accustandard	n.d (at 100)

645

646 **Table 2:** GC-HRMS analytical conditions

Parameters	Settings
GC	
Injection port temperature	300°C
Column temperature (°C)	80°C (0.5 min) → 10°C/min → 330°C (3 min)
Injection mode	Split (split ratio 1:5)
Carrier gas	Helium
Carrier Gas flow	1 mL.min ⁻¹
Transfer line temperature	300°C
MS	
Ion source temperature	300°C
Ionization method	Electron Ionization (EI), 70 eV.
Analytical mode	Full Scan mode (FS)
Scan Range	30.00000 – 750.00000 m/z
Solvent Delay	5 min

647

648 **Table 3:** Kováts retention indices (RI) values and quantitative and qualitative ions for the
 649 selected plastic additives molecules. n.d. = not detected.

Function	Molecules	RI	Quantitative ions	Qualitative ions
Plasticizers	DMP	1469	163.03888	133.02846
	DEP	1608	149.02333	177.05455
	DAIP	1756	149.0231	189.05432
	DIBP	1872	149.02333	161.05917
	DBP	1972	149.02333	160.08830
	ATBC	2160	129.01845	259.15451 ; 137.99502
	DHP	2374	149.02333	234.12006
	BBP	2401	149.02333	206.09376
	DEHA	2404	111.04393	101.05960 ; 129.05444
	DIHP	2380 - 2509	149.02333	265.14313 ; 99.11672
	TEHPA	2477	98.98428	113.13261
	DCHP	2558	149.02333	249.11210
	DEHP	2570	149.02333	279.15909
	DINCH	2630 – 2870	155.07002	109.06474 ; 127.07529
	DIOP	2756	149.02333	261.14876
	DINP	2731 – 2867	149.02323	71.08553
	DNP	2936	149.02333	293.17474
DIDP	2876 - 3010	149.02332	n.d.	
Flames retardants	TEP	1124	98.98432	127.01567 ; 109.00512
	TPP	1383	98.98432	141.03133
	TBP	1650	98.98432	211.10963
	2,4,6,TBP	1656	331.76931	222.85798
	TCEP	1769	142.96611	222.96906 ; 248.98479
	TCPP	1808	125.00023	201.00710 ; 156.98178
	BDE-28	2283	245.96733	139.05414
	TDCPP	2354	98.98432	190.94284 ; 154.96611
	TPhP	2421	325.06296	233.03670 ; 215.02596
	BDE-47	2550	325.87582	323.87792
	TCP	2676	165.07015	243.05746 ; 368.11771
	TCrP	2707		
	BDE-100	2763	403.78613	563.62171
	TTOP	2738	165.07015	243.05746 ; 368.11771
	BDE-99	2823	405.78452	563.62171
	BDE-153	3000	483.69452	242.84599 ; 643.53162
	BDE-154	3092		
BDE-183	3375	563.60352	281.80109	
BTBPE	3453	356.79514	277.87637	
Antioxidants	Irganox® 1081	1366	149.09674	164.12027
	BHT	1520	205.158752	206.16206
	Irganox® 1076	3611	147.08102	263.16534 ; 217.15947
	Lowinox® TBM-6	2795	358.19647	259.07922
UV stabilizers	Uvinul® 3049	2503	151.03903	257.08099 ; 124.05204
	UV-326	2575	300.08972	272.05853
	UV-328	2681	322.19113	351.23003
	UV-327	2692	342.13678	357.16034 ; 286.07428
	Uvinul 3008	2790	213.05461	325.17978 ; 137.02342
Antioxidants; Plasticizers; Stabilizers	4-t-OP	1611	135.08041	206.16644
	NPs	1700 – 1770	135.08041	197.13233 ; 212.15582
	4-NP	1873	107.04916	221.18555
	NP1EO	1969 - 2030	179.10652	193.12220
	BPF	2104	200.08276	n.d.
	4-NP1EO	2146	107.04916	151.07530 ; 264.20834
	BPA	2221	213.09113	228.11452
BPB	2321	213.09065	227.10631	

Function	Molecules	RI	Quantitative ions	Qualitative ions
	NP2EO	2027 - 2321	107.04916	151.07530 ; 264.20834
	BPS	2765.2777	141.00046	110.03627

650

651

652 Table 4: average extraction efficiency percentages and, in parenthesis, standard deviations of
 653 the method following the 1st pyrolysis step, after analyzing the additive content of PLA and PP
 654 samples (n=3). Each sample was successively analyzed 3 times at 350 °C. Bold printed
 655 characters represent average extraction efficiencies >80%. n.d = not detected.

	PLA-A	PLA-B	PP-A	PP-B
DMP	n.d	33 (56)	79 (10)	48 (9)
DEP	90 (17)	95 (9)	70 (4)	65 (9)
DBP	94 (10)	99 (3)	100 (0)	100 (0)
DIBP	98 (3)	98 (3)	100 (0)	100 (0)
DCHP	100 (0)	100 (0)	100 (0)	n.d
DINP	n.d	n.d	87 (2)	88 (4)
DEHA	n.d	90 (18)	59 (36)	93 (2)
TBP	59 (51)	93 (6)	23 (40)	n.d
TCPP	62 (54)	76 (9)	65 (5)	79 (11)
BPB	100 (0)	93 (2)	n.d	n.d

656



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Supplementary Material

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