

Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials

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ABSTRACT

A mixture of polyethylene (PE), polyethylene-terephthalate (PET), polypropylene (PP) and Nylon was submerged in marine water during 12 months. The chlorine content of these plastics was measured through the passing time. Thermobalance was used to look for differences in the thermal decomposition of the plastics during in that time interval. Degradation of PET, PP and Nylon produced changes in the weight loss curve, but behaviour of PE is confusing. Pyrolysis and combustion at 850 °C was finally performed to get knowledge of the possible differences in the emission of main gases, volatiles and semivolatiles including polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (ClBzs), polychlorinated phenols (ClPhs), polybrominated phenols (BrPhs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Results show that the emission of chlorinated species is somewhat not affected by the chlorine content of the plastics mix. The production of PCBs and PCDD/Fs was very low, under 4 pg WHO-TEQ/g.

Keywords: Plastics; PAHs; Dioxins; Marine water; Pyrolysis; Combustion

1. Introduction

The presence of marine debris is a cause for concern due to several reasons. These debris have been identified as harmful to organisms and to human health (Rochman et al., 2013); also these debris have the potential to increase the transport of organic and inorganic contaminants (Avio et al., 2017; Gaylor et al., 2012; Iñiguez et al., 2017; Rochman et al., 2013).

The material most commonly found in marine debris are glass, metal, paper and plastic (Cózar et al., 2014; OSPAR, 2007). The most commonly used plastics are polyethylene, polypropylene and polyethylene terephthalate, therefore, they are the most frequently found in the marine environment too (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Iñiguez et al., 2016; Ruiz-Orejón et al., 2016).

The annual input of plastics in the oceans increases every year. It is estimated that in 2015 around 9.1 million tons were accumulated (Jambeck et al., 2015).

One possible alternative for waste disposal is thermal decomposition through pyrolysis or combustion. These processes provide a reduction in waste volume and involve profitable energetic and/or chemical products. Nevertheless, the possible emission of pollutants during non-controlled plastic thermal degradation may create a serious hazard for human health and for the environment. In this way, it is important to control and reduce the emission of pollutants, and be aware of the chemical mechanisms involved in the thermal decomposition.

Different studies attempt to clarify the effects of chlorine content in waste on the formation mechanisms of polychlorinated pollutants, especially dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (Gullett et al., 2000; Sablier et al., 2010; Wang et al., 2003; Wyrzykowska et al., 2009). The study done in 2003 by Wang et al. showed differences in the emission when the chlorine level in the waste is higher than 0.8-1.1 %. If the level is lower than this threshold level, the formation of PCDDs dominates, probably because the chlorine is used to chlorinate the non-substituted phenol to produce chlorophenols, which are important precursors for PCDDs. In other cases, the PCDFs increase faster. Other authors (Gullett et al., 2000) pointed out a poor correlation between total chlorine in waste streams and formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) during waste combustion., because the active chlorine (Cl) species are strongly dependent upon combustion conditions. Nevertheless, Yasuhara et al. (Yasuhara et al., 2003) showed that the presence of NaCl during the combustion of newspapers increased more than 70 times the emission of PCDD/Fs. Accordingly, Ma et al. (Ma et al., 2010) revealed that the production of chlorinated compounds is affected both by organic and inorganic chlorine.

Regarding the environmental impacts, there are many studies that investigate the pollution associated with plastics combustion and/or pyrolysis (Devaraj et al., 2015; Font et al., 2011; Iñiguez et al., 2017; Poerschmann et al., 2015). However, there is no study investigating the effect of contacting marine water with plastic materials in the thermal decomposition of the wastes. Following this line, the aim of the present work is to study the changes that suffer plastic materials in contact with marine water, and the differences in the emission of pollutants comparing the pyrolysis and the combustion of materials before and after having passed

58 one year in contact with marine water. Also, the chlorine content and the thermal behaviour are monitored
59 during this time.

60 **2. Materials and methods**

61 **2.1. Materials**

62 Four main plastics components usually found in marine litter were studied for thermal decomposition. In this
63 way, PE, PP, PET and Nylon were studied. The plastic components were submerged in marine water, in a 100
64 L drum, during a total period of one year. During this time, different samples were taken to measure the
65 chemical composition and thermal behavior. Specifically, samples were taken at 2, 7 and 12 months, and were
66 compared to the plastics before the treatment.

67 **2.2. Determination of ions and NCV**

68 The Net Calorific Value (NCV) was determined using a calorimetric bomb AC-350 Leco Instruments, and the
69 inorganic anions content of the sample was measured by ionic chromatography following EPA methods 5050
70 and 9056 (US EPA, 1994a, 2007b).

71 **2.3. TG runs**

72 Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal
73 Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in a
74 mixture nitrogen:oxygen = 4:1 (20 % oxygen, simulating air composition) with a total flow rate of 100 mL
75 min⁻¹. Dynamic experiments were carried out at 20 K min⁻¹, from room temperature up to 1173 K. For each
76 run, 4 ± 0.3 mg of sample were used.

77 **2.4. Pyrolysis and combustion runs**

78 The emissions from the thermal decomposition of marine plastic were studied comparing the decomposition
79 before and after having the plastic submerged in the sea water. In this sense, a mixture of the four plastics was
80 prepared in equal proportions, since it was representative of marine litter (Iñiguez et al., 2017). The pyrolysis
81 and the combustion of this mixture were compared before and after passing one year in the marine water
82 drum. During the rest of article, these samples will be named "MIX_original" and "MIX_12months".

83 Combustion and pyrolysis runs of MIX_original and MIX_12months were carried out in a moving tubular
84 reactor, which consists in a quartz tube (10 mm internal diameter) where the material was introduced in three
85 quartz boats (70 mm long each) along the tube. Once the process programmed temperature was reached (850
86 °C in all runs) inside the horizontal furnace and with a constant flow of gas passing through, the boats were
87 introduced in the furnace at constant speed using a horizontal actuator. This experimental system has been
88 previously described in detail (Conesa et al., 2013). Synthetic air (combustion runs) or nitrogen (pyrolysis
89 runs) was introduced in parallel to the sample, with a constant flow of 500 mL min⁻¹ (measured at 1 atm and
90 20 °C). The sample mass in each run was around 0.5 g. Before the decomposition runs, a control containing no
91 sample was carried out using the same experimental conditions (blank). For the combustion runs, an oxygen

92 ratio equal to 0.5 was selected, defined as the fraction between the actual and the stoichiometric air flow rate
93 necessary for a complete combustion (Conesa et al., 2009).

94 The reproducibility of this type of experiments has been tackled in our laboratory. A previous study (Garrido
95 et al., 2016) confirmed a good reproducibility for all compounds analyzed in the emissions from combustion
96 and pyrolysis runs of wastes using a similar laboratory scale horizontal reactor. The obtained standard
97 deviations were small in comparison with the average values; only for some small average values, the
98 standard deviations were somewhat greater, but with relative standard deviations around 5%.

99 The outlet gas stream of each run was sampled to analyze the following pollutants:

100 - Gases and volatile compounds were collected using Tedlar[®] bags (Restek, USA). CO₂ and CO were
101 analyzed by gas chromatography with thermal conductivity detector (GC-TCD) (Agilent 7820). Light
102 hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-
103 17A).

104 - PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs were collected in a polyaromatic Amberlite[®] XAD-2 resin
105 (Supelco, Bellefonte, USA) placed at the exit of the furnace during the whole experiment. The Tedlar[®] bag
106 was located after the resin.

107 Internal standards were employed to calculate the concentration of PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs
108 in the samples. Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) supplied the deuterated standards used for the
109 analysis of the 16 priority PAHs and Wellington Laboratories (Ontario, Canada) supplied the ¹³C-labeled
110 standards for ClPhs, ClBzs, BrPhs and PCDD/Fs. All the internal standards were added to the resin.

111 Next, the resin was successively extracted with a mixture of dichloromethane/acetone (1:1 vol) and toluene by
112 Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the
113 US EPA method 3545A (US EPA, 2000). The extract was divided into two fractions: approximately 30 wt.%
114 was used for the analysis of PAHs, ClPhs, ClBzs and BrPhs (US EPA, 2007a) and the remaining 70 wt.% was
115 employed for the analysis of PCDD/Fs (US EPA, 1994b).

116 PAHs, ClPhs, ClBzs and BrPhs were analyzed by GC-MS (Agilent GC 6890N/Agilent MS 5976N, Agilent
117 Technologies, USA) following the US EPA method 8270D (US EPA, 2007a) as reference. ClBzs, ClPhs and
118 BrPhs were analyzed in the SIR mode and the identification of each isomer was performed comparing the
119 primary/secondary ion area ratio with that obtained in the calibration with the labelled compounds. For the
120 analysis of PCBs and PCDD/Fs, a cleanup step was performed using the Power Prep automated system (FMS,
121 Inc., Boston, MA) with three different columns: multilayer silica, basic alumina and activated carbon. The
122 purified extract was analyzed by HRGC/HRMS. Regarding the analyses of PCBs and PCDD/Fs, the
123 recoveries obtained for the labelled standards were within the ranges established by the reference standards
124 (US EPA, 1994b).

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3. Results and discussion

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3.1. Inorganic anions analysis and net calorific value (NCV).

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Figure 1 shows the main results of the characterization of the plastic materials picked up at the different samplings. The main inorganic anions content and the NCV were measured in samples taken at 0 (original), 2, 7 and 12 months after introducing the plastics in the marine water.

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As can be seen in the Figure, plastics are quickly impregnated with the ions present in the water. In this sense, chloride is mainly incorporated to the plastics, especially PE that increases very quickly its chlorine content. Along time, the chloride content continues increasing, except in the case of PE that shows a high content from very early stages.

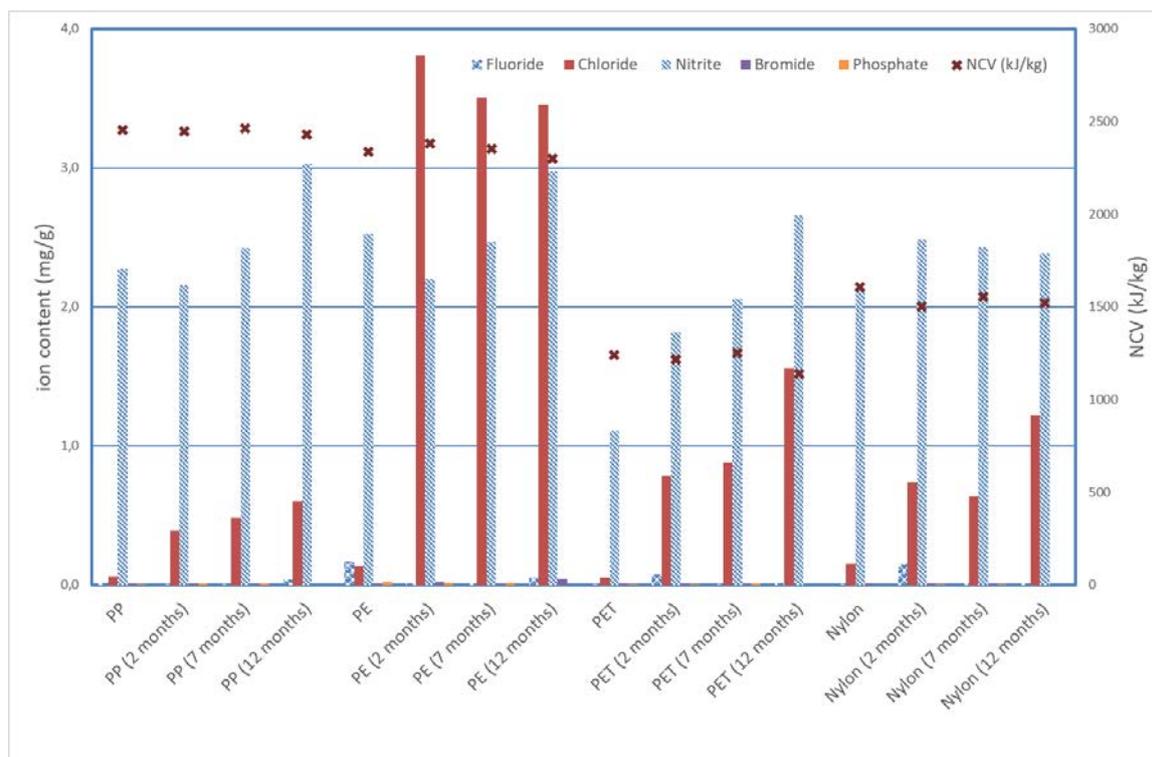
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Respecting to the NCV (represented as 'x' in the graph), is more or less constant for each sample, without being affected by the passage of time. As expected, NCV of PP and PE are much higher than those of PET or Nylon).

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Figure 1. Evolution of inorganic anions content and NCV over time for samples submerged in marine water.

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3.2. Thermogravimetric runs

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Evolution of the thermal behavior of the plastic materials was followed by thermogravimetry. Samples were subjected to decomposition in the thermobalance at 20 K/min and were finally compared. As mentioned

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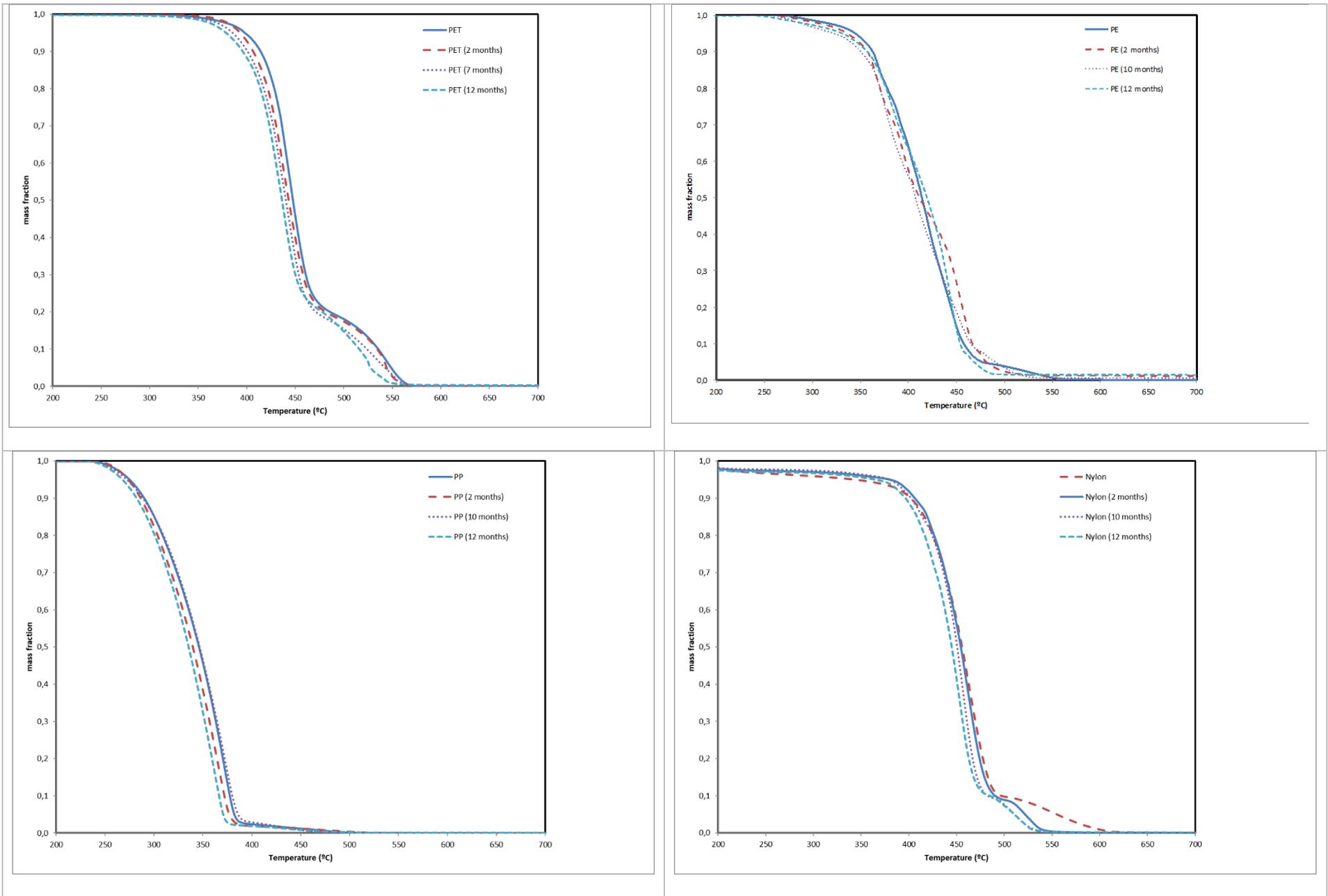
144 before, synthetic air was used as carrier gas to test for the behavior of the samples in combustion conditions
145 (Iñiguez et al., 2017). Measures were duplicated to test for the reproducibility that was very good.

146 Figure 2 shows the results for all plastic materials. As can be seen, all plastics were affected by the contact
147 with the marine water. In general, thermal properties were affected, causing a weakening of the plastic over
148 time. PET was the most affected sample, with Tmax (temperature where the decomposition rate is maximum)
149 going from 446.3 °C (Original PE) to 437.8 °C (sample taken at 12 months). Nylon and PP also have an
150 expected behavior as the degradation is easier as the polymer is submerged in the water.

151 In this way, PP was affected, but in this case the difference between the Tmax values was (373.0-351.3) °C.
152 PE behavior is confusing because it seems that the marine water environment produces a strengthening of the
153 material, as the TG curves are moving to higher temperatures over the time. From the curves, Tmax are
154 calculated at 0, 4, 7 and 12 months, being the values 416, 404, 407 and 418 °C respectively. PE is also the
155 polymer that more quickly increases its chlorine content, as stated before.

156 As can be seen in Figure SM1 of the supplementary material, the decomposition in inert atmosphere of four
157 plastics was also studied in the thermobalance. Generally (Font et al., 2005) the presence of oxygen
158 accelerates the decomposition, as it is the case of the materials studied in the present work.

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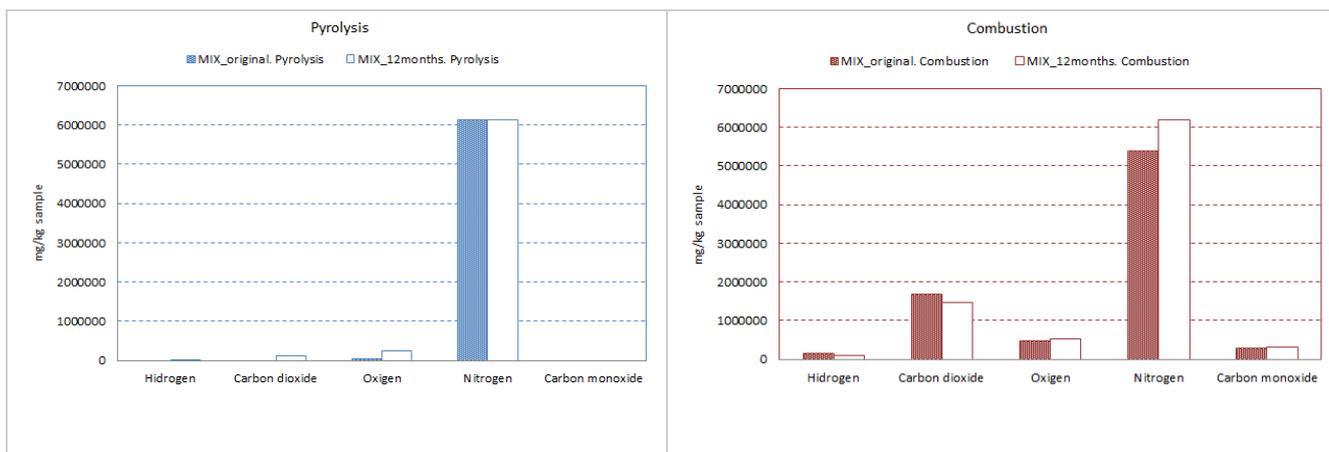
160 Figure 2. Thermal decomposition of the plastic materials at different time after being submerged in marine water.

161 **3.3. Gases and volatile compounds emission during pyrolysis and combustion runs**

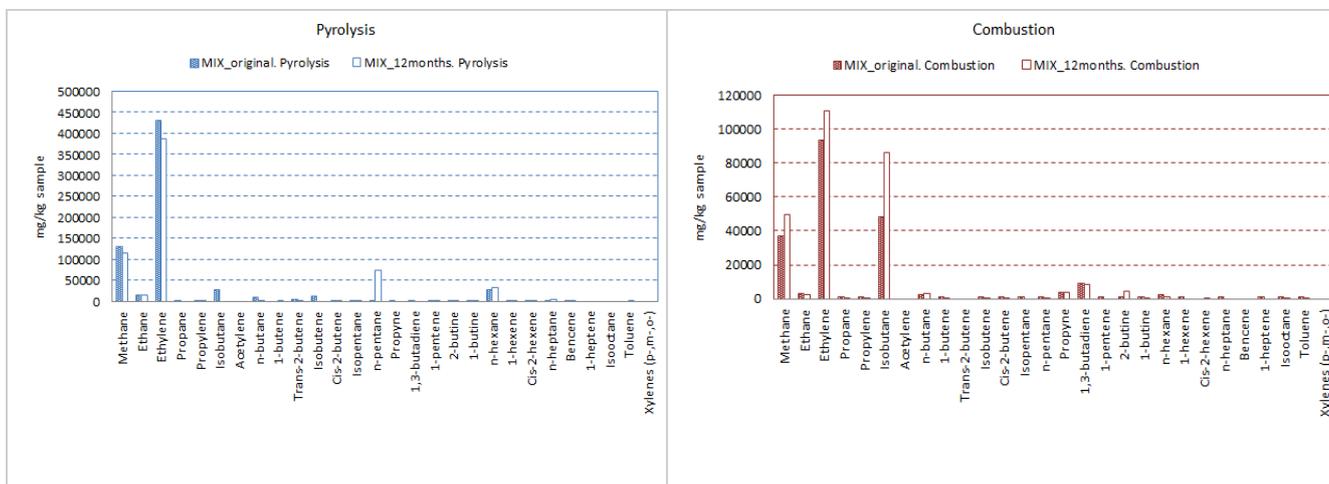
162 As commented before, the sample MIX_12months was subjected to pyrolysis and combustion runs, and was
 163 compared to the MIX_Original decomposition. Figure 3 and Figure 4 show the evolution of the main gases
 164 produced in these runs. Ethylene and methane were the most abundant gases, especially in the pyrolytic
 165 conditions. The presence of oxygen in the combustion runs produces the oxidation of the gases and then the
 166 decrease of the main constituents, as it occurs with other materials (Conesa et al., 2009).

167 Comparing both samples, the differences are not important, in particular in the pyrolysis experiments. It could
 168 be because the Nitrogen content is very high in all samples. However, other authors suggested that the main
 169 factor affecting the emissions is the calculated oxygen ratio and not the flow rate used (Conesa and Domene,
 170 2015). In this sense, it is consider this is not the reason for the small differences found.

171 Differences are shown in the combustion runs, where the production of methane, ethylene and isobutene is
 172 higher in the decomposition of the MIX_12months sample. In both processes, it is important to emphasize the
 173 high production of ethylene, which is expected taking into account the chemical structure of polyethylene. The
 174 CO and CO₂ yields obtained in the combustion runs were much higher than those detected in pyrolysis at 850
 175 °C due to the fact that the increase of oxygen content in the atmosphere intensified the fuel combustion.



176 *Figure 3. Gas emission during the pyrolysis and combustion of the plastics mixtures (GC-TCD).*

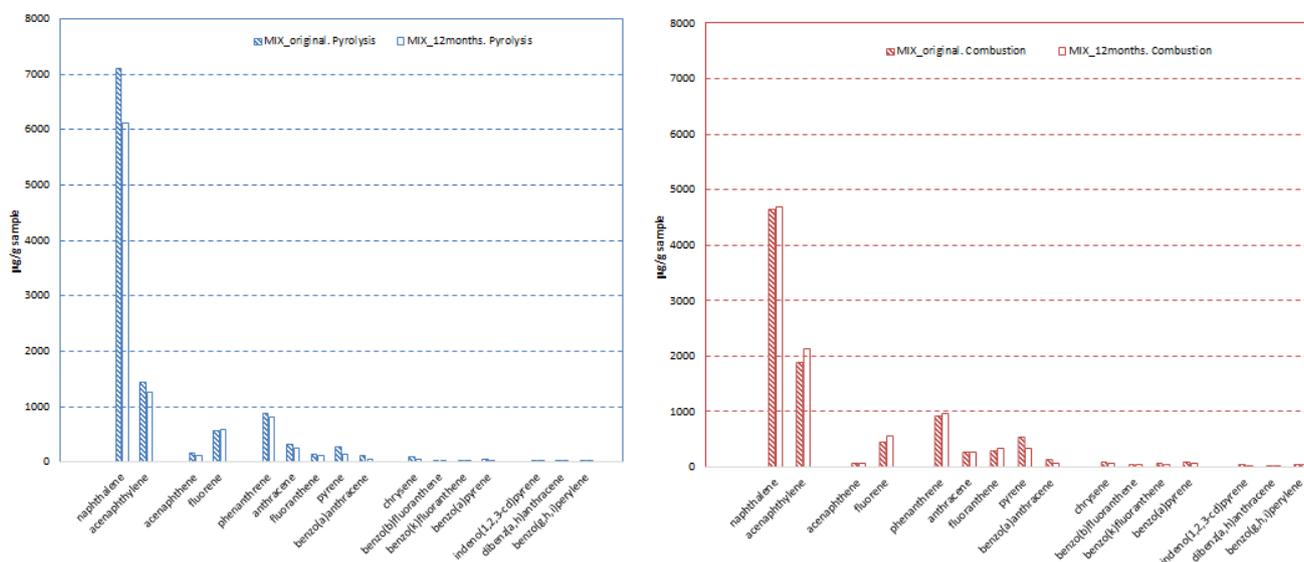


177 *Figure 4. Gas emission during the pyrolysis and combustion of the plastic mixtures (GC-FID).*

178 **3.4. Semivolatile, PAHs and halogenated pollutants**

179 Figure 5 shows the results for the emission of 16 priority PAHs in the pyrolysis and combustion runs. The
180 emission of PAHs from both samples is almost the same. No differences were found.

181 On the other hand, the presence of oxygen affects in different ways the emission of PAHs, as expected (Rey et
182 al., 2016). The emission of naphthalene decreased in the presence of oxygen, as expected since it is known
183 that pyrolytic reactions are the primary source of PAH formation (Thomas and Wornat, 2008), being the
184 naphthalene the mainly compound emitted in all cases. However, other PAHs like acenaphthylene and
185 phenanthrene increased slightly in the combustion runs, but the difference is not significant. Remember that
186 the combustion runs were done with an oxygen ratio of 0.5, i.e., in the presence of 50 % of the stoichiometric
187 oxygen needed for the total combustion.



188 *Figure 5. PAHs emission during the pyrolysis and combustion of the plastics mixtures.*

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190 Tables 1 to 3 presents the emission of chlorobenzenes (ClBz), chlorophenols (ClPh) and bromophenols
191 (BrPh), respectively. The most abundant isomers of ClBz were di-ClBz with maximum values of ca. 200 $\mu\text{g/g}$
192 sample. For all these pollutants, the emission was drastically decreased in the presence of oxygen.

193 The highest yields of ClBzs and ClPhs were observed in pyrolytic conditions; in such a way that the yields
194 decreased with the presence of oxygen, consistent with the profile of PAHs. This tendency occurs also during
195 the thermal decomposition of other wastes (Garrido et al., 2017; Rey et al., 2016). The maximum total yields
196 are also similar lower than those detected with other wastes. In a previous work (Iñiguez et al., 2017) we
197 determined that the content of ClBzs in plastics from marine environment was in the range 0.180–0.215 $\mu\text{g/g}$,
198 being 1,2-dichlorobenzene the most abundant isomer in two different samples. In the present work, a
199 maximum emission of ca. 208 $\mu\text{g/g}$ is shown.

200 Respect to the effect on the emission of the contact with marine water, it is difficult to see a clear trend. From
 201 the data presented in Figure 1, an average value of chlorine content in the samples was calculated. Values of
 202 0.10 mg/g and 1.70 mg/g can be assigned to MIX_Original and MIX_12months respectively. In general,
 203 emission levels of chlorinated pollutants are similar for both samples, indicating that the level of chlorine in
 204 the waste is not correlated with the emission of chlorinated species, at least in the ranges studied in this work.

205 On the other hand, the amount of BrPh evolved is almost nil in all runs performed, as it is the bromine content
 206 of the samples (Figure 1). A maximum value for the emission of total BrPh of 1.2 µg/g can be assigned. The
 207 formation of BrPhs was higher in pyrolytic conditions (1.2-1.0 µg/g) than in oxidative ones (0.4-0.7 µg/g). In
 208 pyrolysis process, the most abundant isomer in two both samples was 3,4-monobromophenol, being 3,4-
 209 dibromophenol the majority compound in the combustion runs. The minimum emission values for pyrolysis
 210 and combustion runs in all the samples were found in the isomer 2,4,5-tribromophenol.

211 Table 1. Chlorobenzenes emission from the pyrolysis and combustion of samples at 850 °C.

ClBz		µg/g sample			
		MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
Mono-	Mono-	2.065	3.495	1.907	1.102
Di-	1,3-	36.67	32.211	69.96	60.26
	1,4-	0.110	0.085	0.149	0.105
	1,2-	79.39	39.260	207.91	84.92
Tri-	1,3,5-	0.046	0.003	0.032	0.016
	1,2,4-	0.324	0.018	0.186	0.129
	1,2,3-	0.058	0.026	0.236	0.127
Tetra-	1,2,3,5-+1,2,4,5-	0.022	0.015	0.058	0.010
	1,2,3,4-	0.019	0.028	0.167	0.016
Penta-	Penta-	0.015	0.011	0.045	0.011
Hexa-	Hexa-	0.039	0.054	0.035	0.052

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221 Table 2. Chlorophenols emission from the pyrolysis and combustion of samples at 850 °C.

	ClPh	µg/g sample			
		MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
Mono-	2-	0.087	0.157	0.091	0.106
	3-+4-	99.91	61.21	245.48	413.48
Di-	2,4-	2.121	0.106	4.605	0.785
	2,5-	1.532	0.074	4.722	0.780
	2,3-	1.320	0.091	2.917	0.729
	2,6-	0.126	0.017	0.170	0.405
	3,5-	0.426	0.157	1.912	2.284
	3,4-	0.205	0.338	3.711	3.990
Tri-	2,3,5-	0.192	0.040	0.038	0.025
	2,4,6-	0.076	0.024	0.192	0.029
	2,4,5-	0.023	0.009	0.044	0.043
	2,3,4-	0.021	0.009	0.031	0.028
	2,3,6-	0.026	0.004	0.028	0.038
	3,4,5-	1.429	0.167	4.455	2.834
Tetra-	2,3,5,6-	0.084	0.041	0.074	0.090
	2,3,4,5-	0.095	0.018	0.066	0.077
	2,3,4,6-	0.053	0.033	0.014	0.007
Penta-	penta-	0.112	0.131	0.201	0.113

222 Table 3. Bromophenols emission from the pyrolysis and combustion of samples at 850 °C.

	BrPh	µg/g sample			
		MIX_original. Combustion	MIX_12months. Combustion	MIX_original. Pyrolysis	MIX_12months. Pyrolysis
MONO-	2-	0.041	0.019	0.151	0.149
	3-+4-	0.049	0.014	0.311	0.280
DI-	2,4-	0.021	0.013	0.099	0.046
	2,3-+2,5-	0.003	0.005	0.003	0.006
	2,6-	0.016	0.018	0.041	0.033
	3,5-	0.065	0.009	0.159	0.039
	3,4-	0.247	0.267	0.207	0.098
	2,3,5-	0.012	0.014	0.054	0.046
	2,4,6-	0.037	0.010	0.014	0.020
	2,3,4-	0.104	0.027	0.056	0.085
TRI-	2,4,5-	0.001	0.001	0.010	0.006
	2,3,6-	0.014	0.001	0.006	0.017
	3,4,5-	0.055	0.047	0.063	0.116
	2,3,5,6-	0.052	0.019	0.012	0.069
TETRA-	2,3,4,5-+2,3,4,6-	0.059	0.022	0.016	0.070
PENTA-	penta-	-	-	-	-

223 **3.5. Polychlorobiphenyls (PCBs) and Dioxins/furans (PCDD/Fs)**

224 Also PCBs and PCDD/Fs were measured in the decomposition runs. The emission levels of these pollutants
225 were very low. Nonetheless, many of the samples presented undetectable amounts of some congeners. Tables
226 SM1 and SM2 (Supplementary Material) show the amounts of the different PCB and PCDD/F congeners
227 emitted, in pg WHO-TEQ/g sample, where a value of the limit of detection was assigned to the non-detects.

228 The total emission of PCDD/Fs was between 0.9 and 2.7 pg WHO-TEQ/g for all the runs, including pyrolysis
229 and combustion runs of samples MIX_Original and MIX_12months. These values were quite lower than the
230 emission measured in a similar experimental system for other materials, as is the case of sewage sludge (630
231 pg WHO-TEQ/g), used oils (80 pg WHO-TEQ/g) or PVC (4500 pg WHO-TEQ/g) and similar to that
232 presented by meal wastes (12 pg WHO-TEQ/g), cotton textiles (8 pg WHO-TEQ/g) and polyester textiles (16
233 pg WHO-TEQ/g) (Conesa et al., 2009). Congener who most contributed to the total toxicity was 1,2,3,4-
234 TCDD in all samples. Respect to the PCBs, a maximum emission level of 0.31 pg/g was detected. This is a
235 very low amount and is not correlated to the level of chlorine in the samples, as is the case of PCDD/Fs.

236 **4. Conclusions**

237 In this work, a mixture of polyethylene, polyethylene-terephthalate, polypropylene and Nylon was submerged
238 in marine water for 12 months. During this time, chlorine was mainly incorporated to the plastics, especially
239 PE, that increased very quickly its chlorine content, reaching the highest value. The NCV of these polymers
240 did not present significant variations over time.

241 In general, thermal properties of all plastics were affected by the contact with the marine water, causing a
242 weakening of the plastic as time goes by. PET was the most affected polymer.

243 Pollutant emissions from thermal decomposition of this sample and the original were studied under inert and
244 oxidizing atmosphere, being methane and ethylene the main compounds emitted in both cases. The yields of
245 these gases were lower in the presence of oxygen.

246 Not differences were found in the emissions of PAHs from both samples (MIX_original and MIX_12
247 months), being the naphthalene the majority compound in all experiments. The highest yields of ClBzs and
248 ClPhs were observed in pyrolytic conditions. The most abundant isomer in all samples was 1, 2-
249 dichlorobenzene. On the other hand, both the bromine content in the samples and the amount of BrPhs
250 evolved are almost nil in all the runs carried out. The emission levels of PCBs and PCDD/Fs were very low
251 too.

252 In general, pollutant emissions are higher when the content of oxygen in the process is lower, that is, in
253 pyrolytic conditions. Otherwise, results show only small differences between MIX_original and
254 MIX_12months. So it can be said that the level of chlorine in the waste is not correlated with the emission of
255 chlorinated species, at least in the ranges studied in this study.

257

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