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Pollutant content in marine debris and characterization by thermal decomposition

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ABSTRACT

Marine debris (MDs) produces a wide variety of negative environmental, economic, safety, health and cultural impacts. Most marine litter has a very low decomposition rate (plastics), leading to a gradual accumulation in the coastal and marine environment. Characterization of the MDs has been done in terms of their pollutant content: PAHs, ClBzs, ClPhs, BrPhs, PCDD/Fs and PCBs. The results show that MDs is not a very contaminated waste. Also, thermal decomposition of MDs materials has been studied in a thermobalance at different atmospheres and heating rates. Below 400–500 K, the atmosphere does not affect the thermal degradation of the mentioned waste. However, at temperatures between 500 and 800 K the presence of oxygen accelerates the decomposition. Also, a kinetic model is proposed for the combustion of the MDs, and the decomposition is compared with that of their main constituents, i.e., polyethylene (PE), polystyrene (PS), polypropylene (PP), nylon and polyethylene-terephthalate (PET).

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1. Introduction

“Marine litter is defined as any persistent, manufactured or processed solid material discarded, disposed or abandoned in the marine and coastal environment” (Coe and Rogers, 1997; Galgani et al., 2010a, 2010b). It consists of items that have been made or used by people and deliberately discarded into the sea or rivers or on beaches; brought indirectly to the sea with rivers, sewage, storm water or winds; accidentally lost, including material lost at sea in bad weather (fishing gear, cargo); or deliberately left by people on beaches and shores (UNEP, 2009).

The presence of marine debris is a cause for concern due to several reasons. It is known to be harmful to organisms and to human health (Coe and Rogers, 1997; Derraik, 2002; Gregory, 2009; Rochman et al., 2013b), it has potential to increase the transport of organic and inorganic contaminants (Gaylor et al., 2012; Holmes et al., 2012; Mato et al., 2001; Rochman et al., 2013a; Teuten et al., 2009), it presents a hazard to shipping, and it is aesthetically detrimental, and thus generating negative socio-economic consequences (Mouat et al., 2010).

The material most commonly found in marine debris are glass, metal, paper and plastic (OSPAR, 2007), and, according to the published literature, it is clearly apparent that, globally, plastic items are consistently the most abundant type of marine debris (OSPAR, 2007; Thompson et al., 2009; UNEP-CAR/RCU, 2008; UNEP, 2005, 2009). The

most commonly used plastics are polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET), 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; Martins and Sobral, 2011).

Recent surveys estimate that between 4.8 and 12.7 million tons of plastic waste ends up in the world's oceans every year (Jambeck et al., 2015). The annual input of plastics in the oceans increases every year. It is estimated that in 2015 around 9.1 million tons were accumulated. By 2025, the annual input of plastics to the sea would be about double what it was in 2010. By then, the total amount of plastic debris accumulated in the oceans around the world is estimated around 155 million tons (Jambeck et al., 2015).

Pyrolysis and combustion have always been considered as attractive alternatives for waste disposal, since these techniques provide a reduction in volume of waste and also involve profitable energetic and/or chemical products. Thermal decomposition of waste can take place both in controlled conditions (incinerators, cement kilns...) and non-controlled conditions, for example, during fires or open-air burning. The substances emitted during non-controlled plastic thermal degradation may create a serious hazard for human health and for the environment (Iñiguez et al., 2016).

Until now plastic fractions of marine debris have been landfilled because it was considered as a waste product with low value; however, today it is known that this waste has a great value and it is suitable for recycling, mainly by chemical or energy recovery, especially attractive for polyolefin waste (Hagstrom et al., 2006).

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Some marine debris cannot be recycled or reused. On most countries, incineration is the most widely used process to treat marine debris (Jung et al., 2010). In this process, the production of air pollutants requires special attention, since incomplete combustion of these can generate harmful gases. Furthermore, due to chlorine, generation of dioxins in this process is important and must be measured.

In the present work, characterization of the pollutant content of the MDs is done, and a kinetic model for their thermal decomposition is proposed, considering the decomposition in different atmospheres and heating rates.

2. Materials

Over several months, it has been carried out the MDs collection in areas near the ports of Torrevieja and Santa Pola (Mediterranean coast). The MDs sample used in this study was selected from the residues collected during one day, and has been considered representative of a conventional marine waste. The selection was made taking into account the major components, especially plastic ones, as well as the proportions in which each of the different collected residues are found in the sea.

Besides of the MDs, the five main plastics components in marine litter were studied for thermal decomposition (Iñiguez et al., 2016). In this way, PE, PP, PET, Nylon and PS were subjected to decomposition in the thermobalance.

3. Methods and equipment

3.1. Characterization of MDs

An elemental analysis was performed to a representative sample (carbon, hydrogen, nitrogen and sulfur) performed by oxidation of the sample to 1000 °C and subsequent detection of combustion products (CO₂, H₂O, N₂ and SO₂) that are separated into specific columns to be thermally desorbed thereafter. The gases pass separately by a thermal conductivity detector which provides a signal proportional to the concentration of each of the individual components of the mixture. The initial weight of the sample was 50 mg, and sulfamethazine was employed as internal standard. The equipment used was a Perkin-Elmer 2400 (Perkin-Elmer, UK); the amount of sulfur detected in this equipment was nil, and so an additional analysis was performed in a Total Carbon and Nitrogen Analyzer “TruSpec CN” LECO, with Sulfur module that used Vanadium Pentoxide. This analysis indicated that the amount of Sulfur is 0.098 wt.%. Also, the humidity of the samples after 2 months at room temperature and the ash content were measured (UNE-EN ISO, 2016). The Net Calorific Value (NCV) was determined using a calorimetric bomb AC-350 Leco Instruments, and the halogen content of the sample was measured by ionic chromatography following EPA method 5050 (US EPA, 2007b).

A detailed analysis of various pollutants contained in the MDs was done in order to characterize the sample and get knowledge of its possible origin. Two different samples were taken and analyzed for the content of polychlorinated biphenyls (PCBs), toxic dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), chlorinated benzenes (ClBzs) and brominated and chlorinated phenols (BrPhs and ClPhs).

In order to determine PAHs, ClBzs, ClPhs and BrPhs in the samples, four different internal standards were added to them before extraction: 5 µL of deuterated PAH Mix 26 (Dr. Ehrenstorfer-Schäfers, Augsburg, Germany), 10 µL of ¹³C-labelled ClPh, 10 µL ¹³C-labelled ClBz and 100 µL ¹³C-labelled BrPh (Wellington Laboratories, Ontario, Canada). Later, extraction was done in a mixture of dichloromethane-acetone (1:1) by Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the U.S. EPA method 3545A (US EPA, 2007a). The extract was concentrated in a rotary evaporator and

with a moderate stream of nitrogen up to 1.5 mL. Finally, 6 µg of anthracene-d10 (AccuStandard, New Haven, USA) was spiked as a recovery standard.

The quantification of the 16 priority PAHs established by U.S. EPA (1998) was done following the U.S. EPA method 8270D (US EPA, 2007b, 2007c) in a GC-MS (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA), in the SCAN mode with a HP-5 MS capillary column (Agilent Technologies, USA). ClPhs, ClBzs and BrPhs were analyzed in the same equipment but employing the SIR mode.

In order to analyze PCDD/Fs and dioxin-like PCBs, U.S. EPA method 1613 (US EPA, 1994b) and U.S. EPA method 1668C (US EPA, 2010) were used, respectively. ¹³C-labelled analogues were added to the samples as internal standards (10 µL of LCS-1613 for PCDD/Fs and 10 µL WP-LCS for PCBs (Wellington Laboratories, Ontario, Canada)) and an accelerated extraction with toluene was performed in an ASE 100 Dionex apparatus.

These extracts were purified and fractionated in an automated Power Prep® system (FMS, Inc., Boston, MA), obtaining two fractions (PCDD/Fs and PCBs). Both fractions were concentrated in nonane with a stream of nitrogen and, finally, recovery standards were added (10 µL of ISS-1613 for PCDD/Fs and 10 µL WP-ISS for PCBs (Wellington Laboratories, Ontario, Canada)). The analytical determination of these compounds used an Agilent HP5890 High Resolution Gas Chromatographer coupled to a Micromass Autospec Ultima NT High Resolution Mass Spectrometer (HRGC-HRMS).

3.2. Decomposition curves of MDs in different atmospheres

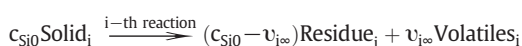
In order to get a better knowledge of the MDs decomposition behavior, thermogravimetric runs were performed in different atmospheres.

Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in different atmospheres such as nitrogen and mixtures of nitrogen and oxygen (4:1 and 9:1) with a total flow rate of 100 mL min⁻¹. The experiments were carried out at heating rates of 5, 10 and 20 K/min for each atmosphere, from room temperature up to 1173 K. For each run, 6 ± 0.3 mg of sample were used.

3.3. Kinetic model optimization method (combustion)

Thermal decomposition of each of the five main plastics components and also of the MDs were studied under N₂:O₂ = 4:1 atm (approx. synthetic air) in order to compare their decomposition curves.

The kinetic model proposed for thermal decomposition of each plastic component considers each material formed by one or two independent parts (depending on the plastic), each one following an independent reaction, as follows:



with $i = 1$ or 2 . In the previous equation, $Solid_i$ refers to different fractions of the original material, $Volatiles_i$ are the gases and condensable volatiles evolved in the corresponding reactions and $Residue_i$ is the possible residue formed in the decomposition of each $Solid_i$. Each fraction has a yield coefficient (considered constant throughout the reaction) representing the maximum mass fraction obtainable by each reaction. In this way, $v_{i\infty}$ is the yield coefficient for the $Volatiles_i$ and $(c_{Si0} - v_{i\infty})$ is the yield coefficient for the $Residue_i$. On the other hand, the sum of initial mass fractions of the components (c_{Si0}) is exactly one minus the final mass fractions of solid (Grønli et al., 2002).

The conversion degree for each reaction is defined as the ratio between the mass fractions of solid reacted at any time ($c_{Si0} - w_{Si}$) and

Table 1

Analysis of marine debris used (wt.% in all cases).

Immediate analysis	
Humidity	9,3
Ashes	29,1
Elemental analysis	
C	38,2
H	4,89
N	0,28
S	0,098
O (by difference)	27,52
Ionic chromatography	
Fluorine	0,00524
Chlorine	1,83
Bromine	0,00786

n.d. = not detected.

the corresponding initial fraction of this component:

$$\alpha_i = \frac{C_{Si0} - W_{Si}}{C_{Si0}}, \quad i = 1, 2.$$

From the mass balance between products and reactants and the conversion degrees, the kinetic equations for decomposition runs can be defined as follows:

$$-\frac{d\left(\frac{W_{Si}}{C_{Si0}}\right)}{dt} = k_i \left(\frac{W_{Si}}{C_{Si0}}\right)^{n_i} \quad \text{or} \quad \frac{d\alpha_i}{dt} = k_i (1 - \alpha_i)^{n_i}$$

with n_i being the reaction order and the kinetic constants following the Arrhenius equation. For the sake of simplicity, and bearing in mind that a great variety of materials follow first order decompositions (Caballero and Conesa, 2011; Várhegyi, 2007), all values of reaction orders have been maintained to unity, i.e., $n_i = 1$ in all cases.

For calculation of the total mass remaining a weighted sum is used:

$$-\frac{dw_s^{\text{cal}}}{dt} = \sum_i C_{Si0} \frac{d\alpha_i}{dt} \quad \text{and} \quad w_s^{\text{cal}} = 1 - \sum_i C_{Si0} \alpha_i$$

The optimization was done by integration of the differential equations presented in the kinetic model by the Euler method considering and testing that the intervals of time were small enough to make the integration errors negligible. The optimization method of the function Solver in a Microsoft Excel spreadsheet was used to minimize the differences between the experimental and calculated mass fraction and their derivatives. The objective function (OF) to be minimized was:

$$\text{OF} = \sum_{m=1}^M \sum_{p=1}^P \left(w_{S,m,p}^{\text{cal}} - w_{S,m,p}^{\text{exp}} \right)^2 + \text{factor} \sum_{m=1}^M \sum_{p=1}^P \left(\frac{dw_{S,m,p}^{\text{cal}}}{dt} - \frac{dw_{S,m,p}^{\text{exp}}}{dt} \right)^2$$

where 'p' represents the experimental data at time 't' in the experiment with a heating rate 'm'. The value of M is the number of runs and P is the number of points in each run. The value of the 'factor' was arbitrarily chosen to be 10^{+3} , in order to give similar contribution to the O.F. to the mass fraction differences and those of the derivatives. Note that with this methodology, a unique set of kinetic constants is calculated from the experimental curves obtained at different heating rates, and it gives kinetic constants valid for the whole set of heating rates used.

The points used for the kinetic analysis, have been selected according to techniques recommended by Caballero and Conesa (2005) so that the derivative of the points is calculated accurately

and correctly, the points are equally spaced on a representation derivative of weight versus temperature and the fitting is simultaneous, with no variation of the kinetic constants, for at least three different heating rates.

With the objective of decreasing the great interrelation existing among the pre-exponential factor, the activation energy and the reaction order, the optimization was carried out using a "comparable kinetic constant" k_i^* instead of optimization of k_{i0} (Martín-Gullón et al., 2003).

$$k_i^* = k_{i0} \exp\left(\frac{-E_i}{RT_{\text{max}}}\right) (0.64)^{n_i}$$

In the previous equation, T_{max} is the temperature where maximum rate of decomposition is experimentally observed, and $n_i = 1$ in the present calculation for all polymers.

In order to explain experimental curves, thermal decomposition in synthetic air of the MDs has been considered as a weighted sum of the decomposition of each of the five main constituents, in such a way that:

$$-\frac{dw_{\text{MD}}^{\text{cal}}}{dt} = \sum_j f_{j0} \frac{d\alpha_j}{dt} \quad \text{and} \quad w_{\text{MD}}^{\text{cal}} = 1 - \sum_j f_{j0} \alpha_j$$

In the previous equation, w_{MD} represents the calculated weigh fraction of the marine debris, and 'j' refers to each component (i.e. PET, PS, PE, PP and Nylon). In the equation f_{j0} represents the weight contribution of each of the components to the total weight.

4. Results

4.1. Characterization of MDs and pollutant content

The results for elemental analysis of a representative sample of MDs are presented in Table 1. In this Table is also shown the humidity of the samples after 2 months at room temperature, the ash content and the halogen content of the sample; it is remarkable the high chlorine content (1,83%), value that is logical bearing in mind that the sample comes from a saline environment. The Net Calorific Value (NCV) was 25.6 MJ/kg.

Details of the analysis of PAHs, ClBzs, BrPhs and ClPhs are shown in Tables SI1, SI2 and SI3 of the Supporting Information. In general, reproducibility of analysis is difficult mainly due to the heterogeneity of the sample. The main PAH present in the sample is naphthalene with a content close to 100 ng/g. Total chlorobenzenes is in the range

Table 2

Dioxin and furans (PCDD/Fs) content (two samples).

Congener	Sample MDs 1 pg/g	Sample MDs 1 pg/g
2,3,7,8-TCDF	0,8	0,7
1,2,3,7,8-PeCDF	0,1	0,2
2,3,4,7,8-PeCDF	0,4	0,4
1,2,3,4,7,8-HxCDF	0,4	1,3
1,2,3,6,7,8-HxCDF	0,2	1,0
2,3,4,6,7,8-HxCDF	3,2	3,2
1,2,3,7,8,9-HxCDF	0,3	0,4
1,2,3,4,6,7,8-HpCDF	1,3	1,4
1,2,3,4,7,8,9-HpCDF	0,6	1,1
OCDF	1,2	0,9
2,3,7,8-TCDD	0,0	0,0
1,2,3,7,8-PeCDD	0,3	0,2
1,2,3,4,7,8-HxCDD	0,0	0,0
1,2,3,6,7,8-HxCDD	0,3	0,6
1,2,3,7,8,9-HxCDD	0,1	0,3
1,2,3,4,6,7,8-HpCDD	3,0	2,7
OCDD	4,6	5,8
Total-toxic PCDD/Fs (pg WHO-TEQ/g)	0,99	1,20

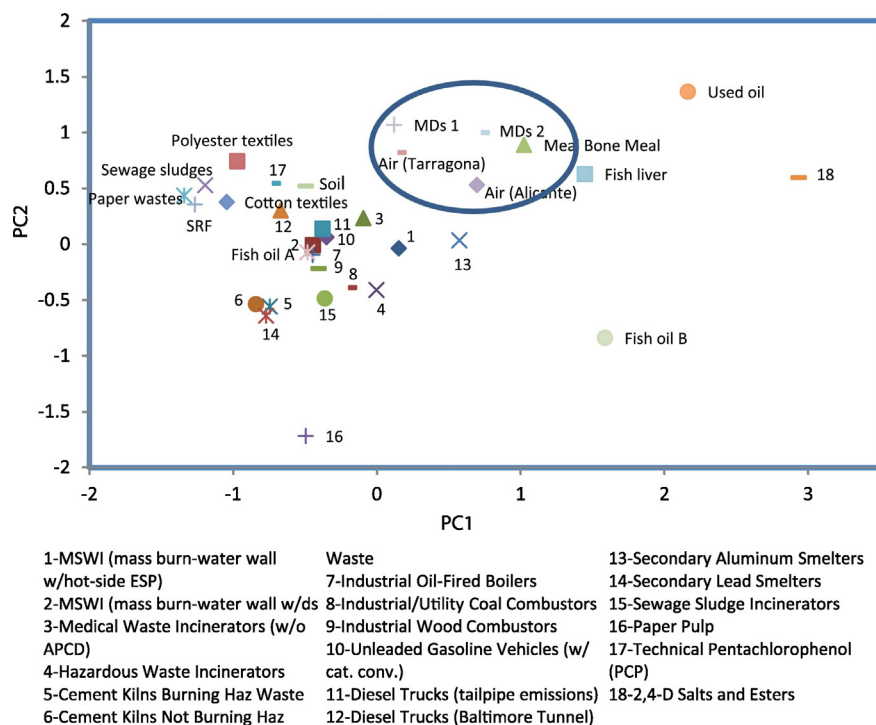


Fig. 1. Scatter plots of the two first principal components. The points represent different sample origins (marked in the text).

180–215 ng/g, being 1,2-dichlorobenzene the most abundant isomer in two different samples. On the other hand, approximate chlorophenols content is 105 ng/g and bromophenols ranged 58–77 ng/g. As comparative data, in our laboratory total amount of chlorophenols measured in furniture wood waste (Moreno et al., 2016) is nearly 100 ng/g whereas not chlorobenzenes were detected. Respect to the PAHs content, furniture wood waste presents a total amount of 645 ng/g whereas solid and pine wood does not present a detectable amount. This shows up that MDs is not a very contaminated waste, the only remarkable difference is the high amount of chlorobenzenes, which may be comparable to that found in vegetable soils (Song et al., 2012) or sediments of rivers (Cai et al., 2007).

The results for the analysis of PCDD/Fs in the two samples of MDs mentioned above are presented in Table 2. The total content of such pollutants is in the range 0.9–1.2 pg WHO-TEQ/g (0.95–1.17 pg I-TEQ/g), similar to other wastes analyzed in our laboratory (Conesa et al., 2008; Fuentes et al., 2007; Moltó et al., 2005; Moltó et al., 2006): cotton and polyester textiles presented a level of 3–10 pg I-TEQ/g, sewage sludge between 5 and 8 pg/g, PVC 0.6 pg/g and meat and bone meals had the lower dioxins and furans content (0.3 pg/g). A reference in literature has been found doing a similar analysis in sediment collected from offshore waters of Central Vietnam (Tri et al., 2016). The total content of such pollutants in these sediments (1.8 pg WHO-TEQ/g) is similar to that obtained in this study.

In order to investigate the congener profile in the MDs samples, a principal component analysis (PCA) has been done considering different profiles published in literature. On the one hand, a study performed in the USA considering different sources (Cleverly et al., 1997) has been used. This study comprises eighteen chlorinated patterns: MSWI (mass burn-water wall w/hot-side ESP), MSWI (mass burn-water wall w/ds), Medical Waste Incinerators (w/o APCD), Hazardous Waste Incinerators, Cement Kilns Burning Haz Waste, Cement Kilns Not Burning Haz Waste, Industrial Oil-Fired Boilers, Industrial/Utility Coal Combustors, Industrial Wood Combustors, Unleaded Gasoline Vehicles (w/ cat. conv.), Diesel Trucks (tailpipe

emissions), Diesel Trucks (Baltimore Tunnel), Secondary Aluminum Smelters, Secondary Lead Smelters, Sewage Sludge Incinerators, Paper Pulp, Technical Pentachlorophenol (PCP), and 2,4-D Salts and Esters. On the other hand, different profiles were taken from literature: cotton and polyester textiles (Moltó et al., 2005; Moltó et al., 2006), meat and bone meal (MBM) (Conesa et al., 2005a), sewage sludges (Conesa et al., 2005b), paper wastes (Conesa et al., 2008), used oils (Fuentes et al., 2007), solid recovered fuel from municipal solid wastes (Conesa et al., 2011), air and soil from Tarragona province (300 km away from the sampling point) (Rovira et al., 2015), air filters taken in our work place (Conesa and Galvez, 2006), fish liver (Orrego et al., 2005) and two different fish oils (Ábalos et al., 2010).

For the PCA nonequivalent toxic units were used, and the amount of each congener is normalized to the total amount of PCDD + PCDF. Fig. 1 presents scatter plot and correlation between all profiles used and first two principal components. Note that MDs congener profile is similar to that found in MBM wastes, and also in air and soil

Table 3
Polychlorinated biphenyls (PCBs) analysis performed in the MDs samples.

Congener	Sample MDs 1 pg/g	Sample MDs 2 pg/g
PCB-81	1,5	1,4
PCB-77	17,3	16,6
PCB-123	11,2	11,0
PCB-118	106,3	105,1
PCB-114	1,3	2,2
PCB-105	39,8	38,9
PCB-126	4,2	4,1
PCB-167	33,7	30,7
PCB-156	35,6	34,4
PCB-157	10,7	5,2
PCB-169	1,8	1,4
PCB-189	14,2	14,2
Total-PCBs (pgWHO-TEQ/g)	0,486	0,457

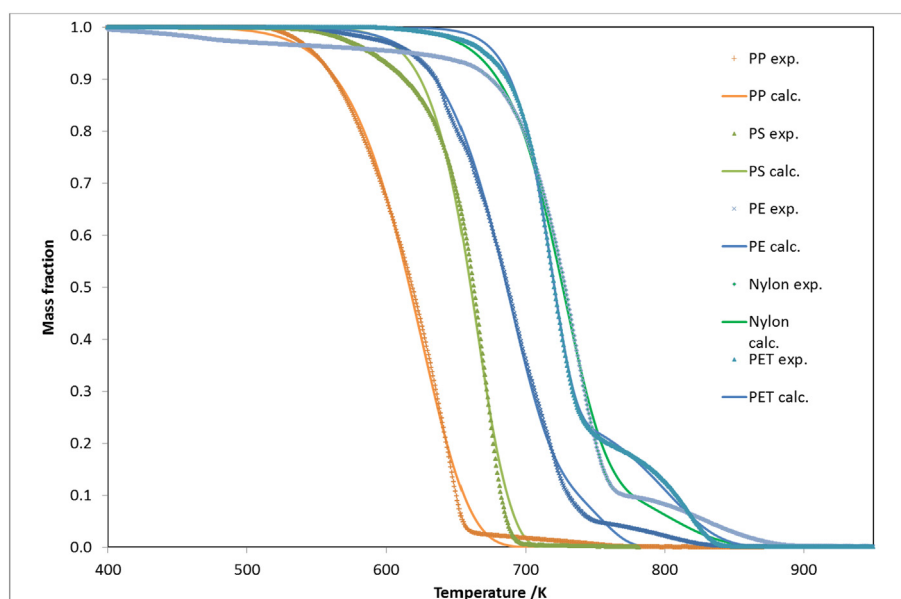


Fig. 2. Thermal decomposition of main plastics found in marine ambient at 20 K/min in $N_2:O_2 = 4:1$ atm. Experimental and calculated curves.

samples from nearby areas, with a predominance of the hepta- and hexa-chlorinated congeners.

Results for the analysis of PCBs in the two samples mentioned above are presented in Table 3. Total toxicity of PCBs is in the range 0.45–0.48 pg WHO-TEQ/g, representing ca. 30% of the dioxin-like compounds toxicity. Literature reports a wide variability on the PCBs contribution to the total WHO-TEQ. For example, PCBs contribution in fish oils ranged from 65 to 80% (Ábalos et al., 2010), whereas the percentage is much lower (ca. 2%) in other wastes as polyester textiles (Moltó et al., 2006).

4.2. Decomposition curves in air atmosphere and kinetic model

Experimental curves for decomposition at 20 k/min of PE, PS, PP and PET together with the calculated ones can be seen in Fig. 2. For the calculated curves, and bearing in mind the form of each curve (Fig. 2), two different fractions ($i = 2$) were considered in the case of PET, Nylon and PE, whereas a single fraction ($i = 1$) was necessary to explain PS and PP decomposition.

The optimized parameters for each plastic material are presented in Table 4. Fig. 2 shows the calculated curves, which explain in a very convenient way the experimental results. In all the decomposition activation energies are in the range 120–230 kJ mol^{−1}, what is the range suggested in literature (Vyazovkin, 2000; Vyazovkin et al., 2011).

On the other hand, Fig. 3 presents the thermal decomposition of the MDs in air atmosphere, at three heating rates. As can be seen, the increase of heating rate shifts the curve to higher temperatures, as usual in other materials.

As mentioned before, the calculation of the MDs decomposition curves, and bearing in mind that each plastic component has already been modelled, is merely to calculate the best values of f_{j0} (note that only 4 values are needed to be calculated). Fig. 3 shows the result of this procedure, with the following contributions to the total weight: 0% PS; 18.8% PET; 12.8% PP; 27.5% PE and 24.8% Nylon, i.e., for the simulation of the decomposition curve there is no need of the PS decomposition as the calculated fraction of this polymer is zero. These are very reasonable contributions and explain very well the obtained curves at the three heating rates used in the present study (see Fig. 3).

4.3. Decomposition curves of MDs in different atmospheres

Fig. 4 shows the thermal decomposition runs at different heating rates in nitrogen and a mixture $N_2:O_2 = 9:1$ (10% Oxygen). As can be seen, below 480–500 K actual atmosphere does not influence thermal degradation because the mass loss is due to vaporization of light components. In other temperature range, the presence of oxygen accelerates the decomposition, as it occurs in other materials (Font et al., 2011; Moliner et al., 2016; Niu et al., 2016), and the mass loss is higher. The introduction of a richer oxygen atmosphere (Fig. 3, previous section) does not produce dramatic changes in the decomposition, and simply a slight acceleration respect to the 10% oxygen atmosphere is observed.

At these higher temperatures it does not occur volatilization but cracking, as the heavy molecules, which are more resistant to the thermo-degradation, are broken, yielding volatiles and char (carbonaceous residue) which accounts for the weight in the thermobalance. This residue is not decomposed in inert atmosphere

Table 4

Kinetic constants for the thermal decomposition of different plastics in $N_2:O_2 = 4:1$ atm.

Nylon	k_{01}, s^{-1}	1.83E + 05
	$E_1, kJ mol^{-1}$	112.46
	c_{s10}	0.17
	k_{02}, s^{-1}	2.85E + 09
	$E_2, kJ mol^{-1}$	158.76
PE	k_{01}, s^{-1}	4.95E + 07
	$E_1, kJ mol^{-1}$	127.28
	c_{s10}	0.86
	k_{02}, s^{-1}	2.05E + 14
	$E_2, kJ mol^{-1}$	232.36
PP	k_{01}, s^{-1}	6.28E + 05
	$E_1, kJ mol^{-1}$	93.51
PET	k_{01}, s^{-1}	1.23E + 07
	$E_1, kJ mol^{-1}$	140.22
	c_{s10}	0.27
	k_{02}, s^{-1}	5.95E + 16
	$E_2, kJ mol^{-1}$	254.21
PS	k_{01}, s^{-1}	1.61E + 11
	$E_1, kJ mol^{-1}$	166.44

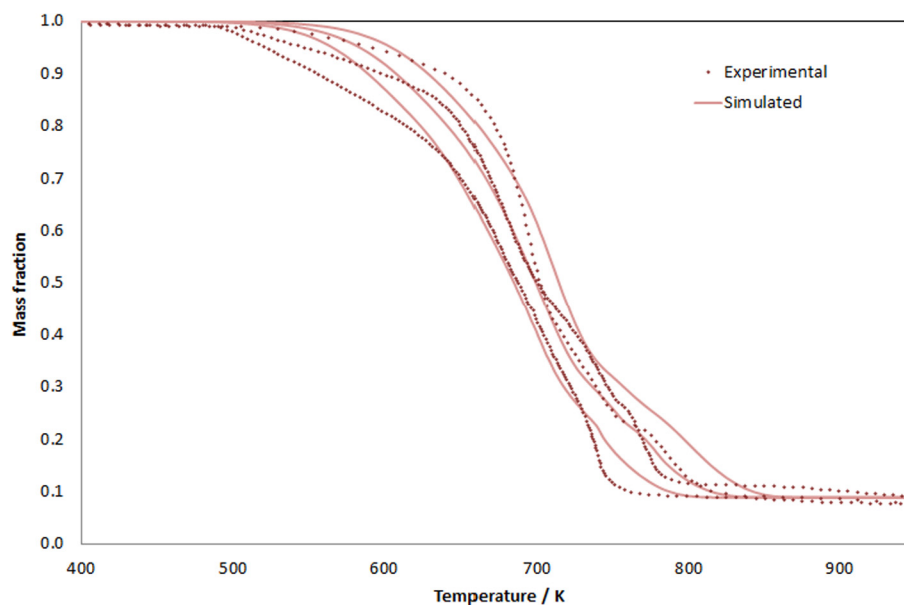


Fig. 3. Thermal decomposition of MDs at 5, 10 and 20 K/min in $N_2:O_2 = 4:1$ atm. Experimental and simulated curves.

but is fast oxidized in the presence of a reacting species as oxygen. For this reason, at temperatures over 700 K the mass loss rate is higher in combustion runs than in pyrolysis.

5. Conclusions

The present study shows up that MDs is not a very contaminated waste. The pollutant content is comparable to other wastes analyzed in our laboratory, or samples collected from rivers or vegetable soils studied by other authors. The sulfur content of the sample is very low and it is notable the high chlorine content, which can be explained by the presence of this waste in seawater.

This study is the first analysis of thermal decomposition performed on a sample of MDs. Our results revealed that below 400–500 K, the atmosphere does not affect the thermal degradation. However, at temperatures between 500 and 800 K the presence of oxygen accelerates the decomposition, so the mass loss rate is higher in combustion than in pyrolysis.

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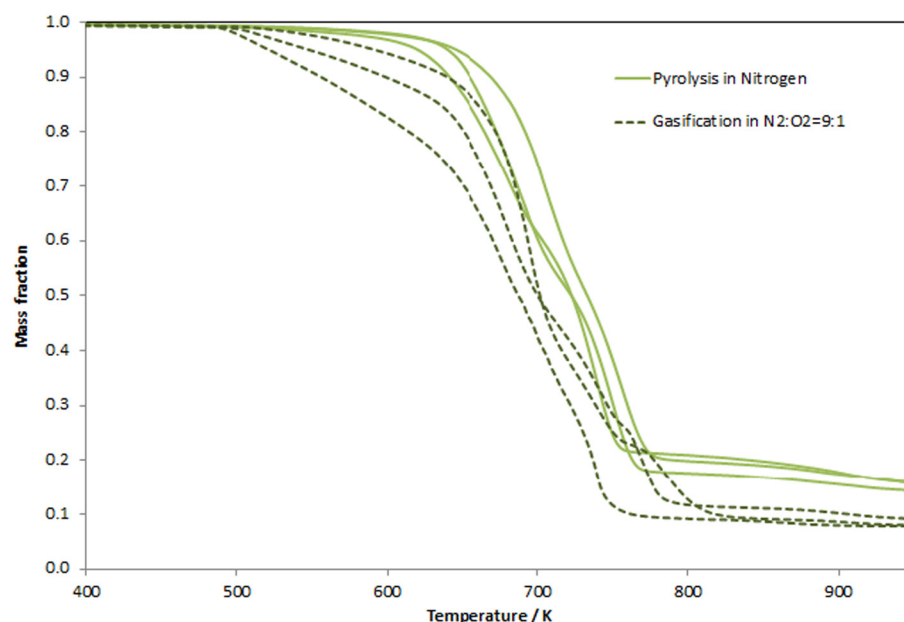


Fig. 4. Thermal decomposition of MDs at 5, 10 and 20 K/min in Nitrogen and in $N_2:O_2 = 9:1$ atm.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marpolbul.2017.02.022>.

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