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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 Torre Vieja 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

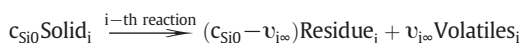
In order to get a better knowledge of the MDs decomposition behavior, thermogravimetric runs were performed in different atmospheres.

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

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