Marine debris characterization and thermal decomposition compared to their main constituents

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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 (as plastics, which are the most abundant type of marine debris), leading to a gradual, but significant accumulation in the coastal and marine environment. Characterization of the marine debris has been done in terms of their pollutant content, including polycyclic aromatic hydrocarbons, chlorobenzenes, chlorophenols, bromophenols, chlorinated dioxins and furans, and dioxin-like PCBs. Also thermal decomposition of marine debris materials has been studied, in a thermobalance at different atmospheres and heating rates. 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 polyethylen-tereftalate (PET). The results show that MDs is not a very contaminated waste. 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.

In the University of Alicante, a research project on the impact of marine debris on the Mediterranean coast is being developed. Over several months, it has been carried out the waste collection in areas near the port. The MDs sample used in this study was selected from which it was collected along one day and considered representative of a conventional marine waste. The selection was made taking into account the major components, especially plastic ones, while maintaining the original proportions by stratified random sampling with proportional allocation. Besides of the MDs, the five main plastics components in marine litter were studied for thermal decomposition (Iñiguez, Conesa et al. 2016). In this way, PE, PP, PET, Nylon and PS were subjected to decomposition in the thermobalance.

An elemental analysis was performed to a representative simple (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). 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 the origin of the sample. The Net Calorific Value (NCV) was 25.6 MJ/Kg.

Table 1. Analysis of marine debris used (wt. % in all cases). n.d. = not detected

Inmediate analysis		Elemental Analysis					Ionic Chromatography		
Humidity	**Ashes**	**C**	**H**	**N**	**S**	**O**	**Fluorine**	**Chlorine**	**Bromine**
9,3	29,1	38	4,9	0,3	n.d.	28	0,00524	1,83	0,00786

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).

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 naphtalene with a content close to 100 ng/g. Total chlorobenzenes is in the range 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 58-77 ng/g. As comparative data, in our laboratory total amount of chlorophenols measured in furniture wood waste 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 or sediments of rivers (Cai, Mo 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: 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. The total content of such pollutants in these sediments (1,8 pg WHO-TEQ/g) is similar to that obtained in this study.

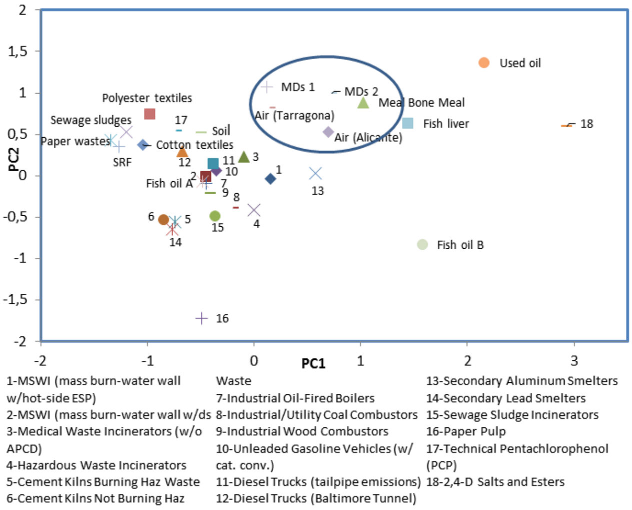

Figure 1. Scatter plots of the two first principal components. The points represent different sample origins (marked in the text).

In order to investigate the congener profile in the MDs samples, a principal component analysis has been done considering different profiles published in literature. For the PCA nonequivalent toxic units were used, and the amount of each congener is normalized to the total amount of PCDD+PCDF. Figure 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 samples from nearby areas, with a predominance of the hepta- and hexa-chlorinated congeners.

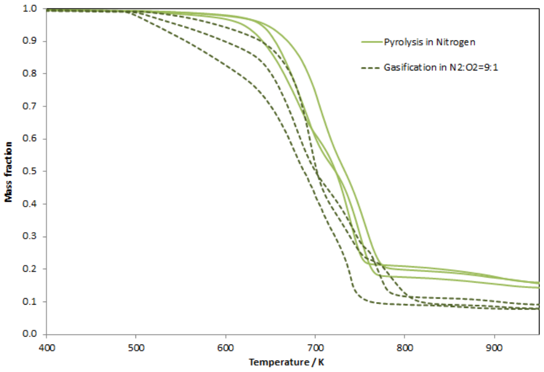

Figure 2. Thermal decomposition of marine debris.

In order to get a better knowledge of the MDs decomposition behavior, thermogravimetric runs were performed in different atmospheres. Figure 2 shows the thermal decomposition runs at different heating rates in nitrogen and in a mixture N_2:O_2= 9:1 (10 % Oxygen). As can be seen, bellow 480 – 500 K actual atmosphere does not influence thermal degradation because the mass loss happens due to vaporization of light components. In other temperature range, the presence of oxygen accelerates the decomposition, as it occurs in other materials (Font, Moltó et al. 2011; Moliner, Bosio et al. 2016; Niu, Chen et al. 2016), and the mass loss is higher. The introduction of a richer oxygen atmosphere (Figure 3, previous section) does not produce dramatic changes in the decomposition, and simply a slight acceleration respect to the 10 % oxygen atmosphere is observed.

In this second phase it does not occur volatilization but cracking. At higher temperatures the heavy molecules, which are more resistant to the thermos-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 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.

Acknowledgements

Support for this work was provided by the CTQ2016-76608-R project from the Ministry of Economy and Competitiveness (Spain) and the PROMETEOII/2014/007 project from the Valencian Community Government (Spain).

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