

## Article

# Effect of Sodium Chloride and Thiourea on Pollutant Formation during Combustion of Plastics

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**Abstract:** Thermal decomposition of different samples containing a mixture of plastics (polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and nylon) combined with NaCl and metal oxides ( $\text{Fe}_2\text{O}_3$ , CuO) was studied under an air atmosphere at 850 °C using a reactor, followed by analysis of the evolved products. Combustion runs were performed to study how the presence of such compounds influences the production of pollutants. Here, we report the analyses of the emissions of the main gases, as well as volatiles and semivolatiles, including polyaromatic hydrocarbons (PAHs), polychlorinated benzenes and phenols, and polybrominated phenols. Results show that the production of chlorinated pollutants did not increase in the presence of NaCl, but the presence of other metals during the decomposition led to the production of a great amount of pollutants. In this regard, the emission of chlorinated phenols increased from 110 to ca. 250 mg/kg when the sample included a small quantity of a transition metal oxide. Additionally, the presence of an inhibitor—thiourea (TUA)—was tested. Results confirm that adding TUA to the sample reduced these emissions to a considerable extent, with the emission of chlorinated phenols amounting to 65 mg/kg.

**Keywords:** plastic mixture; PAHs; ClBzs; NaCl; catalyzed medium; inhibition

## 1. Introduction

Due to the rapid development of the plastics industry, plastic products have become the most abundant material worldwide [1]. The presence of these items in the marine environment has increased dramatically in the last 50 years [2], representing 60–80% of total marine debris [3].

Around 280 million tons of plastic items are produced each year [4,5]. Jambeck et al. estimated that between 4.8 and 12.7 million tons of this waste end up in the world's oceans every year [6]. The polymers most often found in the marine environment are polyethylene, polypropylene, and polyethylene terephthalate, as they are also the most commonly used [7–9].

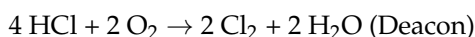
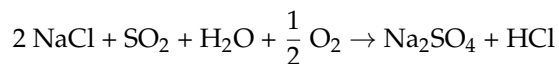
Plastics are hazardous for the marine environment for several reasons. The main reason is their resistance to degradation: it is estimated they need hundreds or thousands of years to degrade [10]. Also important is that plastic debris in the marine environment contains organic contaminants, including polychlorinated biphenyls (PCBs) and dioxins (polychlorodibenzofurans, PCDD/Fs) that are released into the sea during their degradation [11,12]. A lifecycle of marine debris has been described [1], showing the importance of the collection of such materials.

Once removed from the sea, the most common processes used for the treatment of marine debris are combustion or pyrolysis processes. However, during the thermal decomposition of this debris, several pollutants can be emitted into the atmosphere if the process is not properly controlled. Hydrogen chloride and chlorinated aromatic compounds, such as chlorobenzenes (ClBzs), chlorophenols (ClPhs), chlorobiphenyls (PCBs), polychlorodibenzo-*p*-dioxins, and polychlorodibenzofurans (PCDD/Fs), can be produced during pyrolysis and combustion of chlorinated polymers.

The effects of chlorine content in waste on the formation mechanisms of polychlorinated pollutants, especially PCDD/Fs, have been studied by different authors [13–15]. When chlorine content in waste is less than 0.8–1.1%, chlorine can chlorinate the non-substituted phenol to produce chlorophenols, which are important precursors of PCDDs. In this scenario, PCDD formation dominates. However, there can be differences in the emission profiles and quantities of PCDD/Fs when the chlorine level is over 0.8–1.1% [14]. On the other hand, Gullet et al. suggested that active chlorine species are strongly dependent on combustion conditions. Therefore, it seems that there is a low correlation between total chlorine (including inorganic) in waste streams and the formation PCDD/Fs during the combustion process [13]. Nevertheless, other authors have pointed out that both organic and inorganic chlorine affects the production of chlorinated compounds [16,17]. Chern and Bozzelli emphasized that these studies are not appropriate for modern, continuous feed, steady-state municipal solid waste incinerators (MSWIs), and that during primary decomposition, the influence of the presence of NaCl is clear [18].

Altarawneh et al. commented on the necessity of ash-bound inorganic chlorine for the formation of PCDD/Fs. These authors mentioned that adding an aqueous solution of NaCl to fly ash increased the emission of HCl by 50%, which increases the degree of chlorination [19].

The mechanism of the conversion of chlorine contained in NaCl into gaseous HCl is well known [19,20]. The most important points in the conversion are: the availability of water vapor, the presence of clay minerals in the ash, and the temperature and design of the incinerator. Nevertheless, according to Zheng et al., NaCl is an effective chlorine source, but it has no effect without other metallic catalysts, such as  $\text{ZnCl}_2$  or  $\text{CuCl}_2$ . In this regard, Duo and Leclerc [21] proved that although HCl is a combustion product of PVC-containing wastes, NaCl can also be converted into HCl by reactions with  $\text{SO}_2$  or aluminosilicate materials. The subsequent reaction of the HCl product with oxygen, via the well-known Deacon reaction, produces highly reactive  $\text{Cl}_2$ , which chlorinates the intermediate structures:



In fact, it has been proved that HCl is an inactive chlorinating agent in a noncatalyzed medium [19].

On the other hand, it is important to reduce pollutant emissions during thermal decomposition of materials. The effect of the presence of substances acting as inhibitors of these emissions have been studied in several works. In all cases, thiourea (TUA) has shown the best results [22–24].

Following this line of research, the aim of this study is to examine how the presence of NaCl influences the production of pollutants during the thermal decomposition of a mixture of plastic materials. The combustion runs were performed with and without a catalyst mixed with the materials, and the results were compared. In addition, combustions of a mixture of plastics without the presence of NaCl and with 3% content of thiourea (TUA) were carried out. In this way, it was possible to verify whether the presence of thiourea in the sample reduced emissions during the combustion process, as found by other authors. There are studies in the literature where the effect of different inorganic salts has been examined [13,14,16–18], but no reports using plastics or mixtures of plastics have been found.

## 2. Materials and Methods

The decomposition of a mixture of the four most common polymers found in the sea (polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and nylon), was studied. The weight proportion of each plastic was the same, i.e., 25 wt % of each, as this composition is considered characteristic of plastics collected from the seas [1,25].

NaCl used in the study was reactive-grade from VWR (Leuven, Belgium). Iron oxide (III) ( $\text{Fe}_2\text{O}_3$ , Thermofisher, Kandel, Germany) and copper oxide (II) ( $\text{CuO}$ , Panreac Química SA, Barcelona, Spain)

were used as a catalytic medium. A test to reduce the emissions during combustion was also performed using thiourea (TUA) (VWR, Leuven, Belgium).

Combustion runs of different samples were carried out to compare emissions during their thermal decomposition. In this sense, different mixtures were prepared to study the effect of the presence of NaCl in a catalyzed and noncatalyzed medium. Table 1 shows the composition of these samples. They are named “MIX”, “MIX\_TUA”, “MIX\_NaCl”, “MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub>”, and “MIX\_NaCl\_CuO”. As can be seen, the amount of salts used in the present study is much greater than that usually present in marine debris, with the intention of preventing the lack of inorganic chlorine from being a parameter of experimental uncertainty.

**Table 1.** Composition of the samples studied (wt %).

Sample	Composition
MIX	PP, PE, PET and Nylon (25 wt % each)
MIX_TUA	97% MIX 3% thiourea (TUA)
MIX_NaCl	50% MIX 50% NaCl
MIX_NaCl_Fe <sub>2</sub> O <sub>3</sub>	50% MIX 45% NaCl 5% Fe <sub>2</sub> O <sub>3</sub>
MIX_NaCl_CuO	50% MIX 45% NaCl 5% CuO

In each experiment, between 0.25 and 0.50 g of the sample was placed in two quartz boats, each 70 mm long, which were introduced along a quartz tube (10 mm internal diameter). This quartz tube was a moving tubular reactor. The temperature inside the horizontal furnace reached 850 °C before the run. The choice of 850 °C in the experiments is because the EU incineration directive sets a minimum of 2 s at this temperature for the post-combustion zone of treatment plants. The boats were then introduced to the furnace using a horizontal actuator that permits the use of a constant speed and a constant flow of synthetic air (500 mL/min) in parallel to the sample. This flow was measured at 1 atm and 20 °C. The residence time in the hot zone of the furnace is approximately 4 s, taking into account the flow of air and the dimensions of the furnace.

Conesa et al. described this experimental system in detail [26]. The oxygen ratio, which is defined as the fraction between the actual and the stoichiometric air flow rate necessary for a complete combustion, was 0.5. Prior to the decomposition runs, one blank experiment (boats without a sample) was carried out for each of the different experimental conditions. To test the reproducibility of the results, all experiments were duplicated.

The gas produced in each run was sampled to analyze different pollutants. Gases and volatile compounds were collected in Tedlar® bags (Restek, Bellefonte, PA, USA). The gas fraction was analyzed by chromatography, using GC-TCD (Agilent 7820) equipped with two columns: column 1 (HayeSep Q 800/100 (2.44 m × 2 mm)) and column 2 (Molecular Sieve 5A 80/100 (1.83 m × 2 mm)). Analyses to quantify the CO and CO<sub>2</sub> were made in the following conditions: T (oven) = 60 °C, T (detector) = 200 °C, T (injector) = 200 °C, helium flow = 45 mL/min, and septum purge flow = 13.8 mL/min. In addition, to determine light hydrocarbons, a GC-FID (Shimadzu GC-17A) equipped with a capillary column alumina-KCl plot (30 m × 0.32 mm) was used under the following conditions: T (column) = 35 °C, T (injector) = 150 °C, T (detector) = 210 °C, helium total flow = 14 mL/min, helium column flow = 1.2 mL/min, and helium purge flow = 3 mL/min. These GCs were calibrated using a response factor, i.e., with an external calibration. The PAH, ClPh, ClBz, and bromophenol (BrPh) compounds were collected in a polyaromatic resin (Amberlite® XAD-2,

Supelco, Bellefonte, PA, USA). The resin was located just outside the furnace, and the Tedlar bag was situated after the resin.

At the end of each run, the resin was extracted with a mixture of dichloromethane/acetone (1:1 vol) following US EPA Method 3545A and using accelerated solvent extraction (ASE-100 Dionex, Thermo Fisher Scientific, Waltham, MA, USA). Before the extracting process, standards were added to the resin to calculate the concentration of PAHs, ClPhs, ClBzs, and BrPhs. For the analysis of the 16 priority PAHs, deuterated standards were provided by Dr. Ehrenstorfer-Schäfers (Augsburg, Germany), and for the analysis of ClPhs, ClBzs, and BrPhs, <sup>13</sup>C-labeled standards were provided by Wellington Laboratories (Guelph, ON, Canada).

Following its extraction, the extract was concentrated in a rotary evaporator. Later, a moderate stream of nitrogen was used to concentrate it to 1.5 mL. Finally, a recovery standard was added (Anthracene-d<sub>10</sub>, AccuStandard, New Haven, CT, USA).

GC-MS (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, Santa Clara, CA, USA) was used to quantify semivolatile compounds in the samples. PAHs were determined in SCAN mode with an HP-5 MS capillary column (Agilent Technologies, USA). In order to analyze ClPhs, ClBzs, and BrPhs, SIR mode was employed. These analyses were carried out in accordance with US EPA Method 8270D.

### 3. Results

#### 3.1. Gases and Volatile Compounds Emission

As mentioned above, combustion runs were carried out on the different samples. Table 2 shows the yield (mg/kg sample) of the gases emitted during the different runs. In all cases, the main gases to be emitted were carbon dioxide and nitrogen. The mass ratio ( $R_{CO}$ ) between CO and (CO + CO<sub>2</sub>) was also calculated (see Table 2) to check combustion conditions. A low value for this parameter indicates good combustion conditions (i.e., low CO emission). In this regard, combustion was better in the case of samples without NaCl, as inorganic salts require a higher temperature to decompose completely. The ash content after the combustion process was <0.1% in the samples MIX and MIX\_TUA. In the blank run, the only gases detected were N<sub>2</sub> and O<sub>2</sub>.

**Table 2.** Yield of gases and volatile compounds during the combustion experiments at 850 °C ( $\lambda = 0.5$ ). Each run was duplicated ( $n = 2$ ) and average values are presented.

Sample	MIX	MIX_TUA	MIX_NaCl	MIX_NaCl_Fe <sub>2</sub> O <sub>3</sub>	MIX_NaCl_CuO
Compound	mg/kg Sample				
Analysis by GC-TCD					
Hydrogen	nd	nd	1900	1830	1730
Carbon dioxide	1,690,000	1,400,000	137,000	243,000	268,000
Carbon monoxide	417,000	352,000	237,000	180,000	189,000
$R_{CO} = CO/(CO + CO_2)$	0.198	0.200	0.633	0.426	0.413
Analysis by GC-FID					
Methane	26,200	nd	57,100	49,000	45,600
Ethane	1470	21,400	4900	5250	5020
Ethylene	53,400	60,900	129,000	124,000	117,000
Propane	nd	5520	395	550	564
Propylene	nd	nd	146	195	193
Isobutane	29,500	nd	11,500	11,700	11,500
Acetylene	nd	nd	nd	10,700	nd
<i>n</i> -butane	1220	nd	1300	1680	1540
1-butene	1.280	nd	5.250	8.060	4.470
<i>Trans</i> -2-butene	nd	nd	nd	nd	1150
Isobutene	395	2120	1210	1400	501

Table 2. Cont.

Sample	MIX	MIX_TUA	MIX_NaCl	MIX_NaCl_Fe <sub>2</sub> O <sub>3</sub>	MIX_NaCl_CuO
Compound	mg/kg Sample				
<i>Cis</i> -2-butene	nd	2470	144	1500	1820
Isopentane	nd	nd	nd	nd	nd
<i>n</i> -pentane	nd	nd	nd	nd	65
Propyne	2000	nd	11,100	13,400	15,900
1,3-butadiene	1760	nd	nd	nd	nd
1-pentene	nd	nd	nd	nd	nd
2-butene	1420	nd	770	970	909
1-butene	nd	nd	752	111	85
<i>n</i> -hexane	nd	nd	1800	2190	1420
1-hexene	nd	nd	nd	nd	nd
<i>Cis</i> -2-hexene	nd	nd	nd	nd	nd
<i>n</i> -heptane	nd	nd	nd	nd	nd
Benzene	nd	nd	nd	nd	nd
1-heptene	nd	nd	nd	nd	nd
Isooctane	nd	nd	nd	nd	nd
Toluene	1410	3140	915	1440	1170
Xylenes ( <i>p</i> -, <i>m</i> -, <i>o</i> -)	nd	nd	nd	nd	nd
Total	119,000	95,600	221,000	224,000	204,000

nd = not detected (<1 mg/kg sample).

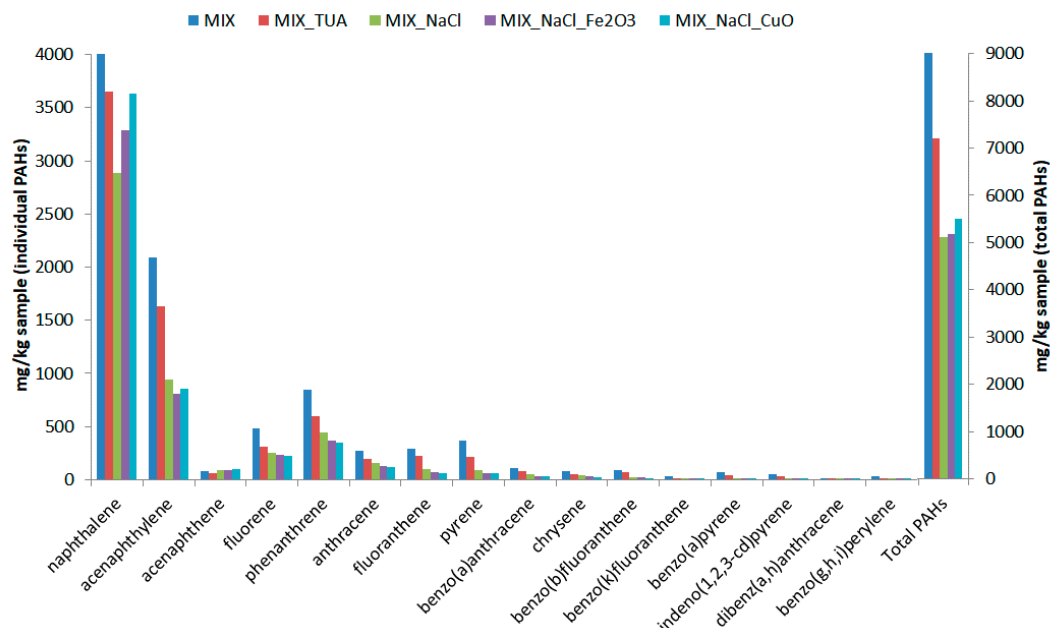
The main light hydrocarbons found in this study were ethylene, methane, and isobutene for all runs. This could be explained by the fact that ethylene and methane are end products of cracking reactions, which take place extensively at high temperatures [27].

These results are similar to those obtained in a previous study [28], in which the pyrolysis and combustion of a similar mixture of plastics (MIX) were analyzed, as well as the effect of the incorporation of chlorine from a marine environment. In both cases, the most abundant product was ethylene in all runs, probably due to the chemical structure of polyethylene.

Regarding the effect of the presence of NaCl and metal oxides in the samples, light hydrocarbons showed higher yields in the presence of NaCl than without it, but the yields were even greater when a small amount of metal oxide was added to the sample (MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub> and MIX\_NaCl\_CuO), indicating that the presence of these oxides improved the catalytic cracking of compounds to low molecular weight species. On the other hand, the addition of a small quantity (3%) of TUA to the mixture of plastics decreased the formation of these hydrocarbons (MIX\_TUA). This was expected, given the findings from previous research, as mentioned before.

### 3.2. PAHs, ClBzs, ClPhs, and BrPhs

The 16 priority PAH profiles are shown in Figure 1. In the blank run, no PAH compounds were detected. In decreasing order of abundance, naphthalene, acenaphthylene, and phenanthrene were the most abundant products in all runs. This result is compatible with results from previous studies performed in our laboratory, in which the combustion of different polymeric materials was carried out under similar conditions [28,29].



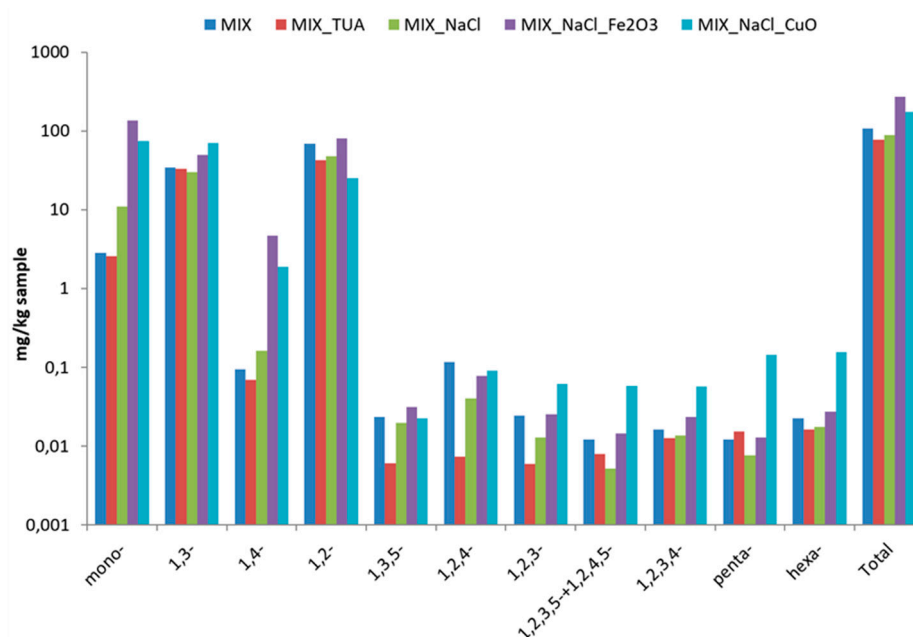
**Figure 1.** Emissions of polyaromatic hydrocarbons (PAHs) during the combustion process at 850 °C (mg/kg sample).

Precursor theory could be used to explain the trend observed in the present study. According to Herrera et al. [30], the concentration of naphthalene is higher than acenaphthylene and phenanthrene because the first aromatic ring (benzene) is formed initially and then begins to grow to high molecular weight polyaromatics.

MIX presented the highest emissions with a total yield of 9318 mg/kg sample. On the other hand, the lowest emission of PAH compounds was observed in the sample of MIX\_NaCl, with a value of 5119 mg/kg sample. The total yield for the rest of the samples was similar.

The seven most carcinogenic PAHs are benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3-cd) pyrene, and dibenz (a,h) anthracene. These compounds presented higher yields in the MIX sample, reaching a total value of 441 mg/kg sample. The presence of sodium chloride with or without the presence of other metal oxides (MIX\_NaCl, MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub>, and MIX\_NaCl\_CuO) showed lower values for these PAHs, presenting a yield of around 100 mg/kg sample.

Figure 2 shows the results of the emissions of ClBzs for all the runs. In the blank runs, the emissions were below the detection limit, which was estimated to be 0.01 µg. This detection limit was calculated by decreasing the PAH concentration of different standards and trying to analyze it. The runs performed in the presence of a small amount of metal oxide showed higher values for ClBz emission than the samples tested in its absence. As a result, MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub> and MIX\_NaCl\_CuO presented the highest total yields, with values of 272 mg/kg sample and 173 mg/kg sample, respectively. Smaller quantities of these compounds were detected in the samples MIX, MIX\_TUA, and MIX\_NaCl during thermal decomposition at 850 °C. In these cases, the total yield varied between 78 and 107 mg/kg sample. This indicates that the mere presence of NaCl is not enough to increase the emission of chlorinated compounds, and that the presence of metal oxides, such as Fe or Cu, catalyzes their formation.



**Figure 2.** Emissions of chlorobenzenes (ClBzs) (logarithmic scale) during the combustion process at 850 °C (mg/kg sample).

According to other studies in which thermal decomposition of other wastes were studied [28,29], mono- and dichlorinated congeners were the main ClBz compounds emitted in all experiments. A relatively low quantity of other isomers of ClBzs was detected.

Chlorophenols (ClPhs) were also analyzed. The results are presented in Table 3, which shows a similar trend to that mentioned for ClBz emission, i.e., the emission was higher in the presence of a catalyzed medium. Therefore, MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub> (248 mg/kg sample) and MIX\_NaCl\_CuO (226 mg/kg sample) showed the highest values. The minimum total yield of ClPhs was obtained in the MIX\_TUA sample, confirming the inhibition effect of TUA on the production of chlorinated pollutants.

**Table 3.** Emissions of chlorophenols (ClPhs) during the combustion process at 850 °C (mg/kg sample). Each run was duplicated ( $n = 2$ ) and average values are presented.

Isomer	ClPh	MIX	MIX_TUA	MIX_NaCl	MIX_NaCl_Fe <sub>2</sub> O <sub>3</sub>	MIX_NaCl_CuO
MONO-	2-	0.123	0.128	0.386	0.391	0.445
	3- + 4-	106	64	141	245	223
DI-	2,4-	0.882	0.038	0.194	0.255	0.287
	2,5-	0.549	0.005	0.011	0.070	0.037
	2,3-	0.458	0.005	0.017	0.021	0.030
	2,6-	0.045	0.005	0.018	0.027	0.020
	3,5-	0.247	0.202	0.209	0.235	0.295
	3,4-	0.152	0.143	0.468	0.608	0.581
TRI-	2,3,5-	0.081	0.030	0.052	0.116	0.093
	2,4,6-	0.033	0.007	0.017	0.031	0.027
	2,4,5-	0.012	0.004	0.007	0.012	0.009
	2,3,4-	0.010	0.002	0.003	0.007	0.008
	2,3,6-	0.013	0.004	0.005	0.005	0.003
	3,4,5-	0.743	0.097	0.851	1.032	1.437
TETRA-	2,3,5,6-	0.040	0.012	0.015	0.011	0.023
	2,3,4,5-	0.053	0.016	0.018	0.025	0.134
	2,3,4,6-	0.021	0.002	0.003	0.001	0.008
PENTA-	penta-	0.075	0.037	0.036	0.047	0.149
	Total	110	65	143	248	226



With respect to the isomer profiles, monochlorinated phenols (3- + 4-) were the highest-emitted ClPh in all samples. This behavior is consistent with literature, as the most common ClPhs in combustion processes are mono-ClPhs [31,32]. The yields of the other isomers were almost negligible in all runs.

Both ClBz and ClPh emissions were substantially higher in the presence of NaCl, but only if a metal catalyst was present. On the other hand, the presence of TUA in the sample reduced the emissions of these compounds, as found by other authors.

Finally, Table 4 shows the results of the emissions of the different BrPhs. As in the case of ClPhs, total yields of BrPhs were almost negligible in all runs. The bromine content of the samples was nil, as expected from the commercial plastics used in the runs. In this regard, the emission of BrPhs was much lower than that of ClPhs, and it is difficult to see a trend when comparing the different samples. The maximum total yield of 0.696 mg/kg sample was obtained in the sample of MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub>. Regarding isomer distribution, 3,4-diBrPh was the most abundant in all samples. At first sight, it seems that the BrPh emissions were slightly higher in the presence of oxides, specifically in the sample with Fe<sub>2</sub>O<sub>3</sub> (MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub>). This would indicate that the reaction of bromine—whereby brominated compounds are formed—is also catalyzed.

**Table 4.** Emissions of bromophenols (BrPhs) during the combustion process at 850 °C (mg/kg sample). Each run was duplicated ( $n = 2$ ) and average values are presented.

	BrPh	MIX	MIX_TUA	MIX_NaCl	MIX_NaCl_Fe <sub>2</sub> O <sub>3</sub>	MIX_NaCl_CuO
MONO-	2-	0.021	0.010	0.036	0.054	0.016
	3- + 4-	0.025	0.008	0.073	0.141	0.050
DI-	2,4-	0.016	0.016	0.026	0.022	0.032
	2,3- + 2,5-	0.004	0.003	0.003	0.002	0.004
	2,6-	0.013	0.015	0.015	0.015	0.017
	3,5-	0.033	0.009	0.012	0.011	0.011
	3,4-	0.311	0.441	0.277	0.349	0.266
TRI-	2,3,5-	0.010	0.007	0.006	0.005	0.003
	2,4,6-	0.020	0.010	0.009	0.010	0.007
	2,3,4-	0.047	0.033	0.011	0.032	0.017
	2,4,5-	0.001	0.001	0.002	0.003	0.001
	2,3,6-	0.006	0.004	0.003	0.003	0.001
	3,4,5-	0.039	0.013	0.021	0.030	0.030
TETRA-	2,3,5,6-	0.027	0.017	0.011	0.011	0.008
	2,3,4,5- + 2,3,4,6-	0.029	0.012	0.008	0.009	0.007
PENTA-	penta-	nd	nd	nd	nd	nd
	Total	0.602	0.599	0.514	0.696	0.470

nd = not detected.

Not many references were found in the literature that would have enabled comparison of the results obtained for PAHs. Furthermore, no data were found on the formation of chlorobenzenes, chlorophenols, and bromophenols during the thermal decomposition of materials combining plastic mixtures, NaCl, and metal oxides.

The data obtained from the present work on the production of pollutants in a laboratory horizontal reactor can be useful for estimating the maximum amounts of such pollutants that can be released from the oven [33]. Nevertheless, the results cannot be directly extrapolated to industrial incineration, as it has been observed that the important aspects influencing emissions in an incinerator are combustion conditions and the air pollution control (APC) devices installed.



#### 4. Conclusions

This study shows the effect of different species (NaCl, TUA, Fe<sub>2</sub>O<sub>3</sub>, CuO) in pollutant emissions resulting from the thermal decomposition of mixtures of plastics under an oxidizing atmosphere at 850 °C.

Carbon dioxide, nitrogen, ethylene, methane, and isobutene were the main compounds emitted during this treatment in all samples. Ethylene was the most abundant light hydrocarbon in all cases, due to the chemical structure of polyethylene.

Regarding the effect of the presence of NaCl and oxides in the samples, light hydrocarbons showed higher yields in the presence of NaCl than without it. However, these yields were even higher in the samples with Fe<sub>2</sub>O<sub>3</sub> and CuO (MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub> and MIX\_NaCl\_CuO). On the other hand, the addition of TUA to the mixture of plastics decreased the formation of these hydrocarbons (MIX\_TUA).

MIX presented the highest emissions of PAH compounds. However, the lowest emissions of PAH compounds were observed in the MIX\_NaCl sample. The yields of ClBzs and ClPhs were substantially higher in the presence of a catalyzed medium. In this case, the presence of TUA in the sample also reduced the emissions of these compounds.

With respect to BrPh emissions, they were nearly negligible in all runs. It was difficult to detect a clear trend between samples, but generally, the emissions were slightly higher in the presence of metal oxides (MIX\_NaCl\_Fe<sub>2</sub>O<sub>3</sub>).

Thus, the tendency to emit pollutants is higher if the sample includes a small quantity of metal oxide. The presence of NaCl in the sample without another catalyst is not enough to increase, in any considerable way, pollutant emissions from a combustion process. Furthermore, it was proven that the presence of TUA in the sample significantly reduces these emissions.

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#### References

1. Iñiguez, M.E.; Conesa, J.A.; Fullana, A. Marine debris occurrence and treatment: A review. *Renew. Sustain. Energy Rev.* **2016**, *64*, 394–402. [[CrossRef](#)]
2. Löhr, A.; Savelli, H.; Beunen, R.; Kalz, M.; Ragas, A.; Van Belleghem, F. Solutions for global marine litter pollution. *Curr. Opin. Environ. Sustain.* **2017**, *28*, 90–99. [[CrossRef](#)]
3. Gregory, M.R. Environmental implications of plastic debris in marine settings—Entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **2009**, *364*, 2013–2025. [[CrossRef](#)] [[PubMed](#)]
4. Rillig, M.C. Microplastic in Terrestrial Ecosystems and the Soil? *Environ. Sci. Technol.* **2012**, *46*, 6453–6454. [[CrossRef](#)] [[PubMed](#)]
5. Koelmans, A.A.; Gouin, T.; Thompson, R.; Wallace, N.; Arthur, C. Plastics in the marine environment. *Environ. Toxicol. Chem.* **2014**, *33*, 5–10. [[CrossRef](#)] [[PubMed](#)]
6. Jambeck, J.R.; Geyer, R.; Wilcox, C.; Siegler, T.R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K.L. Plastic waste inputs from land into the ocean. *Science* **2015**, *347*, 768–771. [[CrossRef](#)] [[PubMed](#)]
7. Martins, J.; Sobral, P. Plastic marine debris on the Portuguese coastline: A matter of size? *Mar. Pollut. Bull.* **2011**, *62*, 2649–2653. [[CrossRef](#)] [[PubMed](#)]
8. Hidalgo-Ruz, V.; Gutow, L.; Thompson, R.C.; Thiel, M. Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. *Environ. Sci. Technol.* **2012**, *46*, 3060–3075. [[CrossRef](#)] [[PubMed](#)]

9. Heo, N.; Hong, S.; Han, G.; Hong, S.; Lee, J.; Song, Y.; Jang, M.; Shim, W. Distribution of small plastic debris in cross-section and high strandline on Heungnam beach, South Korea. *Ocean Sci. J.* **2013**, *48*, 225–233. [[CrossRef](#)]
10. Barnes, D.K.A.; Galgani, F.; Thompson, R.C.; Barlaz, M. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **2009**, *364*, 1985–1998. [[CrossRef](#)] [[PubMed](#)]
11. Fisner, M.; Taniguchi, S.; Moreira, F.; Bicego, M.C.; Turra, A. Polycyclic aromatic hydrocarbons (PAHs) in plastic pellets: Variability in the concentration and composition at different sediment depths in a sandy beach. *Mar. Pollut. Bull.* **2013**, *70*, 219–226. [[CrossRef](#)] [[PubMed](#)]
12. Teuten, E.L.; Saquing, J.M.; Knappe, D.R.U.; Barlaz, M.A.; Jonsson, S.; Björn, A.; Rowland, S.J.; Thompson, R.C.; Galloway, T.S.; Yamashita, R.; et al. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **2009**, *364*, 2027–2045. [[CrossRef](#)] [[PubMed](#)]
13. Gullett, B.K.; Sarofim, A.F.; Smith, K.A.; Procaccini, C. The role of chlorine in dioxin formation. *Process Saf. Environ. Prot.* **2000**, *78*, 47–52. [[CrossRef](#)]
14. Wang, L.-C.; Lee, W.-J.; Lee, W.-S.; Chang-Chien, G.-P.; Tsai, P.-J. Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-*p*-dioxins/dibenzofurans. *Sci. Total Environ.* **2003**, *302*, 185–198. [[CrossRef](#)]
15. Wyrzykowska-Ceradini, B.; Gullett, B.K.; Tabor, D.; Touati, A. PBDDs/Fs and PCDDs/Fs in the Raw and Clean Flue Gas during Steady State and Transient Operation of a Municipal Waste Combustor. *Environ. Sci. Technol.* **2011**, *45*, 5853–5860. [[CrossRef](#)] [[PubMed](#)]
16. Yasuhara, A.; Katami, T.; Okuda, T.; Ohno, N.; Shibamoto, T. Formation of dioxins during the combustion of newspapers in the presence of sodium chloride and poly(vinyl chloride). *Environ. Sci. Technol.* **2001**, *35*, 1373–1378. [[CrossRef](#)] [[PubMed](#)]
17. Ma, W.; Hoffmann, G.; Schirmer, M.; Chen, G.; Rotter, V.S. Chlorine characterization and thermal behavior in MSW and RDF. *J. Hazard. Mater.* **2010**, *178*, 489–498. [[CrossRef](#)] [[PubMed](#)]
18. Chern, H.-T.; Bozzelli, J.W. Comment on “Formation of Dioxins during the Combustion of Newspapers in the Presence of Sodium Chloride and Poly(vinyl chloride)”. *Environ. Sci. Technol.* **2002**, *36*, 2107. [[CrossRef](#)] [[PubMed](#)]
19. Altarawneh, M.; Dlugogorski, B.Z.; Kennedy, E.M.; Mackie, J.C. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* **2009**, *35*, 245–274. [[CrossRef](#)]
20. Zheng, M.H.; Liu, P.Y.; Piao, M.J.; Liu, W.B.; Xu, X.B. Formation of PCDD/Fs from heating polyethylene with metal chlorides in the presence of air. *Sci. Total Environ.* **2004**, *328*, 115–118. [[CrossRef](#)] [[PubMed](#)]
21. Duo, W.; Leclerc, D. Thermodynamic analysis and kinetic modelling of dioxin formation and emissions from power boilers firing salt-laden hog fuel. *Chemosphere* **2007**, *67*, 164–176. [[CrossRef](#)] [[PubMed](#)]
22. Fu, J.-Y.; Li, X.-D.; Chen, T.; Lin, X.-Q.; Buekens, A.; Lu, S.-Y.; Yan, J.-H.; Cen, K.-F. PCDD/Fs’ suppression by sulfur–amine/ammonium compounds. *Chemosphere* **2015**, *123*, 9–16. [[CrossRef](#)] [[PubMed](#)]
23. Fujimori, T.; Nakamura, M.; Takaoka, M.; Shiota, K.; Kitajima, Y. Synergetic inhibition of thermochemical formation of chlorinated aromatics by sulfur and nitrogen derived from thiourea: Multielement characterizations. *J. Hazard. Mater.* **2016**, *311*, 43–50. [[CrossRef](#)] [[PubMed](#)]
24. Chen, T.; Zhan, M.X.; Lin, X.Q.; Fu, J.Y.; Lu, S.Y.; Li, X.D.; Buekens, A.; Yan, J.H. PCDD/Fs inhibition by sludge decomposition gases: Effects of sludge dosage, treatment temperature and oxygen content. *Aerosol Air Qual. Res.* **2015**, *15*, 702–711. [[CrossRef](#)]
25. Iñiguez, M.E.; Conesa, J.A.; Fullana, A. Pollutant content in marine debris and characterization by thermal decomposition. *Mar. Pollut. Bull.* **2017**, *117*, 359–365. [[CrossRef](#)] [[PubMed](#)]
26. Conesa, J.A.; Egea, S.; Moltó, J.; Ortuño, N.; Font, R. Decomposition of two types of electric wires considering the effect of the metal in the production of pollutants. *Chemosphere* **2013**, *91*, 118–123. [[CrossRef](#)] [[PubMed](#)]
27. Atal, A.; Levendis, Y.A.; Carlson, J.; Dunayevskiy, Y.; Vouros, P. On the survivability and pyrosynthesis of PAH during combustion of pulverized coal and tire crumb. *Combust. Flame* **1997**, *110*, 462–478. [[CrossRef](#)]
28. Iñiguez, M.E.; Conesa, J.A.; Soler, A. Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials. *Mar. Pollut. Bull.* **2018**, *130*, 249–257. [[CrossRef](#)] [[PubMed](#)]

29. Soler, A.; Conesa, J.A.; Iñíguez, M.E.; Ortuño, N. Pollutant formation in the pyrolysis and combustion of materials combining biomass and *e*-waste. *Sci. Total Environ.* **2018**, 622–623, 1258–1264. [[CrossRef](#)] [[PubMed](#)]
30. Herrera, M.; Matuschek, G.; Kettrup, A. Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI. *Polym. Degrad. Stab.* **2002**, 78, 323–331. [[CrossRef](#)]
31. Jansson, S.; Fick, J.; Tysklind, M.; Marklund, S. Post-combustion formation of PCDD, PCDF, PCBz, and PCPh in a laboratory-scale reactor: Influence of dibenzo-*p*-dioxin injection. *Chemosphere* **2009**, 76, 818–825. [[CrossRef](#)] [[PubMed](#)]
32. Kaivosoja, T.; Virén, A.; Tissari, J.; Ruuskanen, J.; Tarhanen, J.; Sippula, O.; Jokiniemi, J. Effects of a catalytic converter on PCDD/F, chlorophenol and PAH emissions in residential wood combustion. *Chemosphere* **2012**, 88, 278–285. [[CrossRef](#)] [[PubMed](#)]
33. Conesa, J.A.; Rey, L.; Egea, S.; Rey, M.D. Pollutant formation and emissions from cement kiln stack using a solid recovered fuel from municipal solid waste. *Environ. Sci. Technol.* **2011**, 45, 5878–5884. [[CrossRef](#)] [[PubMed](#)]



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