

Persistent free radicals, heavy metals and PAHs generated in particulate soot emissions and residue ash from controlled combustion of common types of plastic

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Abstract

The production and use of polymeric materials worldwide has reached levels of 150 million tonnes per year, and the majority of plastic materials are discarded in waste landfills where are burned generating toxic emissions. In the present study we conducted laboratory experiments for batch combustion/burning of commercial polymeric materials, simulating conditions of open fire combustion, with the purpose to analyze their emissions for chemical characteristics of toxicological importance. We used common types of plastic materials: poly(vinyl chloride) (PVC), low and high density poly(ethylene) (LDPE, HDPE), poly(styrene) (PS), poly(propylene) (PP) and poly(ethylene terephthalate) (PET). Samples of particulate smoke (soot) collected on filters and residue solid ash produced by controlled burning conditions at 600–750 °C are used for analysis. Emissions of particulate matter, persistent free radicals embedded in the carbonaceous polymeric matrix, heavy metals, other elements and PAHs were determined in both types of samples. Results showed that all plastics burned easily generating charred residue solid ash and black airborne particulate smoke. Persistent carbon- and oxygen-centered radicals, known for their toxic effects in inhalable airborne particles, were detected in both particulate smoke emissions and residue solid ash. Concentrations of heavy metals and other elements (determined by Inductively Coupled Plasma Emission Spectrometry, ICP, method) were measured in the airborne soot and residue ash. Toxic heavy metals, such as Pb, Zn, Cr, Ni, and Cd were relatively at were found at low concentrations. High concentrations were found for some lithophilic elements, such as Na, Ca, Mg, Si and Al in particulate soot and residue solid ash. Measurements of PAHs showed that low molecular weight PAHs were at higher concentrations in the airborne particulate soot than in the residue solid ash for all types of plastic. Higher-ringed PAHs were detected at higher concentrations in the residue solid ash of PVC as compared to those from the other types of plastic. The open-air burning of plastic material and their toxic emissions is of growing concern in areas of municipal solid waste where open-fires occur intentionally or accidentally. Another problem is building fires in which victims may suffer severe smoke inhalation from burning plastic materials in homes and in working places.

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1. Introduction

Polymeric materials are used worldwide in plastic household applications, packaging and electrical and vehicle equipments. Global production of plastics has reached levels of 150 million tonnes per year (from 80 million tonnes in 1990). It is estimated that production of plastics worldwide is growing at a rate of about 5% per year [1]. In 1996 the total plastics con-

sumption in Western Europe was 33.4, in USA 33.9 and in Japan 11.3 million tonnes, respectively [2]. In the year 2004 the consumption of plastic material in Western Europe was 43.5 million tonnes, increasing 3–4% per year [3]. Although 30% of plastic materials (packaging materials, bottles, electrical equipment) are recycled and ~10% are incinerated, 50–60% is discarded in waste landfills or as urban and domestic litter [3,4].

In the last decade plastic waste in Western Europe has become a major environmental problem. In 2003, plastics waste reached 21 million tonnes, of which 50% was recycled or incinerated and the rest was disposed in landfills [5]. A high proportion of

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plastic material worldwide is discarded with municipal waste in landfills or becomes urban litter and domestic trash [6].

Existing municipal waste facilities in many countries are already under pressure by the high volume of plastic and other packaging waste. This situation has led many communities to consider the construction of solid waste incinerators, which can reduce substantially the volume of waste and produce at the same time energy for electricity [7].

The principal types of plastic waste in garbage and litter are: (i) high and low density poly(ethylene) (HDPE, LDPE) used in shopping litter bags, food wrap and films, (ii) poly(vinyl chloride) (PVC) used for bottles, packaging and containers, (iii) poly(ethylene terephthalate) (PET) used in beverage bottles and similar containers, (iv) poly(styrene) (PS) used as a spongy white material for food containers, hot beverage cups, insulating materials, and (v) poly(propylene) (PP) used for yogurt containers, diapers, wrapping films, butter tubs, etc. The majority of these plastics are discarded after use as household waste. It is calculated that around 1000 billion plastic bags are used globally every year [6]. Plastic materials are manufactured by various methods of polymerization with the addition of cross-linking agents, antioxidants, UV and light stability improvers, antistatic agents, heat stabilizers and plasticizers to modify plasticity and pliability and colouring agents [8].

Although plastic materials (consumer goods, household materials, packaging, etc.) are relatively stable, a slow degradation process is taking place and most of their additives can be released in the environment. The main environmental concerns are associated with potential toxic effects, bioaccumulation in aquatic organisms and release of hazardous substances during disposal in municipal waste sites [9]. Burned plastics generate volatile organic compounds (VOCs), smoke (particulate matter), particulate-bound heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dioxins [10–13]. Another aspect of plastic combustion is fires in buildings which can produce increasing amounts of toxic fumes and soot. Victims of fires can suffer from severe smoke inhalation [14,15]. The toxicity of combustion products from burning polymers has been evaluated under experimental conditions [16]. Carcinogenic substances (PAHs, nitro-PAHs, dioxins, etc.) have been identified in airborne particles from incineration or combustion of synthetic polymers such as PVC, PET, PS and PE. These particulates have been found to be highly mutagenic [17].

Greece produces 4.5 million tonnes of municipal solid waste, of which plastic materials (2006) were around 20% [18–21]. Solid waste management in Greece has reached a turning point, plastic and paper waste is mounting, mostly in landfills. Recycling and partly incineration with electricity production are some suggestions proposed in recent studies [22,23].

In the present study the airborne particulate emissions (soot) and solid residue ashes were analyzed for carbonaceous stable free radicals, heavy metals, other elements and PAHs resulting from the combustion of common plastic materials, simulating the conditions of open fire combustion. The most important and widely used types of plastics were used, such as polystyrene, polypropylene, low and high density polyethylene, polyvinyl

chloride and poly(ethylene terephthalate), which were burned at 600–750 °C under controlled laboratory conditions in a well aerated furnace, representing open-air burning conditions.

2. Experimental/materials and methods

2.1. Controlled combustion of selected polymeric materials

Selected plastics from widely used materials were shredded in small pieces. 25 g of each plastic material was weighted and it was placed inside a stainless steel tray (20 cm diameter). The tray was placed inside a heated horizontal chamber-furnace (0.75 m³) with enough air circulating through for batch combustion. We aimed at representative open-air burning conditions. The combustion started by igniting the plastic with a Bünchen burner (natural gas) and left it to burn down until the fire went out. The temperature of the flame from the burning polymeric material was in the range of 600–750 °C. Upon melting, the polymer material burned with luminous envelope flames, whose temperature was measured with a special high temperature thermometer (HANNA instrument HI9063, with thermocouple). The black smoke generated by the self-combustion was collected on a cleaned, preweighed glass fibre filter, from a small top opening (10 cm diameter) of the furnace, supported on a holder and connected with a Hi-Vol air sampler pump (80 m³ h⁻¹). Combustion lasted 2–3 min. The remaining solid residue ash and charred material was collected after cooling down at room temperature. It was estimated that 5–10% (from repeated tests aiming to restrict the escaping fumes only through the opening) of emitted soot escaped in the surrounding environment.

The polymeric material used for batch burning was: poly(styrene) (PS) from spongy light insulating material, poly(vinyl chloride) (PVC) from plastic bottles, low density poly(ethylene) (LDPE) from shopping bags and food wrap, high density poly(ethylene) (HDPE) from trash bags, poly(propylene) (PP) from food containers and poly(ethylene terephthalate) (PET) beverage bottles.

2.2. Collection and extraction of emitted particulates and residue ash

Particulate soot emitted from burning of plastics was collected on a preweighed glass fibre filters (Whatman, 0.3 µm) and filters were dried to a constant weight in a desiccator for 24 h, the mass of the particles was determined gravimetrically. The particulate soot was separated carefully from the filter with a sharp knife. After combustion the remaining solid residue ash in the steel tray was also collected and dried to a constant weight for 24 h in a desiccator.

2.3. Determination of persistent free radicals

Particulate soot (collected on filters) and remaining solid ash after drying to a constant weight were analyzed for persistent free radicals by Electron Paramagnetic Resonance (EPR). A small amount (~0.001 g) was weighed and placed in the bottom of a cylindrical quartz EPR tube. The EPR spectra of all samples

Table 1

Controlled combustion of polymeric material at 600–750 °C (three samples with the same amount were used for each burning-combustion test) under the same conditions

Type of plastic	Production of black smoke	Difficulty in burning	Particulate soot emission (% w/w) (n = 3)	Residue solid ash (% w/w) (n = 3)
PE (HDPE) poly(ethylene)	No	No	0.10–0.25	0.25–0.33
PE (LDPE) poly(ethylene)	No	No	0.10–0.15	0.10–0.2
PP poly(propylene)	No	No	0.2–0.3	0.1–0.1
PS poly(styrene)	Yes	No	0.52–0.65	2.63–2.85
PVC poly(vinyl chloride)	No	Yes	0.21–0.33	9.14–9.62
PET poly(ethylene terephthalate)	No	Yes	0.21–0.25	4.75–5.26

were measured using a Varian E-4 EPR spectrometer. Typical parameters: 100 kHz, X-band; microwave frequency 9.4 GHz; attenuation power 20 mW; modulation amplitude 1–2 G; scan range 100 G; time constant 1 s; scan time 8 min; receiver gain 2.5×10^2 – 5×10^3 . The *g*-values of EPR spectra were calculated from the *g*-value (2.0036) of the stable free radical of 2,2'-diphenyl-1-picrylhydrazyl (DPPH).

The concentrations of radicals, as spins g^{-1} , of representative samples of soot (which represent stable free radicals) were determined by comparison with the stable radical 2,2'-diphenyl-1-picrylhydrazyl (DPPH). EPR spectra of particulate soot and remaining ash of the various plastics are presented in Fig. 1. The area under the EPR, which appears as a single-broad peak was calculated, representing a quantitative measure of radical spins. Comparison was achieved with the EPR spectrum of preweighed samples of DPPH (which is known to be 95% in a stable free radical state). The accuracy of this quantitative estimation is better than 10%. These radicals are embedded in the polymeric matrix of the samples and remained persistent for more than 6 months without change in the intensity of their EPR signal.

2.4. Determination of heavy metals and lithophilic elements

Metals and other elements in particulate soot were determined by Inductively Coupled Plasma Emission Spectrometry (ICP) [ICP Leeman Labs. Inc., PS 950 instrument). For calibration, standards for 26 metals and non-metallic elements (ICP Multi element standard solution V, CentiPUR for wavelength calibration, Merck) was used. 0.5 g of dried sample was added in a conical flask with 9 mL HNO₃, 9 mL HF and 2 mL of H₂O₂. The solution was heated in an electrical plate to dryness and diluted with 25 mL of distilled water. After filtration, the filtrate was transferred to a 50 mL volumetric flask and filled with distilled water. Samples were analyzed automatically and measurements were performed in triplicate. Results are presented in electronic/printed format. Results are presented, for particulate soot in Table 2. Concentrations of metals and other elements are expressed as ppm (mean \pm S.D., *n* = 3).

2.5. Determination of PAHs

Particulate soot from burning of six polymeric materials, was separated from filters and dried to constant weight in a vacuum desiccator. Samples were extracted with dichloromethane for

the determination of polycyclic aromatic hydrocarbons (PAHs) by HPLC.

A sample of 0.2000 g weighted accurately and was extracted with 10 mL CH₂Cl₂ by sonication for 20 min at room temperature. Recovery rates were in the range 88–110%. No further clean-up was performed. The extraction solution was filtrated twice and the crystal-clear extract was evaporated to dryness under reduced pressure in a rotavapor (45 °C) and then 2 mL of CH₃CN was added. The extracted samples were filtered prior to HPLC analysis using Gelman Nylon Acrodisc 0.2 μ m syringe filters. A sample of 20 μ L of the PAHs solution was injected in the HPLC inlet. The HPLC was a reversed-phase HPLC (Agilent 1100 Series, Hewlett-Packard) with UV detector. The chromatographic column was Lichro CART 250 mm \times 4 mm, Lichrospher 100 RP-18, 5 μ m (25 cm \times 4.4 mm) (Merck, Garmstadt, Germany). The mobile phase was acetonitrile:water (85:15) at a flow rate set at 1 mL/min. The UV detector was set at 254 nm.

The 12 PAHs which were selected for determination by HPLC in particulate soot emissions and residue solid ash were: Naphthalene (NAP), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANTH), Chrysene (CHR) and six PAHs with known carcinogenic potential Benzo[*a*]anthracene (B[*a*]An), Benzo[*k*]fluoranthene (B[*k*]Fl), Benzo[*b*]fluoranthene (B[*b*]Fl), Benzo[*a*]pyrene (B[*a*]Py), Dibenzo[*a,h*]anthracene (DiB[*a,h*]An) and Indenol(1,2,3-*c,d*)pyrene (InPy).

HPLC system was calibrated with special preparation in acetonitrile of 16 PAHs (Dr. Ehrenstorfer, reference materials 20951800 PAH-Mix 16), specified in the EPA Method 610 (US EPA, 1977). The precision of all identified species was better than 10% for peak height. Standard solutions of each PAH were used for calibration of peak areas. A peak area was used for the preparation of the 16 PAHs standard curves at four different concentrations. Linearity of regression coefficients were higher than 0.978. Results, expressed as ppm or μ g g^{-1} .

3. Results and discussion

The combustion of six types of plastic showed different patterns of burning. Black smoke was developed during combustion of PS, while HDPE developed initially white smoke. The PP polymeric material melted quickly and charred residue developed in the steel tray. In the case of PVC and PET the plastic material was difficult to burn and needed to keep high tempera-

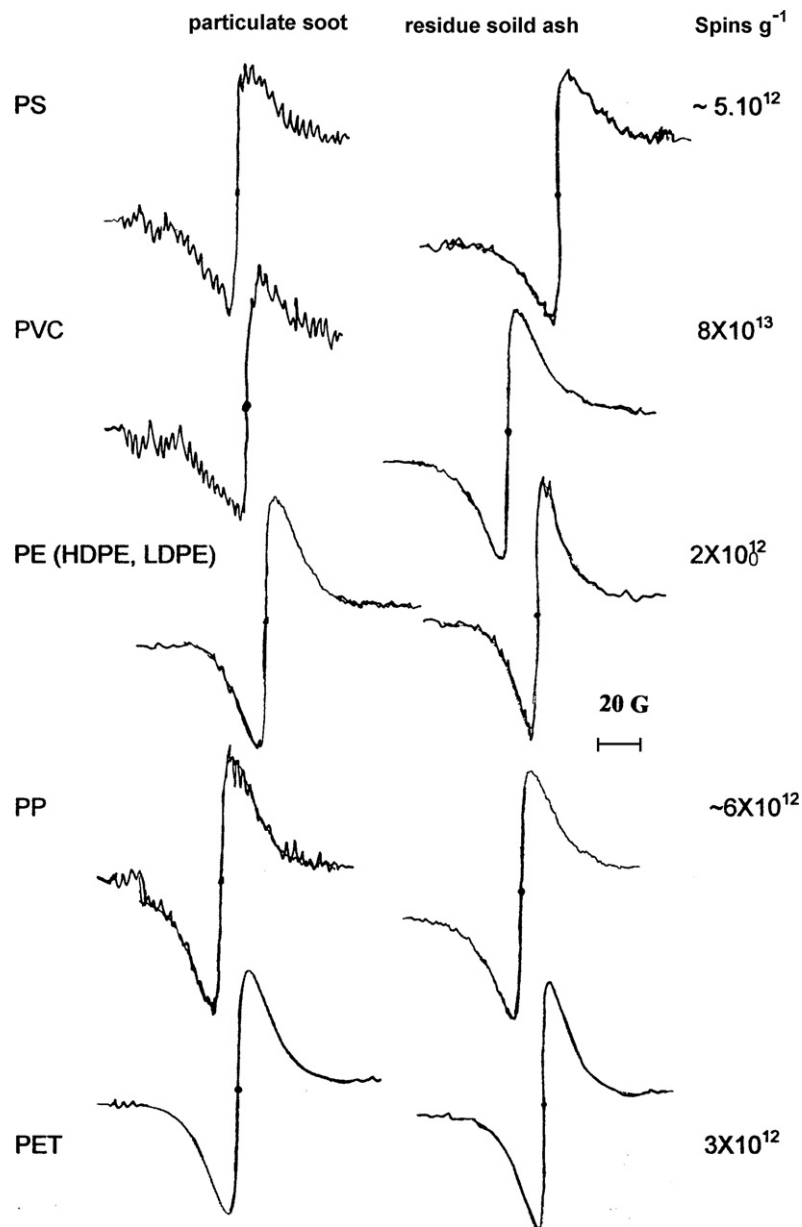


Fig. 1. EPR spectra and free radical concentrations (spins g⁻¹) in particulate soot and residue solid ash of burned polymeric material. The unstructured broad EPR signal contains carbon- and oxygen-centered radical with g in the range of 2.0028–2.0040. Concentration of free radical spins g⁻¹ (with DPPH calibration).

ture conditions. In all cases charred tarry residues were formed. Results of all these combustion characteristics and % of collected soot and residue solid ash are presented in Table 1.

Combustion of PS yielded the highest amounts of emitted soot, which was highly agglomerated, compared to the other polymeric material, and burned very easily without any further heating. Emissions of particulates from PE and PP were very similar and soot was in the form of very fine particles. Combustion of PVC yielded low amount of emitted soot, but left the highest amount of remaining charred material (ash). PVC combustion was slow and leaving it to burn down by itself until the fire went out was difficult, so it needed some extra heating and ignition during the completion of burning. The combustion of PET proceeded with difficulty, it produced small amounts of particulate soot and left relatively 4–5% residue solid ash.

Results from a similar combustion study by Shemwell and Leventis [13], with PS, PE, PVC, PP and PMMA showed different results in the production of particulate soot. PS produced the highest amounts of fine particulates (soot), followed by PP, PE, PMMA and PVC. Burning these plastics with excess oxygen drastically reduced the production of particulate (soot) emissions of PE and PP, substantially reduced those of PS, and mildly reduced those of PVC.

3.1. Persistent free radicals by EPR spectroscopy

The burning of six type of plastics produced particulate soot emissions and residue solid ash (black carbonaceous colour) which indicated the presence of carbon- and oxygen-centered free radicals with a broad unstructured EPR signal at

Table 2

Concentration of heavy metals and lithophilic elements in particulate soot emissions from the controlled combustion of six different plastic materials

Elements	PS	PVC	PE (LDPE)	PE (HDPE)	PP	PET
Al	–	62.2 ± 5.6	1.06 ± 0.35	10.1 ± 0.7	–	0.68 ± 0.1
Ba	0.66 ± 0.30	1.83 ± 0.25	–	–	–	–
Mn	–	–	–	–	–	–
Pb	3.50 ± 65	64.2 ± 6.7	5.91 ± 0.3	5.6 ± 0.2	3.09 ± 0.1	1.4 ± 0.3
Cr	0.58 ± 0.24	9.05 ± 0.5	1.65 ± 0.42	8.13 ± 0.7	0.6 ± 0.09	0.28 ± 0.06
Cd	0.07 ± 0.02	0.17 ± 0.03	0.01 ± 0.005	0.019 ± 0.002	0.009 ± 0.001	0.003 ± 0.001
Cu	–	3.52 ± 0.4	–	–	–	–
Zn	1.49 ± 0.15	13.1 ± 0.5	3.55 ± 0.3	0.68 ± 0.09	0.52 ± 0.07	1.1 ± 0.06
Ni	0.095 ± 0.05	17.2 ± 0.3	1.07 ± 0.3	1.06 ± 0.4	0.5 ± 0.03	0.09 ± 0.02
Na	541 ± 26	285 ± 27	981 ± 10.8	675 ± 6.5	812 ± 18	–
Ca	249 ± 25	1250 ± 15.4	114 ± 1.9	436 ± 3.5	151 ± 12	145 ± 4.5
Mg	26 ± 1.5	122 ± 7.8	17.7 ± 0.8	41.2 ± 2.5	19.8 ± 0.9	13.7 ± 2.4
Fe	0.58 ± 0.20	15.5 ± 0.8	0.61 ± 0.1	1.13 ± 0.2	–	0.34 ± 0.1
Si	49.5 ± 3.7	1160 ± 2.3	12.8 ± 1.2	11.2 ± 0.35	193 ± 2.5	107 ± 2.5
P	5.3 ± 0.7	58.5 ± 3.2	8.54 ± 0.23	11.0 ± 0.68	4.92 ± 0.4	11.5 ± 0.6

Determination by ICP. Values in ppm ($\mu\text{g g}^{-1}$) (mean ± S.D.). Determinations were in triplicate.

$g = 2.0023$ – 2.0036 (spectroscopic splitting factor). The broad EPR signal is overlapped characteristics of carbon-centered radicals (the single electron localized on a carbon atom, aliphatic or organic) and oxygen-centered (mainly quinoid radicals with the single electron localized on the oxygen). These free radicals were very persistent and their EPR spectra remained the same for more than 6 months. The results of EPR spectra are presented in Fig. 1.

Persistent free radicals were measured by EPR spectroscopy. All samples have very similar EPR spectra, with a single unstructured broad EPR signal ($\Delta H_{p-p} = 9.5$ – 10.4 G) and g -value 2.0028 – 2.0040 . The broadness of the EPR signal indicate the presence of several paramagnetic species. The persistent radical species with g -value 2.0028 is consistent with an organic carbon-centered radical, which remains persistent due to its “trapping” inside a polymeric carbonaceous matrix material. The signal with g -value 2.0035 – 2.0038 consists of a group of oxygen-centered radical, which has been identified as semiquinone radicals adsorbed in a polymeric matrix [24].

High concentrations of persistent free radicals have been obtained from all types of charred organic matter (burned in the range of 550 – 650 °C) [25].

Persistent free radicals were first reported and determined by EPR by Pryor et al. [26] in the burned cigarette tar. The presence of these persistent free radicals in the smoke of various materials, and the biological effects of cigarette smoke, wood smoke and smoke from burning of plastics have been investigated [27]. Similar type of persistent free radicals have been found in airborne particulate matter in urban and industrial areas with high levels of atmospheric pollution. These radicals are the result of diesel and gasoline combustion and are considered to be very important for adverse health effects to human lungs [28,29].

3.2. Heavy metals and lithophilic elements

Metals and other elements were determined by ICP. Results of metals after the controlled combustion of six plastic materials in particulate soot emissions are presented in Table 2.

Table 3

Concentration of heavy metals and lithophilic elements in residue solid ash from the controlled combustion of various plastic materials

Elements	PS	PVC	PE (LDPE)	PE (HDPE)	PP	PET
Al	–	82.5 ± 8.6	3.36 ± 1.35	20.5 ± 2.5	–	–
Ba	2.8 ± 0.6	3.5 ± 0.55	–	–	–	–
Mn	–	–	–	–	–	–
Pb	5.7 ± 0.6	44.5 ± 3.8	2.5 ± 0.4	2.6 ± 0.4	2.1 ± 0.2	0.5 ± 0.1
Cr	0.3 ± 0.1	4.3 ± 0.5	0.6 ± 0.2	3.1 ± 0.4	–	–
Cd	–	0.05 ± 0.01	–	–	–	–
Cu	–	2.5 ± 0.3	–	–	–	–
Zn	0.4 ± 0.1	8.0 ± 0.4	2.5 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	0.8 ± 0.2
Ni	–	12.2 ± 1.5	0.7 ± 0.2	0.8 ± 0.3	0.1 ± 0.05	–
Na	640 ± 54	325 ± 37	1.115 ± 53	684 ± 10.5	915 ± 22	23 ± 5
Ca	368 ± 35	1360 ± 38	137 ± 12	554 ± 8.4	234 ± 22	215 ± 15
Mg	15 ± 1.9	105 ± 6.5	8.7 ± 0.6	32.5 ± 1.5	14.3 ± 0.7	11.5 ± 1.4
Fe	3.65 ± 0.60	28.5 ± 2.7	3.64 ± 0.8	6.2 ± 0.4	3.4 ± 0.4	2.35 ± 0.3
Si	78.5 ± 6.8	1240 ± 10.5	32.5 ± 2.6	31.8 ± 2.9	242 ± 8.5	153 ± 4.4
P	7.5 ± 0.9	77.5 ± 6.1	12.8 ± 0.8	19.0 ± 2.2	8.5 ± 1.6	17.5 ± 0.8

Determination by ICP. Values in ppm ($\mu\text{g g}^{-1}$) (mean ± S.D.). Determinations were in triplicate.

Table 4
Polycyclic aromatic hydrocarbon (PAHs) concentrations in particulate soot emissions for six types of plastic

PAHs	PS	PVC	PE (LDPE)	PE (HDPE)	PP	PET
NAP	220 ± 20	340 ± 97	180 ± 35	115 ± 28	110 ± 25	86 ± 15
ACE	35 ± 4	78 ± 6	37 ± 7	26 ± 3	83 ± 7	80 ± 12
FLU	76 ± 11	88 ± 9	113 ± 9	78 ± 7	76 ± 8	45 ± 4
PHE	88 ± 14	92 ± 4	84 ± 9	98 ± 7	65 ± 4	34 ± 5
ANTH	116 ± 22	137 ± 20	55 ± 4	67 ± 6	60 ± 5	39 ± 3
B[a]An ^a	85 ± 9	116 ± 16	43 ± 2	52 ± 10	22 ± 2	LDL ^b
CHR	45 ± 5	135 ± 12	66 ± 5	44 ± 3	34 ± 5	22 ± 2
B[b]Fl ^a	62 ± 4	118 ± 8	35 ± 3	64 ± 7	42 ± 4	18 ± 2
B[k]Fl ^a	154 ± 12	65 ± 4	22 ± 8	73 ± 4	66 ± 7	11 ± 5
B[a]Py ^a	85 ± 14	130 ± 11	56 ± 6	68 ± 4	34 ± 3	28 ± 2
DiB[a,h]An ^a	8 ± 2	23 ± 7	11 ± 4	17 ± 2	LDL ^b	LDL ^b
InPy ^a	92 ± 11	87 ± 9	45 ± 7	63 ± 4	33 ± 5	LDL ^b

Concentrations of 12 PAHs are presented in ppm ($\mu\text{g g}^{-1}$) (mean \pm S.D.). Determinations were in triplicate.

^a PAHs measured are known for their carcinogenic potential: B[a]An, B[k]Fl, B[b]Fl, B[a]Py, DiB[a,h]An and InPy.

^b Lower than detection level.

The results in Table 2 showed that particulate soot contains most of the known toxic metals, such as Pb, Cd, Cr, Cu, Ni and Zn, but their concentrations are relatively low. The particulate soot from PVC contains the highest concentrations of Pb, Ni, Cr, Al and Cu, whereas in the case of the PS, PE, PP and PET soot contains much lower concentrations for these metals. Cd and Cu are found at very low concentrations or are absent in most samples. The presence of chlorine during combustion plays a very important role in the formation of metal chlorides which are very volatile. The presence of chloride salts also contributes to the leaching of metals due to their aqueous solubility. Most studies in the scientific literature examined the role of chlorine in the formation of PCDDs (dioxins) and PCDFs during combustion experiments of polyvinylidene chloride [30,31].

The lithophilic metals Na, Ca, Si, Mg and Fe were found at much higher concentrations than toxic metals in the particulate soot of all plastic materials.

There is a very limited number of controlled combustion studies of plastics and determination of heavy metals in particulate soot emissions and/or residue ash in the scientific literature. These studies were concerned with controlled combustion (in Arapahoe smoke chamber, according to ASTM, D-4100 method) of PVC, rubber and other plastic consumer products. Metals were determined in the smoke and ash phases, but the results were presented in qualitative form (as major, minor and trace). Tests showed the presence of metals, such as Pb, Cd, Pb, Cr, Sn, Ba, Fe, Ti, Ca, Cu and Sb [32–34].

The concentrations of toxic and lithophilic metals in the residue solid ash (bottom ash) left after the end of burning process in the metallic tray of the combustion chamber are presented in Table 3.

The results in Table 3 showed that heavy metals, such as Pb, Cr, Cd, Cu, Ni and Zn are at very low concentrations in the residue solid ash. PVC gave the highest concentrations of Pb, Cr, Ni and Zn in the bottom ash. All other types of plastics contained very low concentrations. Analysis showed very high concentrations in the bottom ash in all types of plastic for the lithophilic elements (in decreasing order) Ca, Na, Si, Mg, P, Al and Fe.

3.3. Selected PAHs in particulate soot and residue ash

The results for selected individual (major) PAH components in particulate soot emissions are presented in Table 4.

The results of Table 4 showed concentrations of PAHs in particulate soot emissions are in the range of 340–8 ppm (or $\mu\text{g g}^{-1}$). The PVC controlled combustion produces the highest amounts of low molecular weight PAHs (3- and 4-ring PAHs) and higher-ringed PAHs compared to the other types of plastic. Prominent among the PAHs present in particulate soot and at in are NAP, B[a]An, B[a]P, InPy, B[b]Fl and B[k]Fl with fused rings.

The results from Table 5 showed that PAHs in the residue solid ash are at lower concentrations compared with these in the particulate ash emissions. If we break down the PAHs into two groups, the results showed that low molecular weight PAHs are at lower concentrations in the residue solid ash, compared to particulate soot emissions. Also, the higher-ringed PAHs were at lower concentrations in the residue ash for the PS, LDPE, HDPE, PP and PET, with the exception in PVC where the opposite is the case. Prominent among the PAHs in the residue ash are B[a]Py, B[a]An, B[b]Fl, B[k]Fl and PHE.

It is well known that the combustion or pyrolysis of polymers is very complex process, since chemical reactions, melting, evaporation, thermal degradation, heterogeneous oxidation, gas diffusion and mass transfer phenomena are taking place. It has been found from other similar studies of combustion/burning plastics in bench-scale furnaces that, temperature of combustion, residence times and supply of oxygen play important roles in the amount of PAH emissions. Also, most researchers emphasize that the combustion parameters of plastics are relatively difficult to replicate [4].

Similar studies with measurements of volatile and semivolatile organic compounds and PAHs from the burning of plastics exist in the scientific literature. Simoneit et al. [6] studied specific trace organic compounds and PAHs by GC–MS in samples of smoke particles from burning of plastic material (shopping bags, roadside trash and landfill garbage) in Chile and the USA. They found that open-burning of plastics gener-

Table 5
Polycyclic aromatic hydrocarbon (PAHs) concentrations in residue solid ash after controlled combustion of six plastic materials

PAHs	PS	PVC	PE (LDPE)	PE (HDPE)	PP	PET
NAP	28 ± 3	80 ± 9	47 ± 5	23 ± 4	12 ± 2	86 ± 9
ACE	23 ± 5	34 ± 3	LDL ^a	LDL ^a	22 ± 4	36 ± 7
FLU	63 ± 7	88 ± 9	23 ± 4	28 ± 4	16 ± 2	45 ± 4
PHE	48 ± 4	92 ± 4	22 ± 5	17 ± 5	19 ± 5	34 ± 5
ANTH	54 ± 7	87 ± 8	34 ± 6	34 ± 7	23 ± 4	39 ± 3
B[a]An ^b	34 ± 4	86 ± 9	39 ± 4	42 ± 6	19 ± 2	LDL ^a
CHR	41 ± 3	90 ± 12	32 ± 5	39 ± 3	24 ± 3	22 ± 2
B[b]Fl ^b	43 ± 7	127 ± 8	55 ± 6	64 ± 7	32 ± 5	18 ± 2
B[k]Fl ^b	57 ± 6	84 ± 4	54 ± 7	73 ± 4	44 ± 6	11 ± 5
B[a]P ^b	66 ± 4	140 ± 8	63 ± 3	77 ± 4	30 ± 2	28 ± 2
DiB[a,h]An ^b	8 ± 2	44 ± 7	8 ± 2	12 ± 2	LDL ^a	LDL ^a
InPy ^b	44 ± 6	136 ± 12	25 ± 3	22 ± 4	28 ± 4	LDL ^a

Concentrations of 12 PAHs are presented in ppm ($\mu\text{g g}^{-1}$) (mean \pm S.D.). Determinations were in triplicate.

^a Lower than detection level.

^b PAHs measured are known for their carcinogenic potential: B[a]An, B[k]Fl, B[b]Fl, B[a]Py, DiB[a,h]An and InPy.

ate particulate smoke which contain various organic compounds and PAHs ranging from phenanthrene to coronene. A study of the combustion of polyethylene, at different operating conditions and for four combustion runs at temperatures 500–850 °C, detected more than 230 volatile and semivolatile organic compounds (by GC–MS), especially olefins, paraffins, aldehydes and light hydrocarbons. PAHs also were detected at low concentrations and most of them were formed at high temperatures [35]. Another study found that the temperature and residence time are considered important factors for PAHs formation in the pyrolysis of polyethylene [36].

Pyrolysis/combustion of PS, PE and PVC particles (with electrically heated furnaces) at gas temperature 900–1200 °C showed that substituted PAHs, oxygenated compounds and chlorinated aromatics are produced in the particulate phase of the combustion products of PVC. PAHs with fused rings were emitted from the combustion of PE and PAHs, either substituted or with fused rings were emitted from the combustion of PS. As the gas temperature and residence times increased, the amount of PAH emissions from all polymers decreased [37]. Controlled-air incineration of PVC, HDPE and PP plastic wastes produced 21 PAHs, which were determined by GC/MS in the gas and particle phases of emissions and in the bottom ash. Excess amounts of air supply in the incineration decreased the concentrations of PAHs both phases. When PVC plastics wastes were incinerated, higher-ringed PAHs constituted a larger percentage in the bottom ash, compared to those from PP and HDPE plastics. Low molecular weight PAHs were found at much lower percentages in the bottom ashes compared to particle phase emissions in the three types of polymers [38].

In another study, polystyrene cups were used in a two-stage furnace combustion (the second furnace was working at 900–1100 °C), the afterburner reduced the soot emissions and PAHs by 20–30% [39]. Polymeric materials (PE, PP, PET and PVC) were burned in the form of free-falling particles in a drop-tube of a laminar-flow furnace poly(ethylene) at gas temperature 750–1150 °C. PAHs were captured in the gas and solid phase using XAD adsorbers and glass fiber filters and analyzed by GC. Changes in PAHs concentrations were mostly related to

postflame conditions [4]. The same paper contains a review of the scientific literature on the combustion and PAHs emissions from plastics [4]. In a study of simulated open filed burning of agricultural plastic (consisted of PE and carbon black) incomplete combustion products were characterized. Alkanes, alkenes, aromatic and PAHs were identified in the volatile, semivolatile and particulate fractions of these emissions. Organic extracts of the particulate samples were moderately mutagenic and comparable to the residential wood burning [40]. Lee et al. studied the mutagenicity of combustion products of PVC, PE, PET and PS. PAHs and nitro-PAHs were identified in particulate phase (in a laboratory combustion process). PVC showed the highest mutagenicity (Salmonella Typhimurium TA98 and TA100 with or without S9 mix) [41].

4. Conclusions

In the last decades social awareness is growing about open-air burning of municipal waste or incinerator emissions which are incinerating in a controlled system various types of toxic waste. Plastics are already a big (~20%) percentage of municipal and toxic waste and their incineration has become a major environmental problem. The results of most studies showed that the controlled combustion of various plastic materials, simulating open-air burning, produces a series of toxic compounds including volatile, semivolatiles, organics and PAHs and toxic metals. Results in this study focused in the analysis of particulate soot emissions and the residue solid ash, after controlled combustion at 600–750 °C. The presence of persistent free radicals which are formed have obvious toxicological implications for inhalation of emissions during open-air burning of plastic waste and building fires. Another important toxicological factor in the particulate soot emissions and residue ash are the toxic metals, such as Pb, Cd, Cr, Cu, Ni, although their concentrations were found to be very low. PAHs have been detected in the particulate soot at relatively high concentrations. Considering that some PAHs are carcinogenic and mutagenic there is a very important health implication from the burning of plastic waste in municipal waste landfills, especially in unregulated ones and near urban areas.

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