

# Occupational Risk Assessment in E-Waste Plant: Progress Achieved over Years <sup>†</sup>

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**Abstract:** The present paper deals with the risk assessment of exposure of workers to polybrominated diphenyl ethers, polychlorobiphenyls and some brominated flame retardants detected in both settled dust and airborne particulate matter collected in an e-waste recycling plant. The concentration values of target analytes were used to perform the risk assessment by considering the three different exposure routes: inhalation, ingestion and dermal absorption of particles. Both carcinogenic and non-carcinogenic risk factors were determined to estimate human health risk associated to study site and to evaluate how plant improvements affected air quality and reduced risks for workers involved in recycling operations.

**Keywords:** risk assessment; flame retardants; human health; WEEE plant

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## 1. Introduction

The rapid economic growth, urbanization, industrialization, and increased demand for consumer goods makes the electric and electronic equipment central to the discussion of resource sustainability and management of the resulting waste stream. The European Directive 2012/19/EU mandates all member states to promote separate collection and resource recovery from e-waste in order to reduce the disposal waste volume by ensuring their re-entry into the market. E-waste can be considered a secondary raw material for the recovery of valuable components, such as precious metals, plastics, glass, ceramics etc. Nevertheless, it is characterized by the presence of chemicals harmful to the environment and to the waste disposal workers [1]. Halogenated flame retardants (HFRs), commonly added to electric and electronic equipment to delay fire ignition or contain its diffusion, can cause adverse effects such as skin disease, damage to the nervous system, endocrine disruption, etc. [2,3].

Among HFRs, polybrominated diphenyl ethers (PBDEs) and polychlorobiphenyls (PCBs), widely used over the years, were banned from manufacture and use and replaced with alternative compounds of similar structure (BFRs) [4]. Nevertheless, PBDEs and PCBs are still detected in e-waste recycling facilities where outdated equipment are processed [5]. In these plants, risks associated with the treatment of waste from electrical and electronic equipment (WEEE) are mostly due to disassembly and shredding steps because of formation of high amounts of dust on which harmful substances can be absorbed [6].

Therefore, the aim of present paper was to estimate the exposure of workers to PBDEs, PCBs and some BFRs detected in both settled dust and airborne particulate matter (PM) collected in an e-waste recycling plant located in Central Italy. In 2017 and 2022, two

measure campaigns were carried out to evaluate how plant improvements affected air quality and reduced risks for workers involved in recycling operations. The concentration values of target analytes were used to perform the risk assessment by considering the three different exposure routes: inhalation, ingestion and dermal absorption of particles [7].

## 2. Materials and Methods

### 2.1. Sampling

PM<sub>10</sub> and settled dusts were collected in an e-waste recycling plant where TV, PC, monitor and small appliances were processed. The samplings were performed in 2017 and 2021 after plant modification designed to achieve higher safety standards. In 2017, e-waste was delivered to an area where it was carried out both the manual disassembly of TV, PC, monitor and the mechanical shredding of small appliances. In 2021, waste treatment area was divided in two separated blocks: the first dedicated to the handling of TV, PC, monitor (Z1); the second to the processing of small household appliances (Z2). Accordingly, work organization was also changed, and workers were divided into two groups: those employed in Z1 and those occupied in Z2.

PM<sub>10</sub> was sampled with SKC impactors on 37 mm teflon filters (Merck Millipore S.p.A., USA) using a Leland Legacy sample pump (SKC Inc., USA) operating at 10 L/min. Before and after samplings, filters were conditioned in an Activa Climatic Cabinet (Aquaria srl, Italy) at 20 °C and 50% of relative humidity and weighted with a microbalance (Sartorius Lab Holding GmbH, Germany).

Settled dusts were collected with a brush from work surfaces, homogenized, sieved at 63 µm and stored in glass bottles.

### 2.2. Analytical Methods

The detailed method was described in previous papers [5,8,9]. Briefly, both filters and dusts were extracted by an accelerated solvent extractor ASE200 (Thermo Fisher Scientific Inc., USA) with n-hexane (1:1) (two cycles) followed by ethyl acetate (two cycles) at 100 °C and 1500 psi. The extracts were evaporated, re-dissolved with 50 µL of toluene and stored at -18 °C. PCBs, BDEs and BFRs, reported in Table 1, were analyzed using an Agilent Technologies 7890B gas chromatograph (GC) coupled with a 5977B mass selective detector (MS) (Agilent Technologies Inc., USA) operating in negative chemical ionization.

**Table 1.** List of target analytes.

PCBs	PBDEs	BFRs
PCB77 (3,3',4,4'-Tetrachlorobiphenyl)	BDE47 (2,2',4,4'-Tetrabromodiphenylether)	BATE (2-bromoallyl 2,4,6-tribromophenylether)
PCB99 (2,2',4,4',5-Pentachlorobiphenyl)	BDE99 (2,2',4,4',5-Pentabromodiphenylether)	TBECH (1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane)
PCB101 (2,2',4,5,5'-Pentachlorobiphenyl)	BDE100 (2,2',4,4',6-Pentabromodiphenylether)	BTBPE (1,2-bis(2,4,6-tribromophenoxy)ethane)
PCB105 (2,3,3',4,4'-Pentachlorobiphenyl)	BDE153 (2,2',4,4',5,5'-Hexabromodiphenyl ether)	DPTE (2,3-dibromopropyl-2, 4, 6-tribromophenylether)
PCB110 (2,3,3',4',6-Pentachlorobiphenyl)	BDE183 (2,2',3,4,4',5',6-Heptabromodiphenylether)	HBCD (hexabromocyclododecane)
PCB114 (2,3,4,4',5-Pentachlorobiphenyl)		HCDBCO (hexachlorocyclopentadienyldibromocyclooctane)

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PCB126	PBEB
(3,3',4,4',5-Pentachlorobiphenyl)	(2,3,4,5,6-pentabromoethylbenzene)
PCB138	TBCO
(2,2',3,4,4',5'-Hexachlorobiphenyl)	(1,2,5,6-tetrabromocyclooctane)
PCB146	ATE
(2,2',3,4',5,5'-Hexachlorobiphenyl)	(Allyl-2,4,6-tribromophenylether)
PCB151	
(2,2',3,5,5',6-Hexachlorobiphenyl)	
PCB156	
(2,3,3',4,4',5-Hexachlorobiphenyl)	
PCB157	
(2,3,3',4,4',5'-Hexachlorobiphenyl)	
PCB167	
(2,3',4,4',5,5'-Hexachlorobiphenyl)	
PCB169	
(3,3',4,4',5,5'-Hexachlorobiphenyl)	
PCB170	
(2,2',3,3',4,4',5-Heptachlorobiphenyl)	
PCB177	
(2,2',3,3',4',5,6-Heptachlorobiphenyl)	
PCB180	
(2,2',3,4,4',5,5'-Heptachlorobiphenyl)	
PCB183	
(2,2',3,4,4',5',6-Heptachlorobiphenyl)	
PCB187	
(2,2',3,4',5,5',6-Heptachlorobiphenyl)	
PCB190	
(2,3,3',4,4',5,6-Heptachlorobiphenyl)	

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GC separation was carried out on an HP5-MS (5% phenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm i.d., 0.25 µm film thickness) fused silica capillary column (Agilent Technologies Inc., USA). One µL splitless injections were performed with an injector temperature of 280 °C. Oven temperature program was as follows: 100 °C increasing at 25 °C/min to 310 °C held for 8 min. The helium carrier gas was at a constant flow of 1 mL/min. Quadrupole, ion source and transfer line temperatures were set at 150, 230 and 300 °C, respectively. The reagent gas was methane at 40 mL/min. The MS was operated in selected ion monitoring (SIM) mode for quantitation of target compounds. The analytes were identified on the basis of their mass spectra using the base peak and at least one qualifier ion depending on the compound and quantified by internal standard method and matrix-matched calibration curves. Quality control, consisting of blank measures and calibration verifications, was carried out routinely.

### 2.3. Human Health Risk Assessment

As described in the USEPA risk assessment guidance [7,10], potential risks via ingestion, dermal contact and inhalation were estimated.

Carcinogenic risk (CR) for each exposure route was evaluated using the following equations:

$$CR_{inhalation} = \frac{C_i \times EF \times ET \times ED}{AT \times 365 \times 24} \times IUR$$

$$CR_{ingestion} = \frac{C_i \times IngR \times EF \times ED}{BW \times AT} \times CF \times SFO$$

$$CR_{dermal} = \frac{C_i \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \times SFO / GIABS$$

where  $C_i$  is the contaminant concentration for each compound in PM ( $\mu\text{g}/\text{m}^3$ ) and in settled dust ( $\mu\text{g}/\text{g}$ ),  $EF$  is the exposure frequency (225 d/y),  $ET$  is the daily exposure time (8 h/d),  $ED$  is the exposure duration (25 y),  $AT$  is the average time (25,550 d for carcinogenic risks),  $IUR$  is the inhalation unit risk ( $\mu\text{g}/\text{m}^3$ )<sup>-1</sup>,  $IngR$  is the ingestion rate (mg/day),  $BW$  is the average body weight (70 kg),  $SFO$  is the oral slope factor (mg/kg/day)<sup>-1</sup>,  $SA$  is the skin surface area (cm<sup>2</sup>/day),  $GIABS$  is the gastrointestinal absorption factor (dimensionless),  $AF$  is the skin adherence factor (mg/cm<sup>2</sup>),  $ABS$  is the dermal absorption factor (dimensionless).

Non-carcinogenic risk, named hazard quotient (HQ), was determined using the following equations:

$$HQ_{inhalation} = \frac{C_i \times EF \times ET \times ED}{AT \times 365 \times 24 \times 1000} / RfC$$

$$HQ_{ingestion} = \frac{C_i \times IngR \times EF \times ED \times CF}{BW \times AT} / RfD$$

$$HQ_{dermal} = \frac{C_i \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} / RfD \times GIABS$$

where  $RfC$  is the inhalation reference concentration (mg/m<sup>3</sup>),  $RfD$  is the reference dose for ingestion/dermal contact (mg/kg/d),  $AT$  is the average time (9125 d for non-carcinogenic risks).

Parameter values used for risk assessment are displayed in Table 2. However, since for some analytes, these values are lacking, the human health risk was determined using the data of compound with similar chemical–physical characteristics or belonging to same class of contaminants and with comparable toxicity and similar potential for bioaccumulation.

**Table 2.** (a) Parameter values specific for each class of compound [7–8,10–12]. (b) IUR, RfC and RfD values for each compound [7–8,10–12].

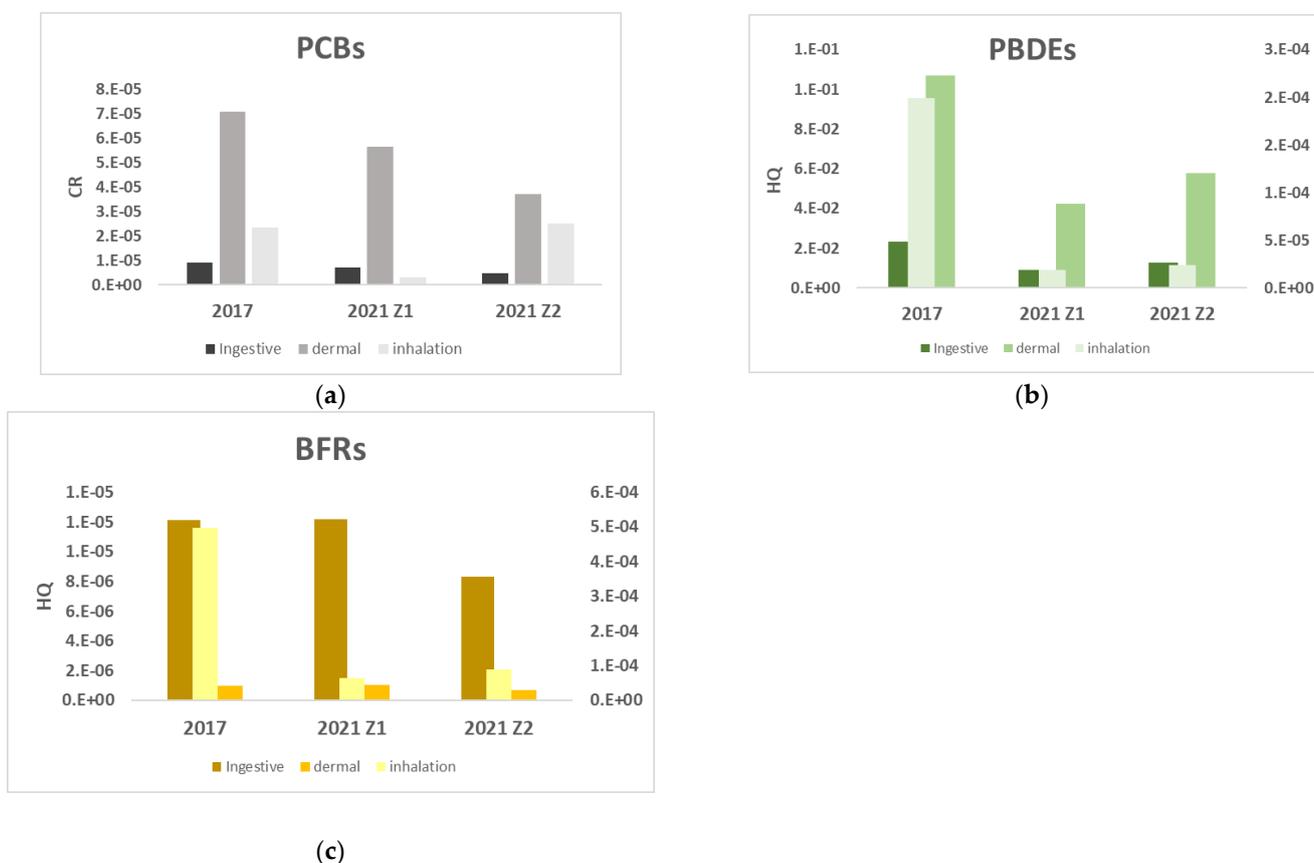
	IngR	SFO	SA	GIABS	AF	ABS	CF (kg/mg)
PCBs	100	2	3300	0.1	0.2	0.1	1 × 10 <sup>-6</sup>
PBDEs	30	7 × 10 <sup>-4</sup>	5700	1	0.2	0.1	1 × 10 <sup>-6</sup>
BFRs	20	7 × 10 <sup>-3</sup>	4615	1	0.01	0.03	1 × 10 <sup>-6</sup>
PCBs	IUR (μg/m <sup>3</sup> ) <sup>-1</sup>	PBDEs	RfC (mg/m <sup>3</sup> )	RfD (mg/kg/day)	BFRs	RfC (mg/m <sup>3</sup> )	RfD (mg/kg/day)
PCB126	3.8E+00	BDE47	1.1E-02	1.00E-04	BATE	1.1E-02	2.4E-01
PCB169	1.1E+00	BDE99	0.007	1.00E-04	TBECH	1.1E-02	2.4E-01
Other PCBs	1.1E-03	BDE100	7.0E-03	1.00E-04	BTBPE	1.1E-02	2.4E-01
		BDE153	1.1E-02	2.00E-04	DPTE	1.1E-02	2.43E-01
		BDE183	1.1E-02	2.00E-03	HBCD	1.1E-02	2.0E-01
					HCDBCO	1.1E-02	2.0E-01
					PBEB	1.1E-02	2.4E-01
					TBCO	1.1E-02	2.4E-01
					ATE	1.1E-02	2.4E-01

Total carcinogenic risk (TCR) and total non-carcinogenic risk (THQ) were calculated by summing the individual risks obtained for every compound class and for the three exposure routes [5].

TCR data were compared to values recommended by USEPA [10] that, for public health protection, suggests  $CR < 1 \times 10^{-6}$  as acceptable risk level and  $< 1 \times 10^{-4}$  as a tolerable risk level [13,14]. Likewise, THQ values were compared those suggested from USEPA [10]. If  $HQ < 1$  no appreciable risk of non-carcinogenic effects may occur, while  $HQ > 1$  indicates chance of non-carcinogenic effects [13].

### 3. Results

Figure 1 displays CR and HQ values for each class of compounds and for the three exposure routes.



**Figure 1.** Carcinogenic and non-carcinogenic risk for PCBs (panel a) PBDEs (panel b) and BFRs (panel c) for the three exposure routes over years. For PBDEs and BFRs, inhalation HQ is displayed on the secondary axis.

For PCBs (panel a), CR due to dermal contact shows the highest values in both 2017 and 2021. However, after e-waste treatment area was divided in two separated blocks, CR decreases for the three exposure routes, except for the inhalation in Z2 where CR values are comparable to those of 2017.

Regarding PBDEs (panel b), 2021 HQ results highlight a significant decrease for all the exposure routes. For this class of pollutants, HQ values due to dermal contact are the highest ones, whereas the inhalation route contributes to a lesser extent.

As for BFRs (panel c), although the inhalation HQ shows higher values both in 2017 and 2021, the renovation carried out in 2021 highlights a significant improvement. Conversely, for the ingestion and dermal contact, HQ values do not appear to decrease significantly. Table 3 shows the total carcinogenic and non-carcinogenic risk compared with USEPA

**Table 3.** Total carcinogenic and non-carcinogenic risk over years compared to USEPA recommended values.

	2017	2021-Z1	2021-Z2	USEPA Recommended Values
TCR	1.03E-04	6.67E-05	6.68E-05	CR < 1 × 10 <sup>-6</sup> acceptable risk CR < 1 × 10 <sup>-4</sup> tolerable risk
THQ	1.31E-01	5.18E-02	7.09E-02	HQ < 1 no appreciable risk HQ > 1 appreciable risk

In 2017, TCR data exceeded the tolerable values set by USEPA, whereas THQ results were lower than acceptable risk limits. In 2021, both TCR and THQ are lower than recommended values and about 60% below those found in 2017. Therefore, the plant modifications seem to have resulted in a risk reduction for the workers involved in the treatment of e-waste.

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