Proceeding Paper

Microplastics: An Emerging Pollution Source in E-waste Recycling Facilities †

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Abstract: In the recent years, scientific community is focused on~~-~~the potential adverse effect of microplastics (MPs) particles on the human health.~~-~~However, few studies have been conducted concern the MP emissions in industrial sites where plastic materials are processed. In this regard, e-waste recycling plants can be a significant source of MPs and could cause toxic effects for workers involved in waste treatment steps. Therefore, the aim of present study is to estimate the carcinogenic and non-carcinogenic risk to which workers employed in e-waste recycling plants can be exposed. Through the analysis of some plastic additives commonly used in polymer-based products such as PCs, monitors, TV screens etc., the possible contribute of MPs to exposure was assessed.

Keywords: Microplastics; carcinogenic risk; e-waste; plastic additives

1. Introduction

Waste of electrical and electronic equipment (WEEE) are the fastest growing waste streams in our society and can be considered a secondary raw material for the recovery of valuable components [1]. However, their composition and the industrial recycling processes to which e-waste is subjected can lead to health risks for both workers and population living close to the plants[2]. In particular, a high percentage of EEE is made up of plastic and, following disassembly, tearing and shredding operations, large quantities of dust containing micro- and nano-plastics can be produced[3]. MPs, defined as particles with diameters <5 mm, including nanoplastics (NPs) with diameters <1 μm, are characterized by large specific surface area and high hydrophobicity~~. In addition~~, The properties of polymers used in EEE often need to be improved by adding various chemical additives that can act as plasticizers, flame retardants, stabilizers, reinforcements etc., depending on their use [4]. Therefore, a study of plastic additive concentration profiles detected in dust samples collected in the different processing areas of three e-waste treatment plants and could help to evaluate the potential use of additives as chemical tracers of MP sources and her possible role of carriers of harmful organic substances added to plastic polymers [5]. Among several additives, phthalate acid esters (PAEs) are major plasticizing agents used to improve flexibility, extensibility and workability of polymers. Due to their widespread diffusion and use, PAEs can be found at significant concentrations in all environmental matrices and prolonged exposure to these chemicals is associated with many adverse effects such as endocrine disruption, reproductive toxicity, cancer, asthma, etc. [6]. However, these contaminants are not always chosen as plastic tracers because they are ubiquitous and present in many products, not allowing, therefore, a unique association

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with the presence of MPs in indoor environments. Nevertheless, in complex sites such as those examined in the present paper where plastic component is pre-dominant, it may be interesting to analyze some plasticizers and to assess occupational exposure to chemicals known endocrine disruptors and harmful to human health.

Therefore, the aim of present paper was to estimate the exposure of workers to PAEs determined in settled dust collected in e-waste recycling plants. Settled dust was sampled during working hours close to the e-waste process lines. 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. Therefore, the present paper highlights the need to evaluate MP contribution to occupational risk in order to adopt suitable prevention and protection measures.

2. Materials and Methods

2.1. Site Description and Sampling

Settled dusts were collected in three e-waste recycling plants (named WP1, WP2 and WP3) chosen according to the type of treatment and processed waste. In WP1, PC and monitors were disassembled manually, and recoverable components were selected; in WP2, small household appliances were opened and shredded mechanically; in WP3, fluorescent tubes and linear lamps were processed.

Dust was collected from work surfaces with a brush, previously cleaned with ultrapure water and pure ethanol. Then, the samples were sieved at 63 μm to remove larger particles and divided in 1 g sub-samples after homogenization. The sub-samples were stored in amber glass bottles at -18 °C.

2.2. Analytical Methods

The detailed method was described in previous papers [7]. Briefly, dusts were extracted by an accelerated solvent extractor ASE200 (Thermo Fisher Scientific Inc., USA) with n-hexane (two cycles) followed by ethyl acetate (two cycles) at 100 °C and 1500 psi. The clean-up was carried out filling ASE cells with florisil as sorbent. The final extracts were filtered, evaporated, re-dissolved with 50 μL of toluene and stored at −18 °C. PAEs, 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 electronic ionization (EI).

Table 1. List of target analytes.

PAEs	Abbreviation
Dimethyl phthalate	DMP
Diethyl phthalate	DEP
Dipropyl phthalate	DPrP
Diisobutyl phthalate	DiBP
Dibutyl phthalate	DBP
Benzyl butyl phthalate	BBP
Bis-2-ethylhexyl phthalate	DEHP
Diheptyl phthalate	DHepP
Bis-2-ethylhexyil terephthalate	DEHT
Di-n-octyl phthalate	DnOP
Diphenyl phthalate	DPhP

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. 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 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.

2.3. Human Health Risk Assessment

Carcinogenic (CR) and non-carcinogenic (HQ) risks were calculated by determining the daily intake of PAEs via dust inhalation, ingestion and dermal absorption according to the following equations [6, 8-10]:

$$ADD_{inhalation} = \frac{C_d * InhR * EF * ED}{BW * AT * PEF}$$

$$ADD_{ingestion} = \frac{C_d * IngR * EF * ED * 10^{-6}}{BW * AT}$$

$$ADD_{dermal} = \frac{C_d * SA * AF * ABS * EF * ED * 10^{-6}}{BW * AT}$$

where ADD is the average daily dose ((mg/(kg*d)) and C_d is the concentration (mg/kg) of each contaminant in settled dust.

Table 2 shows the values of exposure factors applied for ADD determination [8-10].

Table 2. Definition and values of exposure parameters for health risk assessment.

Factor	Definition	Value (Unit)
EF	Exposure Frequency	225 d y^{-1}
ED	Exposure Duration	25 y
AT	Average Time	25550 d (carcinogenic risk) 9125 d (non carcinogenic risk)
PEF	Particle Emission Factor	$1.36*10^9$ m^3 kg^{-1}
InhR	Inhalation Rate	20 m^3 d^{-1}
IngR	Ingestion Rate	100 mg d^{-1}
BW	Body Weight	70 kg
SA	Skin Surface Area	4250 cm^2
AF	Skin Adherence Factor	0.07 mg $(cm^2$ $d)^{-1}$
ABS	Dermal Absorption Factor	0.001

d: day; y: year

CR and HQ were evaluated for each exposure routes as follows:

$$CR_i = ADD_i * SF$$

$$HQ_i = \frac{ADD_i}{RfD}$$

where RfD is the reference dose (mg/(kg*d)), SF is the slope factor $(mg/(kg*day))^{-1}$ [9-10]. Total carcinogenic risk (TCR) and total non-carcinogenic risk (THQ) were determined as sum of individual risks calculated for each compound and for each exposure routes.

Both TCR and THQ data were compared to values recommended by USEPA [10] that, for public health protection, suggests $CR < 1 \times 10^{-6}$ as acceptable risk level; CR <1 ×

10^{-4} as a tolerable risk level; HQ < 1 for no appreciable non-carcinogenic effect and HQ > 1 for possible non-carcinogenic effects.

3. Result and Discussion

Table 3 shows concentration values of target analytes in settled dusts collected in the three plants of e-waste treatment.

Table 3. PAE concentration (mg/kg) in dust samples collected in the three plants.

PAEs	WP1	WP2	WP3
DMP	0.80	2.9	0.046
DEP	n.d.	0.76	n.d.
DPrP	n.d.	0.33	0.14
DiBP	612	287	n.d.
DBP	76	86	16
BBP	5.8	4.9	0.26
DEHP	462	70.6	92.2
DHepP	0.45	0.47	0.29
DEHT	50	55	8.8
DnOP	1.2	1.3	0.36
DPhP	0.057	n.d.	0.044

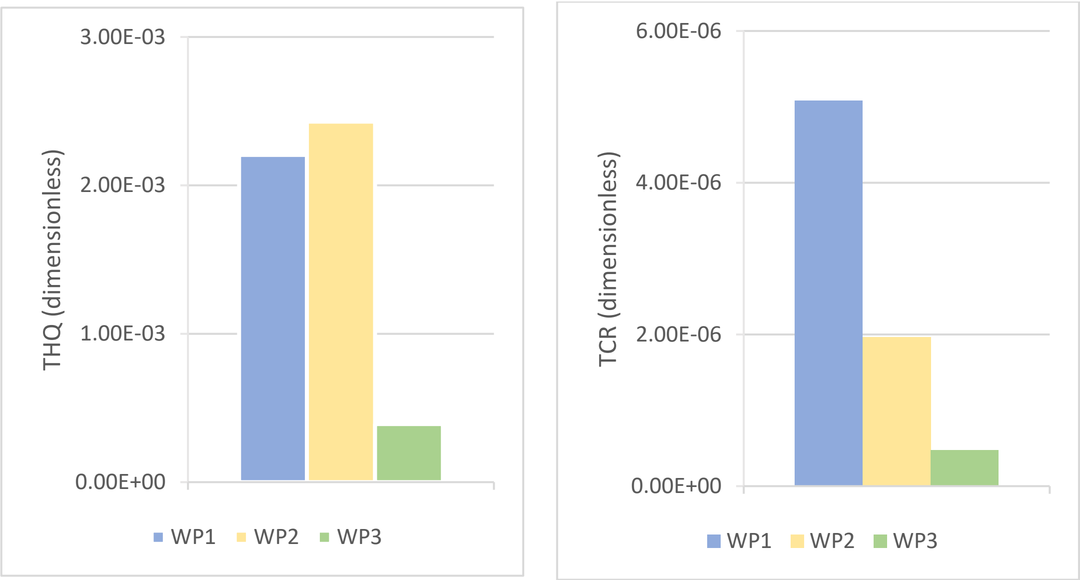
n.d.: not detectable

PAE profile is comparable in WP1 and WP2 and the most abundant compounds are DiBP, DBP, DEHP and DEHT. Instead, in WP3 only DEHP is detected at significant concentration, counting for 78% of total PAEs. This can be due to e-waste processed in this plant mainly comprising fluorescent tubes and linear lamps. DEHP is a plasticizer for wire coatings and electrical cables in PVC and, nevertheless restriction on its use, it is still widely detected in environment [12]. DEHT is alternative plasticizer to DEHP and is used in coatings, electric connectors, plastic toys etc. DiBP and DBP are widespread in polymers of computers, cameras, monitors, refrigerators etc. [4].

Figure 2 shows the values of THQ and TCR as sum of individual risks calculated from compound concentrations in settled dust collected in the three plants of e-waste treatment.

THQ values are comparable in WP1 and WP2, while TCR is higher in WP2. Regarding HQ, the major contribution is given by DEHT whose concentrations are similar in the two plants. Instead, DiBP and DEHP, which contribute significantly to the CR since potential carcinogens, have the highest concentration in WP1. WP3 shows the lowest value of risk factors in agreement with kind of e-waste processed in this plant and characterized mostly by inorganic contaminants.

Furthermore, THQ and TCR are always below limits recommended by USEPA [10], suggesting a low risk for waste treatment workers. In addition, predominant exposure route appears to be dust ingestion, contributing about 90% to the total risk. However, in this preliminary risk assessment, contaminant concentrations in airborne dusts were not included and, since the processes carried out in the three plants can generate considerable quantities of dust, this exposure route could be not negligible.



a)

(**b**)

Figure 2. Total non-carcinogenic risk (panel **a**) and total carcinogenic risk (panel **b**) computed as sum of individual risks for each compound and for each exposure routes in the three plants.

4. Conclusion

The present paper highlighted the presence of some legacy and novel plasticizers in settled dust samples collected in e-waste treatment plants. Nevertheless, the values of risk factors are always below limits recommended by USEPA. Therefore, the preliminary results does not seem to show health risks for both workers and population living close to the plants. However, since the contaminant concentrations in airborne particulate matter were neglected at this initial stage, the future developments will be addressed to evaluate the worker exposure via inhalation considering airborne particulate, as well.

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