detritus | Multidisciplinary Journal for Waste Resources & Residues

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ASSESSMENT OF THE DEGREE AND SOURCE OF POLYOLEFIN RECYCLATES CONTAMINATION

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Article Info:
Received:
13 September 2021
Revised:
26 November 2021
Accepted:
26 November 2021
Available online:
19 December 2021

Keywords:
Plastic
Recycling
Contamination
PAHs
Assessment

ABSTRACT

This study has the aim of analysing the degree of contamination of recycled polyolefin purchased from the market by focusing on the content of polycyclic aromatic hydrocarbons (PAHs). Additionally, the impact of the mechanical recycling process on the polyolefin chemical quality was investigated. Results indicated that recycled polyethylene (PE) had higher PAHs concentrations by 10 to 20 folds in comparison to the pristine PE. Similarly, recycled polypropylene (PP) indicated higher PAHs concentrations in comparison to the virgin polypropylene, yet with lower degree of difference. Analysing the 8 indicators assigned by the Regulation EU 1272/2013 amending REACH Annex XVII, all recycled specimens showed concentrations lower than the limit of 0.5 mg kg^{-1}, which indicates that there is no restriction in material's utilisation. This study functioned as a preliminary assessment to check the suitability of recycled plastics for their further utilisation. Additionally, the study indicates that polyolefin can experience quality deterioration when uncontrolled recycling conditions are applied.

1. INTRODUCTION

Due to the need for high quality of recycled plastics from the heterogeneous waste stream, deficiencies of the recyclates quality should be identified and avoided when possible, in particular with the assessment of the up-to-date regulations on substances, mixtures and products (Alassali et al., 2020a). Generally, the occurrence of unwanted substances that can migrate and accumulate in the plastic's cycle is a significant limitation and risk to its closed-loop recycling (Eriksen et al., 2019).

Contamination can occur throughout the whole plastic value chain. The main sources of plastic contamination are: degradation products generated during material ageing or exposure to different conditions (Alassali et al., 2018; Alassali et al., 2020c), addition of chemical substances in the form of additives to obtain a specific quality (Sanchez et al., 2020), or contamination by use or application (Hahladakis and Iacovidou, 2019).

The application of the circular economy concept on plastic waste requires the consideration of its recycling, where resources are maintained as long as possible and the maximum value is recovered after disposal. Plastic waste could be recycled mechanically, chemically or thermally. Yet, the mechanical recycling is the preferred option, due to the preservation of the material.

Many factors limit the mechanical recycling of plastic waste, especially the fact that plastics are organic components that are highly sensitive to elevated temperatures and mechanical stress (Al-Salem et al., 2009). Additionally, plastic waste contamination could be a significant challenge when considering plastic waste recycling. Hence, identifying contaminants and their possible sources in plastics will define the gaps in the plastic's value-chain. Consequently, the application of circular economy could be boosted on the plastic waste stream, while ensuring sustainability, high quality, and safety of products.

Compared with natural sediments, hydrophobic organic contaminants have greater affinity for a range of plastics like polyethylene (PE), polypropylene (PP), or polyvinylchlorid (PVC) (Teuten et al., 2007). Polycyclic aromatic hydrocarbons (PAHs) are among the contaminants of concern. They have toxic, carcinogenic and mutagenic characteristics. Most of the PAHs are categorised as persistent, bio-accumulative and toxic (PBT) substances. These substances do not degrade and can remain for extended periods in the environment (German Environment Agency, 2016). The presence of PAHs in plastics is mainly a result of the additives added during the production and the manufacturing stages (i.e. carbon black and extender oils) (Lassen et al., 2012). Additionally, plastics could accumulate PAHs from the surrounding environment as a result of their organic nature, which increases their affinity to a variety of

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Detritus / Volume 17 - 2021 / pages 42-48
https://doi.org/10.31025/2611-4135/2021.15145

organic pollutants (Rochman et al., 2013).

On December 6th, 2013, the European Commission published the Commission Regulation (EU) No. 1272/2013 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). The regulation banns articles containing rubber or plastic fractions with certain levels of PAHs from being placed on the market for sale to the general public in the European Union. The regulation declares that defined articles cannot contain more than 1000 μg kg^{-1} of the 8 selected PAHs. On the other hand, toys and children articles have the restriction limits of 500 μg kg^{-1} (European Commission, 2006). Accordingly, the content of PAHs in recycled plastic should be controlled in order to be allowed on the European market.

The objective of this paper is to evaluate the chemical quality of the recycled polyolefin samples by studying the existence and the concentration of polycyclic aromatic hydrocarbons (PAHs) in comparison to virgin new samples. Furthermore, the impact of diluting recycled plastics with new plastics was studied to provide solutions for enhancing the recyclates quality in case of contamination. On the other hand, the study assessed if the mechanical recycling process is a source of plastics contamination with PAHs. In the context of this research, plastics extrusion was applied to simulate the effect of the mechanical recycling.

2. MATERIALS AND METHODS

2.1 Recycled polyolefin

The recycled plastics used in this study were obtained from recyclers. The samples used are representative since they are of a quality that is offered on the market and meeting the European standards. The samples were tested before and after undergoing further recycling cycles.

2.1.1 Recyclates without further processing

The quality of recycled plastics (available on market) in terms of contamination with PAHs was analysed. The aim was to test their application viability in consumer products and children's articles. For that reason, the recyclates shown in Table 1 were purchased.

PP1, PP2 and PE1 acquire a high level of purity. A selective recycling technology is applied, including degassing and filtration. PP1, PP2 and PE1 are products made from pre-sorted plastics (by colour and polymer type). On the other hand, the recycled polyethylene sample PE2 is a test set of recyclates originating from foils used in construction sites.

2.1.2 The impact of dilution on the chemical quality of recyclates

In the second part of the experiment, the chemical quality of the recycled material was studied in relation to the product's composition (i.e., the fraction of recycled plastic to virgin plastic: Recycled/Virgin (%)). The aim was to assess the effect of mixing the recycled plastic with virgin plastic on the total concentration of PAHs. Based on the decrease in the degree of contamination, an indication to the best dilution factor could be provided. To arrange the test sets (samples with different compositions (RE:VI)), five main mixtures were prepared as shown in Figure 1.

The extrusion was conducted using HAAKE™ Rheomex CTW 100 OS, a twin-screw extruder. The applied extrusion was done at a rotation speed of 25 rpm, with the heat profile of: 170-175-180-190 and 210°C at the die.

The produced filaments were separately shredded by Retsch SM 300 to the size of 4 mm x 4 mm. The shredded material of each mixture was separately collected for further testing.

2.2 Pristine polymers

In order to avoid the influence of additives on the chemical quality of plastics, pristine PE and PP samples were used in this section. In the context of this research, plastics extrusion was applied to simulate the effect of plastic's mechanical recycling. Three extrusion cycles were executed. The first one simulated the conditions plastics endure during the production process. The second extrusion cycle simulated the effects plastics undergo during the first recycling, and the third extrusion resembled a second recycling cycle. The pristine polymers used in this study were low-density polyethylene (LDPE) granules and PP pellets. The LDPE granules and PP pellets were purchased from INEOS Olefins and Polymers Europe.

The extrusion of plastics was performed using ZSE 27maxx (a twin-screw extruder from Leistritz), with a screw torque of 134 Nm screw^{-1}, total power of 46 kW and 12 heating zones (including the die). The applied rotational speed ranged between 100 and 150 rpm, with an extrusion speed of 3 kg h^{1}. The first extrusion cycle was applied on 5 kg of pristine granules. After each extrusion cycle, 1 kg of material was separated for testing purposes and the

TABLE 1: Recyclates purchased from the market.

PE1: Dark	**PE2: Black**	**PP1: Black**	**PP2: Dark**
			

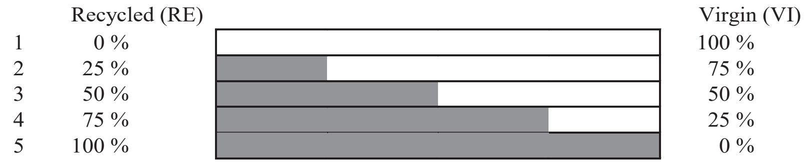

FIGURE 1: The composition of the 5 mixtures (study samples).

rest was dried overnight in BINDER ovens before shredding and further extrusion. This was repeated until the three extrusion cycles for each polymer were accomplished. The extrusion was achieved at a temperature range of 190 to 210°C for both polymers.

2.3 Extraction of PAHs from the plastic's matrix

Samples were extracted using a Randall extractor to be able to analyse the PAHs content. This method is simple, cost-effective, and time saving. Literature showed that this method can reach improved extraction efficiencies with higher reproducibility (Geiss et al., 2018).

The samples were weighed in duplicates in 33 x 60 cellulose extraction sleeves (thimbles) obtained from VWR. The weight of the test samples ranged between 0.1 and 0.5 g, weighed by Sartorius CP balance. The thimbles were manually fixed inside the metallic frames which attach to the magnetic height-adjustable holders (see Figure 2). The reaction vessel, in which the extract is collected, was filled with 70 mL of toluene, purchased from J.T. Baker®, and three to four boiling stones were added before connecting it to the condenser by screwing.

The upper part of the apparatus acts like a reflux cooler, which condensates the solvent's vapours to rinse the sample and bring the extract into the reaction vessel (see Figure 2).

The extractions were performed in duplicates. Randall hot extraction consists of three main steps: immersion, rinsing, and evaporation. The immersion step was conducted at 150°C for 120 min, where the sample is entirely in contact with the extraction solvent. Afterwards, the thimble was pulled out of the sump (reaction vessel) using the height-adjustable holder, while applying a temperature of 175°C to rinse the sample for 60 min. The evaporation was done at the same temperature (i.e. 175°C) for as long as needed to reach a solution's volume of ≤ 20 mL. The time of evaporation in this setup ranged between 20 and 40 min.

2.4 Extract preparation and clean-up

40 µL of an internal standard was added to the solution to calculate the recovery (concentration of 40 ng mL^{-1}). The internal standard was Phenanthrene-d$_{10}$ 98 atom % D, 98% (CP) from Sigma-Aldrich. The extract was then filtered to remove the plastic particles. Finally, the extract was evaporated by a 0.7 bar nitrogen (N_2) stream. Drying was applied until the solution reached a volume of ~500 µL. The clean-up was achieved using solid phase extraction (SPE). For that, silica gel Bakerbond™ disposable extraction columns were utilised.

2.5 PAHs analysis

The analysis of the samples was performed using a gas chromatograph HP 6890 coupled with a single ion monitoring mass selective detector. Before conducting the analysis, a calibration step preceded. The calibration was done prior to analysing each of the samples' sets. For the calibration, different established concentrations between 10 and 1000 ng mL^{-1} of an external standard containing the 16 US-EPA PAHs – naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene – were analysed, and the respective responses were measured.

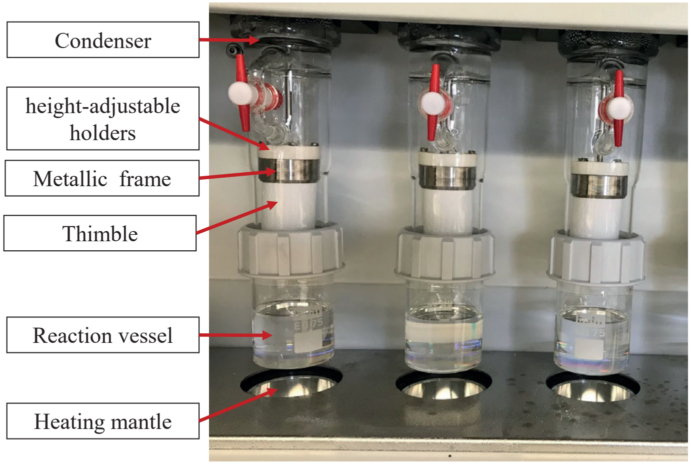

FIGURE 2: The setup of PAHs extraction using Randall extractor.

3. RESULTS AND DISCUSSION

3.1 PAHs in recycled polyolefin

3.1.1 Polyethylene

The content of the total 16-US-EPA PAHs in recycled HDPE was significantly higher in comparison to pristine (virgin) HDPE samples (Figure 3). The concentration of the total analysed PAHs in pristine samples was 155 ± 37.9 μg kg^{-1}. The highest PAHs concentration was observed in PE1 (3043 ± 837 μg kg^{-1}), a sample of a mixed source. A thorough analysis of the 16-US-EPA PAHs showed significant variances in the concentrations of phenanthrene and pyrene. Phenanthrene's concentration was 1200 μg kg^{-1} in PE1 in comparison to 310 μg kg^{-1} in PE2. Likewise, pyrene's concentration in PE1 was 2.7 times the concentration in PE2 (741 μg kg^{-1} in comparison to 271 μg kg^{-1}). Like most PAHs, phenanthrene is present in manufactured dyes and plastics. Hence, its high concentration is attributed to the contamination of the source material. Pyrene is found in high concentrations in crude oil and in extender oil. Accordingly, its presence is a result of the plastics manufacturing process. The difference between PE1 and PE2 is the source material. PE1 originates from a mixed source (post-consumer, commercial, or post-industrial waste), where PE2 originates from foils used at construction sites. Hence, the chemical quality of the two samples is different due to the additives in the source material. As was reported by Camacho and Karlsson (2000), the concentration of aromatic hydrocarbons in the recycled resin is approximately five times higher in comparison to virgin polyolefin. The results of this experiment indicated that the total content of the 16-US-EPA PAHs is 20 times and 10 times higher in PE1 and PE2, respectively, when compared to pristine resins, depending on the materials' source and the efficiency of the applied sorting.

Among the 16 US-EPA PAHs, 6 belong to the REACH 8 priority PAHs (i.e. benzo(a)anthracene, chrysene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and dibenz(a,h)anthracene). The concentrations of the 6 priority PAHs in PE1 and PE2 were ranging between 300 and 400 μg kg^{-1} (see Figure 4). The threshold limits for the 8 priority PAHs are 500 μg kg^{-1} for children articles, and 1000 μg kg^{-1} for all other consumer products (Geiss et al., 2018). Hence, samples PE1 and PE2 might show risks if applied in children articles (Alassali, 2020). Nonetheless, their application in consumer products shows limited risks.

3.1.2 Polypropylene

The two tested recycled PP samples are of undefined sources. The concentration of the 16-US-EPA PAHs in the purchased PP recyclates showed an increase by 173% for PP1 and by 264% for PP2, in comparison to the pristine PP samples (see Figure 5). The black sample showed lower concentrations of the 16-US-EPA PAHs in comparison to the dark grey sample. However, considering the 6 out of the 8 priority PAHs, PP1 had higher concentration of ben-

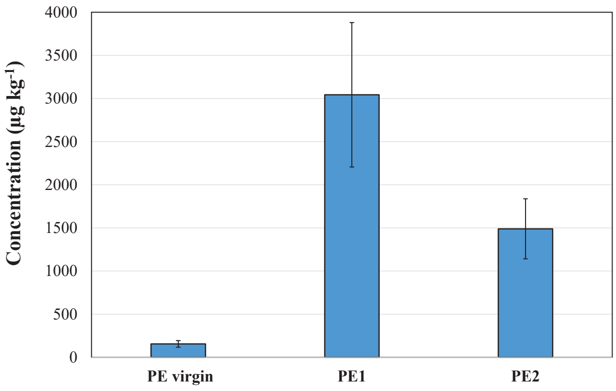

FIGURE 3: The concentration of the 16-US-EPA PAHs in different HDPE samples.

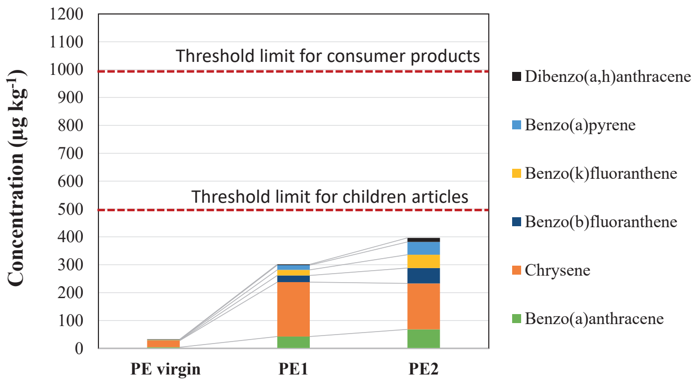

FIGURE 4: The content of 6 out of 8 priority PAHs in the recycled and virgin HDPE samples.

zo(a)pyrene. Additionally, PP1 (black in colour) contained dibenzo(a,h)anthracene, which was missing in PE2. Dibenzo(a,h)anthracene is mainly found in crude oil, which is an indication of the presence of crude oil residues, probably through the plastic manufacturing process. All in all, the concentrations of the 6 priority PAHs were always below the REACH-indicated threshold limits, for both children articles and consumer products. Hence, and due to the low contamination risk, the recycled PP samples indicate suitability for application without restriction (see Figure 6).

The concentration of the priority PAHs in recycled PP ranges between 0.3 to 0.5 of the concentration in recycled PE. This could be explained by the higher degradability of PE in comparison to PP under the recycling conditions, or by the higher affinity of PAHs to the polymer PE.

3.2 Does the mechanical processing per se generate PAHs in the plastic matrix?

In this section, the impact of plastic recycling was simulated in the lab on new and pure polymers (LDPE and PP). The content of PAHs was then compared between new plastic samples and 3-times extruded samples (as the worst case).

For PE 3x-extruded sample, the 16-US-EPA PAHs concentrations increased by 185% (from 155 ± 37.9 µg kg^{-1} to 442 ± 133 µg kg^{-1}). A similar factor of increase was obtained for the 6-priority PAHs, showing that there is a general trend of increase (see Figure 7). The increase of the concentrations of naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene were most significant in comparison to the rest of analysed PAHs (increasing by 200 to 300%) (Alassali, 2020; Alassali et al., 2020b). This proves that exposing polyethylene to the heat and stress involved in the mechanical recycling process may result in polymer degradation, oxidation and the formation of new chemical groups. As was reported by Alassali et al., 2018, the degradation of LDPE can be detected by one or more of the following evidences: increase in the crystallinity, decrease in the molecular weight, increased chain scissoring, oxidation (i.e., formation of C-O, C=O, ether, aldehyde, ketone and/or carboxylic acid products) and a minor decrease in the tensile strength. Another reason of contamination could be the high affinity of the PAHs to the PE and PP polymers (Teuten et al., 2007), which could be absorbed from the surrounding environment during the extrusion process.

The same trend was observed for PP. After extruding the pristine PP, a minor increase in the total concentration of PAHs was observed. However, the percentage of increase was lower by a factor of 43.6% than that for the LDPE polymer. Even a lesser percentage of increase was obtained by the 6-priority PAHs (29.5%) (see Figure 8). Nonetheless, the PAHs content was tangibly below the threshold limits for children articles as well as consumer products for PE

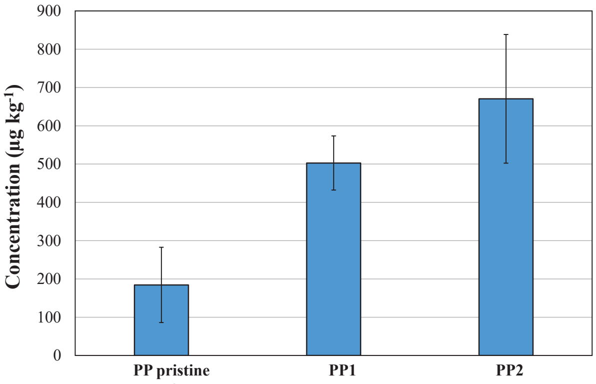

FIGURE 5: The concentration of the 16-US-EPA PAHs in different PP sample.

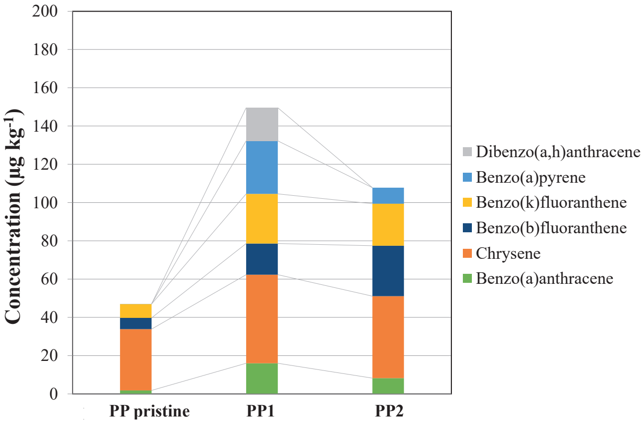

FIGURE 6: The content of 6 out of the 8 priority PAHs in the recycled and pristine PP samples.

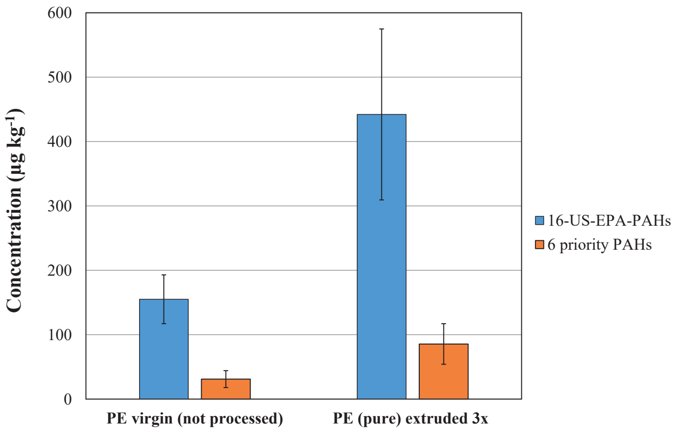

FIGURE 7: A comparison in the PAHs content between pristine PE and 3-cycles extruded pure PE.

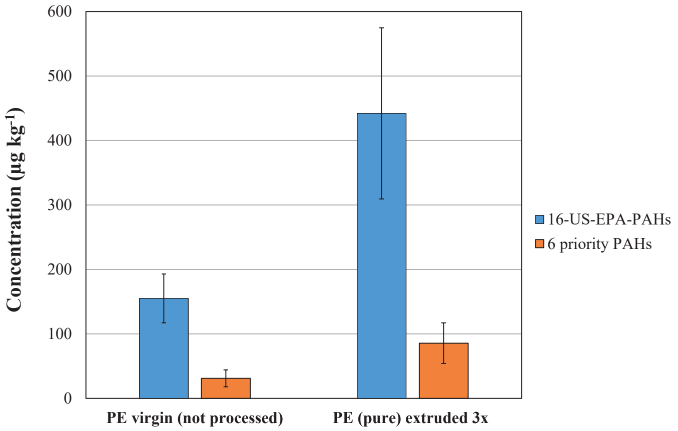

FIGURE 8: A comparison in the PAHs content between pristine PP and 3-cycles extruded pure PP.

and PP samples that are recycled without the presence of additives (Alassali et al., 2020b).

3.3 The impact of mixing recycled plastics with pristine polymers (dilution) on the PAHs content

Generally, recyclates dilution with pristine polymers resulted in a decrease in the total concentration of the 16-US-EPA PAHs. It was observed that the decrease was 16% for the 50%-RE sample and improved by almost the double (decrease by 30%) for the 25%-RE (see Figure 9).

Phenanthrene was lost in both diluted samples (i.e. 50%-RE and 25%-RE). This could be attributed to the low melting point of phenanthrene (99°C) (National Center for Biotechnology Information), resulting in its evaporation during the extrusion process. Additionally, the dilution of the material resulted in further decrease in its concentration to be undetectable.

Analysing the 6-priority PAHs showed an insignificant decrease in their concentration when the PE2 was diluted by a 50%-factor. When the 6-priority PAHs were separately evaluated, a tangible increase in the chrysene concentration and a minor increase in the acenaphthene concentration were observed in the 50%-RE sample. This is explained by the additional extrusion step the 50%-RE sample has undergone, in comparison to the 100%-RE sample (original sample, which was not further extruded in the lab). The same trend was not observed in the 25%-RE sample, because of the additional dilution of the sample with pure and new material, resulting in a substantial dilution in the PAHs content (Alassali et al., 2020b).

4. CONCLUSIONS

The aim of this study was to analyse the impact of the mechanical recycling of plastics on the degree of their contamination by polycyclic aromatic hydrocarbons (PAHs). Firstly, recyclates purchased from recyclers were tested to assess for the quality of recycled plastic put on the market. Results showed that HDPE and PP recyclates had higher concentrations of PAHs in comparison to pristine samples. HDPE recyclates originating from mixed sources had higher concentrations of the 16-US-EPA PAHs than those recyclates originating from one defined source. This indicates the importance of controlling the plastic waste streams put for recycling. Similarly, recycled polypropylene (PP) indicated higher PAHs concentrations in comparison to pristine material, yet with lower degree of contamination than that for HDPE, which could be explained by the less affinity it has to PAHs in comparison to the PE polymer. Considering 6 out of the 8 priority PAHs indicators (assigned by the Reg-

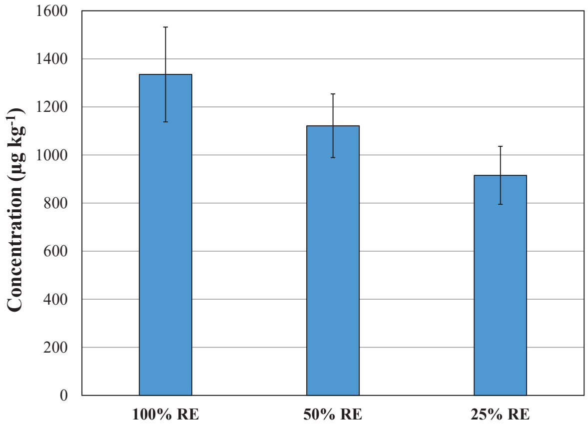

FIGURE 9: The concentration of the 16-US-EPA PAHs in PE recyclates, before and after dilution (by a 50% and 75% factor).

ulation EU 1272/2013 amending REACH Annex XVII), recyclates were most of the times complying with the threshold limits for consumer products.

Taking everything into account, the recycling process contributes to the formation and accumulation of PAHs in plastics, yet the increase is insignificant in pure plastics, due to the absence of organic additives and dyes. The PAHs content can be intensified in recycled plastics when the source material comes with higher degrees of contamination. As a result, the quality and source of plastic waste define the quality of produced recyclate. Adding pristine resin to the recycled plastic can enhance the chemical quality of the end product by obtaining less contamination risks.

AKNOWLEDGEMENTS

We thank Ms. Anja Scholz for her help in developing and optimising the extraction procedure.

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