



Full length article



Decontamination efficiencies of post-consumer high-density polyethylene milk bottles and prioritization of high concern volatile migrants

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ARTICLE INFO

Keywords:

Polyolefins recycling
HDPE
Decontamination
Volatile compounds
Food contact use
Migration

ABSTRACT

High-density polyethylene (HDPE) milk bottles are well-distinguished from other plastics in the mix-collected plastic waste and have potential to be closed-loop recycled. To evaluate this option, volatile substances present in various recycled HDPE (rHDPE) pellets and flakes from postconsumer milk bottles were analysed for similarities between different industrial recycling companies and batches. All substances found were classified in five different levels based on toxicity, from level I to level V (high toxicity). Chemicals present in the samples from different recyclers varied considerably, while those from different batches of a given recycler gave similar results. However, the study of rHDPE stream mixed with high volume of non-milk-bottles provided significant differences between batches. Washing the rHDPE twice and applying extra decontamination techniques reduced to a half the intensities for most chemicals detected, including two toxicity level V substances, butylated hydroxytoluene and diethyl phthalate. Nevertheless, other two high concern compounds, octocrylene, and 2-ethylhexyl-4-methoxycinnamate were not significantly reduced and thus deserve special attention when decontaminating rHDPE and evaluating its feasibility for food contact uses. Extra decontamination was able to reduce the intensities of 1-dodecene and 1-tetradecene. In total, 265 substances were detected in migration tests (95% ethanol and 3% acetic acid) and 58 of them were prioritized by toxicity. Regarding volatile migrants, rHDPE with low content of non-milk-bottle could be safe for direct contact with low-fat content food. For high-fat foods, the main concerns could come from 1-tetradecene, octocrylene, and 2-ethylhexyl-4-methoxycinnamate.

1. Introduction

Plastic recycling is one of the important topics in the European plastic strategy in a circular economy (EC, 2018). Globally, it is also well accepted as an essential way to tackle increasingly prominent environmental issues posed by plastic pollution. Mechanical recycling, as one of the well-established and widely used approaches, only accounts for 14–18% plastic waste recycling rate at global level (OECD, 2018) and 31% in Europe (d'Ambrières, 2019) and requires further improvements.

Comprising 39.6% of plastic demand and 46.7% of global primary plastic waste generation (PlasticsEurope, 2012, 2020), the plastics used in packaging sector are vital in the way to a circular economy. Before being authorized for food contact uses, recycled materials should comply with Framework Regulation EC 1935/2004 (EC, 2004) and EU 10/2011 (EC, 2011) requiring that they may not pose risk to human health. Currently, only a few of post-consumer polyolefins are closed-loop recycled for food contact uses (Silano et al., 2018a), and most of the recycled plastics for food contact are referred to

polyethylene terephthalate (PET), thanks to their promising high purity and low levels of contaminants (Strangl et al., 2019). Compared to PET, polyolefins, which represent 70% of plastic packaging (PlasticsEurope, 2019), are more challenging to be closed-loop recycled as they have much higher chemical sorption capacity, faster diffusion of chemicals through them, and thus higher migration potential than PET (Palkopoulou et al., 2016). Consequently, cleaning procedures that work well on PET, e.g., the so-called super-clean PET recycling system, cannot be simply extrapolated to polyolefins (Palkopoulou et al., 2016). Further developments and investments in innovative recycling systems are required to satisfy the high quality demands of industry (Strangl et al., 2019).

Polyolefins are widely used in food packaging in various forms, for example, polyethylene (PE) films or thermal sealing layers in multilayer packages, polypropylene (PP) crates/trays, high-density polyethylene (HDPE) milk bottles, etc. Amongst them, HDPE milk bottles could be the first candidate for closed-loop recycling (Welle, 2005) since they could be easier to collect and sort from a kerbside collection system and might

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<https://doi.org/10.1016/j.resconrec.2021.105640>

Received 5 February 2021; Received in revised form 20 April 2021; Accepted 25 April 2021

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have less contaminants compared to others. Bottle-to-bottle recycling (separated collection of post-consumer HDPE milk bottles) might come back with minimum contamination, but it requires a major update of the whole recycling systems since HDPE milk bottles are currently mix-collected with other plastics. Similar to PET bottles, HDPE milk bottles are well-distinguished from others in the mixed plastic waste collection (Silano et al., 2018b, 2018c) and therefore could have less contamination from non-food grade plastics. However, knowledge about the compounds present and their concentration in post-consumer plastics, and the capabilities of various recycling processes to remove them, are crucial for the design of efficient HDPE recycling process (Welle, 2005). As far as we know, research studies on this topic are limited. Some of them mainly focused on the odorants, which is also important for food contact uses, but chemicals of high safety concern were not considered (Demets et al., 2020; Strangl et al., 2018, 2019). Extraction as well as migration from various recycled HDPE were investigated (Coulter et al., 2007; Devlieghere et al., 1998; Dutra et al., 2011; Huber and Franz, 1997; Welle, 2005). However, these studies are outdated as some of them are more than 20 years old. Technological development in analytics allows generating value-added information. There could be progress made in the plastic industry as well. Recently, a highly sensitive direct immersion – solid-phase microextraction coupled to gas chromatography – mass spectrometry (DI-SPME-GC-MS) method was developed for the untargeted screening of (semi-)volatile migrants in different food simulants (Su et al., 2020). This analytical procedure enabled getting a deeper insight into chemicals present in rHDPE that might endanger human health.

Consistency of chemicals present between different batches of sorted HDPE bottles in the recycling plant could be one of the key points for the quality control of recycled materials. Thus, the first objective of this work was to evaluate the batch effect in the recycling industry (samples collected at different time) on the chemicals present in flakes and pellets from rHDPE milk bottles by hierarchical clustering (HCA). The second objective was to evaluate the efficiency of two cleaning processes (washing twice and extra decontamination) on the removal of chemicals present in the rHDPE samples and to deeply understand the factors largely affecting the cleaning efficiency. Thirdly, with the aim to find out the most concerning chemicals in rHDPE from milk bottles samples, a highly sensitive DI-SPME-GC-MS method was employed for the untargeted screening of migrants coming from these rHDPE samples in both 95% ethanol (v/v) and 3% (w/v) acetic acid food simulants. The large number of migrants identified was then prioritized and quantified when available. Finally, several substances with prioritized concern were listed and addressed with particular attention for rHDPE samples with the aim to provide useful information for developing effective decontamination techniques and establishing legislation to assure high quality rHDPE.

A schematic overview of the analytical strategy applied in this study is shown in Fig. 1. The research has been distributed in two sections, one deals with the first and second objectives by employing sample extraction from both flakes and pellets, HCA, and fold change analysis, while the other one concerns the third objective via migration study from pellets, prioritization, and quantification of high concern substances.

2. Materials and methods

2.1. Reagents and samples

Butylated hydroxytoluene (CAS 128-37-0), diethyl phthalate (84-66-2), naphthalene (91-20-3), diisobutyl phthalate (84-69-5), 2-ethylhexyl-4-methoxycinnamate (5466-77-3), diphenyl ether (101-84-8), 1-dodecene (112-41-4), alpha-terpineol (98-55-5), 2,6-diisopropyl-naphthalene (24,157-81-1), 1-tetradecene (1120-36-1), 1-methyl-naphthalene, (1321-94-4), octocrylene (6197-30-4), 3-methyl-1,1'-biphenyl, (643-93-6), 1-chloro-decane, (1002-69-3), 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (82,304-66-3),

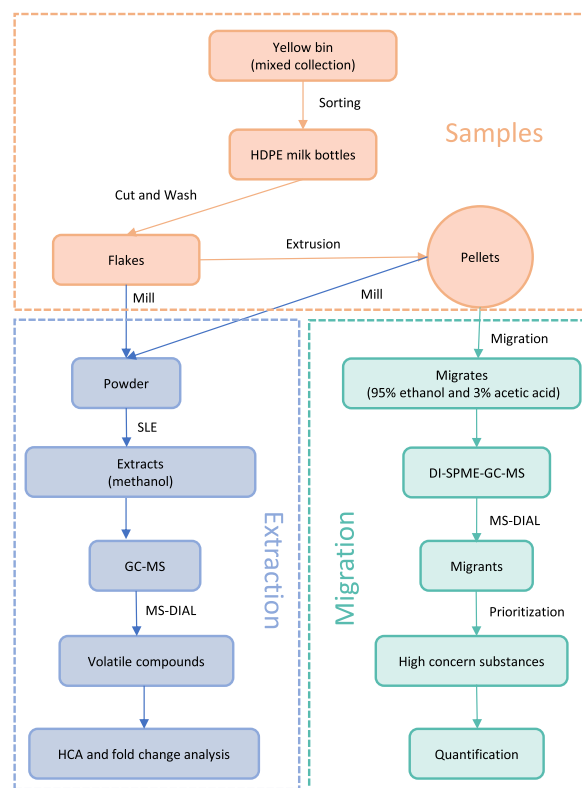


Fig. 1. Schematic overview of the analytical strategy applied in this study.

2,4-dichloro-benzenamine (554-00-7), biphenyl (92-52-4), 2,4-dichlorobiphenyl (33,284-50-3), 3-phenyltoluene (643-93-6), o-hydroxybiphenyl (90-43-7), pyrimethanil (53,112-28-0), (+)-2-bor-nanone (464-49-3), 2-tridecanone (593-08-8), benzophenone (119-61-9), 2-ethylhexyl salicylate (118-60-5), ethyl dodecanoate (106-33-2), 1-octadecanol (112-92-5), 1,1'-oxybis-octane, (629-82-3), 1-octadecanol (112-92-5), D-limonene (5989-27-5), dl-menthol (89-78-1), isoborneol (507-70-0), alpha-terpinene (99-86-5), N,N-dimethyltetradecylamine (112-75-4), diisooctyl phthalate (27,554-26-3) and 2,4-dimethyl-benzenamine, (95-68-1) were from Sigma-Aldrich (Madrid, Spain).

Post-consumer HDPE milk bottles in flakes and pellets (abbreviated as F and P, respectively) forms were provided by 3 Spanish plastic recyclers located in different provinces and autonomies. According to the recyclers, rHDPE milk bottles were kerbside collected (yellow container in Spain) and separated from other plastics in sorting plants. HDPE milk bottles (white with slightly black colour inside, see Appendix A Fig. A.2, first 3 bottles) can be well-distinguished from other PE bottles (totally white, see Appendix A Fig. A.2, last bottle). Besides, most of the collected bottles still keep their labels. Thus, they are visually distinguishable and therefore can be manually sorted. They were then cut up and washed with water to attain the flake samples. Pellets were then obtained by directly extruding the flakes without additional decontamination steps, except otherwise specified. The appearances of the samples are shown in Appendix A Fig. A.1, while detailed information of the samples is depicted in Fig. 2. Samples P1.3' and F1.3' were obtained directly from P1.3 and F1.3, respectively, by applying an extra decontamination technique which is a non-destructive deodorization process by heating. The appearance of both pellets and flakes did not change after this step. However, no more details are available for extra decontamination due to confidential reasons. Samples P2.1, P2.2, P2.3, F2.4, F2.5, and F2.6 were washed twice with water. However, samples were collected on various days as specified in Fig. 2. Notably, although P2.2, P2.3, F2.4, F2.5, F2.6 were collected on the same day, there were no direct correspondences, e.g., P2.2 was not related to F2.4, F2.5, nor F2.6.

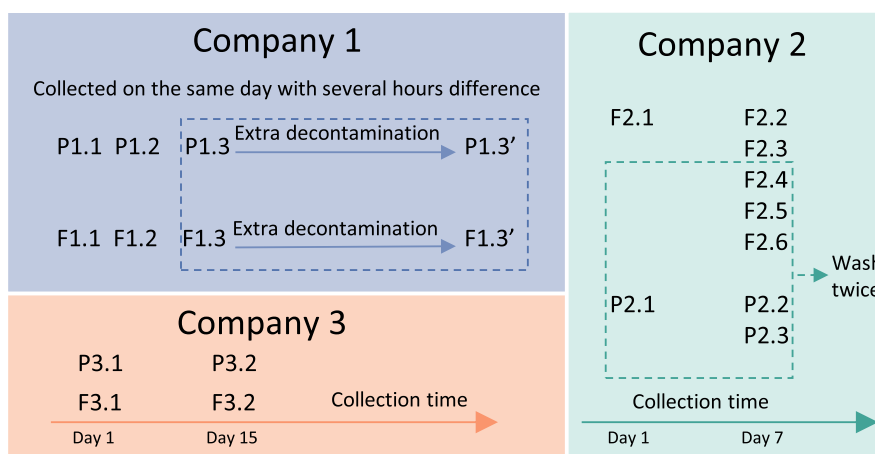


Fig. 2. Detailed sample information including collection time and additional processes applied.

Furthermore, to explore the possible origin of octocrylene and 2-ethylhexyl-4-methoxycinnamate, 3 bottles of milk and 1 bottle of liquid yogurt packaged in HDPE bottles were bought from the local supermarkets (Zaragoza, Spain). The samples collected are shown in Appendix A Fig. A.2. The bottles were then cleaned with water and dried for the extraction as described below.

2.2. Sample extraction

Samples of both flakes and pellets were milled into powders by an ultra-centrifugal mill (Retsch ZM 200; Haan, Germany) using a perforated plate sieve with aperture size of 0.5 mm. The milled samples (1.00 g) were then extracted with 5 mL of dichloromethane for 1 h by ultrasonic bath (Brasonic 3510-MTH; Connecticut, USA). Three consecutive extractions were applied by adding fresh dichloromethane in each case, and the extracts were then mixed and evaporated to dryness with a gentle nitrogen flow at 40 °C (Techne DB-3; Staffordshire, UK). Subsequently, 0.4 mL of methanol was added to re-dissolve the extract under ultrasonic bath (5 min). Finally, the extract was vortexed for 30 s and filtered by a 0.2 µm Acrodisc GHP syringe filter (Waters, New York, USA) prior to GC-MS analysis. Owing to instrumental capacity limitation, samples from each company were grouped and processed under the same lot to minimize the potential batch effect in the extraction process. Samples and procedural blanks were simultaneously prepared in triplicate. Quality control (QC) sample pooled from the filtered extracts (50 µL from each sample) was employed for sample alignment and normalization to minimize the effect of instrumental variation during injections and thus to have more robust statistical analysis.

2.3. Migration tests

For pellet samples, the protocol proposed in our previous article (Su et al., 2021) was used. In short, the surface area of each pellet was estimated based on their cylinder-like shape (Appendix A Fig. A.1). The size of the pellet samples is shown in Appendix A Table A.1. The number of pellets needed for 18 mL food simulant (the size of the migration container) was then calculated accordingly. For flakes, weight method (average weight of the pellets used for migration) was utilized owing to the difficulty to calculate the corresponding surface area. Two food simulants, namely 95% ethanol (v/v) and 3% (w/v) acetic acid were used as fatty and acidic food surrogates, respectively, as the worst-case scenarios. The migration test was conducted under 60 °C for 10 days according to the Commission Regulation EU No. 10/2011 (EC, 2011). Samples including procedural blanks were prepared in duplicate.

2.4. Fourier-transform infrared (FTIR) spectroscopy analysis

The flakes from company 2 contained many non-milk bottle plastics. To evaluate the types of polymer present, the flakes (ca. 50 g) were manually separated into 5 fractions (Appendix A Fig. A.6) and the polymer types (5 pieces from each fraction) were measured by an FTIR spectrometer (Cary 630, Agilent, USA). Attenuated total reflectance (ATR) sampling was used in all the cases. The FTIR absorbance spectrum from 4000 to 650 cm^{-1} was measured in the samples with a resolution of 4 cm^{-1} and 64 scans. Identity of polymer in each case was carried out by comparison of the FTIR spectra obtained to the spectra in the commercial polymer libraries.

2.5. Direct-immersion solid-phase micro-extraction (DI-SPME)

The DI-SPME procedure was optimized and used in our previous studies (Su et al., 2020, 2021). Briefly, 95% ethanol samples were 9.5 times diluted to prevent SPME fibre damage, while neutralization with NaOH was applied to 3% acetic acid samples prior to DI-SPME. SPME conditions were as follows: pre-incubation at 70 °C for 5 min, extraction for 55 min by a DVB/CAR/PDMS fibre Supelco (PA, USA), desorption in the GC inlet (250 °C) for 8 min, and fibre cleaning at 270 °C for 2 min. The DI-SPME processes were automatically achieved by a CTC Analytics CombiPAL autosampler (Zwingen, Switzerland) connected to the GC-MS.

2.6. Quantification of prioritized migrants

Quantification of prioritized migrant was done under the same conditions as mentioned in Section 2.5. Calibration plots were done from each pure standard corresponding to each identified compound. Substances found in 95% ethanol migration were quantified in 10% ethanol by DI-SPME-GC-MS as above described, in order to avoid any damage to the SPME fibre. The final concentration was recalculated considering the dilution factor of the samples. In the case of 3% acetic acid migration, pre-neutralized 3% acetic acid was used instead.

2.7. GC-MS analysis

A gas chromatography Agilent 6890 N coupled to a mass spectrometer Agilent 5975 was used for this purpose. The separation was carried out in an Agilent DB-5 MS capillary column (30 m × 0.25 mm id, 0.25 µm film thickness) with the following temperature program: started at 50 °C, it increased to 100 °C at 15 °C/min, then slowly rose to 200 °C at 2 °C/min, and finally climbed to 300 °C at 15 °C/min. Carrier gas was helium (99.999%) at 1.0 mL/min. The inlet temperature was set at 250

°C and splitless mode was employed. Mass scan range was 40–700 Da. Test mixture 2 for apolar capillary columns according to Grob (Sigma Aldrich) was injected prior to each sequence of samples to control the correct performance of the system. The QC sample (Section 2.2) was injected twice at the beginning and the end of the sequence as well as every 10 injections.

2.8. Data analysis

All GC–MS data were processed by MS-DIAL version 4.36 (Tsugawa et al., 2015) by applying the following settings: minimum peak height of 1000, sigma window of 0.5 and EI spectra cut-off of 1 for deconvolution; alignment was done with 10 retention index (RI) tolerance and 85% EI similarity; features with sample max / blank average fold change lower than 10 were removed. NIST 14 spectral library in NIST MS search format (*.MSP) including RI information was used for identification. Experimental semi-polar RI was retrieved, averaged, and assigned to each spectrum when available. When no experimental RI is available, predicted RI using a deep convolutional neural network (Matyushin et al., 2019) was calculated. Identification was done before alignment with 80% spectrum similarity and 85% total score cut-off to reduce false positive. The identified table list was manually curated to assure identification, alignment, peak area integration, and to check the presence of a certain substance in each sample. Locally estimated scatterplot smoothing (LOESS) algorithm was then utilized to normalize batch or amplitude drifts within MS-DIAL. Subsequently, the normalized peak area table was exported for further multivariate analysis. Missing values were replaced with 1/10 of minimum peak area over all samples.

Multivariate analysis including hierarchical clustering and fold change analysis was carried out by MetaboAnalyst (Chong et al., 2019). Data transformation (log or cube root transformation) and scaling (mean, auto, pareto, or range scaling) were selected for each subset of analysis by visually assessing how Gaussian the data distribution appeared according to the MetaboAnalyst tutorial. False discovery rate (FDR) adjusted p-values based on Benjamini-Hochberg procedure was used. Data visualization was accomplished by ggplot2 package (Hadley Wickham, 2016) in R programming. Chemical classification was done by ClassyFire (Djoumbou Feunang et al., 2016). Migrants were prioritized as previously proposed in our study (Su et al., 2021). In short, migrants listed as carcinogenic, mutagenic, and reprotoxic chemicals (CMR, categories 1A, 1B, and 2 in the classification, labelling, and packaging (CLP) regulation) (European Union, 2008), substances of very high concern (SVHC) from European Chemicals Agency (ECHA) (<https://echa.europa.eu/candidate-list-table>), endocrine disrupting chemicals (EDC) (IPCP, 2017), and/or having specific migration limit (SML) as ND (not detectable at 0.01 mg/kg) in the positive list of EU regulation (EC, 2011) (positive list for short below) obtained toxic level V. The CMR, SVHC and positive list were last updated on 15th of September 2020. Toxtree (version 3.1.0.1851) based on Cramer rules (Patlewicz et al., 2008) was utilized for toxicity estimation when the migrant is not present CMR, SVHC, EDC or positive list. Cramer class III or SML between 0.01 and 0.1 mg/kg migrant was level IV; Cramer class II or SML between 0.1 and 1 mg/kg attained level III; Cramer class I or SML between 1 and 60 mg/kg got level II and migrants having SML equal to 60 mg/kg constituted level I.

3. Results and discussion

The number of pellets or the weight of flakes, respectively, can be employed for migration tests as an approximation method. However, the contact surface in each sample could vary because of the irregular shape of samples. Consequently, it is difficult to normalize the chromatographic response of each chemical in the migration samples either by weight or by contact surface. As it is known, the contact surface to food simulant volume ratio in migration test, which is set in Europe to 6 dm² to 1 kg food simulant, is vital and could have great effect on chemical

migration. Hence, using migration results for the following multivariate analysis might, to some extent, add uncertainties to the results. In this sense, multivariate analysis described below using extraction data will be more robust. For extraction, all samples were milled into powders to have identical shape and LOESS normalization was employed to minimize instrumental variation during analysis. Chemicals identified in the extracts and their normalized peak area are shown in Appendix B.

3.1. Compositional similarities among samples

Compositional similarities (number of chemicals present and their corresponding intensities) of the rHDPE samples provided by 3 different recyclers were evaluated. In addition, samples from a same company were collected at different time (from hours to weeks). Therefore, differences between batches of waste HDPE bottles could be assessed as well. The compositional similarities were evaluated by hierarchical clustering of the chemicals detected in the extracts using their normalized chromatographic peak areas. As illustrated in Fig. 3, various batches of samples (both pellets and flakes) from company 1 were quite similar, and for company 3 alike (example chromatograms in Appendix A Fig. A.3). The batch difference was even smaller than the distinction between replicates. Samples from company 1 were collected on the same day with only few hours of difference. However, samples from company 3 were collected within 15 days. Although the composition from these 2 companies varied considerably, batches within the same company showed consistency, which is very positive for the industries. As expected, P1.3' and F1.3' were from company 1, but they were not clustered into the same group with other samples because they had been cleaned by the so-called extra decontamination technique.

In contrast, the situation was more complicated for company 2 samples. Sample P2.1 was quite different from P2.2 and P2.3 (see comparison of chromatograms in Appendix A Fig. A.4). Sample F2.1 was dissimilar from F2.2 and F2.3 as well. The main difference amongst them was that P2.1 and F2.1 were collected 7 days before the others. Sample F2.4, F2.5, and F2.6 were collected on the same day and they were similar to each other. The results suggest that for company 2, samples from the same day were somehow consistent, while those from different days could vary considerably. The phenomenon is interesting and deserves further evaluation. Looking in depth into the sample difference from each company (Fig. 4), we found that samples from companies 1 and 3 were rather clean (mainly from milk bottles) while company 2 samples contained many colour pieces e.g., various films with printing inks. Apart from HDPE flakes, isotactic PP films and flakes were found in company 2 samples by FTIR analysis (Fig. 4). Obviously, these colour pieces did not come from milk bottles per se. Their presence in the so-called recycled milk bottles is most likely the consequence of poor separation capability during the recycling process. Hence, the significant chemical variation of company 2 samples collected on different days could be explained by the complexity of the samples because of the non-milk-bottle plastic contamination.

3.2. Efficiency of washing twice on the removal of chemicals

Washing with water is a simple way to clean up contaminants attached on the surface of the recycled plastics. However, one-time washing might not be sufficient. For this reason, we have tested if washing the rHDPE twice with the same procedure would provide additional chemical removal capability. Sample F2.1 was excluded for this comparison since it was not collected on the same day than others and showed a different GC–MS profile as aforementioned in Section 3.1. As intuitively shown in Appendix A Fig. A.5, smaller peak size was observed for the majority of peaks after employing second wash. More specifically, the chromatographic peak area of 63.3% of chemicals including two level V substances, butylated hydroxytoluene (BHT) and diethyl phthalate (DEP) was halved after washing the flakes twice with water (Fig. 5A). Benzene and substituted derivatives, organooxygen

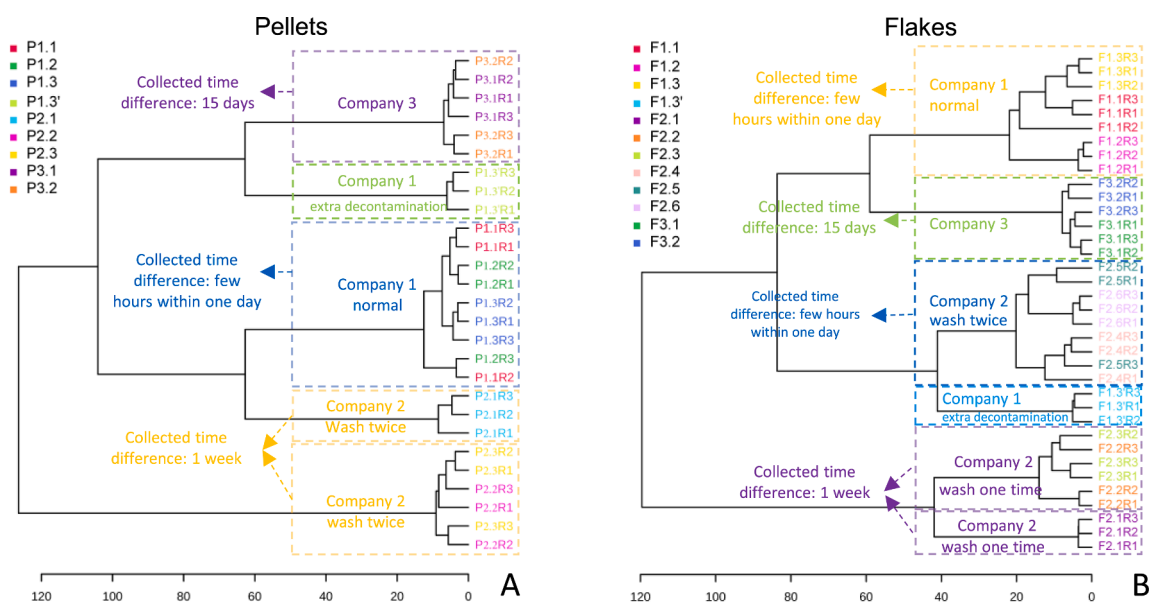


Fig. 3. Hierarchical clustering of pellet (A) and flake (B) samples.

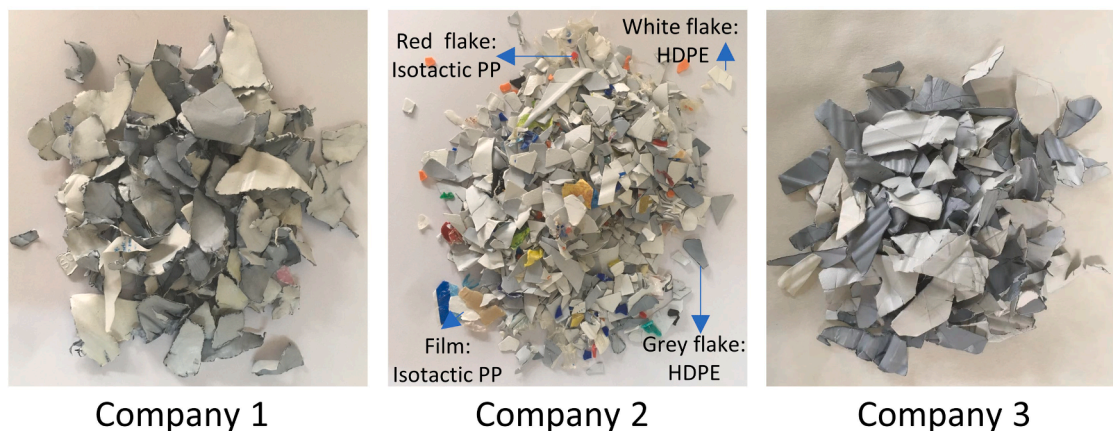


Fig. 4. Flake samples from each company.

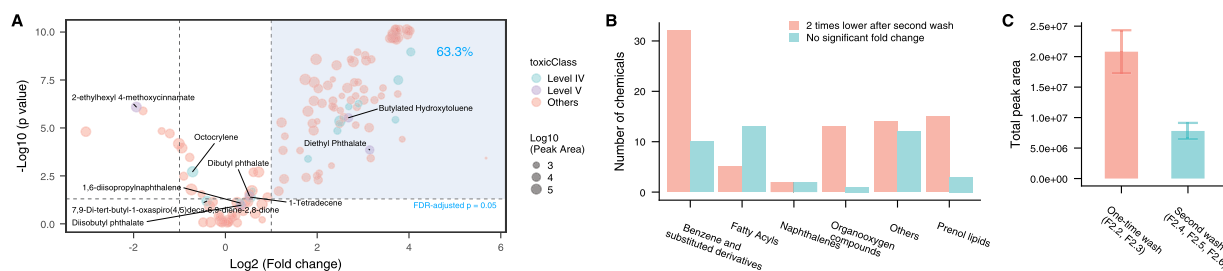


Fig. 5. Efficiency of washing twice: fold change analysis by volcano plot (A), chemical classes distribution (B), and total chromatographic peak area (C) Note: Fold change is expressed as one-time wash versus twice wash; the size of the circles is mapped to the average peak area of the samples that applied second wash.

compounds, and prenol lipids were the 3 classes of chemicals more easily removed (Fig. 5B). Besides, the total chromatographic peak area dropped more than a half (Fig. 5C).

As aforementioned, flakes from company 2 contained high proportion of non-milk-bottle plastics, e.g., coloured films, coloured flakes, etc. Each type of plastic might have different contaminants. For example, coloured films might have more contaminants (chemicals from printing inks) than milk bottle flakes. To assess whether the percentage of each type of plastics has changed after the second wash, flakes from company

2 were manually separated into 5 fractions, namely, milk bottle flakes, transparent flakes, coloured flakes, coloured films, and transparent films (Appendix A Fig. A.6), and the weight of each fraction was calculated. As shown in Table 1, the percentage of milk bottle fraction significantly increased from 54% to 84% after the second wash, which means that high amount of non-milk bottle plastics was removed in this step. This could be one of the important reasons why much less and lower peaks were observed for samples subjected to a second wash. However, we speculate that more cleaning processes, e.g., sink float separation, might

Table 1

The percentage of each fraction of polymer before and after second wash.

Polymer fractions	One time wash (%)			Wash twice (%)		
	F2.1	F2.2	F2.3	F2.4	F2.5	F2.6
transparent film (PE, PP)	2.4	3.2	2.7	0.3	0.4	0.3
transparent flake (pe)	32.1	36.8	37.3	4.1	4.7	4.2
colour film (pp and others)	3.5	3.6	3.3	1.3	1.0	1.2
colour flake (pe, pp)	5.8	3.1	3.0	12.0	8.8	8.2
milk bottle (HDPE)	56.3	53.6	54.2	82.3	85.4	86.3

have been applied in the so-called second wash as those non-milk bottle fractions might not be easily removed by simply washing with water.

Unlike DEP, two heavier phthalates, dibutyl phthalate (DBP) and diisobutyl phthalate (DiBP) were more difficult to remove. Moreover, 2-ethylhexyl-4-methoxycinnamate, which is an EDC, as well as octocrylene and 1-tetradecene, which had been reported to have excess migration values (SML 0.05 mg/kg) in recycled polyolefins (Su et al., 2021) were not easy to clean neither (Fig. 5A). The compound 2-ethylhexyl-4-methoxycinnamate had significantly higher intensities after second wash probably because of sample heterogeneity (see also Appendix A Fig. A.7). Albeit samples collected on the same day had similar GC-MS profiles (as mentioned in 3.1), it does not mean that they were exactly the same. In fact, several chemicals varied their chromatographic intensities.

3.3. Efficiency of the extra decontamination technique

To examine the effectiveness of the extra decontamination step, P1.3 and F1.3 were processed by this technique, and corresponding cleaned samples P1.3' and F1.3' were obtained, respectively. Appendix A Fig. A.8 gives the intuitive sight of the efficacy of extra decontamination. Many peaks had lower intensities after extra decontamination. Explicitly, 48.5% and 81.4% compounds in flakes (Fig. 6A) and pellets (Fig. 6D), respectively, got less than half chromatographic response after being treated with the extra decontamination technique. Interestingly, much higher cleaning efficiency was observed for pellets, as evidenced by their total peak area decrease (Fig. 6C and F). Firstly, there were more substances (118 vs 103) detected and higher total peak area observed ($2.8 \cdot 10^7$ VS $1.4 \cdot 10^7$) in pellets than in flakes before applying extra decontamination. Therefore, it is reasonable to have higher cleaning efficiency in the most contaminated samples (pellets). For example,

most of the benzene and substituted derivatives were sufficiently cleaned (fold change higher than 2) in pellets but not in flakes (Fig. 6B and E). By plotting only this class of chemicals (Appendix A Fig. A.9), we can understand that 37.8% of benzene and substituted derivatives had fold change between 1.5 and 2 in flakes with low p-values, which means that their intensities were actually reduced. However, their intensities in flakes were already small (Fig. 7) making it more difficult to be further reduced. Secondly, higher efficiency in pellets could also be the result of polymer degradation during extrusion which is well known in plastic recycling (Schyns and Shaver, 2020; Singh et al., 2017). Because of the thermal conduction and viscous shearing applied to polymers with an extruder, polymer chain length and mechanical properties are reduced (Schyns and Shaver, 2020), causing increased diffusion of chemicals within the polymer. As such, chemicals in the degraded polymer (pellet) could be more easily extracted and cleaned, which also explains why there were more substances and higher intensities detected in pellet samples.

Washing twice was effective for reducing the concentration of DEP and BHT, whereas DBP, DiBP as well as 1-tetradecene remained almost constant. On the other hand, extra decontamination demonstrated to be effective for these compounds. Nevertheless, extra decontamination did not sufficiently decrease the content of octocrylene and 2-ethylhexyl-4-methoxycinnamate neither. Quite significantly, N-phenyl-2-naphthalenamine, which is a suspected carcinogen, had much higher

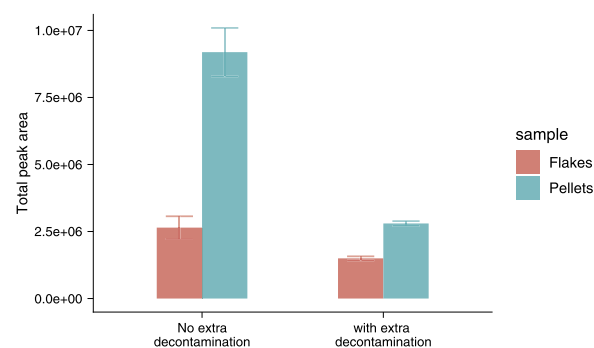


Fig. 7. Efficiency of extra decontamination on benzene and substitute derivatives: total peak area before and after extra decontamination in flakes and pellets.

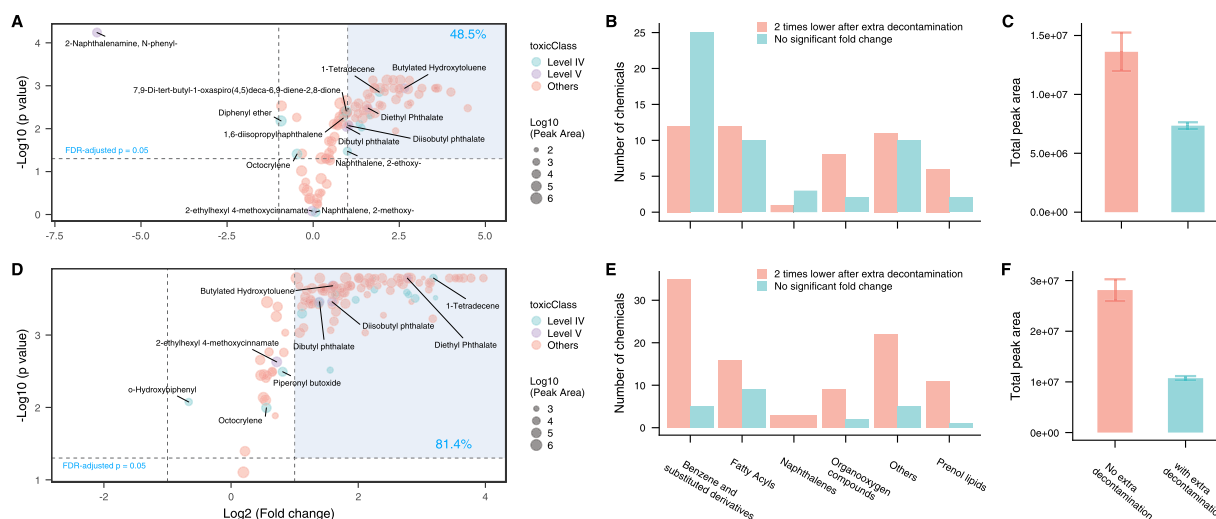


Fig. 6. Efficiency of extra decontamination: fold change analysis by volcano plot on flakes (A), chemical classes distribution on flakes (B), and total chromatographic peak area on flakes (C), fold change analysis by volcano plot on pellets (D), chemical classes distribution on pellets (E), and total chromatographic peak area on pellets (F) Note: Fold change is expressed as no extra decontamination versus extra decontamination; the size of the circles is mapped to the average peak area of the samples that applied extra decontamination.

response in flakes after extra decontamination (Fig. 6A left-top). As shown in Fig. 8, this compound was actually detected in both F1.3' and P1.3', which were the only two samples subjected to extra decontamination. However, it was only identified in F1.3' by MS-DIAL because it had too low intensity to have a representative spectrum in P1.3'. Since it was not observed in samples F1.3 and P1.3, it is speculated to be a contaminant or a newly formed substance during the extra decontamination process. As far as we know, this is the first time to report the presence of this compound in recycled plastics after certain treatments.

It is worth mentioning that the cleaning efficiencies of the two methods were not directly comparable, as they were not applied to the same samples, and the degree of contamination in samples was also different. In contrast to company 1 samples, those from company 2 were more contaminated. The numbers of chemicals considered in Fig. 5A and Fig. 6A were 128 and 103, respectively. Moreover, total peak areas of the flakes before applying second wash and extra decontamination were $2.1 \cdot 10^7$, and $1.4 \cdot 10^7$, respectively.

3.4. (Semi-)quantification of prioritized migrants

The use of a sensitive DI-SPME screening method enhances the capability of finding compounds of human health concern. On the other hand, it also increases the number of noise substances which are sensitive and of low toxicity, e.g., alkanes, and therefore distracts us from focusing on migrants of real concern. Hence, the long list of migrants detected was prioritized by toxicity class, detection frequency, and maximum response as proposed in our previous work (Su et al., 2021). There were 265 migrants detected overall (Appendix C). In agreement with previous studies (Dutra et al., 2011; Huber and Franz, 1997; Welle, 2005), commonly used plastic additives (BHT, DEP, DBP, etc.), degradation products (7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione), various saturated/unsaturated oligomers, aliphatic esters, fatty alcohol/aldehyde, as well as some favour compounds (galaxolide, camphor, 1,8-cineole, etc.) were detected in these samples. At the end, 58 prioritized migrants (all toxicity level V and IV compounds) and their concentrations in all pellet samples were quantified/semi-quantified where available (Table 2) since such samples are intended to be used for the manufacture of final products, thus being more representative. Some level IV substances (Cramer class III) were excluded from this list because they are commonly used as flavouring ingredients and have low migration values ($\mu\text{g}/\text{kg}$ level) compared to their uses as food additives and therefore should not pose threats to consumers. The quantification detail including standard used for quantification, limit of detection (LOD), limit of quantification (LOQ), and coefficient of determination (R^2) in each food simulant are included in Appendix D. In addition, many level III and II compounds are listed and quantified in Appendix D as well since they were detected in almost all samples, suggesting their commonalities in rHDPE. Fortunately, most of them have low migration levels (below 1 mg/kg) which is safe for these classes of compounds.

Among the prioritized migrants, many of them were only found in company 2 samples, for example metolachlor (herbicide), 2-(methylmercapto)benzothiazole (fungicide), and pyrimethanil (fungicide). Moreover, one polychlorinated biphenyl (3,3'-dichloro-1,1'-biphenyl) and many chemical intermediates (for dyes or pesticides) including 4-chloro-benzonitrile, 2,4-dichloro-phenol, 3,4-dichloro-benzenamine, and hexadecanenitrile were unique in company 2 samples as well. Their

presence could be the result of the inclusion of many non-milk-bottle-origin rHDPE owing to the poor separation of the input in the recycling plant (Fig. 4). These pesticides imply the presence of plastic waste from agricultural field or from bottles used for pesticides in the rHDPE flow, including misuses. Furthermore, two alkenes, 1-dodecene and 1-tetradecene, had migration values higher than their SML (50 $\mu\text{g}/\text{kg}$).

Samples from companies 1 and 3 were much cleaner than those from company 2 in terms of appearances of flakes as well as the detected migrants. The compound 1-dodecene had migration ranged from 21 to 106 $\mu\text{g}/\text{kg}$, which is similar to a previous study (Coulter et al., 2007) where migration test was carried out with isooctane at 20 °C for 2 days. For company 3 samples, one insecticide, chlorpyrifos, was detected in 95% ethanol migration test as well. Additionally, octocrylene and 1-tetradecene migrated about 170 and 70 $\mu\text{g}/\text{kg}$ in 95% ethanol, respectively, which is higher than their SML (50 $\mu\text{g}/\text{kg}$). The EDC UV filter, 2-ethylhexyl-4-methoxycinnamate had relatively high migration (about 70 $\mu\text{g}/\text{kg}$) as well. As for 3% acetic acid migration, the main concern comes from the three phthalates for their possible EDC properties. DiBP and DBP had very low migration ($< 1 \mu\text{g}/\text{kg}$) and should not be problematic. However, DEP has relatively high migration ($> 10 \mu\text{g}/\text{kg}$, which is the SML for the non-listed substances in EU 10/2011). Fortunately, the concentration of this compound can be reduced several times by either washing twice or extra decontamination as previously discussed (Fig. 5 and 6). DEP and DBP were previously detected in the extracts of rHDPE (Dutra et al., 2011; Huber and Franz, 1997), however, their higher potential to migrate into acidic food simulants was not demonstrated.

No pesticides were detected in the migration from company 1 samples though, slightly high migration values were observed for 1-tetradecene and DEP in the samples without applying extra decontamination, which is similar to company 3 samples. However, their migrations were much lower after applying extra decontamination (P1.3') and do not represent a human risk. It is worth noting that these 2 compounds could also be reduced by washing twice the post-consumer flakes. Further, many other prioritized compounds, such as BHT, 1-dodecene, and 1,6-diisopropyl-naphthalene had much lower migration or were even not detected after extra decontamination. Similar to company 3 samples, the two UV filters octocrylene and 2-ethylhexyl-4-methoxycinnamate had relatively high migration, 57.5 and 71.9 $\mu\text{g}/\text{kg}$, respectively. Unfortunately, extra decontamination did not work well on these two compounds as above discussed. Nevertheless, they were not detected in 3% acetic acid migration implying that they prefer to migrate into fatty foods. The results show that these rHDPE could not be used for high-fat content food packaging, but it could be adequate for acidic foods in terms of migration of (semi-)volatile compounds. It is interesting that octocrylene and 2-ethylhexyl-4-methoxycinnamate are common UV filters in cosmetics, but they were found in all rHDPE samples originated from milk bottles. The result suggests that they could be incorporated in the formulation of rHDPE milk bottles to protect fat matter in milk from light oxidation which causes bitter taste. However, as far as we know, this is the first time that these UV filters are reported in rHDPE. To evaluate whether they came from the HDPE milk bottles or from contamination, 4 HDPE milk bottles from various brands were purchased from the local supermarkets and tested. Neither octocrylene nor 2-ethylhexyl-4-methoxycinnamate were detected in any sample. Therefore, they might be common contaminants from cosmetic

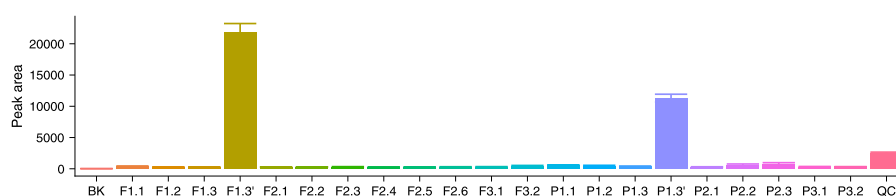


Fig. 8. Bar chart of N-phenyl-2-naphthalenamine across samples.

Table 2
 Prioritized migrants and their concentrations ($\mu\text{g}/\text{kg}$) from each company's pellet samples into 95% ethanol and 3% acetic acid food simulants.

Name	Company 1								Company 2						Company 3				Remarks
	EP 1.1	EP1.2	EP1.3	EP1.3'	HP1.1	HP1.2	HP1.3	HP1.3'	EP2.1	EP2.2	EP2.3	HP2.1	HP2.2	HP2.3	EP3.1	EP3.2	HP3.1	HP3.2	
Butylated hydroxytoluene	4.1 ± 0.2	4.2 ± 0.2	4.9 ± 0.1	2.1 ± 0.1	n.d.	n.d.	n.d.	n.d.	12.2 ± 0.1	2.3 ± 0.3	1.9 ± 0.1	n.d.	n.d.	n.d.	< 1	< 1	n.d.	n.d.	V
Diethyl phthalate	n.d.	n.d.	n.d.	n.d.	8.7 ± 3.9	11.4 ± 2.5	11.9 ± 3.7	2.3 ± 0.2	n.d.	n.d.	n.d.	47.4 ± 3.1	25.5 ± 1.7	28.2 ± 1.3	n.d.	n.d.	13.7 ± 1.6	13.3 ± 1.8	V
Naphthalene	n.d.	n.d.	n.d.	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	n.d.	14.6 ± 1.8	12.1 ± 0.1	n.d.	3 ± 0.03	2.9 ± 0.1	n.d.	n.d.	0.5 ± 0.1	n.d.	V
Diisobutyl phthalate	n.d.	n.d.	8.8 ± 1.1	n.d.	0.6 ± 0.1	0.8 ± 0.1	0.8 ± 0.2	0.4 ± 0.03	10.7 ± 0.2	24.4 ± 0.5	30.6 ± 4.2	0.8 ± 0.02	1 ± 0.3	0.9 ± 0.1	10.5 ± 0.7	12.4 ± 0.3	0.9 ± 0.1	0.9 ± 0.1	V
Dibutyl phthalate	n.d.	n.d.	n.d.	n.d.	0.1 ± 0.04	0.1 ± 0.03	0.2 ± 0.1	0.1 ± 0.01	n.d.	n.d.	n.d.	0.3 ± 0.01	0.2 ± 0.01	0.3 ± 0.1	n.d.	n.d.	0.2 ± 0.02	0.2 ± 0.01	V
2-ethylhexyl 4-methoxycinnamate	43.4 ± 25	43.9 ± 17	39.5 ± 17	71.9 ± 25	n.d.	n.d.	n.d.	n.d.	82.8 ± 10	212.4 ± 74	309.5 ± 13.4	n.d.	n.d.	n.d.	64.9 ± 22	70.7 ± 6.6	n.d.	n.d.	V
Diphenyl ether	104.8 ± 1	51 ± 1.9	58.2 ± 1.9	9.5 ± 0.7	3.7 ± 0.7	3.9 ± 0.5	4.3 ± 0.4	1.8 ± 0.2	595.7 ± 15	76.7 ± 16	62.3 ± 0.8	20.3 ± 0.2	3.8 ± 0.9	3.6 ± 0	123.1 ± 10	151.7 ± 12	9.4 ± 0.1	9.2 ± 0.3	IV; Flavouring ingredient
Galaxolide	–	–	–	–	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	–	–	–	–	n.d.	n.d.	IV; Fragrance in soaps
1-Dodecene	21.2 ± 2.1	33.5 ± 8.8	27.1 ± 1.2	< 1	< LOQ	< LOQ	–	–	57.8 ± 3.8	105.9 ± 1	90 ± 5.1	–	–	–	36 ± 7.6	46.5 ± 11	–	–	IV; SML 50 $\mu\text{g}/\text{kg}$
Tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol	n.d.	n.d.	n.d.	n.d.	–	–	–	–	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	–	–	IV
2-Methoxy-naphthalene	–	–	–	n.d.	–	–	–	–	–	–	–	–	–	–	–	–	–	–	IV; Emulsifier, stabilizer
Alpha-terpineol	n.d.	n.d.	n.d.	n.d.	32.8 ± 0.5	31.2 ± 0.1	32 ± 2	9.5 ± 1.5	n.d.	n.d.	n.d.	62.9 ± 0.6	133.7 ± 3	119.1 ± 9	n.d.	n.d.	67.7 ± 5	80.6 ± 12	IV; Flavouring ingredient
2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-Indene	–	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	IV
1,6-diisopropyl-naphthalene	4.8 ± 0.2	4.8 ± 0.2	5.4 ± 0	3.8 ± 0.3	n.d.	n.d.	n.d.	n.d.	3.6 ± 0.2	2.1 ± 0.1	2.1 ± 0.1	n.d.	n.d.	n.d.	3.7 ± 0.1	4.3 ± 0.3	n.d.	n.d.	IV
1-Tetradecene	52.2 ± 4.2	52.6 ± 3.9	52.9 ± 5.5	12.5 ± 0.5	–	–	–	–	58.6 ± 1.1	78.3 ± 2.2	64.7 ± 0.4	–	–	–	68.7 ± 17	84.1 ± 16	–	–	IV; SML 50 $\mu\text{g}/\text{kg}$
1-Methyl-4-(1-methylethyl)-3-cyclohexen-1-ol	n.d.	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	5.7 ± 0.3	10.9 ± 0.1	9.3 ± 1.1	n.d.	n.d.	< LOQ	< LOQ	IV; Flavouring ingredient
1-Methyl-naphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 0.1	n.d.	44.4 ± 7.9	40.7 ± 1.1	n.d.	2.6 ± 0.2	2.5 ± 0.04	< 1	< 1	< 0.1	< 0.1	IV; Flavouring ingredient
2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-	n.d.	n.d.	n.d.	n.d.	–	–	–	–	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	–	–	IV; NIAS
Octocrylene	39.4 ± 28	44.6 ± 27	35.7 ± 18	57.5 ± 26	n.d.	n.d.	n.d.	n.d.	99.6 ± 20	407 ± 277	770 ± 180	n.d.	n.d.	n.d.	160.7 ± 27	195.2 ± 31	n.d.	n.d.	IV; SML 50 $\mu\text{g}/\text{kg}$
3-Methyl-1,1'-biphenyl	< 1	< 1	< 1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.9 ± 0.7	8.4 ± 0.3	n.d.	0.1 ± 0.01	0.1 ± 0.01	< 1	< 1	n.d.	n.d.	IV
Bicyclo[4.2.0]octa-1,3,5-triene	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	n.d.	n.d.	–	n.d.	–	n.d.	n.d.	–	–	IV
1,4,6-Trimethyl-naphthalene	n.d.	n.d.	n.d.	< 1	n.d.	n.d.	n.d.	n.d.	n.d.	46.9 ± 4	43.4 ± 1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
1-Chlorododecane	< 1	< 1	1.1 ± 0.1	n.d.	n.d.	n.d.	n.d.	n.d.	15.7 ± 2.2	13.1 ± 1.2	10.3 ± 0.1	n.d.	n.d.	n.d.	2.4 ± 0.3	2.7 ± 0.3	n.d.	n.d.	IV
2,2,2-Trichloro-1-phenylethyl acetate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	IV
1,6-dimethyl-naphthalene	< 1	< 1	< 1	n.d.	n.d.	n.d.	n.d.	n.d.	< 1	31.2 ± 2.7	30.7 ± 1.2	n.d.	n.d.	n.d.	< 1	< 1	n.d.	n.d.	IV
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	n.d.	n.d.	n.d.	n.d.	n.d.	30.3 ± 26	55.4 ± 21	13.5 ± 1.5	n.d.	< LOQ	n.d.	n.d.	39.9 ± 4.6	45.9 ± 0.5	n.d.	n.d.	15.3 ± 1.2	13.4 ± 1.1	IV; NIAS

(continued on next page)

Table 2 (continued)

Name	Company 1				Company 2								Company 3				Remarks		
	EP 1.1	EP1.2	EP1.3	EP1.3'	HP1.1	HP1.2	HP1.3	HP1.3'	EP2.1	EP2.2	EP2.3	HP2.1	HP2.2	HP2.3	EP3.1	EP3.2		HP3.1	HP3.2
Dodecanenitrile	–	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
o-Chloroaniline	n.d.	n.d.	n.d.	n.d.	2.9 ± 0.1	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	2.1 ± 0.01	24.5 ± 0.6	21.8 ± 2.3	n.d.	n.d.	n.d.	n.d.	IV; Intermediate
2-Methyl-2-nonanol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	–	n.d.	IV
Diphenylmethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 0.1	< 0.1	n.d.	n.d.	< 0.1	< 0.1	IV
2,4-Dichlorobenzenamine	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.5 ± 0.1	10.5 ± 0.5	12 ± 0.4	n.d.	n.d.	n.d.	n.d.	IV; Intermediate
3,3'-dichloro-1,1'-biphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.6 ± 0.1	8.9 ± 0.1	9.1 ± 0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV; PCB 11
Hexadecanenitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV; Intermediates
2-Methyl-naphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	181.1 ± 29	141.6 ± 10	n.d.	4.4 ± 0.6	4.2 ± 0	n.d.	n.d.	n.d.	n.d.	IV
Di-(p-tolyl)methane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
3,4-Dichlorobenzenamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	117.8 ± 18	124.8 ± 8	n.d.	n.d.	n.d.	n.d.	IV; Intermediate
4,4'-Dimethylbiphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16.8 ± 0.7	16.5 ± 0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
3,3'-Dimethylbiphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.9 ± 1	12.6 ± 0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
2-Methyl-9H-fluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
1,6,7-Trimethyl-naphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	65 ± 4.6	64.1 ± 3.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
2,7-Dimethyl-quinoline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV
2,4-Dichlorophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV; Intermediate
1,1'-Ethylidenebis-benzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV
1-Methyl-7-(1-methylethyl)-naphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.2 ± 0.5	15.1 ± 0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
1,2-Dimethyl-naphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.4 ± 1.1	11.6 ± 0.4	n.d.	0.5 ± 0.02	0.5 ± 0.01	n.d.	n.d.	n.d.	n.d.	IV
1-Methyl-3-[(4-methylphenyl)methyl]-benzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
o-Hydroxybiphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31.7 ± 1.8	33.9 ± 0.9	n.d.	n.d.	n.d.	n.d.	IV; Flavouring ingredient
Metolachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV; Herbicide
2-(Methylmercapto)benzothiazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV; Fungicide
2-(2-Methylphenyl)-1-phenyl-(Z)-1-propene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	IV
4-Chlorobenzonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV; Intermediate
2-Phenyl-pyridine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV
Ambrox	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	n.d.	n.d.	IV
Pyrimethanil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.3 ± 0.1	4.4 ± 0.3	n.d.	n.d.	n.d.	n.d.	IV; Fungicide
2-(2-Methylpropyl)-quinoline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV
1-(2-Chlorophenyl)-ethanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV
Chlorpyrifos	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	IV; Insecticide
3-(Trifluoromethyl)-benzenamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–	–	n.d.	n.d.	n.d.	n.d.	IV

Note: the values are expressed as mean ± sd in duplicates; E represents 95% ethanol migration while H stands for 3% acetic acid migration; roman numerals in the **Remarks** column are the toxic classes assigned for the corresponding migrants, detailed in Appendix C; - means detected but not quantified, while n.d. stands for not detected.

packaging waste but are not intentionally added to the HDPE milk bottles. This fact demonstrates that better classification of the input is required to get only postconsumer milk (or food in general) bottles. Considering their high concern and the difficulty to remove them from rHDPE, measures to mitigate cross contaminations from cosmetic/personal care packaging could be of great help to get high quality rHDPE. Additionally, these two compounds had much lower sensitivities (LOD) than many other migrants (Appendix D), and thus could be easily overlooked when manually picking peaks of concern in chromatograms based on peak size.

4. Conclusions

In the present work, hierarchical clustering analysis was employed to investigate whether the chemical compositions of various batches of rHDPE milk bottles from 3 recyclers vary considerably. As anticipated, the compositions from the 3 recyclers were different. In addition, well classified samples from companies 1 and 3 (with negligible non-milk-bottle rHDPE contamination) showed rather consistent chemical composition between batches, while poorly classified samples from company 2 (containing many non-milk-bottle rHDPE) varied remarkably amongst batches. The chemical removal efficiencies of two cleaning procedures were evaluated by fold change analysis. Both washing twice and extra decontamination techniques showed comparable efficiencies. About 50% of chemicals had half chromatographic responses after applying the two techniques. However, the two techniques are not directly comparable since they were not applied to the same samples. A noticeable discrepancy was that extra decontamination was able to reduce the migration of 1-tetradecene to a safe level while washing twice did not.

Quantitative analysis of the prioritized migrants showed that impure milk bottle rHDPE samples (from company 2) were contaminated with several pesticides and one polychlorinated biphenyl, which are of very high concern. Besides, many prioritized migrants were only detected in this set of samples and some of them had migration values several times higher than their SML. Consequently, this type of rHDPE might not be suitable for food contact uses. Samples from companies 1 and 3 had negligible non-milk-bottle rHDPE contamination and much less prioritized chemicals were detected in migration tests. However, there were still migrants of high concern, with relatively high migration, such as 1-dodecene, 1-tetradecene, octocrylene, and 2-ethylhexyl-4-methoxycinnamate. The former two can be sufficiently lowered by extra decontamination, while the latter two cannot be reduced by either washing twice or extra decontamination. Octocrylene, and 2-ethylhexyl-4-methoxycinnamate have molecular weight 360 and 290 Da, respectively. As it is reported (Palkopoulou et al., 2016), decontamination yield in polyolefins strongly drops with increasing molecular weight.

The present work contributes to the scientific knowledge by demonstrating that fold change analysis constitutes a good way to examine the efficacy of decontamination techniques applied to recycling of plastics, allowing the evaluation of intensity changes for every detected compound, and focusing on the changes of high concern substances combined with toxicity data.

From a practical point of view we have pointed out that special attention should be paid for octocrylene and 2-ethylhexyl-4-methoxycinnamate when recycling HDPE from milk bottles for new food contact uses in terms of decontamination as well as legislation. Deeper studies are required to know whether they are common in rHDPE milk bottles samples or not. In the worst cases, while they are not easy to remove, additional decontamination procedures at industrial level should be considered, although we can suggest enhancing sorted collection as the most interesting and simple option to avoid cross contamination, which constitutes the main limitation of the present system for collecting and recycling HDPE.

To better understand the main factors affecting the decontamination efficacy, accessible process decontamination conditions will be helpful.

It has to be mentioned that the present work used pellets for migration tests, which would overestimate the results. In this sense, further research focused on migration tests by using real bottles manufactured from rHDPE will surely provide more realistic results. Despite the huge amount of information generated in this study, it has been limited to the determination of volatile compounds. A similar work with focus on non-volatile organic compounds as well as metals, would give an overall knowledge conducting to an optimum harnessing of HDPE bottle. This will be the subject of further research.

CRediT authorship contribution statement

Qi-Zhi Su: Conceptualization, Methodology, Visualization, Investigation, Writing – original draft. **Paula Vera:** Conceptualization, Investigation, Writing - review & editing. **Jesús Salafraña:** Investigation, Writing - review & editing. **Cristina Nerín:** Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Qi-Zhi Su has received a grant from the China Scholarship Council (201706780010). The authors acknowledge Funds given by ECOEMBES, Gobierno de Aragón and European Social Funds to GUIA group T53_20R (University of Zaragoza) and Project RTI2018–097805-B-I00 financed by Ministerio de Ciencia e Innovación, Spain.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2021.105640](https://doi.org/10.1016/j.resconrec.2021.105640).

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