Safety concerns of recycling postconsumer polyolefins for food contact uses: Regarding (semi-)volatile migrants untargetedly screened

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Abstract:

Plastic recycling is one of the important ways to mitigate plastic pollution. However, chemicals present in recycled plastics is one of the key qualities affecting their potential uses and deserves more attention. 475 migrants coming from 15 postconsumer recycled polyolefins were identified by direct immersion-solid-phase micro-extraction gas chromatography mass spectrometry (DI-SPME-GC-MS) and atmospheric pressure-gas chromatography-quadrupole-time of flight-mass spectrometry (APGC-QTOF-MS). About 60 % of them might not be of human risk because they were food additives/components or they are saturated hydrocarbons, fatty acyls, or prenol lipids. Most of them had molecular weight (MW) between 150 and 210 Da, though, high concern substances with high MW (e.g. octocrylene) implied that high MW surrogates are required to study the efficiency of recycling processes for polyolefins. The mean predicted octanol/water partition coefficient (XLogP) was about 6.5 and 3.5 for 95 % ethanol and 3 % acetic acid food simulants, respectively. Octocrylene, 1-tetradecene, 1-dodecene, dodecyl acrylate, 2,4-di-tert-butylphenol, 1,4-benzenedicarboxylic acid, diethyl ester, benzenamine, 2,4-dichloro-, and diethyl phthalate were of high concern depending on the potential food contact use of the materials. The results presented are informative and can be of great help for recyclers and law makers to recycle polyolefins for safe food contact use.

1. Introduction

Environmental issues posted by extensive accumulation of plastic wastes in oceans, landfills, and other terrestrial compartment as a price of the current linear economy, have been reported to deteriorate the ecosystems and impact wildlife and possibly human health (Lithner et al., 2011). Packaging accounted for 39.9 % of plastic demand in 2018 (PlasticsEurope, 2019). The European Plastic Strategy (EC, 2018) recommends recycling most of the plastic packaging and in this frame, polyolefins, which constitute about 70% of plastic packaging (PlasticsEurope, 2019), occupy an important place to mitigate environmental pollution and to reduce raw materials input to the packaging sector. The main challenge to recycle packaging waste into new food packaging is that chemical migration, from the recycled materials to the food in contact with them, can be higher

compared to virgin materials, and therefore pose potential risks to human health (Geueke et al., 2018). For example, additives accumulated and their degradation products (Coulier et al., 2007), oligomers of the raw materials (Ubeda et al., 2018), printing inks (Clemente et al., 2016), adhesives (Canellas et al., 2017) from labels and multilayers as well as products resulting from misuse of plastic packaging (Biedermann and Grob, 2013), etc. could be present in the recycled materials. Within EU, the use of recycled plastics for food contact is subjected to various regulations, e.g. the framework Regulation No 1935/2004 (EC, 2004) and Commission Regulation 10/2011 (EC, 2011). Food contact use of recycled polyethylene terephthalate (rPET) bottles has been well established in the last decades with the use of so-called super-clean recycling (Welle, 2011). However, the rich data available for rPET cannot be simply extrapolated to polyolefins in terms of safety issues (Palkopoulou et al., 2016). For a given substance, the diffusion coefficient is orders of magnitude higher in polyolefins than in PET (Dole et al., 2006). Hence, the absorption of chemical substances into polyolefins and their migration from the materials can be higher, and the decontamination step will be much more challenging. As a consequence, decontamination, challenge test, and quality control test should be tailored for recycled polyolefins (rPO) based on careful scientific studies (Palkopoulou et al., 2016).

Knowledge about the chemical compositions of postconsumer polyolefins is crucial for the design of appropriate recycling systems to improve the quality of rPO regarding safety (Welle, 2005). As far as we know, research data on this topic is limited. Existing studies mainly focused on the screening of (semi-)volatile extractables from recycled high density polyethylene (HDPE) milk bottles by Soxhlet extraction and/or headspace - solid-phase micro-extraction gas chromatography mass spectrometry (Devlieghere et al., 1998; Dutra et al., 2011; Nerín et al., 1998; Welle, 2005). Recently, odorant compositions of postconsumer bags and films have been well investigated as well (Cabanes et al., 2020; Strangl et al., 2020). However, chemical migration from these materials is rarely studied. Migration test from recycled materials can be an interesting topic as human exposure is more related to chemical migration rather than extraction. The present study aims to evaluate the potential of using rPOs for food contact uses regarding safety concerns. (Semi-)volatile compounds migrating from various postconsumer polyolefins into two simulants (3 % acetic acid and 95 % ethanol) were untargetedly screened by a sensitive analytical method, namely direct immersion-solid-phase micro-extraction gas chromatography mass spectrometry (DI-SPME-GC-MS). Atmospheric pressure-gas chromatography-quadrupole-time of flight-mass spectrometry (APGC-QTOF-MS) together with MS-FINDER (Tsugawa et al., 2016) were applied to characterize peaks that cannot be simply identified by normal GC-MS as well as to improve identification confidence by confirming molecular formulas of the tentatively identified substances where no experimental RI is available. Chemical classes, molecular weight (MW), predicted toxicities (Cramer rules) in the absence of experimental toxicity data and octanol/water partition coefficient (XLogP) distributions of identified substances were analysed. Their possible origins were investigated by searching food related, plastic packaging related, as well as cosmetic related databases. In addition, a strategy was proposed to prioritize chemicals of higher concern obtained by nontargeted screening. Quantification of some prioritized migrants was done when available. **2. Materials and methods** *2.1. Reagents and samples* Authentic standards including diphenyl ether (101-

84-8), 2,6-diisopropylnaphthalene (24157-81-1), octocrylene (6197-30-4), 2,4- diphenyl-4-methyl-1-pentene (6362-80-7), benzophenone (119-61-9), benzenamine, 2,4-dichloro-(554-00-7), UV 531 (1843-05-6), decane, 1- chloro- (1002-69-3), 1,1′ -biphenyl, 3-methyl- (643-93-6), 2,4-di-tert-butylphenol (96-76-4), 2-ethylhexyl salicylate (118-60-5), hexanedioic acid, bis(2-ethylhexyl) ester (103-23-1), bis(2-ethylhexyl) phthalate (117-81-7), dodecanoic acid, ethyl ester (106-33-2), hexadecanoic acid, methyl ester (112-39-0), diethyl phthalate (84-66-2), 1-octadecanol (112-92-5), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (6846-50-0), isoborneol (124-76-5), 9-octadecenoic acid, methyl ester, (E)- (112-62- 9), benzaldehyde, 4-propyl- (28785-06-0), 1,4-benzenedicarboxylic acid, diethyl ester (636-09-9), caryophyllene (87-44-5), d-Limonene (5989-27-5), 2-propenoic acid, 1,7,7-trimethylbicyclo[2.2.1] hept-2-yl ester, exo- (5888-33-5), 2-tridecanone (593-08-8), 1-tetradecanamine, N,N-dimethyl- (112-75-4), benzenamine, 2,4-dimethyl- (95-68-1), morpholine, 4-octadecyl- (16528-77-1), 1,1′ -biphenyl, 2,4-dichloro- (2050-67-1), biphenyl (92-52-4), 1-tetradecene (1120-36-1), 1-dodecene (112-41-4), dodecyl acrylate (2156-97-0), 2-ethylhexyl acrylate (103-11-7), isobornyl acrylate (5888-33-5), Tinuvin 326 (3896-11-5), and octadecanamide (124-26-5) were purchased from Sigma-Aldrich (Madrid, Spain). There were 6 and 9 postconsumer recycled polyolefin pellets from Spain and China, respectively (Table 1). For Spanish samples, recycled plastics were collected from the yellow bin that contains only packaging. Flexible PO fraction was then separated from the collected materials, cut, washed with cold water containing detergent, and dried to obtain the flakes (Appendix A Fig. A.1). The flakes were then fed into an extruder to produce the corresponding pellets under vacuum. S1 to S6 pellet samples were collected at different time, which means that they were various batches from the same company. Company 1 and 2 locates in Qingyuang and Suzhou, China, respectively. According to the companies, C1 was made from HDPE bottles and turnover box, C2 was from bottles and LDPE films, C3 comprised of 90 % bottles and LDPE films and 10 % virgin PE, C9 consisted of 70 % HDPE bottles and turnover box and 30 % virgin PE, and C4 was made of mixed PE materials. The rest (C5 to C8) were purchased from company 3 which is a distributor but not a recycler and details about these samples remain unknown due to commercial confidentiality. *2.2. Migration test* Migration tests were conducted following the EU regulation (No 10/ 2011) on plastic materials and articles intended to come into contact with food (EC, 2011). Based on the conventional assumption of 6 dm2 surface area in contact with 1 kg of food, the amount of each plastic used for total immersion migration test (18 mL food simulant) was calculated. Both 95 % ethanol and 3 % acetic acid food simulants were used to simulate fatty and acidic food, respectively. All migration tests were carried out for 10 days at 60 ∘C as an accelerated standard test for long time storage (> 6 months) at room temperature according to the EU regulation. Samples and procedural blanks were simultaneously prepared and only migrants that had peak area 10 times higher in samples than that in blanks were counted. *2.3. Direct-immersion solid-phase micro-extraction (DI-SPME)* DI-SPME was optimized by response surface methodology (RSM) in our previous study (Su et al., 2020). The optimized conditions were as follows: 95 % ethanol samples were diluted 9.5 times into 10 % ethanol to avoid damage to the SPME fibre while 3 % acetic acid samples were neutralized by NaOH prior to DI-SPME. Samples were pre-incubated in an agitator (70 ∘C) for 5 min, extracted for 55 min by a DVB/CAR/PDMS fibre Supelco (PA, USA), and finally thermally desorbed in the GC inlet (250 ∘C) for 8 min. Subsequently, the fibre was cleaned in a needle heater (270 ∘C)

for 2 min prior to the next extraction. All DI-SPME processes were automatically done by a 6500 CTC autosampler connected to both GC-MS and APGC-QTOF-MS.

2.4. GC-MS analysis GC-MS profiles were obtained from a gas chromatography (6890N) coupled to mass spectrometry (5975). A semi-polar DB-5 MS column (30 m × 0.25 mm id, 0.25 μm film thicknesses) from Agilent (California, USA) was employed for separation. The temperature ramp was as follows: initiated 50 ∘C for 3 min, followed by increasing to 300 ∘C at the rate of 3 ∘C/min, and finally remained for 2 min. Helium (99.999%) was the carrier gas running at a constant flow rate of 1.0 mL/min. The inlet temperature was set at 250 ∘C and splitless mode was employed. Mass scan range was from 40-700 Da. Test mixture for apolar capillary columns according to Grob (Sigma Aldrich) was injected every time prior to sample analysis for the control of the system. *2.5. Identification of migrants by MS-DIAL* Recycled polyolefins are quite complex and the number of migrants coming from each sample was huge (example chromatogram is shown in Appendix A Fig. A.2). Therefore, manual interpretation of those GC-MS profiles one by one can be considerably time-consuming and tedious. The use of MS-DIAL (Tsugawa et al., 2015) can facilitate such kind of data interpretation by automatic peak detection (chromatographic deconvolution), alignment, blank subtraction, and identification. MS-DIAL parameters were: minimum peak height of 2000, sigma window of 0.5 and EI spectra cut off of 1 for deconvolution and identification was done before alignment by comparing spectra against NIST 14 library with score cut off of 85 % to reduce false positive. Alignment was done with 0.1 min retention time tolerance and 70 % EI similarity. Features with sample max / blank average fold change lower than 10 were removed. The generated list of compounds was then manually checked to assure identification (retention index with tolerance of 30 when available) and to mark down which samples did really contain that migrants. *2.6. APGC-QTOF-MS analysis* Gas chromatography (A7890; Agilent, California, USA) and high-resolution mass spectrometer Xevo G2 QTOF (Waters, Massachusetts, USA) were interfaced with an atmospheric pressure soft ionization, namely APGC. The setting of gas chromatography was the same as that of GC-MS, except for the gas flow rate which was 1.8 mL/min in APGC-QTOF-MS to achieve high comparability of chromatograms between GC-MS and APGC-QTOF-MS. Source temperature, corona current, cone and auxiliary gas flow were 150 ∘C, 1.0 μA, 20 and 175 L/h, respectively. Mass range for both MS1 and MS2 function was from 40 to 700 Da. MSE positive acquisition mode was applied with low energy at 6 V and high energy at 10-40 V. APGC-QTOF-MS data interpretation was explained in our previous article (Su et al., 2019) with one exception, where MS-FINDER (version 3.42) was used for in-silico fragmentation herein. Unlike LC-QTOF-MS, no mass correction in real time is available in the APGC-QTOF-MS. Masses of each spectra have to be manually corrected as previously detailed (Su et al., 2019). The corrected spectra were then imported into MS-FINDER for structural elucidation. *2.7. Data processing and prioritization of important migrants* Hierarchical clustering of samples and their correlations were calculated by MetaboAnalyst (Xia and Wishart, 2016) using peak areas of tentatively identified migrants. If two samples have similar migrants and intensities, then they will be in a same cluster and have high correlation (red). InChIKey, MW, molecular formula, and XlogP, of all identified migrants were retrieved from PubChem using *webchem* (Eduard Sz¨ocs et al., 2020) package in R. Classification of migrants was done by ClassyFire developed by Fiehn lab (Djoumbou Feunang et al., 2016). Databases

namely "Substances added to food", "EU cosmetic ingredients inventory", and "Colorants dyes and pigments" were downloaded from EPA as well. Moreover, "Chemicals associated with plastic packaging" database which contain chemicals likely (List A) and possibly (List B) associated with plastic packaging was downloaded (Groh et al., 2019) as well. "Food database" containing a long list of food components was downloaded from FooDB (http://foodb.ca, accessed on 20/02/2020). The list of migrants was then searched against these 5 databases by matching InChIKey characters to get a general idea about their possible origins. Besides, the list of carcinogenic, mutagenic, and reprotoxic chemicals (CMR, category 1A, 1B, and 2) was extracted from the Annex VI of the CLP Regulation (European Union, 2008) (accessed on 20/05/2020). Substances of very high concern (SVHC) database was downloaded from ECHA (https://echa.europa.eu/candidate-list-table, accessed on 20/05/2020). The list of endocrine disrupting chemicals (EDC) was extracted from the UN review report II (IPCP, 2017) about EDC. The specific migration limit (SML) of the migrants were obtained by consulting the EU10/2011 regulation (last updated on 29.08.2019). The toxicity of a migrant, if it is not in CMR, SVHC, or EDC lists and does not have SML value, was estimated by Toxtree (version 3.1.0.1851) based on Cramer rules (Patlewicz et al., 2008). In an attempt to prioritize the migrants based on their toxicities, each migrant was assigned to a toxicity level with the following rules: chemicals that have SML as ND (not detectable at 0.01 mg/kg) or be included in CMR, SVHC, or EDC list have level V; chemicals that have Cramer III or have SML between 0.01 and 0.1 mg/kg obtain level IV; chemicals that have Cramer II or have SML between 0.1 and 1 mg/kg have level III; chemicals that have Cramer I or have SML between 1 and 60 mg/kg get level II; chemicals that have SML equal to 60 mg/kg get level I. Once toxicity levels were designated, the migrants were prioritized first by detected frequency (from high to low separated by 60 %), followed by toxicity level (from level V to I), and finally by average S/N calculated by MS-DIAL. *2.8. Quantification of migrants* Prioritized migrants were quantified by authentic standards (external calibration) when available. Calibration curves were prepared in 10 % ethanol solution for migrants that had maximum response in 95 % simulant, and the final concentration was calculated considering the dilution of sample (9.5 times); while prepared in pre-neutralized (pH = 7) 3 % acetic acid for migrants that had maximum response in 3 % acetic acid sample. The standard solutions were then analysed by DI-SPME-GC-MS as the samples did and procedural blanks have been subtracted (detail in Appendix C). **3. Results and discussion** *3.1. Identification by APGC-QTOF-MS* APGC-QTOF-MS allows for structural elucidation by monitoring the exact masses of precursor and product ions. As an example, the peak at 47.682 min (RI 1896) in GC-MS matched quite well to nimorazole in MS-DIAL (total spectrum similarity 90.8). However, nimorazole has reference RI 1803, which did not match to this peak. Therefore, this identification was ruled out (Fig. 1 A). When carefully inspected the APGC-QTOF-MS chromatogram of the same sample, a corresponding peak was found at 47.50 min with precursor ion 256.2641 m/z (Fig. 1 B). The correspondence was evidenced by a shared major fragment (100 m/z) in both systems and by a tolerable retention time shift. The structure of this unknown was then elucidated by MS-FINDER. The GC-MS spectrum of the unknown was predominated by 100 m/z. Looking in depth, numerous compounds have quite similar spectra in NIST 14 library and all of them have the same substructure (marked in Appendix A Fig. A.3). The finding implies that the unknown could have this substructure as well. There were many compounds that had in

silico MS/MS spectra matched well (score > 6 with 10 in total) to the unknown though, some of them have considerably different EI spectra

compared to the unknown, e.g., palmitamide (Appendix A Fig. A.4), and must not be the right identification. Among them, only one, namely 4- dodecylmorpholine contain this substructure. Moreover, predicted RI of 4-dodecylmorpholine using a deep convolutional neural network (Matyushin et al., 2019) was 1890, which is quite close to the experimental RI (1896). 4-dodecylmorpholine is an indirect additive used in food contact substances. Hence, it is reasonable to be present in postconsumer rPO. The identification was indirectly confirmed by 4-octadecylmorpholine which is a homolog of 4-dodecylmorpholine with longer alkyl chain. They have same fragments and precursor patterns ([M+H]+ and [M-H+O]+) as shown in Appendix A Fig. A.5 *3.2. Tentatively identified migrants, their classification, and possible origins* There were 1893 features detected by MS-DIAL though, the result should be interpreted carefully, since a feature does not necessarily mean an individual compound. Many of the features can be artefacts, duplicates of other features based on the parameters used for data processing, e.g. sigma window used for automatic deconvolution. For this reason, using all detected features as the total number of chemicals present in samples could be misleading and exaggerated. This situation can be even worse in LC-MS/MS profiling considering that there could be plenty of adducts and in-source fragments. With the help of MS-DIAL, NIST 14 library, and APGC-QTOF-MS, 475 migrants coming from these 15 postconsumer rPO were tentatively identified in total with high confidence and 34 of them were confirmed by authentic standards. The whole list and their detailed information are shown in Appendix B. The number of migrants detected in each sample ranged from 150 (C6) to 251 (C9) which indicates the complexities of the samples regarding chemicals present. As classified by ClassyFire, there were mainly 9 classes of chemicals (Fig. 2). As the highest hit class (24.6%), fatty acyls compounds are mainly fatty acid/acid ester/alcohol and have toxicity level II, which might not be risky concerning human health. Benzene and substituted derivatives together with naphthalenes account for 22.4 % of the migrants. Many of them have class V or IV, e.g. phthalates and chlorobenzenamines, which can be toxic and deserve attention. There were many alkyl benzenes/naphthalenes though, no typical chromatograms of MOAH were found and the presence of MOAH can be excluded. Prenol lipids was the third largest class but most of them (58.8 %) were found to be food components or food additives. Aiming to understand possible origins of those migrants, they were searched against the 5 aforementioned databases to check if they are food/plastic packaging/cosmetic related. Fig. 3 shows the number of migrants found in each group. There were 186 migrants (39.2 %) found to be food related (either in food additives or food component database). They might not be of safety concern but their migration could change the organoleptic properties of the contacting food (Vera et al., 2020). Among them, fatty acid esters merit specific attentions for their high intensities and frequencies detected. Moreover, 55 compounds were found to be plastic packaging related (either in List A or B of Chemicals associated with plastic packaging database) omitting those already defined as food related, e.g. bis(2-ethylhexyl) phthalate and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, which are used as plasticizer in plastics. Leaving out those regarded as food/plastic packaging related, 30 migrants might come from cosmetic. For example, 2-ethylhexyl trans-4-methoxycinnamate which is used as sunscreen in cosmetics, was detected in 40 % of the samples and had high average

intensity. Finally, only 4 migrants were found in the colorant, dye, and pigments database, and all of them were food related as well. *3.3. Correlations among samples and regional differences* By comparing tentatively identified migrants in both 95 % ethanol and 3 % acetic acid food simulants by GC-MS, one can get a general idea

found. Blue region represents the significant differences, while red colour indicates high similarity in GC profile between samples. It is not unexpected that 95 % ethanol and 3 % acetic acid had significantly different migration profiles (blue region in Fig. 4), as the two simulants have diverse polarities and affinities to various chemical structures. There were 251 migrants only detected in 95 % ethanol simulant and 134 migrants only in 3 % acetic acid, while only 91 migrants were detected in both simulants. With respect to distinctions within the same simulant, certain patterns can be seen. It is clear that samples from Spain were quite different from those from China, but they were remarkably similar to each other, possibly because they all came from the same company but only from different lots. The results suggest that chemical compositions of postconsumer rPO from this company are uniform to some extent. It is good for the company since compositional uniformity is vital for controlling the quality of recycled materials. The result could come from its relatively steady input of recycled materials. For a well-developed recycling company, the input of recycled materials can be consistent to some degree once it has a fixed area to collect the postconsumer materials, because the consumption structure in a particular area can be steady in a certain stage and thus, chemicals coming from related pre-consumer plastic and residues from foods can be similar in a large scale. However, huge shifts of collection area might provide different inputs. As for samples from China, they were not consistent to each other as they came from 3 different companies and possibly several polymer types. As can be seen, C1, C8 and C9 were classified into a same cluster while sample C2, C3, C5, and C7 were in another cluster in both simulants possibly because these two clusters represented two types of polyolefins. As it is known, C1 and C9 were mainly consisted of HDPE while C2 and C3 comprised of LDPE. Interestingly, there were 219 (46.1 %) migrants detected in both Spanish and Chinese samples, suggesting that they are probably common in rPO. However, there were 192 (40.4 %) and 67 (14.1 %) migrants that were only present in Chinese and Spanish samples, respectively. The result depicts that some compounds might be region related, e.g. isoborneol (detail in 3.5). *3.4. Molecular weight distribution of detected migrants* In light of the correlation analysis, samples were divided into 5 groups for the evaluation of MW and predicted octanol/water partition coefficient (XLogP). Spanish samples were group 1; C1, C8, and C9 were group 2; C2, C3, C5, and C7 were group 3; C4 and C6 were designated as group 4, and group 5, respectively. Interestingly, MW concentrated on around 150 - 210 Da in all groups (Fig. 5). As it is known, the smaller the molecules the easier they can be absorbed into and released from the polymers (Fang and Vitrac, 2017). At this point, common surrogates with MW ranging from 92 to 298 Da for rPET challenge test (EFSA, 2011) seems sufficient to check the ability of a recycling procedure to remove the majority of contaminants. However, this is not the case of polyolefins, where there were also high concern substances with higher MW detected. For example, octocrylene has MW 361.5 Da. It was detected in 60 % of samples (both Spanish and Chinese samples) and its highest concentration was ca. 0.17 mg/kg, which is 3 times higher than its SML (0.05 mg/kg). Further, less high MW compounds detected can also result from the limitation of the analytical techniques (GC-MS in this case) (Palkopoulou

et al., 2016). It was shown that decontamination efficiency strongly decreases with increasing MW regardless of the investigated technologies (Palkopoulou et al., 2016). Therefore, decontamination of polyolefins should be carefully optimized to remove all chemical substances of concern including high MW substances. *3.5. Distribution of predicted octanol/water partition coefficient (XLogP) of migrants* With regard to XLogP distribution (Fig. 6), the differences between the two simulants were significant. The XLogP of migrants focused on 6.5 in 95 % ethanol while on 3.5 in 3 % acetic acid in all groups. The result can be expected because of the polarity difference between the two simulants as above mentioned. Hence, high XLogP compounds have higher potential to migrate into 95 % ethanol while low XLogP substances to 3 % acetic acid. Further, polyolefins are nonpolar polymers and have a good affinity to apolar chemicals while they have low affinity to polar molecules (Palkopoulou et al., 2016). As such, the absorption of more polar contaminants into polyolefins during their entire lives could be low. This could be one of the reasons why the number of migrants (less polar) in 95 % ethanol is about twice higher than that in 3 % acetic acid (251 VS 134) as above mentioned (3.2). Therefore, based on the potential uses (in contact with fatty or aqueous food) of rPO, various decontamination techniques can be developed. Moreover, this result can also be informative for the optimization of LC-ESI-HRMS for non-targeted screening of migrants in different food simulants since hydrophobicity (LogP) is one of the key factors that affecting ionization efficiency in electrospray (Liigand et al., 2014). *3.6. Prioritization to high concern migrants and their concentrations* The huge number of detected migrants in these samples is informational for understanding classes, MW, and XLogP distribution of rPO contaminants, which can be instructive for developing appropriate rPO decontamination techniques. However, it might also distract us from focusing on key migrants regarding human health. The prioritized migrants including their highest concentration in samples are presented in Table 2. Detailed information about the (semi)-quantification was displayed in Appendix C. Regarding the possible origin of a component, it is not easy to know the true one. Here, the priority was given to food related, followed by plastic related and cosmetic related, since once it is food related, it is more acceptable to be detected in food contact materials and it might not be of safety concern. Food additives do not necessarily mean safe though, they were regarded as acceptable here, as their migration into the contacting food (normally in ppb level) could be much lower in comparison to the amount of addition as food additives. When no such relationship was found, functional uses described in Pubchem was marked down. There were 53 migrants considered as high concern. Many fatty acid esters were included in the list regardless of their low toxicities (level II) because of their high average S/N. Their highest concentrations ranged from 0.03 to 0.36 mg/kg, which are far away from the TTC value for Cramer rule Class I components (1.8mg/Kg). Hence, they might not represent a human health risk. However, most of them are used as flavouring agents in foodstuff, and so their high migration may alter the organoleptic properties of the contacting food (Strangl et al., 2018), and thus should be avoided. With respect to regulation compliance, there were several compounds that exceeded their SML and should be emphasized. As a photostabilizer, octocrylene was detected in 60 % of samples with highest concentration at ca. 0.17 mg/kg which is 3 times higher than its SML (0.05 mg/kg) in the regulation (EU 10/ 2011), while another commonly used photostabilizer UV 531 had migration much lower than its SML (6 mg/kg). Octocrylene can also be the result of contamination from cosmetic packaging as it is widely used as UV filter in cosmetics as well. It is not

surprising to detect 1-tetradecene and 1-dodecene as they are two olefin monomers. However, they were observed in all samples and their highest migrations were 3-5 times higher than their SML (0.05 mg/ kg). A similar result was observed by a previous study where 2 out of 5 recycled PP samples had 1-dodecene migration ca. 3 times higher than its SML (Coulier et al., 2007). As it is known, acrylates are common monomers of plastics, adhesives, and paints. There were few of them mainly found in Chinese samples. Dodecyl acrylate and 2-ethylhexyl acrylate were detected in ca. 40 % of samples, but the former one exceeded its SML (twice) while the latter one did not. Besides, isobornyl acrylate got quite high migration (7.4 mg/kg), but fortunately, it was only observed in one sample. Other migrants, e.g. benzophenone, that have SML value in the regulation, were below the limit and should not be of human health concern. 2,4-Di-tert-butylphenol, likely coming from the degradation of antioxidant tris(2,4-ditert-butylphenyl) phosphite (Irgafos 168) or [3- [3-(3,5-ditert-butyl-4-hydroxyphenyl)propanoyloxy]-2,2-bis[3-(3,5-ditert-butyl-4-hydroxyphenyl)propanoyloxymethyl]propyl]   3-(3,5- ditert-butyl-4-hydroxyphenyl)propanoate (Irganox 1010), was found in all samples except for EC1, and its highest migration even reached 2.26 mg/kg, which is higher than the TTC value for Cramer I components. As a NIAS, 2,4-Di-tert-butylphenol has been reported to increase with increasing recycling steps (Coulier et al., 2007). According to Pubchem, isoborneol is used as a flavouring, fragrance, to make other chemicals, and in traditional Chinese medicine. It had relatively high migration level (maximum 0.62 mg/kg) as well. However, it is interesting that this component was detected in all samples coming from China but not from Spain which is a good example for region related contaminants. Besides, high level of migration was recorded for d-limonene. Limonene has been reported as a degradation product of di-tert-butylphenol in many recycled HDPE samples (Welle, 2005). However, it is also widely used as flavouring in food and fragrance in parfum. Hence, it can also be residue from the previous uses as it was in rPET (Nerin et al., 2003). Its high migration can be problematic as well regarding the organoleptic properties of the contacting food. As plasticizers and additives, phthalates are commonly used in many consumer products and they have been reported for endocrine-disrupting and reproductive effects in animal studies (Wang et al., 2019). Moreover, many of them are in the CMR, SVHC, and/or EDC lists and therefore deserve attentions. There were ten phthalates detected in this set of samples. Among them, dibutyl phthalate (DBP), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), phthalic acid, bis(7-methyloctyl) ester (DINP branched), and phthalic acid, 5-methylhex-2-yl nonyl ester were detected in more than 60 % of samples. Compared to the former four phthalate, the latter two were less commonly detected in recycled plastics (Devlieghere et al., 1998; Geueke et al., 2018; Huber and Franz, 1997). DEHP had concentration lower than their SML while DEP hit 0.32 mg/kg and has no SML and thus merits more attention. Furthermore, three terephthalates and one isophthalate were identified. They, especially 1,4-Benzenedicarboxylic acid diethyl ester, were present in 80 % of samples at high concentration (7.0 mg/kg), which is much higher than the TTC value for Cramer II compounds. This compound can be formed by a transesterification reaction between PET chain and ethanol or be a side product formed during PET polymerization (Alin and Hakkarainen, 2013). Its high concentration in rPO could be the result of cross contamination from PET and/or inclusion of PET in these recycled

plastics. There were sixteen amines detected and five of them were listed in the Table 2. As we explained in our previous article (Su et al., 2020), amines could have very low response in GC-MS because many of them can be strongly adsorbed on the column or injector. Hence, their detection in the samples might suggest relatively high concentration. For example, benzenamine, 2,4-dichloro- was detected in 86.7 % of samples with concentration as high as 0.16 mg/kg, which is twice higher than the TTC value for Cramer III compounds. It is commonly used as intermediates for pesticides, dyes, etc., and thus can be counted as NIAS as well. As far as we know, it is the first time to report their migration from recycled plastics. 1-tetradecanamine, N,N-dimethyl-, had high average S/N though, its concentration was not that high possibly because of its high response factor. As expected, most of amines were only detected in 3% acetic acid simulant. In consequence, they might be risk when in contact with acidic but not fatty food. Furthermore, there were one pesticide named cyclopropanecarboxylic acid, 3-(2, 2-dichlorovinyl)-2,2-dimethyl-, (3-phenoxyphenyl)methyl ester, (1R-trans)-, and two insecticides named chlorpyrifos and bifenthrin detected, but these compounds were only observed in C1, C8, and C9 samples implying that these samples might contain plastic flow from agricultural field. This could be also the reason why these 3 samples were grouped together in 3.2. Last but not least, couples of chlorine-containing compounds were detected. For example, dodecane, 1-chloro-, which is used as intermediate for many other basic organic chemical manufacturing, was detected in 66.7 % of samples with 0.024 mg/kg as the highest migration, which is lower than the TTC value for Cramer III compounds. One polychlorinated biphenyl (PCBs), 1,1′ -Biphenyl, 3,3′ -dichloro- was found in 33.3 % of samples (both Spanish and Chinese samples), but its maximum concentration was lower than 0.01 mg/kg. Although the production of PCBs was banned in 1970s across most of the world, their residues in the environment are still present in some regions (Song et al., 2018). For this reason, this compound was assumed to be an environmental contaminant. **4. Conclusions** Among the 475 migrants detected in various recycled polyolefins, 39.2 % were food related and 24.1 % were found as saturated hydrocarbons, fatty acyls, or prenol lipids, which might not be human risk. Molecular weight distribution analysis shows that most migrants have MW between 150-210 Da. However, using surrogates similar to PET with MW up to 300 Da is insufficient for challenge test of recycled polyolefins as evidenced by high migration of octocrylene (MW 361.5 Da) and heavier compounds such as octocrylene, hexadecanoic acid dodecyl ester and triacontane with molecular weight of 361.5, 424.7, and 422.8, respectively, among others, could be used as surrogates as well. Predicted octanol/water partition coefficient (XLogP) distribution illustrates that chemicals that can migrate into different food simulants vary a lot. Therefore, the decontamination strategy for recycled polyolefins can be driven by their intended uses (e.g., for fatty or acidic food). Looking in depth into particular migrants, octocrylene, 1-tetradecene, 1-dodecene, and dodecyl acrylate exceeded their SML. Besides, 2,4-di-tert-butylphenol and 1,4-benzenedicarboxylic acid, diethyl ester were of high concern in 95 % ethanol (fatty food) migration concerning their detected frequency and highest concentration. For 3 % acetic acid simulant (acidic food), benzenamine, 2,4-dichloro- and diethyl phthalate deserve more attention. This study presents a fundamental input of chemicals that can migrate out from postconsumer recycled polyolefins as well as their MW and XLogP distribution. The prioritization strategy helps us concentrate on higher risk migrants. This database as well as the data

analysis is beneficial for developing sufficiently clean recycled polyolefins for food contact and thus closing the loop.

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Figures and tables

Table 1: Detail information of samples (n=5).

Company	Spanish company	Chinese company 1				Chinese company 2	Chinese company 3			
Sample name	S1, S2, S3, S4, S5, S6	C1	C2	C3	C9	C4	C5	C6	C7	C8
Diameter (mm)	5.2 ± 0.2	3.8 ± 0.2	3.3 ± 0.2	6.2 ± 0.2	5.0 ± 0.1	3.7 ± 0.2	3.2 ± 0.3	3.5 ± 0.3	4.7 ± 0.3	3.5 ± 0.3
Height (mm)	2.3 ± 0.2	3.4 ± 0.2	4.1 ± 0.2	2.3 ± 0.3	2.8 ± 0.3	3.0 ± 0.1	3.1 ± 0.2	3.3 ± 0.4	2.1 ± 0.2	3.0 ± 0.1

Note: diameter and height were expressed as mean ± standard deviation (n=5)

Table. 2 Prioritized important migrants and their concentrations

| RT	Name	Freq	ToxL	S/N	Con. (μg/kg)	Note (SML unit: mg/kg)
66.157	Bis(2-ethylhexyl) phthalate	100.0	V	1573.2	47.6 ± 38.1	CMR; SVHC; EDC; SML: 1.5
49.626	Dibutyl phthalate	100.0	V	587.2		CMR; SVHC; EDC; SML: 0.3
46.584	Diisobutyl phthalate	66.7	V	526.9		CMR; SVHC; EDC
36.906	Diethyl Phthalate	100.0	V	412.8	315.8 ± 34.7	EDC
29.124	Diphenyl ether	93.3	IV	692.8	69.2 ± 5.7	food related
69.129	Octocrylene	60.0	IV	518.8	166.6 ± 22	SML: 0.05
43.781	2,4-Diphenyl-4-methyl-1-pentene	60.0	IV	470.4	< 10	plastic related
26.054	Benzenamine, 2,4-dichloro-	86.7	IV	348.8	158.9 ± 5.6	intermediate for other chemicals
46.092	Galaxolide	66.7	IV	269.6		plastic related
47.682	4-Dodecylmorpholine	93.3	IV	187.2	21.5 ± 0.7	additive in food contact substances
28.991	1-Tetradecene	100.0	IV	140.0	272.0 ± 17.8	SML: 0.05
32.148	Dodecane, 1-chloro-	66.7	IV	116.4	23.7 ± 0.3	intermediate
20.126	1-Dodecene	100.0	IV	89.3	181.8 ± 9.9	SML: 0.05
30.37	Diphenylmethane	60.0	IV	28.8		cosmetic related
32.514	1,1'-Biphenyl, 3-methyl-	73.3	IV	27.9	18.0 ± 0.2	
53.328	Oleanitrile	73.3	IV	11.6		plastic related
38.016	Benzophenone	100.0	III	355.3	68.1 ± 5.2	SML: 0.6
30.766	Phenol, 2,6-bis(1,1-dimethylethyl)-	86.7	III	151.7		plastic related
28.049	Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester	66.7	III	117.3		plastic related
33.92	2,4-Di-tert-butylphenol	93.3	II	19693.1	2257.8 ± 284.8	plastic related
33.605	1-Dodecanamine, N,N-dimethyl-	80.0	II	9345.4	43.1 ± 0.6	plastic related
50.995	Hexadecanoic acid, ethyl ester	100.0	II	6413.2	355.6 ± 41.2	food related
44.407	Tetradecanoic acid, ethyl ester	93.3	II	5102.0	192.4 ± 24.7	food related
44.644	2-Ethylhexyl salicylate	66.7	II	4957.1	143.8 ± 0.3	cosmetic related
62.456	Hexanedioic acid, bis(2-ethylhexyl) ester	100.0	II	3678.8	122.1 ± 59.9	SML: 18
20.91	Benzaldehyde, 2,5-dimethyl-	100.0	II	1121.0	125.5 ± 10.1	
31.18	1-(4-tert-Butylphenyl)propan-2-one	93.3	II	859.3	120.4 ± 5	
55.98	Linoleic acid ethyl ester	66.7	II	826.0	774.5 ± 270.6	cosmetic related
40.011	n-Hexyl salicylate	93.3	II	733.0	377.6 ± 9.6	plastic related
47.951	Dimethyl palmitamine	60.0	II	708.6		plastic related
58.004	Hexadecanoic acid, 2-hydroxyethyl ester	60.0	II	578.7		cosmetic related
25.156	4-(t-Butyl)benzaldehyde	100.0	II	523.6	59 ± 0.5	
37.128	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	100.0	II	318.7	182.1 ± 16.2	SML: 5
18.311	Isoborneol	60.0	II	279.3	615.9 ± 26.3	food related
56.248	Ethyl Oleate	100.0	II	266.2	926.2 ± 57	food related
71.258	UV 531	60.0	II	246.5	184.8 ± 80.5	SML: 6
39.121	1,4-Benzenedicarboxylic acid, diethyl ester	80.0	II	126.78	70055.4 ± 2399.1	plastic related
12.51	D-Limonene	100.0	II	117.76	2022.4 ± 155.5	food related
73.078	Phthalic acid, bis(7-methyloctyl) ester	80.0	II	59.3		plastic related
60.297	2-Ethylhexyl trans-4-methoxycinnamate	40.0	V	13689.1		EDC
29.055	Phenol, 4-(1,1-dimethylpropyl)-	46.7	V	1067.7		SVHC
51.022	1H-Pyrazole, 4,5-dihydro-1,3-diphenyl-	40.0	IV	1190.7		
40.105	1,7-di-iso-propylnaphthalene	53.3	IV	535.5	14.3 ± 0.3	plastic related
38.512	N,N-Dimethyldodecanamide	46.7	IV	496.4		slip agent
42.931	1,1'-Biphenyl, 3,3'-dichloro-	33.3	IV	51.0	4.4 ± 0.1	Polychlorinated biphenyl in PCB
40.704	Dodecyl acrylate	40.0	IV	28.1	102.3 ± 3.9	SML: 0.05
21.844	2-Ethylhexyl acrylate	33.3	IV	26.2	33.5 ± 4.5	SML: 0.05
28.115	2-Propenoic acid, 1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, exo-	53.3	III	548.1	97.7 ± 3.6	plastic related
41.12	1-Tetradecanamine, N,N-dimethyl-	33.3	II	4578.0	11.7 ± 1.2	cosmetic related
65.938	Tinuvin 326	26.7	II	377.2	319.2 ± 138.7	SML: 30
56.94	Terephthalic acid, ethyl 2-ethylhexyl ester	33.3	II	345.2	2870.5 ± 352.9	
18.709	Benzenamine, 2,4-dimethyl-	53.3	II	240.4	451.8 ± 35.2	plastic related
14.376	Aniline, N-methyl-	20.0	II	29.3	47.6 ± 38.1	food related
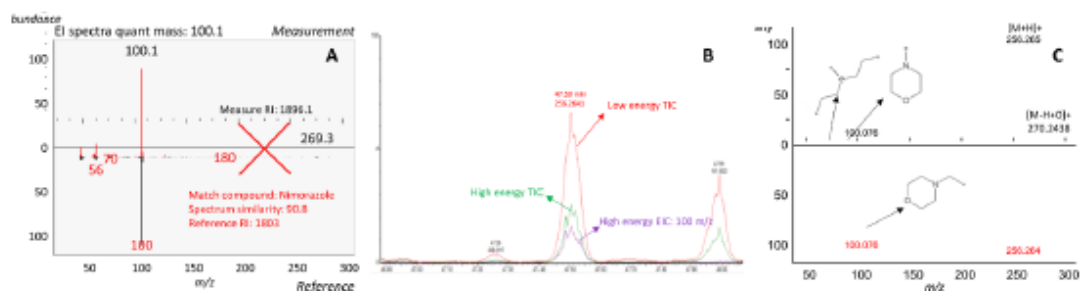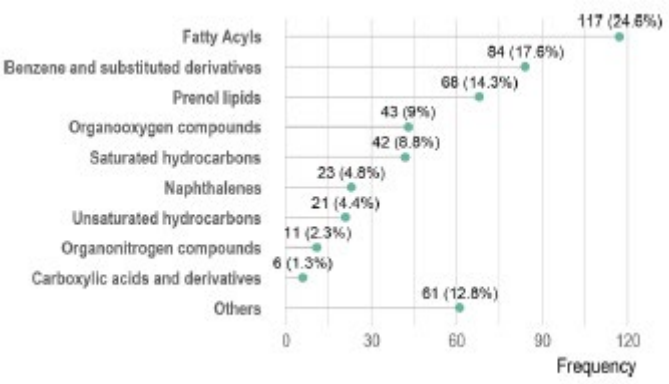
Fig. 2. Chemical classes distribution of detected migrants. Absolute frequency with relaltive frequency (%) in bracket

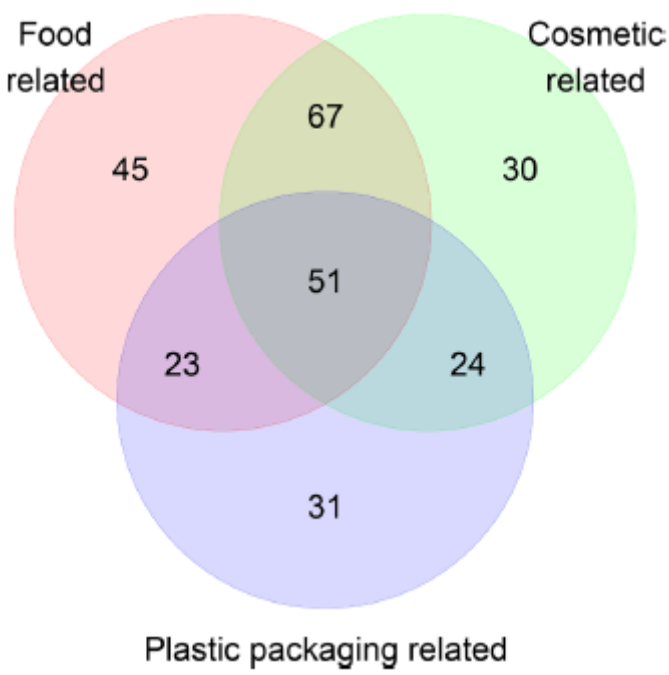**Fig. 3.** Possible origins of detected migrants

Fig. 4. Hierarchical clustering of samples (marginal diagram) and their correlations using peak areas tentatively identified migrants. Note: H represents acetic acid migration while E stands for 95 % ethanol migration

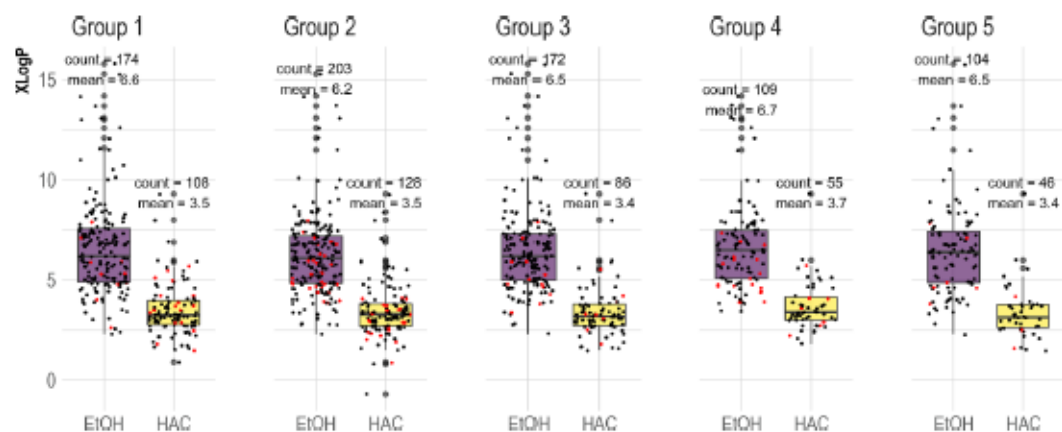**Fig. 5.** Molecular weight distribution of detected migration by groups

Fig. 6. XLogP distribution of detected migrants by groups and simulants. Note: EtOH and HAC are the migration into 95 % ethanol and 3 % acetic acid food simulants, respectively. Dots in red are chemicals that have toxicity level V and IV.