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Title page

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ABSTRACT

The demand for high quality recycled polymers in the European plastic industry is on the increase, likely due to the EU's Plastic Strategy intended to implement the circular economy model in this sector. The problem is that there is not enough recycled plastic in the market. In terms of volume, post-consumer plastic waste could be key to meet the current and future demand. Nevertheless, a high level of contamination originated during the product's life cycle restricts its use. The first step to change this must be identifying the undesired substances in post-consumer plastics and performing an effective risk assessment. The acquired knowledge will be fundamental for the development of innovative decontamination technologies.

In this study, 134 substances including volatile and semi-volatile compounds have been identified in recycled LDPE and HDPE from domestic waste. Headspace and solvent extraction followed by GC/MS were used. The possible origin of each substance was studied. The main groups were additives, polymer and additives breakdown products, and contamination from external sources. The results suggest that recycled LDPE contains a broader number of additives and their degradation products. Some of them may cause safety concerns if reused in higher added value applications. Regarding recycled HDPE, the contaminants from the use phase are predominant creating problems such as intense odors. To reduce the number of undesired substances, it is proposed to narrow the variety of additives used in plastic manufacturing and to opt for separate waste collection systems to prevent cross-contamination with organic waste.

Keywords: mechanical-recycling, plastics, domestic-waste, polyolefins, NIAS, IAS.

1. Introduction

Plastic products have reached almost all areas of our lives. The demand for plastics is continuously growing owing to a broad range of properties such as lightness, versatility and durability. In the EU, 51.2 million tons were consumed in 2017 for new product manufacturing. Packaging is the most important sector, representing almost 40 % of the total plastic demand. Plastic wraps and containers contribute largely to reduce food waste generation, transportation costs and emissions, raw materials consumption, etc. Although their main function is to protect the product inside, primary packaging also plays a pivotal role in product commercialization. The package must capture the attention of the consumers and distinguish the product from other brands, for which purpose high-quality raw materials are needed. High density and low-density polyethylene (HDPE and LDPE) cover the largest demand in the plastic

packaging sector, but in different applications (PlasticsEurope, 2018). For rigid packaging, HDPE is preferred while LDPE is largely used for flexible film-related uses. This derives in higher use of HDPE as a bottle container of cleaning agents and care products (Mudgal et al., 2011), while LDPE is commonly used for flexible packaging in food-contact grade applications, carrier bags, as well as for shrink and stretch film (Plastics Recyclers Europe, 2019). A growing amount of multilayer packaging is used in the sector. Around 1.89 million tons were produced in Europe in 2016 (Katharina Kaiser et al., 2018). Additionally, the demand for polyethylene terephthalate (PET) is also significant since it is used for beverage packaging.

Besides the benefits that these materials brought to our society, we cannot ignore that plastic packaging contributes enormously to waste generation and environmental pollution. This can be attributed to the fact that these products are generally produced as single-use items with short service life. As a consequence, plastic packaging amounts to approximately 70 % of the total weight of plastics in the municipal solid waste (MSW) stream (Mudgal et al., 2011). It has been estimated that 36 % of household plastic waste is composed of bottles and flasks, 36 % of which are made of HDPE, and another 40 % corresponds to plastic films mainly produced with LDPE (69 %). The rest corresponds to a smaller fraction that includes pots, tubs and trays (Hestin et al., 2017).

In addition to increasing waste generation, post-consumer packaging from households is highly contaminated and heterogeneous. Common contaminants are inks, coatings, dust, organic waste, etc, which present a great challenge, especially for domestic plastic waste recovery. Indeed, conventional recycling processes are not able to mitigate the chemical contamination of post-consumer waste, leading to the use of recycled products in lower grade applications e.g. construction, agriculture or piping (Maurizio Crippa et al., 2019). Recycled plastics from post-consumer sources are unlikely to be applied in more demanding applications (for instance, packaging industry) since nowadays these materials cannot fulfill the requirements of this sector regarding color, odor (M. Strangl et al., 2018), migration of unknown substances such as organic substances (V. García Ibarra et al., 2018), and the accumulation of metals in recycled polymers may also be an issue for their introduction into the market (Eriksen, M. K. et al., 2018). Moreover, the purification of polyolefins is more difficult compared to PET because of the higher permeability, leading to a faster migration of the contaminants from external sources to the inner layers of the polymer (Geueke, Birgit et al., 2018).

Closing the loop, which means using the recycled plastic for the same application as the original material, may produce substantial savings to the environment (Ping Hou et al., 2018). Nevertheless, the possibility

of migration of potentially hazardous substances from the recycled packaging to the product is a matter of concern for the stakeholders; not only in the food packaging sector but also in other sectors such as hygienic packaging sector. These undesired chemicals are tagged as non-intentionally added substances (NIAS) (Geueke, Birgit et al., 2018). The origin of NIAS can be the degradation of the polymeric material and its additives, as well as the contaminants resulting from the migration of external sources (C. Nerin et al., 2013). Some results have been reported until now regarding NIAS in post-consumer plastic packaging e.g. in HDPE milk bottles and PET bottles. In the case of post-consumer HDPE bottles, Welle (2005) reported that the most predominant NIAS are related to oligomers of the polymer material itself, degradation products from antioxidant additives (e.g., di-*tert*-butylphenol), and odorants such as limonene. In the case of PET bottles, acetaldehyde, formaldehyde, 2-methyl-1,3-dioxolane as well as PET oligomers were found as NIAS of the PET material itself. Toluene and xylenes were also detected and were related to monomers and additive impurities or processing aids. Finally, cyclopentanone and isophthalaldehyde were found in PET because of using polyamides as an oxygen barrier in the packaging. The only compounds present in post-consumer PET but not in the virgin were 4-iso-propyltoluene and limonene (R. Franz et al., 2004). Therefore, the NIAS are not exclusively present in recycled plastic, but also in the original plastic products. In recycled plastics, the generation of NIAS is not the only issue. Intentionally added substances (IAS) during the manufacturing process (e.g. catalysts, additives, inks, fillers, etc.) can pose a risk to consumers, especially, when their quality is low. For instance, brominated flame retardants can come from non-food grade materials due to inefficient collecting schemes and missorting (Geueke, Birgit et al., 2018). A large list of additives exists in the market, such as plasticizers, antioxidants, lubricants, flame retardants, etc. The selection of the proper additives and their quality (or grade) depends greatly on the final application of the plastic product. For instance, substances intended to be used in food contact materials must meet the highest quality requirements subject to regulation EU 10/2011.

Conventional plastic recycling consists of several mechanical processes such as grinding, washing, drying and extrusion. During the recycling of post-consumer plastic waste, an efficient washing unit is crucial to remove dirtiness and obtain high-quality pellets. Although processes for recycling PET have been accepted by the European Food Safety Authority (EFSA) to use the outcoming recyclates in food-grade applications (EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF), 2019) this does not apply to polyolefins. The cleaning of polyolefins e.g. polyethylene (PE) products is limited to washing with cold or hot water, which is not enough to remove undesired odor, color or other NIAS. Therefore, new technologies capable of upgrading the quality of recycled PE by decontamination

could be key to reach the ambitious EU targets: more than 50 % of plastic waste recycled (European Commission, 2018) and 30 % of recycled plastic incorporated in new products manufacturing by 2030 (European Commission, 2019b). However, few technologies currently exist intended to remove contaminants from plastic recyclates, namely deinking of plastic films using surfactants (Fullana Font and Lozano Morcillo, 2013), extraction of impurities with supercritical carbon dioxide (C. S. Castro Issasi et al., 2019), or stripping volatile compounds with hot air (Sebastian-Scarola and Gordon-Angell, 1996) are some of them.

Based on the abovementioned facts, the lack of knowledge about the composition of the contaminants remaining in the polymer matrix after use as well as the limiting technology for recycling at present are the main bottlenecks for the reuse of recycled post-consumer plastic waste. For this reason, this paper aims to identify the contaminants or in other words, the non-intentionally added substances (NIAS) containing in post-consumer HDPE and LDPE packaging. We think that uncovering the substances present in the most widely used post-consumer packaging materials will contribute to providing a database of hazardous and unwanted substances that may remain in the recycled polymers. These substances can be used as indicators for determining the decontamination efficiency of recycling processes. Specifically, in this research, we analyze the volatile and semi-volatile fractions of organic compounds by extracting them with headspace and solvent extraction techniques followed by their analyses utilizing gas chromatography and mass spectrometry (GC/MS).

2. Materials and methods

2.1. Samples

The two samples used in this study were recycled pellets obtained from post-consumer low-density polyethylene (PC-LDPE) and high-density polyethylene (PC-HDPE) from yellow sack collection in Germany. PC-LDPE waste consisting of single layer LDPE bags and films, and PC-HDPE consisting of rigid bottles from detergents, shampoo and other cleaning products. Both, PC-LDPE and PC-HDPE wastes were supplied to the recycling company, previously sorted in the waste management facility. The pellets were produced by a recycling company. The recycling protocol consisted of a washing step only using cold water and no additional surfactants, then drying by centrifugation, and finally, the polymer was extruded using a melt filter and a degassing step, obtaining pellets with 5 mm diameter. The percentage of post-consumer LDPE and HDPE in the recycled pellets is 100 %. The LDPE and HDPE samples used are a mixture of the granules from three different lots produced by the recycling company.

2.2. Analysis of volatile organic compounds with headspace solid phase microextraction and gas chromatography and mass spectrometry

2.2.1. Extraction of volatile organic compounds by means of headspace solid phase microextraction

To determine the VOCs remaining in the polymer matrix, the headspace solid phase microextraction (HS-SPME) technique was applied. An amount of 20 ± 0.01 g of recycled plastic pellets were introduced in a glass vial of 100 mL volume sealed with a 20 mm diameter teflon/silicone septum. Following, a SPME syringe with a 75 μ m Carboxen/Polydimethylsiloxane fiber was injected through the septum and held in the headspace of the vial while adsorbing the volatile organic compounds (VOCs) emitted by the plastic sample. The VOCs extraction was facilitated by heating the sample in a water bath at 60°C for 1 hour meanwhile the SPME fiber was placed inside (C. Dutra et al., 2011). Only one analysis of each sample has been carried out since the goal of this work is to perform a qualitative assessment of the composition of the recycled pellets. The results will be used in future to conduct a quantitative analysis of target compounds. Then, replicates of each sample will be needed.

2.2.2. Analysis of volatile organic compounds by gas chromatography and mass spectrometry

The VOCs adsorbed on the fiber were desorbed in the injection port of the gas chromatograph Agilent 7890A (GC), where the volatiles were separated using a non-polar HP5 capillary column (30 m length, 0.25 mm diameter, supplied by Agilent Technologies), after which the mass spectrum of each peak was obtained with the Mass Spectrometer Agilent 5975C (MS). The method set in the GC/MS for the VOCs analysis is described in Table 1. Temperature program and injection temperature were defined according to Dutra et al. (2011).

Table 1: Operating conditions in the gas chromatography mass spectrometry device for VOCs identification.

GC Conditions			
Split mode	5:1		
Injector temperature	280 °C		
Desorption time	10 min		
Flow rate	1 mL/min		
Temperature program	T(°C)	Rate (°C/min)	Hold (min)
	40		5
	130	3	0
	250	6	0
	300	20	1
MS Conditions			

Solvent delay	0.5 min
Scan mode	35 m/z – 300 m/z
Method of ionization	Electron impact

2.3. Analysis of semi-volatile organic compounds with solvent extraction, gas chromatography and mass spectrometry

2.3.1. Extraction of semi-volatile organic compounds into solvents

Semi-volatile organic compounds (SVOCs) were obtained from the plastic samples by extraction into a solvent. Plastic pellets were grounded to powder using a cryogenic grinder to increase the contact area. An amount of 1.0 ± 0.02 g of grounded plastic was introduced into a 20 ml vial with 10 ± 0.05 mL of dichloromethane (DCM). The vials were sealed, and the sample was stirred for 24 hours. After the extraction period, the sample was decanted from the solvent and stored for 12 hours at 4°C to separate the remaining solids. The extracts were then concentrated under a stream of nitrogen up to 1.5 mL (Pasvial sample vial concentration JSD). DCM (HPLC quality) was purchased from VWR Chemicals (Barcelona, Spain). The analysis was carried out once for each sample since this is a qualitative study.

Two standards were added to make possible the comparison between the samples since the extraction method can create differences regarding the abundance of the substances, especially, during the concentration stage. Therefore, the area of each substance has been corrected with the area of the nearest compound from the standard. In total, 10 µL of internal standard Mix26 from Dr. Ehrenstorfer in DCM and 5 µL of anthracene-d₁₀ from AccuStandard Inc in DCM were added. The Mix26 is composed of 6 deuterated compounds: 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 in DCM. The concentration of each compound is 4000 µg/mL, which has been used to perform a semi-quantification of the substances identified in the samples. Standards were purchased from Sigma Aldrich Química (Barcelona, Spain).

2.3.2. Analysis of semi-volatile organic compounds by gas chromatography and mass spectrometry.

Gas chromatography (Agilent 7890A) coupled with a quadrupole mass spectrometer (Agilent 5975C) was used to identify the SVOCs extracted from the plastic samples. The same HP5 column was used as the one described in section 2.2.2. The method set in the GC/MS for the SVOCs analysis is described in Table 2.

Table 2. Operating conditions in the gas chromatography-mass spectrometry device for SVOCs identification.

GC Conditions			
Split mode	Splitless		
Injector temperature	250 °C		
Flow rate	1 mL/min		
Temperature program	T(°C)	Rate (°C/min)	Hold (min)
	40		5
	290	12	6
	320	20	10
MS Conditions			
Solvent delay	8 min		
Scan mode	35 m/z – 550 m/z		
Method of ionization	Electron impact		

2.4. Methodology for volatile and semi-volatile organic compounds identification.

The VOCs and SVOCs were identified via GC/MS assisted by the NIST library with the previous deconvolution of the chromatogram using AMDIS software. To facilitate the data treatment of the results, a programming code in MATLAB was developed in order to manipulate the document provided by AMDIS and organize the organic compounds identified in all the samples simultaneously.

Of the total detected compounds, only the ones with a match quality higher than 80 % were determined as tentatively identified compounds, and the ones with a match quality between 65 and 80 % were considered as low quality tentatively identified compounds. The parameter of quality refers to the probability of an identified mass spectrum to match the mass spectrum of the reference compound from the NIST library, for which we used NIST MS search 2.0 software.

3. RESULTS

3.1. Volatile organic compounds

3.1.1. Overall volatile emissions

The chromatograms of recycled HDPE and LDPE pellets from post-consumer waste resulting from the analysis of the volatile fraction performed with HS-SPME-GC/MS technique are presented in Figure 1. At a glance, we can see that post-consumer LDPE presents a substantially lower content of VOCs than post-consumer HDPE recycled pellets. In detail, the overall area in the chromatogram of post-consumer HDPE is 9-fold higher than that of the post-consumer LDPE. For the first identification of every organic

compound detected, the mass spectrum obtained experimentally was compared with the NIST library, and the VOCs were classified as hydrocarbons, oxygenated compounds and others. As a result, it was obtained that the total chromatogram area of VOCs in both cases (LDPE and HDPE) was mainly covered by hydrocarbons, including aliphatic hydrocarbons, cyclic and phenyls, as well as by oxygenated compounds such as carboxylic acids, ketones and aldehydes. Particularly, 44 % of VOCs in post-consumer HDPE correspond to hydrocarbons and 51 % to oxygen-containing compounds. In the case of post-consumer LDPE, 42 % of VOCs are formed by hydrocarbons and 45 % by oxygen-containing compounds.

Figure 1: Chromatogram of post-consumer LDPE (purple) and post-consumer HDPE (green) recycled pellets obtained by HS-SPME-GC/MS

Secondly, the VOCs were classified according to their volatility, for which the chromatograph was divided into 3 sections according to the time the molecules remain (t_R) inside the HP5 capillary column of the GC. These three groups correspond to $t_R < 15$ minutes, $15 < t_R < 30$ minutes and $30 < t_R < 45$ minutes (see Figure 2). As a result of this distribution, post-consumer HDPE pellets indicate a higher amount of heavy VOCs, as more than 50 % of volatiles detected fell in the region of 30 to 45 minutes residence time, while the VOCs corresponding to the post-consumer LDPE sample were mostly detected at residence times lower than 30 minutes.

Figure 2: Profile of VOCs according to the residence time (tR) that the molecules remain in the HP5 capillary column

3.1.2. Identified substances

In the overall chromatogram, more than 1000 substances were detected, but not all of them provided a reliable match with the NIST library reference compounds.

Overall, in the post-consumer LDPE and post-consumer HDPE samples, 105 compounds were tentatively identified with match quality >65%. These VOCs are presented in Table 3 classified by their molecular structure as alcohols (5), aldehydes (10), alkylbenzenes (16), ketones (14), lactones (5), esters (36), ethers (10), carboxylic acids (2) and one phthalate, diethyl phthalate, beside another seven substances such as pyridines, hexene or dimethyl trisulfide. The abundance of each substance is represented by the level of intensity of the peak in the chromatogram distinguishing among low (1), medium (2) and high (3). The levels have been established by dividing the chromatogram in 3 equal parts between 0 and the highest peak of the two samples.

Of the total number of VOCs, 83 were identified with a match quality above 80 % and 22 with a match quality between 65 and 80 %. The groups with the largest number of substances are esters and alkylbenzenes. Specifically, 81 substances were identified in the post-consumer HDPE sample and 43 in the LDPE sample with match quality > 65%. Of these, 18 compounds were found in both samples, which include octanal (no. 7), alkylbenzenes (no. 15, 16, 18, 20, 23 and 25), ketones (no. 31, 32, 35 and 43), esters (no. 50, 60, 80 and 83), ethers (no. 88 and 93), and the compound 2,6-diisopropylnaphthalene (no. 104).

Regarding the amount of the VOCs (low quality) tentatively identified in each sample, we can see in Figure 3 that the dominant groups in post-consumer LDPE are aldehydes, carboxylic acids and ketones,

while in post-consumer HDPE the groups of esters and ethers outlined over the rest. According to the level of intensity, all the identified VOCs fall in the region of low-level intensity except for benzyl acetate (no. 62) and 2-phenoxyethanol (no. 81). Both were identified in the post-consumer HDPE sample. Though the VOCs identified in the LDPE sample are all rated with low intensity, it is worth mention that 5-methylfurfural (no. 6) followed by acetic acid (no. 96) have the maximum peak areas compared to the rest of compounds in this sample.

The nature of these compounds, though mentioned in Table 3, will be detailed in the discussion section.

Figure 3: Chromatogram area of the different groups of volatile organic compounds identified with match quality >65 % in post-consumer LDPE (purple) and HDPE (green) samples, including aldehydes, alkylbenzenes, carboxylic acids, esters, ethers, ketones, lactones and others

Table 3: List of VOCs tentatively identified by GC/MS originating from post-consumer HDPE (PC HDPE) and post-consumer LDPE (PC LDPE). Q is the match quality percentage and RT is the retention time. PC means post-consumer source. A= additive; AD=additive degradation product; PD=polymer degradation product; C=contaminant; deg = degradation. Peak intensity: 1=low, 2=medium, 3=high.

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
Alcohols									
1	furfuryl alcohol	98-00-0	75	6.06		1	C	Food aroma	(H. E. Hoydonckx et al., 2000)
2	2-butoxyethanol	111-76-2	68	8.45	1		C	Cosmetics	(European Commission, 2019c)
3	dihydromircenol	18479-58-8	75	16.76	1		C	Cosmetics	(European Commission, 2019c)
4	butylated hydroxytoluene (BHT)	128-37-0	71	36.25	1		A or C	Antioxidant Cosmetics	EU 10/2011 (European Commission, 2019c)
Aldehydes									
5	furfural	98-01-1	66	5.10		1	C	Cosmetics Food aroma	(European Commission, 2019c; H. E. Hoydonckx et al., 2000)
6	5-methylfurfural	620-02-0	93	10.87		1	C	Cosmetics Food	(J. A. Maga and I. Katz, 1979; European Commission, 2019c)
7	octanal	124-13-0	90	13.02	1	1	PD or C	Cosmetics	(European Commission, 2019c; Hamid, 2000)
8	nonanal	124-19-6	81	18.33	1		PD or C	Polyethylene Cosmetics	(European Commission, 2019c; Hamid, 2000)
9	anisaldehyde	123-11-5	70	25.24	1		C	Cosmetics	(European Commission, 2019c)
10	piperonal	120-57-0	76	28.70	1		C	Cosmetics	(European Commission, 2019c)
11	3-(4-isopropylphenyl)-2-methylpropionaldehyde	103-95-7	90	34.18	1		C	Cosmetics	(European Commission, 2019c)
12	α -amylcinnamaldehyde	122-40-7	93	40.04	1		C	Cosmetics	(European Commission, 2019c)
13	3,5-di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	82	42.41		1	AD	Irganox 1076 oligomer	(E. Reingruber and W. Buchberger, 2010; M. Biedermann et al., 2014)

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
14	2-(phenylmethylene)octanal	101-86-0	96	42.66	1		C	Cosmetics	(European Commission, 2019c)
Alkylbenzenes									
15	(1-butylhexyl)benzene	4537-11-5	96	36.92	1	1	C	Surfactant deg	(Kosswig, 2000)
16	(1-propylheptyl)benzene	4537-12-6	87	37.18	1	1	C	Surfactant deg	(Kosswig, 2000)
17	(1-ethyloctyl)benzene	4621-36-7	81	37.82	1		C	Surfactant deg	(Kosswig, 2000)
18	(1-butylheptyl)benzene	4537-15-9	90	39.68	1	1	C	Surfactant deg	(Kosswig, 2000)
19	(1-pentylhexyl)benzene	4537-14-8	92	39.70	1		C	Surfactant deg	(Kosswig, 2000)
20	(1-propyloctyl)benzene	536-86-1	88	39.87	1	1	C	Surfactant deg	(Kosswig, 2000)
21	(1-ethylnonyl)benzene	4536-87-2	84	40.49	1		C	Surfactant deg	(Kosswig, 2000)
22	(1-methyldecyl)benzene	4536-88-3	72	41.32	1		C	Surfactant deg	(Kosswig, 2000)
23	(1-pentylheptyl)benzene	2719-62-2	95	41.79	1	1	C	Surfactant deg	(Kosswig, 2000)
24	(1-butyloctyl)benzene	2719-63-3	89	42.03	1		C	Surfactant deg	(Kosswig, 2000)
25	(1-propylnonyl)benzene	2719-64-4	91	42.18	1	1	C	Surfactant deg	(Kosswig, 2000)
26	(1-ethyldecyl)benzene	2400-00-2	92	42.71	1		C	Surfactant deg	(Kosswig, 2000)
27	(1-butylnonyl)benzene	4534-50-3	87	44.02	1		C	Surfactant deg	(Kosswig, 2000)

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
28	(1-propyldecyl)benzene	4534-51-4	88	44.25	1		C	Surfactant deg	(Kosswig, 2000)
29	(1-ethylundecyl)benzene	4534-52-5	91	44.66	1		C	Surfactant deg	(Kosswig, 2000)
30	(1-hexyloctyl)benzene	4534-54-7	91	45.65	1		C	Surfactant deg	(Kosswig, 2000)
Ketones									
31	acetophenone	98-86-2	67	16.17	1	1	C	Cosmetics/ Catalyst	(European Commission, 2019c; PubChem, 2019)
32	2-nonanone	821-55-6	91	17.54	1	1	PD	Polyethylene	(Bradley and Coulier, 2007)
33	3-decanone	928-80-3	92	22.40	1		C or PD	Cosmetics/ polyethylene	(Bradley and Coulier, 2007; European Commission, 2019c)
34	benzylacetone	2550-26-7	75	24.83	1		C	Cosmetics	(European Commission, 2019c)
35	2-undecanone	112-12-9	88	27.05	1	1	PD	Polyethylene	(Bradley and Coulier, 2007)
36	2,2,4,4,6,8,8-heptamethylnonanone	4390-04-9	83	28.03		1	C or PD	Cosmetics Polyethylene	(European Commission, 2019c; Bradley and Coulier, 2007)
37	3-dodecanone	1534-27-6	95	31.41	1		PD	Polyethylene	(Bradley and Coulier, 2007)
38	1-(4-tert-butylphenyl)propan-2-one	81561-77-5	93	33.67	1		Possible AD	Phenyl type antioxidant	
39	2,6-di-tert-butyl-1,4-benzoquinone	719-22-2	83	34.06		1	AD	Oxidation phosphite additives	(Bradley and Coulier, 2007)
40	α -methyl ionone	7779-30-8	84	36.44	1		C	Cosmetics	(European Commission, 2019c)
41	lilial	80-54-6	76	36.66	1		C	Cosmetics	(European Commission, 2019c)
42	β -methylionone	127-43-5	75	38.23	1		C	Cosmetics	(European Commission, 2019c)
43	benzophenone	119-61-9	89	39.34	1	1	A or C	UV	EU 10/2011

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
								antioxidant Cosmetics	(European Commission, 2019c)
44	3,5-di-tert-butyl-4-hydroxyacetophenone	14035-33-7	85	43.67	1		AD	Pentaerythritol tetrakis oligomer	(Bradley and Coulier, 2007)
Lactones									
45	butyrolactone	96-48-0	92	8.37		1	C	Cosmetics Food	(European Commission, 2019c; J. A. Maga and I. Katz, 1976)
46	γ -valerolactone	108-29-2	86	10.38		1	C	Cosmetics Food	(European Commission, 2019c; J. A. Maga and I. Katz, 1976)
47	δ -valerolactone	542-28-9	81	15.26		1	C	Cosmetics Food	(European Commission, 2019c; J. A. Maga and I. Katz, 1976)
48	γ -nonalactone	104-61-0	81	30.11	1		C	Cosmetics Food	(European Commission, 2019c; J. A. Maga and I. Katz, 1976)
49	γ -undecalactone	104-67-6	71	38.10	1		C	Cosmetics	(European Commission, 2019c)
Esters									
50	methyl methacrylate	80-62-6	87	2.44	1	1	A		EU 10/2011
51	methylhexanoate	106-70-7	76	9.16		1	C	Cosmetics/ food related	(PubChem, 2019; European Commission, 2019c)
52	methyl pyruvate	600-22-6	96	2.67		1	C	Food-related	(The Good Scents Company, 2018)
53	methyl lactate	2155-30-8	89	2.79		1	C	Cosmetics	(European Commission, 2019c)
54	butyl acetate	123-86-4	92	4.78	1		A or C	Additive/ cosmetics	EU 10/2011 (European Commission, 2019c)
55	butyl 2-propenoate	141-32-2	81	7.82		1	A or C	Additive/	EU 10/2011

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
								cosmetics	(European Commission, 2019c)
56	hexyl acetate	142-92-7	88	13.90	1		C	Cosmetics	(European Commission, 2019c)
57	dimethyl butanedioate	106-65-0	97	14.99	1		C	Cosmetics	(European Commission, 2019c)
58	methyl-2-ethylhexanoate	816-19-3	96	15.06		1	C	Fungi growth	(F. Van Lancker et al., 2008)
59	allyl hexanoate	123-68-2	84	17.33	1		C	Cosmetics	(European Commission, 2019c)
60	methyl benzoate	93-58-3	79	17.53	1	1	A or C	Antioxidant/ Cosmetics	EU 10/2011 (European Commission, 2019c)
61	methyl octanoate	111-11-5	85	19.14		1	C	Cosmetics	(European Commission, 2019c)
62	benzyl acetate	140-11-4	92	21.22	3		C	Cosmetics	(European Commission, 2019c)
63	allyl heptanoate	142-19-8	91	22.14	1		C	Cosmetics	(European Commission, 2019c)
64	methyl salicylate	119-36-8	89	22.46	1		C	Cosmetics	(European Commission, 2019c)
65	α -methylbenzyl acetate	93-92-5	70	22.67	1		C	Cosmetics	(European Commission, 2019c)
66	tetrahydrolinalyl acetate	20780-48-7	89	24.51	1		C	Cosmetics	(European Commission, 2019c)
67	dimethyl hexanedioate	627-93-0	98	25.15	1		C	Cosmetics	(European Commission, 2019c)
68	ethyl salicylate	118-61-6	95	26.02	1		C	Cosmetics	(European Commission, 2019c)
69	dimethylbenzylcarbiny acetate	151-05-3	90	28.28	1		C	Cosmetics	(European Commission, 2019c)
70	methyl anthranilate	134-20-3	77	29.10	1		C	Cosmetics	(European Commission, 2019c)
71	ethyl decanoate	110-38-3	85	31.78	1		C	Cosmetics	(European Commission, 2019c)
72	methyl 2- (methyldamino)benzoate	85-91-6	92	31.94	1		C	Cosmetics	(European Commission, 2019c)
73	benzyl dimethylcarbiny butyrate	10094-34-5	78	35.41	1		C	Cosmetics	(European Commission, 2019c)
74	indan-1,3-diol monopropionate	17511-60-3	93	36.34	1		C	Cosmetics	(European Commission, 2019c)
75	2-phenoxyethyl isobutyrate	103-60-6	94	36.46	1		C	Cosmetics	(European Commission, 2019c)

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
76	amyl salicylate	2050-08-0	72	38.10	1		C	Cosmetics	(European Commission, 2019c)
77	hexyl salicylate	6259-76-3	85	39.61	1		C	Cosmetics	(European Commission, 2019c)
78	methyl 2-(3-oxo-2-pentylcyclopentyl)acetate	24851-98-7	83	40.26	1		C	Cosmetics	(European Commission, 2019c)
79	methyl tetradecanoate	124-10-7	81	41.70		1	C or AD	Cosmetics/ Lubricant impurity	(European Commission, 2019c; Bradley and Coulier, 2007)
80	ethyl tetradecanoate	124-06-1	92	43.15	1	1	C or AD	Cosmetics/ Lubricant impurity	(European Commission, 2019c; Bradley and Coulier, 2007)
81	isopropyl myristate	110-27-0	90	43.89	1		C	Cosmetics	(European Commission, 2019c)
82	methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	6386-38-5	92	45.95	1		C	Cosmetics	(European Commission, 2019c)
83	ethyl palmitate	628-97-7	83	46.83	1	1	C or AD	Cosmetics/ Lubricant	(European Commission, 2019c; Bradley and Coulier, 2007)
84	ethylene brassylate	105-95-3	93	47.11	1		C	Cosmetics	(European Commission, 2019c)
85	isopropyl palmitate	142-91-6	85	47.33	1		C	Cosmetics	(European Commission, 2019c)
Ethers									
86	1-methoxy-2-propanol	107-98-2	90	2.04		1	C	Cosmetics/ solvent inks	(European Commission, 2019c; DOW, 2012)
87	1-ethoxy-2-propanol	1569-02-4	82	3.00		1	C	Solvent polymers	(ECHA, 2019b)
88	1-butoxy-2-propanol	5131-66-8	90	9.99	1	1	C	Cosmetics/ solvent inks	(European Commission, 2019c; ECHA, 2019a)
89	2-(2-ethoxyethoxy)ethanol	111-90-0	93	13.14		1	C	Cosmetics/ solvent inks	(Stoye, 2000; European Commission, 2019c)

No	Compound Name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
90	(2-methoxyethyl)-benzene	3558-60-9	93	17.08	1		C	Cosmetics	(European Commission, 2019c)
91	2-phenoxyethanol	122-99-6	93	23.91	3		C	Cosmetics	(European Commission, 2019c)
92	anethole	104-46-1	77	26.74	1		C	Cosmetics	(European Commission, 2019c)
93	diphenyl ether	101-84-8	89	31.46	1	1	C	Cosmetics	(European Commission, 2019c)
94	4-allyl-1,2-dimethoxybenzene	93-15-2	82	32.10	1		C	Cosmetics	(European Commission, 2019c)
95	methyl 2-naphthyl ether	93-04-9	78	33.50	1		C	Cosmetics	(European Commission, 2019c)
Carboxylic acids									
96	acetic acid	64-19-7	90	1.60		1	C	Organic waste	(C. Zhang et al., 2014)
97	propanoic acid	79-09-4	98	2.35		1	C	Organic waste	(C. Zhang et al., 2014)
Phthalates									
98	diethyl phthalate	84-66-2	70	38.73	1		A or C	Plastizicer/ Cosmetics	(PubChem, 2019; European Commission, 2019c)
Others									
99	hexane	110-54-3	84	1.60	1		PD		(Hamid, 2000)
100	pyridine	110-86-1	86	2.86		1	C	Fungi growth	(E. Kaminski et al., 1974)
101	dimethyl trisulfide	3658-80-8	98	10.84		1	C	Rotten food, aroma	(J. K. Parker, 2015)
102	dipropylene glycol	110-98-5	96	14.13		1	C	Cosmetics	(European Commission, 2019c)
103	2-acetyl pyridine	1122-62-9	94	14.59	1		C	Food aroma	(The Good Scents Company, 2018)
104	2,6-diisopropyl naphthalene	24157-81-1	87	41.76	1	1	C	Paper labels	(Geueke, Birgit et al., 2018)
105	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	90	45.53	1		AD	Antioxidant	(M. Biedermann et al., 2014; Bradley and Coulier, 2007)

3.2. Semi-volatile organic compounds

3.2.1. Overall semi-volatile emissions

The chromatograms of PC-HDPE and PC-LDPE show that apparently the amount of SVOCs is higher in the LDPE sample (Figure 4), which is opposite to the results of VOCs emissions depicted in section 3.1.1. The total area under the LDPE chromatogram is around 5 times higher than the total area of HDPE. The identified compounds are divided into three main groups: hydrocarbons, oxygenated and nitrogenous. The 66 % of the total PC-LDPE area corresponds to substances containing oxygen while the remaining area is almost equally represented by hydrocarbons and nitrogen-compounds (around 16 % each). Regarding PC-HDPE, the largest group is also formed by oxygenated compounds amounting to 45 % of the total area. The percentage of hydrocarbons and nitrogen-compounds is also similar in this sample, 26 % and 25 % respectively.

Figure 4. Chromatogram of post-consumer LDPE (purple) and post-consumer HDPE (green) recycled pellets obtained by solid-liquid extraction and GC/MS.

Regarding the volatility of SVOCs, PC-LDPE presents a higher concentration (almost 80 %) of compounds with t_R between 15 and 30 minutes. Less volatile compounds ($30 < t_R < 45$ minutes) represent around 20 % of the total mass. These two groups cover nearly the totality of detected SVOCs since the percentage of substances between 0 and 15 minutes is barely 0.2 %. The PC-HDPE sample shows a similar proportion of compounds in the medium ($15 < t_R < 30$ minutes) and low volatility ($30 < t_R < 45$ minutes) region, around 48 % and 46 % respectively. The remaining fraction corresponds to compounds detected between 0 and 15 minutes (Figure 5).

Figure 5. Profile of SVOCs according to the residence time (tR) that the molecules remain in the HP5 capillary column.

3.2.2. Identified substances

In the sum of the two samples, 7 of all organic compounds detected by GC/MS have been tentatively identified with match quality over 80 % (Table 4). The largest group is represented by esters (no. 14, 20, 22, and 26). All of these substances have been detected in the PC-LDPE sample, and only the last one is present in the PC-HDPE sample. The remaining three substances belong to a different functional groups such as alkylbenzenes (no. 4), azoles (no. 27) and glycols (no. 1). Therefore, in total, 6 substances have been tentatively identified over 80 % in PC-LDPE and 3 substances in PC-HDPE.

Regarding the substances with lower match quality identification, in total, 25 compounds have been identified with a match quality between 65 and 80 % (Table 4). Specifically, 20 substances were found in PC-LDPE and 13 substances in PC-HDPE. In this case, 8 compounds were detected in both samples. The groups with the largest number of substances are esters (no. 13, 15-19, 21, and 23-25) and carboxylic acids (no. 7-9). Other smaller groups are ketones (no. 11 and 12), alkylbenzenes (no. 5 and 6), aldehydes (no. 3), amides (no. 28) and phthalates (no. 29). The rest contain different substances such as 2,2,4,4,6,8,8-heptamethylnonane (no. 30), 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (no. 31) and diphenyl sulfone (no. 32).

Finally, 6 substances have been detected in high concentration, but with a poor match quality (under 65 %). These substances cannot be identified with certainty, however, they are worth to mention due to their high abundance (no. 33-38 in Table 4).

286 Unlike VOCs, the abundancy of SVOCs is based on the concentration of each substance semi-
287 quantified with the internal standard. Nevertheless, the levels of abundancy are the same: low (1),
288 medium (2) and high (3).

Table 4. List of SVOCs tentatively identified by GC/MS originating from post-consumer HDPE (PC HDPE) and post-consumer LDPE (PC LDPE). Q is the match quality percentage, and RT is the retention time. PC means post-consumer source. A= additive; AD=additive degradation product; PD=polymer degradation product; C=contaminant; deg=degradation. Peak intensity: 1=low, 2=medium, 3=high.

No	Compound name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification Type	Origin	Source
Glycols									
1	diethylene glycol	111-46-6	89	9.92		1	AD	Antioxidant	(Bradley and Coulier, 2007)
2	dipropylene glycol	110-98-5	77	10.93		1	AD	Antioxidant	(Bradley and Coulier, 2007)
Aldehydes									
3	2-(phenylmethylene)-heptanal	122-40-7	66	18.49	1		C	Cosmetics	(European Commission, 2019c)
Alkylbenzenes									
4	(1-butylheptyl)benzene	4537-15-9	82	18.31	1	1	C	Surfactant deg	(Kosswig, 2000)
5	(1-ethyldecyl)benzene	2400-00-2	67	19.56	1	1	C	Surfactant deg	(Kosswig, 2000)
6	(1-methylundecyl)benzene	2719-61-1	75	19.91	1		C	Surfactant deg	(Kosswig, 2000)
Acids									
7	dodecanoic acid	143-07-7	71	17.54	1	1	A or C	Processing aid/Surfactant	EU 10/2011 (European Commission, 2019c)
8	tetradecanoic acid	544-63-8	77	19.46		1	A or C	Processing aid/Cleansing	EU 10/2011 (European Commission, 2019c)
9	n-hexadecanoic acid	57-10-3	69	21.18	1	1	A or C	Processing aid/Emollient	EU 10/2011 (European Commission, 2019c)
10	tert-butyl-(4-tert-butylphenyl)phosphinic acid	25097-42-1	71	23.69	1		AD	Antioxidant	(Frontier Laboratories Ltd, 2020)
Ketones									
11	benzophenone	119-61-9	74	18.37		1	A or C	UV absorber/Cosmetics	EU 10/2011 (European

No	Compound name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification Type	Origin	Source
									Commission, 2019c)
12	2-acetyl-5-methylfuran	1193-79-9	75	20.70	1		C	Odor compound	(L. Paravisini et al., 2015)
Esters									
13	ethyl tetradecanoate	124-06-1	72	19.72	1	1	C or AD	Cosmetics/ Lubricant impurity	(European Commission, 2019c; Bradley and Coulier, 2007)
14	2-ethylhexyl salicylate	118-60-5	85	19.94		1	C	Cosmetics	(European Commission, 2019c)
15	methyl hexadecanoate	112-39-0	72	20.86		1	AD	Lubricant	(Bradley and Coulier, 2007)
16	ethyl palmitate	628-97-7	76	21.42		1	C or AD	Cosmetics/ Lubricant	(European Commission, 2019c; Bradley and Coulier, 2007)
17	isopropyl palmitate	142-91-6	69	21.65	1	1	C	Cosmetics	(European Commission, 2019c)
18	propyl hexadecanoate	2239-78-3	70	22.17		1	AD	Lubricant	(Bradley and Coulier, 2007)
19	methyl octadecanoate	112-61-8	72	22.45	1	1	AD	Lubricant	(Bradley and Coulier, 2007)
20	tributyl acetylcitrate	77-90-7	86	23.48		1	A	Plasticizer	EU 10/2011 (Bradley and Coulier, 2007)
21	propyl octadecanoate	3634-92-2	71	23.66		1	AD	Lubricant	(Bradley and Coulier, 2007)
22	methyl abieta-8,11,13-trien-18-oate	1235-74-1	82	24.24		1	AD	Adhesives	(C. Nerin et al., 2013)
23	dodecyl hexadecanoate	42232-29-1	70	28.56		1	AD	Lubricant	(Bradley and Coulier, 2007)
24	glycerol tricaprylate	538-23-8	67	29.43	1		C	Cosmetics	(European

No	Compound name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification Type	Origin	Source
									Commission, 2019c)
25	hexadecyl hexadecanoate	540-10-3	76	33.39		1	AD	Lubricant	(Bradley and Coulier, 2007)
26	octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	2082-79-3	82	35.99	1	1	A	Antioxidant	EU 10/2011
Azoles									
27	bumetrizole	3896-11-5	85	25.62	1		A or C	UV absorber/Cosmetics	EN 10/2011 (European Commission, 2019c)
Amides									
28	13-docosenamide, (z)-	112-84-5	65	27.02	1	1	A	Slip agent	EN 10/2011
Phthalates									
29	bis(2-ethylhexyl) isophthalate	137-89-3	72	26.80		3	A	Plasticizer	(Frontier Laboratories Ltd, 2020)
Others									
30	2,2,4,4,6,8,8-heptamethylnonane	4390-04-9	80	15.05		1	C PD	Cosmetics Polyethylene	(European Commission, 2019c; Bradley and Coulier, 2007)
31	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	79	20.93	1	1	AD	Antioxidant	(M. Biedermann et al., 2014; Bradley and Coulier, 2007)
32	diphenyl sulfone	127-63-9	73	21.07		1	C	Thermosetting plastics	(Tiwari and Mhaisekar, 2019)
Predominant SVOCs with match quality < 65 %									
33	6-octadecenoic acid, (z)-	593-39-5	23	22.67		2	AD	Possible lubricant	(Bradley and Coulier, 2007)
34	ethyl oleate	111-62-6	23	22.81		2	A	Possible plasticizer	(W. Waskitoaji et al., 2012)
35	di-n-octyl phthalate	117-84-0	22	25.49		2	A	Possible plasticizer	(PubChem, 2019)

No	Compound name	CAS No	Q (%)	RT (min)	PC HDPE	PC LDPE	Classification Type	Origin	Source
36	9-octadecenamide, (z)-	301-02-0	33	25.62	1	1	AD	Possible slip agent	(Bradley and Coulier, 2007)
37	methylenebis(2,4,6-triisopropylphenylphosphine)	EPA-159591	62	34.11	1	1	AD	Possible antioxidant	(Bradley and Coulier, 2007)
38	methyl 3,5-dicyclohexyl-4-hydroxybenzoate	55125-23-0	23	36.14	3	3	AD	Possible antioxidant	(Bradley and Coulier, 2007)

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3.3. Compounds identified by headspace and solvent extraction techniques

Overall, 10 substances were identified by both techniques, VOCs and SVOCs analyses, including 2,2,4,4,6,8,8-heptamethylnonanone, benzophenone, 2-(phenylmethylene)heptanal, ethyltetradecanoate, ethylpalmitate, isopropylpalmitate, (1-butylheptyl)benzene, (1-ethyldecyl)benzene, dipropylene glycol and 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione. In detail, 2,2,4,4,6,8,8-heptamethylnonanone, 2-(phenylmethylene)heptanal, ethyltetradecanoate, (1-butylheptyl)benzene and dipropylene glycol were identified in the same samples by both techniques, headspace and solvent extraction. However, isopropylpalmitate, (1-ethyldecyl)benzene and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione were only identified in the post-consumer HDPE sample by means of the analysis of VOCs but in both samples when analyzing with the SVOCs technique. The reason why these organic compounds may not appear in PC-LDPE with HS-SPME-GC/MS technique may be due to the low volatility of these compounds. Additionally, benzophenone and ethyl palmitate were identified in both samples when using VOCs analysis and uniquely in the post-consumer LDPE sample when applying the SVOCs analysis.

4. DISCUSSION

Recycled plastics demand is on the increase in EU due to factors like social pressure and special European incentives and support measures. In 2015, the EU launched a pledging campaign to ensure that 10 million tons of recycled plastic are used for new products manufacturing by 2025, which means to triple the demand (European Commission, 2018). In total, 70 companies and business associations have shown their interest in participating. Among them, important brand owners of food and non-food applications can be found (e.g., Danone, LIDL, P&G, Unilever, etc.). Despite the efforts made, it has been estimated that in 2019 only 6.4 million tons were recycled (European Commission, 2019a). The main barriers to increase plastics' recyclability are the low quality of recycled plastics and the lack of traceability, which brings uncertainty about the chemical composition.

Food packaging covers over 50% of the European plastic market (Eriksen, Marie Kampmann et al., 2019). Therefore, introducing a recycled content in this application can boost the demand, as well as economic and environmental benefits. Nevertheless, quality and safety requirements are very high, and all recycling processes must be authorized by EFSA. Until now, around 90% of approved

technologies are made for PET recycling. Regarding polyolefins, 4 processes have been approved by the EFSA Panel on food contact materials, enzymes, flavourings and processing aids (CEF) (2010; 2012; 2013b; 2013a) for recycling of PP and HDPE crates for fruits and vegetables. Additionally, another recycling process was approved by the EFSA (2015) for recycling milk and juice bottles, as well as trays for fruit and vegetables or animal products made of HDPE. Recycling of polyolefins for food contact applications is progressing, albeit slowly. Therefore, most recycled plastics must be allocated for non-food applications. However, more forgiving applications and lack of specific legislation on using recycled plastics do not mean that there is no concern about chemical contaminants present in the recycled pellets, especially, when they come from post-consumer waste. For instance, Burberry, a British luxury fashion house, has elaborated a list of product restricted substances applicable to any finished product or raw material used (Burberry, 2018). The list includes bisphenol A, chlorobenzenes, chlorophenols and phthalates among others. Consumer safety is also important in the hygienic sector. For example, P&G (an American multinational specialised in personal care and hygienic products) claims that they do not use ingredients like alkylphenols, benzenes, bisphenol A and PAHs (polycyclic aromatic hydrocarbons) (Procter & Gamble, 2020). As all these substances could migrate from the plastic package produced with recycled pellets, studying the composition of post-consumer recycled plastics is imperative when it comes to high added value application, both food and non-food.

4.1. Origin of the identified substances

The different substances identified in the post-consumer HDPE and LDPE samples were categorized by their origin in four groups, including additives, polymer degradation products, additives degradation products and contaminants. The additives are considered IAS because they are part of the original formulation of the plastic product. The NIAS are substances originated from the additives and material degradation and contaminants migrating from the environment or filled goods (Geueke, B., 2018). The contaminants identified in the PC-HDPE and PC-LDPE samples are mainly associated with cosmetics, food aromas, organic waste or inks, as detailed hereafter.

The total number of compounds (VOCs and SVOCs) detected in the PC-HDPE sample is higher than the number of compounds in the PC-LDPE sample (105 versus 79). The contaminants constitute the largest group in both samples and most of these substances were detected by HS-SPME-GC/MS technique. The number of contaminants in the PC-HDPE sample is almost twice the number of contaminants in the PC-LDPE sample. Regarding the additives and their degradation

products, the largest number was detected in the PC-LDPE sample (32 versus 21). In this case, the solvent extraction followed by GC/MS technique was more sensitive. Finally, the polymer degradation products were mainly detected in the volatile fraction and the number of substances of this group is similar in both samples (7 in PC-HDPE and 5 in PC-LDPE).

This imply that existent technologies capable of decreasing the content of VOCs in polymers could reduce the concentration of NIAS in the recycled plastics, such as applying high temperature and high vacuum during extrusion (EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF), 2015; EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF), 2019) or the Extruclean process developed for the removal of hazardous substances in PE packaging using supercritical CO₂ during extrusion (García-Muñoz, 2017)

4.1.1. Additives

Only 6 of the substances identified (quality>80 %) in the volatile fraction (Table 3) are associated with additives (no. 39, 50, 54, 55, 87 and 88). Of which, 2 (no. 54 and 55) are included in the European Union list of substances allowed to be used in materials intended to come in contact with food (Regulation EU 10/2011 with reference no. 300 and 325 respectively). Likewise, butylated hydroxytoluene (no. 4) and methyl benzoate (no. 60) were identified with a match quality 65-80 % and appear as antioxidant additives used for food packaging applications according to Regulation EU 10/2011 (no. 315 and 171 in the positive list, respectively). In addition, the plasticizer diethyl phthalate (no. 98) was identified with a match quality lower than 80 % as well, but this is not included in the positive list of additives from the Regulation EU 10/2011.

Regarding semi-volatile fraction, a total of 10 substances were related to plastic additives, three of which with a match quality higher than 80 % (no. 20, 26 and 27). The substances with a match quality between 65 and 80 % reported as additives are 6 (no. 7, 8, 9, 11, 28, and 29), of which only the latter one is not included in the list from Regulation EU 10/2011. Additionally, possible additives found as major compounds but identified with an approximate molecular structure in the chromatogram (match quality < 65 %) are ethyl oleate (no. 34) and di-n-octyl phthalate (no. 35). These two are neither included in the list from Regulation EU 10/2011. The additives which do not comply with the food contact regulation usually come from less demanding applications and, therefore, might pose safety issues to consumers of recycled products. In addition, the presence of composite materials containing inks, coating, functional barriers, etc. increases the number of

substances in recycled plastics. Nevertheless, the amount of multilayer and composite materials in the studied samples is negligible since these plastics are usually removed during the sorting stage owing to their low recyclability (O. Horodytska et al., 2018). In sum, the lack of traceability in post-consumer plastic waste represents currently an obstacle for the implementation of the circular economy through closed-loop recycling (McKinnon et al., 2018).

The additives identified in this study are mainly antioxidants, plasticizers and processing aids, as well as a UV absorber and slip agent to a less extent (see Table 3 and Table 4).

4.1.2. Polymer degradation products

Polymer and additives degradation products are usually generated due to excessive heat and irradiation energies (C. Nerin et al., 2013). In general, the major functional groups obtained in the screening of volatile substances from LDPE and HDPE are ketones and aldehydes, followed by alkanes and alkenes which can be formed as a result of thermal oxidation of the polymer (Bradley and Coulier, 2007). In total, 8 substances were tentatively identified as polymer degradation products in the volatile fraction (no. 7, 8, 32, 33, 35, 36, 37 and 99 in Table 3). Only 2,2,4,4,6,8,8-heptamethylnonanone (no. 30 in Table 4) was detected with the analysis of SVOCs.

4.1.3. Additives degradation products

Regarding additives degradation products, 7 VOCs (Table 3) were identified, all of them with match quality over 80 % (no. 13, 39, 44, 79, 80, 83 and 105). In the semi-volatile fraction (Table 4) a total of 17 substances were classified as additive degradation products. Of which, 2 substances were identified with match quality over 80 % (no. 1 and 22), 11 substances between 65 % and 80 % (no. 2, 10, 13, 15-16, 18, 19, 21, 23, 25, and 31) and, finally, 4 substances under 65 %, (no. 33, 36, 37, and 38). The chemical structure of the substances with low quality match are approximate. Nevertheless, based on their chemical structure, it has been suggested that they are possible degradation products of lubricants, slip agents and antioxidant additives (see Table 4). The substance 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione appears in both VOCs and SVOCs fractions (no. 105 in Table 3 and no. 31 in Table 4).

4.1.4. Contaminants from external sources

This is clearly the predominant group of substances among all the VOCs identified. The majority of esters were identified as contaminants originating from cosmetics ingredients, just to name some,

methyl lactate (no. 53), hexyl acetate (no. 56) and dimethyl butanedioate (no. 57), among others (no. 50 - 85). Another contamination related to cosmetic ingredients are α -methylionone (no. 40), 3-(4-Isopropylphenyl)-2-methylpropionaldehyde (no. 11), α -amylcinnamaldehyde (no. 12), (phenylmethylene)octanal (no. 14) and dipropylene glycol (no. 102). In addition, all the identified ethers from the volatile fraction are registered in the CosIng database as cosmetics ingredients (no. 86-95). Moreover, the group of alkylbenzenes (no. 15-30) may belong to breakdown products produced by the degradation of alkylbenzene sulfonates, widely used as anionic surfactants in detergents and cleaning agents (Kosswig, 2000). Substances that were identified as polymer degradation products or additives may also be related to contamination of cosmetics ingredients according to the CosIng database (no. 4, 7, 8, 33, 36, 43, 54, 55, 60, 80, 83 and 98). Regarding contamination related to food, the lactones (no. 45-49) as well as 5-methylfurfural (no. 6), furfural (no. 5) and methyl hexanoate (no. 51) can derive from food flavors as well as from cosmetics ingredients. However, the presence of furfuryl alcohol (no. 1), methyl pyruvate (no. 52) and 2-acetyl pyridine (no. 103) is uniquely associated with food flavors. The VOCs associated with rotten food products include methyl-2-ethylhexanoate (no. 58), acetic acid (no. 96), propanoic acid (no. 97), pyridine (no. 100) and dimethyl trisulfide (no. 101). Other volatile substances (no. 86-89) are used as ink and polymer solvents as well as in cosmetics and, therefore, the derived contamination could be originating from these three sources. Additionally, the compound 2,6-diisopropyl-naphthalene (no. 104) may come from paper labels that remain in contact with the polymer after being recycled.

Some of the VOCs identified in this study were previously reported by Strangl et al. (2017; 2018; 2019) and Cabanes et al. (2020) qualified as odor causative substances originating from post-consumer LDPE and HDPE; namely, acetic acid, dimethyl trisulfide, anethole, anisaldehyde, octanal, nonanal, 2-methoxynaphthalene, 2-acetyl pyridine, as well as an array of lactones and ionones.

Among the SVOCs, 14 substances were tentatively identified as plastic contaminants, 3 with match quality over 80 % (no. 4, no. 14, and no. 27) and 11 with match quality between 65 % and 80 % (no. 3, no. 5-6, no. 7-9, no. 11-12, no. 17, no. 24, and no. 32). Again, several substances (no. 27, no. 11, and no. 7-9) have been classified as additives and contaminants simultaneously. This is because these substances appear in several data sources, for instance, in the list of substances permitted as additives for food packaging (EU 10/2011) and in the CosIng database (cosmetic

ingredients). Most contaminants belong to the group of cosmetics, including surfactants, cleaning agents and emollients, as well as to their degradation products. Other contaminants can be incompatible thermosetting plastics as a result of cross-contamination, for instance, diphenyl sulfone (no. 32).

4.2. Distribution of identified compounds regarding source generation and material

4.2.1. Concentration of volatile organic compounds identified in PC-LDPE and PC-HDPE

The peak areas of the VOCs from PC-HDPE and PC-LDPE samples is presented in Figure 6, where the compounds are classified in 4 groups: contaminants, polymer degradation products, additives and additives degradation substances. In the PC-HDPE sample, the area of the chromatogram belongs mainly to the VOCs identified as contaminants, followed by polymer and additive degradation substances and finally the compounds classified as additives present the lowest content in the light fraction. In the PC-LDPE sample, as explained in the section 3.1.1, the total area is much lower than that corresponding to PC-HDPE, but the distribution of the compounds is quite the same except for the additives than in this case their concentration in the sample is higher compared to the additives degradation products and the polymer degradation products.

Figure 6: Chromatogram area of VOCs related to contaminants, polymer degradation, additives and additive degradation products in post-consumer HDPE and LDPE

4.2.2. Concentration of semi-volatile organic compounds identified in PC-LDPE and PC-HDPE

The use of internal standards allows performing a semi-quantification of the concentration (substance weight per sample weight). Regarding the concentration of SVOCs, it has been found

that the overall mass of substances (reported in Table 4) per mass of the plastic sample is around 4 times higher in PC-LDPE than in PC-HDPE. The group of additives shows the highest concentration, followed by additive degradation products (Figure 7). The concentration of contaminants is significantly lower, and the concentration of polymer degradation products is almost negligible. This is due to the fact that the majority of these substances are volatile and therefore appear in the light fraction. The concentration of the substances identified with low quality (under 65 %) was also considered for the overall mass calculation.

The most abundant additive in the PC-LDPE sample is bis(2-ethylhexyl) isophthalate (no. 29), commonly used as a plasticizer, with 272.0 µg/g, approximately. As mentioned in section 4.1, this additive is not included in the positive list of additives accepted for food contact materials manufacturing (EU 10/2011). Therefore, its migration from the final recycled product should be studied together with an appropriate risk assessment. Two additional substances with high concentration were identified as possible additives although with a match quality lower than 65 %: ethyl oleate (no. 34) with 160.0 µg/g and di-n-octyl phthalate (no. 35) with 170.0 µg/g. Regarding additive degradation products, the most abundant substances were identified with low match quality: 6-octadecenoic acid, (Z)- (no. 33) with 146.3 µg/g and methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38) with 343.7 µg/g.

Among the additives tentatively identified in the PC-HDPE sample, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 26), used as an antioxidant, presents the highest concentration (around 15.0 µg/g), followed by (Z)-13-docosenamide (no. 28), with nearly 14.0 µg/g. Both substances appear on the Union list of Regulation EU 10/2011, however, only the former presents a specific migration limit (SML), which determines the maximum amount permitted of the additive accumulated in the packed food. The slip agent (Z)-13-docosenamide, must comply with an overall migration limit of 10 mg of total constituents per dm² of the food contact surface. Additives degradation products with the highest concentration were identified with low match quality: 9-Octadecenamide, (Z)- (no. 36) with 23.0 µg/g, methylenebis(2,4,6-triisopropylphenylphosphine) (no. 37) with 60.0 µg/g and methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38) with 239.0 µg/g.

Figure 7. Concentration of substances detected by solid extraction followed by GC/MS according to their nature.

4.3. Differences between post-consumer LDPE and HDPE

The results show that the PC-HDPE sample contains a high number of contaminants such as cosmetic ingredients including fragrances and surfactants. This is because HDPE is commonly used in home and personal care packaging production. Organic compounds from the packaged product are absorbed into the plastic container lowering its potential to be upcycled. It has been shown in this study that current recycling technologies based on cold wash cannot ensure that the contaminants are removed. The risk of migration of hazardous and undesired substances from the recycled products hamper the implementation of the circular economy due to irreversible quality loss. Therefore, the development of more sophisticated recycling processes is essential for material decontamination.

Regarding PC-LDPE, plastic additives and their degradation products are present in high concentrations. The mixture of plastics from different applications during waste collection increases the variety of additives in the recycled material. A few of them, for instance, some phthalates, can affect human health (S. Benjamin et al., 2017). Thus, recycled pellets cannot be used in high-value applications such as food packaging. In this case, removing the undesired substances by washing is even more challenging. Therefore, the solution to facilitate the upcycling of plastic waste could involve source separation and restriction on the use of certain additives that cannot be applied to produce food packaging materials. Additionally, a significant number of unwanted substances were found in PC-LDPE, some of which could appear during the use phase of the original product (for instance, food leftovers on the packaging), and others may appear due to

cross-contamination in waste containers. This is the case of cosmetics and surfactants which were identified in PC-LDPE but are more commonly used in the products packed with rigid HDPE and flexible multilayer films. The last ones were removed from the waste stream during the sorting stage due to their low recyclability.

5. Conclusion

The results of this study show that the substances classified as contaminants and polymer degradation products are mainly volatile, thus HS-SPME sampling technique should be used for their identification. On the other hand, additives and their degradation products have low volatility and, therefore, solvent extraction appears to be the most appropriate sampling technique. GC/MS has proven to be an effective analytical technique for the identification of VOCs and SVOCs. Nevertheless, in future research studies, complementary methods such as liquid chromatography (LQ) should be used to identify larger compounds.

Recycled post-consumer LDPE and HDPE NIAS differ in amount and source which could be given by their distinguished applications. LDPE is more generally used for flexible packaging while HDPE is usually applied for bottles of detergents and cleaning agents. Accordingly, the contaminants obtained in the HDPE sample show a greater amount of cosmetic ingredients and surfactant oligomers due to its previous use. In the case of LDPE, the variety and concentration of additives and their degradation products are higher than in the HDPE sample, which could be an obstacle to its reuse in high added value applications.

In sum, the key to recovering plastics materials could not be only in the upgrading of the recycling technology but also in the presorting at household levels to avoid cross-contamination. Or even in the implementation of a general regulation for additives in plastics to foster the transition to a circular economy. For instance, the separate collection schemes are intended to gather plastics used for food and non-food packaging, which are subsequently sorted by type. These materials cannot be recycled in a closed-loop due to the high variety of additives likely to be present. As the regulation for food contact materials is more restrictive, uniquely the additives under Regulation EU 10/2011 should be used for plastic packaging manufacturing. Thereby, non-food packaging could be used for food packaging after recycling, covering a broader range of applications.

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- 134 substances were tentatively identified in HDPE and LDPE recycled pellets.
- The origin of each substance was studied, and four main groups were established.
- The variety of additives used in LDPE manufacturing should be reduced.
- Separate collection and decontamination should be implemented for rigid HDPE.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: