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Development and application of an analytical method to quantify odour removal in plastic waste recycling processes

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ABSTRACT

Europe is strongly committed to the recycling of plastics, especially packaging. In the development of closed loop recycling processes, recyclates must have appropriate properties, including lack of odour. The main objective of this study was to develop a technique to qualitatively and semi-quantitatively analyse the volatile contaminants in these complex plastic waste matrices before and after washing procedures. Three sampling methods were explored, SPME and purge and trap methods (activated carbon with solvent desorption and Tenax-TA with thermal desorption). All analyses were then carried out using gas chromatography – mass spectrometry. SPME was not repeatable due to the heterogeneity of the waste samples and the static character of the method. Solvent desorption with CS_2 (RSD 14,5 %) and thermal desorption (RSD 13,4 %), were capable of measuring the removal efficiency of pollutants in a semi-quantitative way. A broad spectrum of chemically different, but mostly apolar volatiles can be detected. In addition, it became clear that also the analysis of the less volatile components is essential, as these are strongly adhered to the hydrophobic polymer matrix. A post-consumer film waste stream was analysed, before and after washing and pelletizing. A general decrease of 97 % and 44 %, was measured with respectively thermal and solvent desorption for the screened components. However, after reprocessing potentially odour-causing compounds are again released or formed, showing the complexity of odour removal processes in plastic recycling.

1. Introduction

Reuse and recycling of plastics are key in the transition towards a circular economy. Europe targets a 70 % recycling rate for packaging waste by 2030, and specifically 55 % for plastic materials (European Council, 2018). To reach the ambitious European target, a more advanced recycling of post-consumer packaging materials is inevitable.

Indeed, post-consumer polymers, especially those originating from household waste, are typically a mixture of different plastic types (Ragaert et al., 2017). Besides this cross contamination, the particular waste plastics are dirty, contaminated and have mostly undergone degradation. Possible non-plastic constituents are inks, coatings, additives and adhesives. These components are not necessarily part of the basic polymer structure, but can also be added during processing. Other impurities (dust, soil, grease, organic waste) can adhere to the polymer surface during its use phase (Horodytska et al., 2018). All the aforementioned contaminations cause recycling issues, such as immiscibility of polymers during reprocessing, glues from labels, lack of freedom in colours of recycled products due to mixtures of inks resulting in a dark colour, etc (Horodytska et al., 2018; Ragaert et al., 2017).

One particular problem is the odour of plastic waste. The uptake and degradation of polluting substances, and breakdown of the polymer chains and added substances during the plastic life cycle lead to the formation of a complex mixture of contaminants, which are often odour-causing volatiles. Presence of such odorous constituents is clearly one of the reasons why large volumes of plastic waste are currently only suitable for downcycled applications (Horodytska et al., 2020).

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Therefore, there is a growing interest in more advanced washing procedures. To quantify the efficiency of washing processes however, it is not clear yet which analytical method is most suitable to measure this complex mix of potential odour-causing components on plastic waste.

The domain of odour and flavour research mainly focuses on food and beverages analysis (Capelli et al., 2008; Souza-Silva et al., 2015; Woolfenden, 2010, 1997) and environmental air, water and soil monitoring (Callejón et al., 2016; Grosch, 1994; Jeleń et al., 2012; Song and Liu, 2018; Zellner et al., 2008). Studies on odour characterisation and removal in plastic waste recycling are scarce (Strangl et al., 2020, 2019, 2018, 2017). Especially plastic waste is highly challenging as a consequence of its heterogeneous physicochemical properties, such as specific shape (from trays to films to pellets), polarity (from PE to PVC) and additivation including inks and possible degradation products that are also stated to cause odour (Bledzki et al., 1999; Hodgson et al., 2000; Huber et al., 2002; Welle et al., 2002). Because of this complexity, and the fact that plastic recycling is a rather new research field, there is a lack of insight in the entire odour profile of plastic waste and the analysis thereof.

Typically volatile organic compounds (VOC) can be divided into three groups based upon volatility defined by their boiling temperature (Tb): very volatile organic compounds ($Tb < 100°C$), volatile organic compounds ($100°C < Tb < 240°C$) and semi-volatile organic compounds ($240°C < Tb < 400°C$) (Ahn et al., 2011). The whole range of components is not easy to remove during recycling and the resulting organoleptic properties play an important role in the suitability of these materials to be recycled in higher quality applications. However, it should be noted that not all VOCs have a smell. Odour strongly depends on the concentration and chemical structure of the specific component. VOCs often occur together and can intensify each other in terms of smell (Buettner, 2017).

VOCs are known to be measurable by gas chromatography (GC). However, due to the low concentrations of the volatiles and the heterogeneity of the waste, a good sampling technique is essential, in which the concerned components are extracted and concentrated. Solid-phase microextraction (SPME) followed by GC-analysis proved itself as a rapid, inexpensive and solvent-free method for the determination of volatile components from both solid and liquid matrices. Most research on this topic has focused on the thermo-oxidative degradation products originating from plastics, such as PE and PP (Hopfer et al., 2012), LDPE films (Hakkarainen et al., 1997), agricultural film (Khabbaz et al., 1999, 1998; Khabbaz and Albertsson, 2000) and recycled LDPE (Stangenberg et al., 2004), virgin and recycled polyamide 6.6 (Gröning and Hakkarainen, 2002, 2001), PMMA (Rogalewicz and Voelkel, 2005), polysulfide (Vance et al., 2006) and foamed polysiloxane rubber (Hall and Patel, 2006). Research was also conducted on packaging materials, as these should not transmit undesirable pollutants to the packaged good (Vera et al., 2014). The quantitative analysis of volatile organic compounds with head-space (HS)-SPME was successfully executed on multilayer (cellulose/PE/aluminum/PE) packaging by Ezquerro et al. (2003a, 2003b). Ortiz and Tena (2006) used headspace SPME coupled to GC-MS for the identification of volatile compounds originating from cosmetics, migrated in polyethylene packaging material. HS-SPME was also used in the work of Sides et al. (2001) to identify the components responsible for off-odour in pharmaceutical packaging. More recently the SPME technique was applied for the analysis of recycled PET and HDPE packaging (Dutra et al., 2011), PE and PVC cling films (Panseri et al., 2014) and LDPE and LLDPE packaging (Cozzi et al., 2018).

Extraction of the volatile components present on plastic waste, is also possible by using dynamic headspace sampling, in which the compounds are captured on traps by flushing the material. In the work of Yamashita et al. (2009, 2007) the VOC emissions of heated virgin (LDPE, PP and PS) and waste pellets are sampled on thermal desorption tubes and analyzed by GC-MS. Fabris et al. (2010) used Tenax-TA tubes followed by n-hexane elution for the measurement of volatiles present in post-consumer PET samples. Besides these direct headspace sampling techniques, the use of solvents to extract the contaminants directly from the plastic matrix, can be applied. Direct solvent extraction was used for the identification of contaminants in post-consumer HDPE (Camacho and Karlsson, 2000; Welle, 2005). More recently, Strangl et al. (2019, 2018, 2017) did an extensive characterization and quantification of the odorants present in post-consumer packaging waste, by means of solvent extraction followed by solvent assisted flavour evaporation (SAFE). The odour profile and its intensity in different streams was examined using sensory evaluation with trained panelists and GC-Olfactometry. Most of these studies are focused on the qualitative determination of contaminants and their odour character. Quantitative description and comparison require the use of more expensive and time-consuming methods like odour panels, stable isotope dilution analysis (SIDA) or comparative odour extract dilution analysis (cOEDA).

The aforementioned papers give a good overview of different potential odorous substances, from virgin and in some sources also from waste plastics. However, the growing interest in the recycling of heavily contaminated post-consumer plastics goes along with the demand for a technique capable of measuring odour removal of a wide range of odour-causing constituents during washing procedures. It is essential that such a technique is fast, reliable and robust, as each plastic waste stream significantly varies in composition.

The main objective of this study is therefore the development of a sampling method coupled with GC-MS analysis towards measurement of potentially odour-causing contaminants on complex plastic waste streams. Therefore, it is important to get insight in the range of different contaminants present and their (physico)chemical diversity. This is important towards the determination and optimization of efficiency of possible washing procedures to remove the odour. Three sampling techniques (SPME, sampling on activated charcoal followed by $CS2$ desorption and sampling on Tenax-TA followed by thermal desorption) are investigated with a view to their potential to quantify removal efficiency of the pollutants. Two post-consumer plastic film waste streams and an agglomerated material thereof, are used in the development of the dynamic sampling methods and subsequent GC-MS analyses. Furthermore, the techniques are applied in a case study to monitor the potential odour-causing components throughout a recycling chain. This application takes into account dirty mixed plastic films, the washed films and the pellets after regranulation from a waste processing company.

2. Materials and methods

2.1. Chemicals and standards

All used chemicals were of analytical grade (purity of > 98 %) and were applied without any preceding purification. A C7-C40 alkane standard (Supelco) was used to determine the Kovats indices. For the solvent desorption method acenaphthene-d_{10} was used as an internal standard. The internal standard toluene-d_8 was utilized in the thermal desorption method.

2.2. Plastic waste materials for method development

Two waste streams are chosen that originate from operational large scale anaerobic digestion plants in Belgium (Waste stream 1) and France (Waste stream 2). The streams mainly consist of flexible post-consumer plastic packaging waste. We have also used the agglomerated version of Waste stream 1 to take into account the formed components after potential thermal degradation. These materials are selected for development of the analytical methods. Table 1: shows an overview of the used materials.

2.2.1. Waste stream 1 sample

The first waste stream is plastic waste originating from source separated food waste. Food products are de-packed, after which the organic fraction goes to anaerobic digestion. The waste plastic packaging could potentially be recycled. This stream consist mainly of plastics (> 70 wt%). In addition, it contains smaller fractions of organic material, inert materials, wood and textiles. Based on our analysis by Fourier-transform infrared spectroscopy (FTIR), the plastic fraction is composed of PE, PP, PET, PS, PA and multilayers.

2.2.2. Waste stream 2 sample

The second waste stream is the light fraction (mainly plastics) originating from municipal solid waste collected in France. This municipal solid waste is anaerobically digested – after preliminary purification. Afterwards the non-digestible impurities are separated in a light and heavy fraction. This light fraction can be divided into plastics (about 50 %), textiles, wood, inert materials, organic materials and a fraction smaller than 5 mm. These small particles mainly consist of plastics, fine organic material and sand. The plastic fraction comprises PE, PP, PET, PS, PVC, multilayer and others.

2.2.3. Agglomerated material

This material originates from Waste stream 1. The plastic waste stream underwent a water sink-float step, after which the light fraction was compacted into agglomerated material (Plastcompactor HV (Herbold)). It is therefore expected to contain mostly polyolefins.

2.2.4. Case study

To follow the odour profile throughout the plastic recycling chain, we have sampled three streams in a Belgian waste processing company (Table 1:). The plastic film waste (dirty films) is first rinsed and then passes a friction washer and sink-float system, all with tap water. The film material is then flash dried using hot air (washed films). Finally, these materials are regranulated using an extruder at 200°C with vacuum degassing (regranulated material).

2.3. Sampling

All plastic waste samples (2-3 kg) were shredded (MDS 340/150 (Hellweg Maschinenbau)) to a size of less than 5 mm. In that way uniform and more homogeneous samples were obtained. Glasswork used during sampling, was always dried and preconditioned in an oven to avoid contaminations.

2.3.1. Headspace – solid phase micro extraction

Two SPME fibres, 100 µm Polydimethylsiloxane (PDMS) and 75 µm Carboxen/Polydimethylsiloxane (CAR/PDMS) (fused silica fibre core, Supelco), were used and compared. Prior to sampling the fibres were conditioned at respectively 250°C and 300°C. Blank tests were performed to exclude carry-over. Three gram of waste was introduced in a 40 ml vial and sealed with a Mininert valve. Before SPME fibre extraction, the vials were preconditioned at 50°C in a thermal bath for 5 min. Then, the fibre was introduced in the headspace of the vial for 15 min, still in the thermal bath (50°C). The loaded fibre was desorbed in the inlet of the GC apparatus (300°C) through a Supelco direct type, unpacked liner with straight design (Figure 1:a).

2.3.2. Purge and trap followed by solvent desorption

For the purge and trap method, 3 g of waste material was weighed in 40 ml vials. The vials were preconditioned at 60°C in a thermal bath for 5 min. Next, an Activated Charcoal (AC) Tube Type NIOSH (Dräger) was used to adsorb the (semi-)volatiles of the waste fraction (Figure 1:b). Focus is on the contaminants present in the headspace of the plastics, as these contribute to the odour profile of the materials. The AC tubes have a 100 mg adsorption layer of coconut shell charcoal and a 50 mg backup layer. Hereby, the vial was flushed with pressurized air at a constant flow rate of 100 ml/min during 60 min. Then, the 100 mg adsorption layer (eventually also the backup layer) were transferred into 1,5 ml microvials. 1 ml of CS_2 is added to the vials in order to desorb the adsorbed (semi-)volatiles. The CS_2 is spiked with the internal standard acenaphthene-d_{10} to a concentration of 50 ppm. This internal standard was chosen because of the targeted higher boiling components in this method. The microvials are then sealed with PTFE caps and allowed to desorb for 30 min with intermittent shaking. Finally, 1 µL of CS_2 was injected (splitless) in the inlet of the GC device through a Supelco split/splitless type, wool packed liner with single taper design.

2.3.3. Purge and trap followed by thermal desorption

As a preparation of thermal desorption, 3 g of waste was introduced in a gas washing bottle connected on one side to a Tedlar bag filled with nitrogen gas and on the other side to a sampling pump (GilAir 3 Personal Air Sampler). Between the gas washing bottle and the pump, a Tenax sorbent tube (Tenax-TA, mesh 35/60) was installed (Figure 1:c). All connections were made of Teflon. The Tenax-TA sorbent tubes were conditioned for 1 h at 300°C under helium flushing. The tubes were then spiked with the internal standard Toluene-d_8 (10.8 ng), according to the procedure described in (Demeestere et al., 2008). Again, the samples were preheated for 5 min at 60°C. The (semi-)volatiles were actively pumped on the Tenax-TA tubes for 15 min at a flow rate of 10 ml/min.

2.4. Analysis

2.4.1. SPME-GC-MS and solvent desorption-GC-MS

The SPME and solvent desorption measurements were performed on an Agilent 6890 GC coupled to Hewlett Packard mass selective detector 5973. NIST mass spectral library was used for compound identification. More information on component identification is given in the supplementary material. For the CS_2 samples the automatic injector 7683 was used. The GC apparatus is equipped with a cross-linked (5%-Phenyl)-methylpolysiloxane (HP-5ms, Agilent) column (30 m × 0,25 mm, 0,25 µm). The column oven temperature was initially programmed at 50°C and kept at this temperature for 1 min. Next, the temperature increased at a rate of 5°C/min to 175°C and held for 1 min. Further, the temperature ramped to 325°C at a rate of 25°C/min. The total run time of the analysis amounted 33 min. The components were separated using helium as a carrier gas at a constant flow rate of 1 ml/min. When measuring solvent desorbed samples the solvent delay was set at 4 min. The measurements were done in scan and Selective Ion Mode (SIM) for the semi-quantitative analysis. The components and their respective ions were selected based on the outcomes of the SPME analysis. The output signals were processed in Instrument Analysis MSD Chemstation (Agilent).

2.4.2. TD-GC-MS

The analytes, preconcentrated on the Tenax-TA sorbent tubes, were desorbed using a Unity series 2 Thermal Desorption system (Markes). Hereby, the tubes were first prepurged with helium (20 ml/min) for 2 min. Next, thermal desorption was performed for 10 min at 260°C and a helium flow rate of 20 ml/min. The desorbed analytes were captured on a cold trap (-10°C) filled with Tenax-TA 35/60. The refocused analytes were then flash-heated (280°C) and transferred under a split flow of 40 ml/min to the GC apparatus (Focus GC, Thermo Scientific) equipped with a 100 % polydimethylsiloxane capillary column (FactorFour VF-1ms) (30 m × 0,25 mm, 1 µm). The samples were separated under constant pressure (50 kPa) of the helium flow. The initial oven temperature was set at 35°C and held for 10 min, then increased to 60°C (2°C/min). Next, ramped to 170°C (8°C/min) and finally heated to 240°C (15°C/min) and maintained at this temperature for 10 min. The GC was coupled (240°C) with a DSQII Single Quadrupole MS (Thermo Scientific). For the first 10 min ion masses between 15 – 300 (m/z) were recorded in full scan mode. Afterwards, the mass range was narrowed to 29 – 300 (m/z). Data processing was done using Xcalibur 2.2 software (Thermo Scientific).

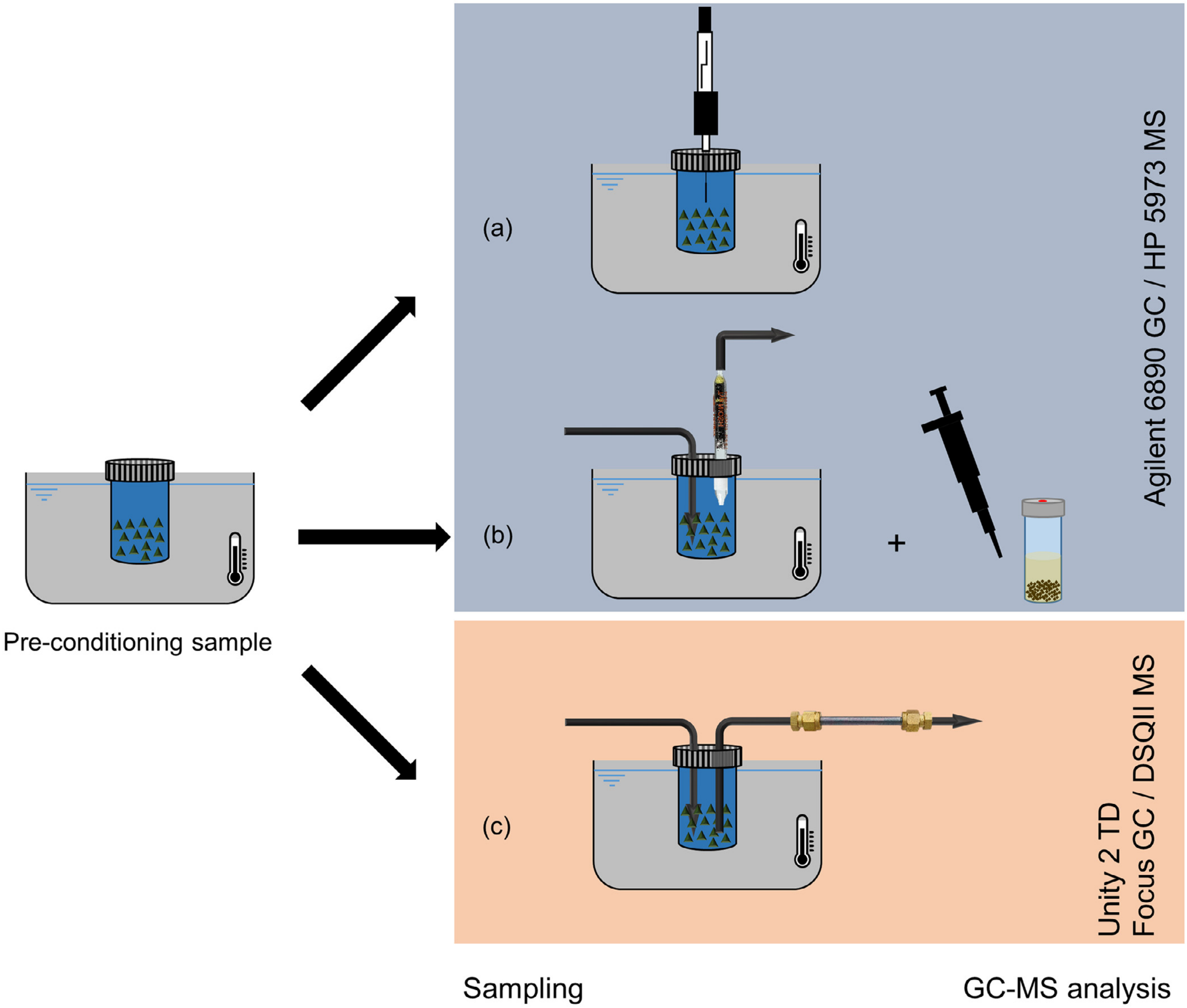

Fig. 1.. Overview of the applied sampling techniques: (a) SPME sampling; (b) Activated charcoal sampling and solvent desorption; (c) Sampling on Tenax-TA tubes and thermal desorption.

3. Results and discussion

3.1. Assessment of the sampling methods

This research compares three sampling techniques, prior to GC-MS analysis, capable of measuring the potentially odorous components in the headspace (HS) of complex plastic waste matrices in a semi-quantitative way. Three sampling techniques are explored: HS-SPME, active sampling on activated charcoal followed by solvent desorption (CS_2) and active sampling on Tenax-TA tubes followed by thermal desorption.

3.1.1. SPME

The HS-SPME-GC-MS technique shows that it is possible to identify (Kovats indices and mass spectra) a wide range of (semi-)volatiles in a fast way. The efficiency of SPME sampling depends on multiple parameters, such as type of fibre, extraction temperature and time, humidity and type of matrix (Dutra et al., 2011; Ezquerro et al., 2002; Ortiz and Tena, 2006). We compared two types of fibres, a CAR/PDMS fibre (75 µm) and a PDMS fibre (100 µm) (Fig. 2). The PDMS fibre is an absorbent type of fibre, in contrast to the CAR/PDMS type, which captures components by ab- and adsorption. Due to the adsorbent character, a limited number of active sites are available on the CAR/PDMS fibre. The CAR/PDMS fibre showed in comparison to the PDMS type good capture for the faster eluting compounds (15 min at 30°C) (Fig. 2a/2b). The more volatile components, like ethanol, acetic acid, 1-butanol and pentanal, were indeed identified with GC-MS on the CAR/PDMS fibre. These compounds were not measured with the PDMS fibre at 30°C, but this SPME fibre showed good absorption for the less volatile substances (e.g. fatty acids and esters) in the headspace. Higher sampling temperatures (50°C) were applied to more effectively desorb the trapped components, shifting their equilibrium towards the headspace. However, the increase in temperature causes an undesirable enrichment in (branched) alkanes and fatty acids for the CAR/PDMS type of fibre (Fig. 2d). The SPME with a PDMS fibre is more suitable for sampling at higher temperatures (Fig. 2c). Fig. 3 shows that sampling at 50°C with a PDMS type of fibre allows the identification of a wide range of components. Even polymer additives, like dibutyl phthalate, are observed with the PDMS fibre (Fig. 3). For the purpose of quantitative measurements, the adsorbent nature of the CAR/PDMS fibre has a negative impact, which can be ascribed to the competitive sorption mechanism. The different analytes will compete for the active positions on the adsorbent. With longer sampling times or higher extraction temperatures,

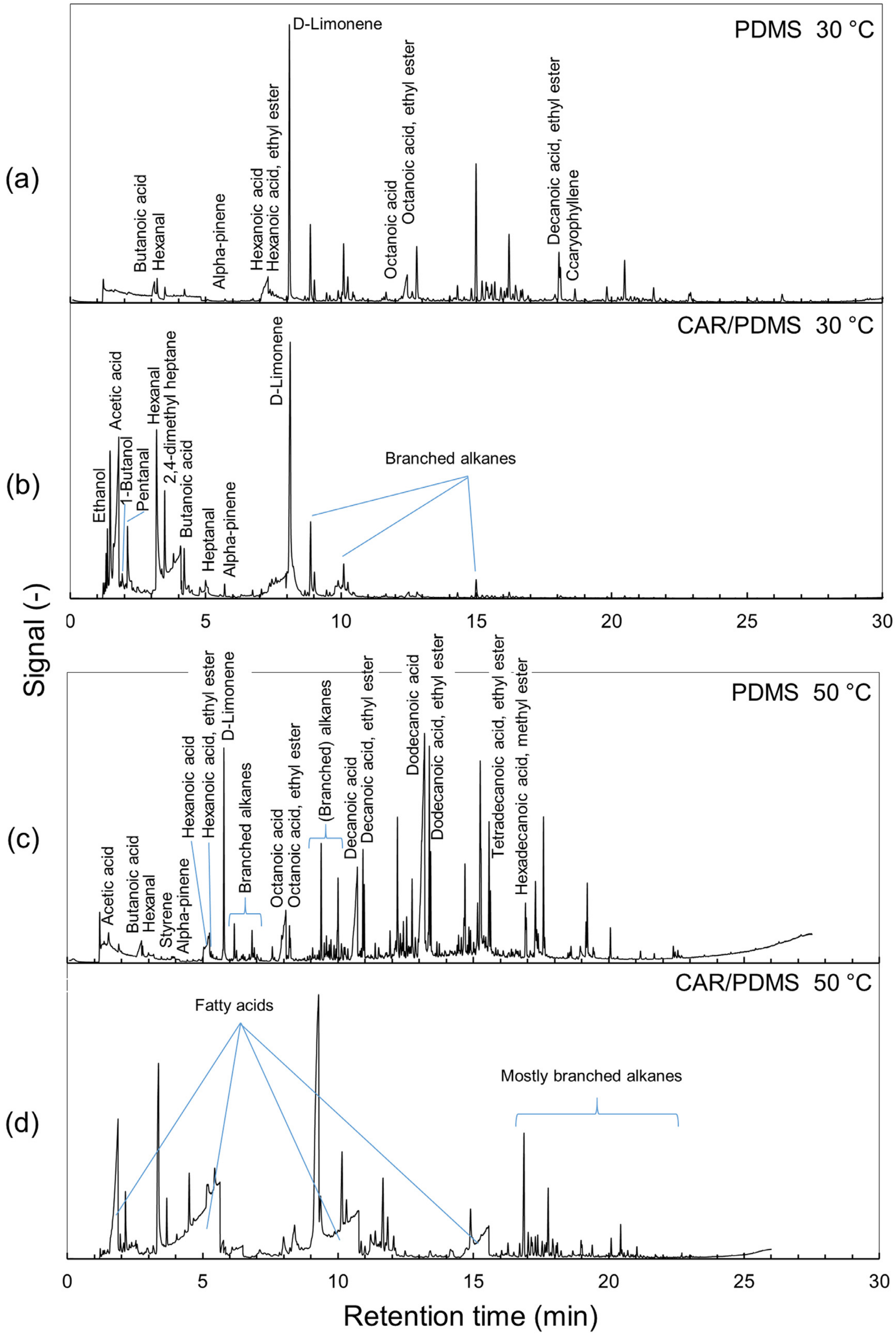

Fig. 2.. SPME measurements on the agglomerated material: (a) Sampling temperature 30°C with PDMS fibre (b) Sampling temperature 30°C with CAR/PDMS fibre (c) Sampling temperature 50°C with PDMS fibre (d) Sampling temperature 50°C with CAR/PDMS fibre.

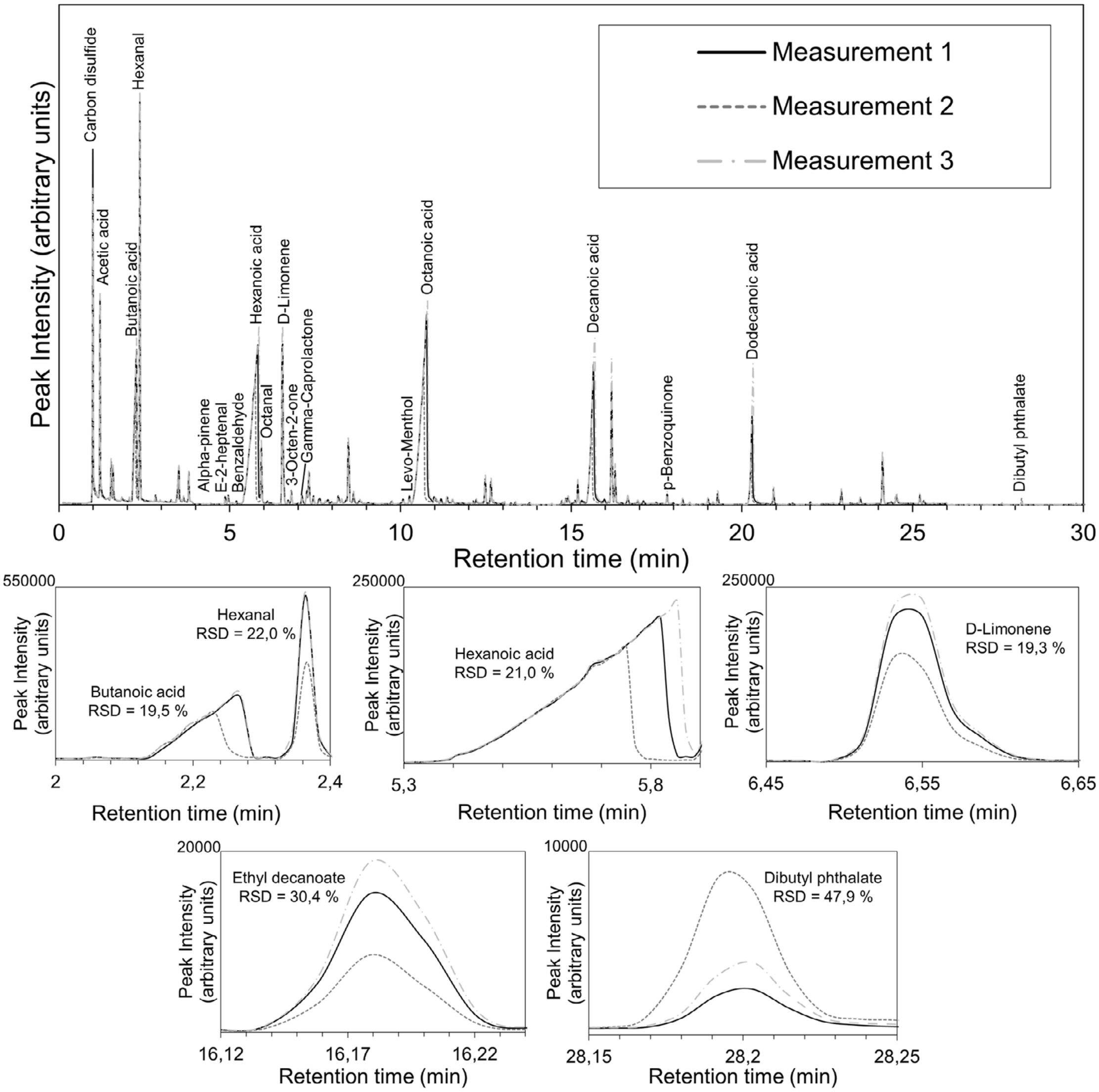

Fig. 3.. Three consecutive SPME measurements (sampling at 50°C with PDMS fibre) exposing the non-repeatabillity.

Table 1.
Overview of the used samples.

Samples		Description
Method optimisation and development	Waste stream 1	Mainly plastic film waste material coming from depacked food products
	Waste stream 2	Mainly plastic film waste from municipal solid waste
	Agglomerated material	Compacted material from the light fraction ($\rho < 1$ g/ml) of waste stream 1
Case study	Mixed films	Dirty post-consumer plastic waste films
	Washed mixed films	The washed and thermally dried mixed films
	Regranulated material	The pellets after extrusion (with degassing) from the washed films

low molecular compounds are displaced by high molecular ones (Murray, 2001).

The SPME sampling seems suited for qualitative screening of (semi-) volatiles in the headspace of complex plastic waste streams. On the other hand, the quantitative potential of the static SPME sampling for plastic waste is onerous. This can be attributed to the complexity of the investigated waste streams. The absorptive capacity of the PDMS fibre is insufficient. The linear and branched alkanes and the fatty acids present in the headspace competes with the collection of potentially odour-causing constituents (Fig. 2d). This competitive sorption leads to non-repeatable measurements using SPME sampling, as can be concluded from Fig. 3. A direct quantitative determination is in addition difficult in the absence of blank reference matrices. Developing such a blank and mixing VOCs and internal standards in solid matrices with a view to spiked samples is very difficult, especially for the heterogeneous physicochemical composition of plastic waste.

3.1.2. *Solvent desorption*

This dynamic headspace sampling method uses activated charcoal tubes to adsorb the potentially odorous components, followed by solvent desorption with CS_2. Activated charcoal is selected as the suitable adsorbent, as it is capable of capturing a wide range of volatiles and semi-volatiles (Dräger Safety AG & Co. KGaA, 2011). This requirement is necessary since odour is caused by a whole range of components

Table 2.
Overview of the detected components in the different waste streams for Thermal and Solvent sampling. The measurements were executed in triplicate.

	Component	Sampling	Agglomerate		Waste stream 1		Waste stream2	
			Relative Peak Area	RSD	Relative Peak Area	RSD	Relative Peak Area	RSD
	Terpenes							
1	Alpha-pinene	Thermal	0.92	2.2	59.60	29.5	39.57	3.8
		Solvent	0.70	10.3	16.26	14.4	20.76	10.9
2	Beta-pinene	Thermal	1.47	3.2	17.70	28.1	12.51	2.5
3	3-Carene	Thermal	0.59	0.6	14.06	30.0	9.95	1.8
		Solvent	0.24	6.4	N.D.	-	0.03	25.2
4	(R)-(+)-Limonene	Thermal	46.65	2.8	98.12	30.5	81.69	4.2
		Solvent	73.34	5.4	38.38	17.0	84.87	8.4
5	Linalool	Thermal	N.D.	-	0.57	11.7	0.57	17.0
6	Alpha-cubebene	Solvent	0.26	3.8	0.07	19.4	0.13	17.6
7	Alpha-curcumene	Solvent	0.33	18.8	N.D.	-	N.D.	-
8	Caryophyllene	Solvent	0.43	6.5	N.D.	-	0.09	26.3
	Sulphurous							
9	Carbon disulfide	Thermal	0.02	7.4	0.10	13.2	0.23	4.8
	Oxygenated							
10	Acetone	Thermal	1.30	19.1	1.42	16.0	11.60	10.2
11	Isopropanol	Thermal	0.14	7.1	N.D.	-	1.58	20.0
12	2 –Methyl-2-propanol	Thermal	0.11	2.9	0.99	52.3	1.32	8.0
13	Isobutyraldehyde	Thermal	0.01	11.4	0.15	72.8	0.16	4.5
14	Butanal	Thermal	0.07	4.1	0.01	-	0.43	7.7
15	2-Butanone	Thermal	0.03	11.1	0.12	66.2	1.60	2.3
16	Ethyl acetate	Thermal	0.05	11.6	N.D.	-	0.05	13.6
17	3-Methylbutyraldehyde	Thermal	0.02	3.1	0.26	60.5	0.22	5.7
18	1-Butanol	Thermal	0.67	1.9	N.D.	-	2.27	20.4
19	2-pentanone	Thermal	N.D.	-	0.02	-	0.55	1.5
20	Pentanal	Thermal	0.61	3.7	0.02	-	2.34	2.1
21	3-Methyl-1-butanol	Thermal	0.18	9.4	0.12	-	0.34	9.4
22	1-Pentanol	Thermal	N.D.	-	N.D.	-	3.31	16.0
23	2-Hexanone	Thermal	N.D.	-	N.D.	-	0.21	4.2
24	Hexanal	Thermal	6.15	1.9	0.05	31.7	5.31	4.7
25	Butanoic acid	Thermal	6.35	9.0	0.17	140.5	N.D.	-
26	1-Hexanol	Thermal	N.D.	-	N.D.	-	5.07	15.0
27	2-Heptanone	Thermal	0.22	2.3	N.D.	-	0.32	2.3
28	Heptanal	Thermal	1,01	2.4	N.D.	-	0.76	5.3
29	Benzaldehyde	Thermal	0.97	7.6	N.D.	-	0.59	6.4
30	E-2-heptenal	Solvent	N.D.	-	0.07	5.4	0.10	5.0
31	Ethyl hexanoate	Solvent	1.47	2.1	N.D.	-	N.D.	-
32	Octanal	Solvent	0.46	6.3	0.71	14.2	0.51	8.8
33	2-Ethyl-1-hexanol	Thermal	N.D.	-	2.08	30.2	9.34	5.7
		Solvent	N.D.		N.D.	-	7.55	10.9
34	Gamma-caprolactone	Solvent	20.22	8.6	0.79	31.1	1.00	1.6
35	Acetophenone	Thermal	0.59	13.9	0.27	11.8	0.56	13.1
36	2-Nonanone	Solvent	0.30	13.1	N.D.	-	0.04	8.5
37	Nonanal	Thermal	0.80	6.7	0.15	20.4	0.36	15.2
38	Methyl octanoate	Solvent	1.79	7.6	N.D.	-	N.D.	-
39	5-methyl-2-(1-methylethyl)-cyclohexanone	Solvent	0.77	61.6	0.09	56.9	0.35	11.6
40	Levomenthol	Solvent	0.65	6.0	0.16	21.2	0.49	9.5
41	Ethyl octanoate	Solvent	3.91	1.1	N.D.	-	N.D.	-
42	Ethyl decanoate	Solvent	4.05	9.8	N.D.	-	N.D.	-
43	Ethyl dodecanoate	Solvent	1.61	20.5	N.D.	-	N.D.	-
	Halogenated							
44	Chlorobenzene	Thermal	0.01	19.9	0.05	3.5	0.10	8.3
	Aromatic							
45	Toluene	Thermal	0.27	3.7	1.28	12.9	3.18	11.5
46	Ethylbenzene	Thermal	0.41	1.1	2.86	13.1	5.12	8.5
47	p-Xylene	Thermal	0.67	1.7	2.58	12.8	3.70	6.2
48	Styrene	Thermal	1.97	7.7	5.67	30.7	10.39	6.3
49	o-Xylene	Thermal	0.35	4.4	1.30	19.3	1.63	6.7
50	Propylbenzene	Thermal	0.18	5.6	0.61	18.4	0.83	12.4
51	1-Ethyl-4-methyl-benzene	Solvent	N.D.	-	N.D.	-	0.65	11.3
52	2-Pentylfuran	Solvent	4.37	6.3	0.67	3.1	1.74	17.3
53	1,2,4-trimethylbenzene	Thermal	0.31	10.0	2.16	33.3	2.20	11.7
54	1-Methyl-3-(1-methylethyl)benzene	Thermal	3.02	8.5	22.13	32.6	21.38	5.9
		Solvent	6.62	5.0	13.61	13.6	40.90	7.5
55	1,3-Bis(1,1-dimethylethyl)benzene	Solvent	6.41	1.4	0.25	23.2	0.43	13.8
	(Cyclo-)alkanes/alkenes							
56	n-Pentane	Thermal	0.17	10.6	0.49	17.8	0.93	6.7
57	n-Hexane	Thermal	0.16	4.5	0.24	22.6	0.21	6.2
58	Cyclohexane	Thermal	N.D.	-	0.29	20.1	0.40	10.0
59	n-Heptane	Thermal	0.03	7.0	0.66	13.9	0.80	11.0
60	Methylcyclohexane	Thermal	N.D.	-	0.21	17.1	0.19	7.5
61	n-Octane	Thermal	0.05	6.4	1.56	14.2	1.05	7.3
62	2,4-Dimethylheptane	Thermal	4.08	2.8	3.63	22.3	2.60	1.2

(*continued on next page*)

Table 2. (*continued*)

	Component	Sampling	Agglomerate Relative Peak Area	RSD	Waste stream 1 Relative Peak Area	RSD	Waste stream2 Relative Peak Area	RSD
63	2,4-dimethyl-1-heptene	Thermal	0.39	3.2	1.11	22.0	1.02	3.1
64	4-Methyloctane	Thermal	6.35	1.7	2.47	25.1	2.02	1.1
65	n-Nonane	Thermal	0.07	0.5	0.75	26.9	0.44	3.5
66	n-Decane	Thermal	0.89	4.6	9.41	33.6	5.05	0.5
		Solvent	0.42	5.9	1.87	14.1	1.53	5.5
67	E-3-dodecene	Solvent	1.14	4.2	N.D.	-	0.08	26.0
68	6-Ethyl-2-methyloctane	Solvent	2.64	8.5	0.12	8.7	0.20	9.7
69	n-Undecane	Thermal	1.60	9.7	3.15	10.8	1.35	15.4
		Solvent	16.26	13.0	1.38	29.7	1.34	5.4
70	n-Dodecane	Thermal	1.36	20.1	6.78	15.9	1.92	13.8
		Solvent	5.87	12.5	7.11	18.4	3.67	5.6
71	n-Tridecane	Solvent	2.99	2.3	0.45	21.0	0.74	18.2
72	n-Tetradecane	Solvent	11.82	87.7	0.83	10.1	1.81	27.7
73	n-Hexadecane	Solvent	1.50	26.7	0.14	14.6	0.65	10.3

(Buettner, 2017; Wypych, 2017).

The identified (semi-)volatiles from three SPME-GC-MS measurements of waste stream 1, waste stream 2 and agglomerated material are compared with the detected components after solvent desorption sampling and GC-MS analysis. From these measurements a list of 49 potentially odour-causing contaminants and precursors could be produced. These components are identified based upon their mass spectra (NIST mass spectral library). The sensitivity decreases due to the dilution in CS_2. Besides, the most volatile components are not observed in the solvent desorption technique. In this study, this is caused by the solvent delay which was set to protect the mass spectrometer. Considering that an apolar column is used, and that the (semi-)volatiles present are generally quite apolar, it is reasonable to link the retention times to the volatility. A Selective Ion Monitoring (SIM) method was developed for the selected constituents.

The solvent desorption measurements were repeated in triplicate on new batches of the respective waste streams (Table 2). An internal standard (acenaphthene-d_{10}) was added to the CS_2 desorption solvent to reduce the error on each measurement, as a consequence of variation in sampling and GC-MS instrument. For each measurement, the peak areas of the analytes were divided by the peak areas of the internal standard. These measurements on freshly sampled waste fractions were carried out to validate the constructed method. 30 components of the 49 implemented in the SIM method were found across the three samples. This again indicates the variable and complex nature of plastic waste streams. The RSD values on the relative peak areas are generally lower than 20 %, which indicates good repeatability for these complex matrices. The higher RSD values can be attributed to compounds with a low peak response (e.g. E-3-Octen-2-one, 2,6-dimethylundecane). The high RSD values for the low volatile components may be ascribed to the lower desorption characteristics from activated charcoal towards CS_2.

The application of this method can make it possible to map the removal of contaminants through the plastic recycling chain, with the focus on the less volatile fraction. In addition, it should be noted that this method can easily be extended to components present in other plastic waste streams. This is essential as each plastic waste flow can change considerably in terms of composition and odour character.

3.1.3. Thermal desorption

In order to get more insight into the more volatile substances, a thermal desorption technique is explored (Demeestere et al., 2008). The components present in the headspace above the plastic fractions are captured on a sorbent (Tenax-TA). The trapped volatiles are then transferred onto the GC column. The sampling and analysis were performed in triplicate to evaluate the possibilities of this method for semi-quantitative determination of odorants in complex plastic waste flows. The results are presented in Table 2.

The used processing method is capable of analysing 80 VOCs. Ten extra compounds (acetone, 2-methyl-2-propanol, 2-pentanone, pentanal, methylcyclohexane, butanoic acid, 2,4-dimethylheptane, 2,4-dimethyl-1-heptene, 4-methyloctane, beta-pinene and 1-methyl-3-(1-methylethyl)-benzene) found in the respective waste streams, were added to the method based upon their mass spectra. With this method, 51 volatile compounds were detected across the three waste streams (Table 2). The volatiles cover a wide range of chemical species: oxygenated components (23), (cyclo-)alkanes (13), aromatics (8), terpenes (5), halogenated (2) and sulphurous (1) components. A large quantity of these components has a characteristic odour and will thus contribute to the smell of the different waste streams.

For the agglomerated material and waste stream 2 acceptable ($<$ 20 %) RSD values on the peak areas are obtained from three-fold repeated experiments. These materials are quite homogeneous and thus result in low RSD values. However, the measurements on Waste stream 1 show RSD values of more than 30 %, which can be attributed to the heterogeneity of the material. Further reducing the material size, by means of cryogenic grinding for example, can offer a solution. It must be ensured that there is no major loss of volatiles during these processes.

Like the solvent desorption technique, the use of the thermal desorption technique also makes it possible to carry out a semi-quantitative analysis of the more volatile components present. However, it is important that the sample is sufficiently homogeneous.

3.2. Comparison of the methods

When comparing the three applied GC/MS headspace sampling techniques, several parameters must be taken into consideration. With a view to the valorisation of waste plastics, it is important to have a reliable measurement method to monitor the volatile and semi-volatile fraction, responsible for the malodour. These volatile substances have their origin in a number of processes, namely thermal degradation during (re)processing, microorganism activity, contact with spoiled food, degradation of additives… (Gröning and Hakkarainen, 2001; Strangl et al., 2019, 2018, 2017; Wypych, 2017; Yamashita et al., 2007). Besides the vast amount of linear and branched alkanes and alkenes, the thermal oxidation degradation products of PE and PP materials consists of aldehydes, ketones, alcohols, esters and acids having a larger odour potential (Hoff and Jacobsson, 1982, 1981; Hopfer et al., 2012). The qualitative interpretation of the agglomerate material (Table 2) reveal that a wide range of different chemical structures are detected. The analysis shows a vast fraction of alkanes and alkenes, fatty acids, as well as some of their methyl and ethyl esters, oxygenated compounds like linear aldehydes, alcohols and ketones. Furthermore, monoterpenes and sesquiterpenes represent a large proportion of the possible odour-causing components. Aromatic compounds are also measured.For both post-consumer waste streams (Table 2), large portion of the headspace is composed of (branched)

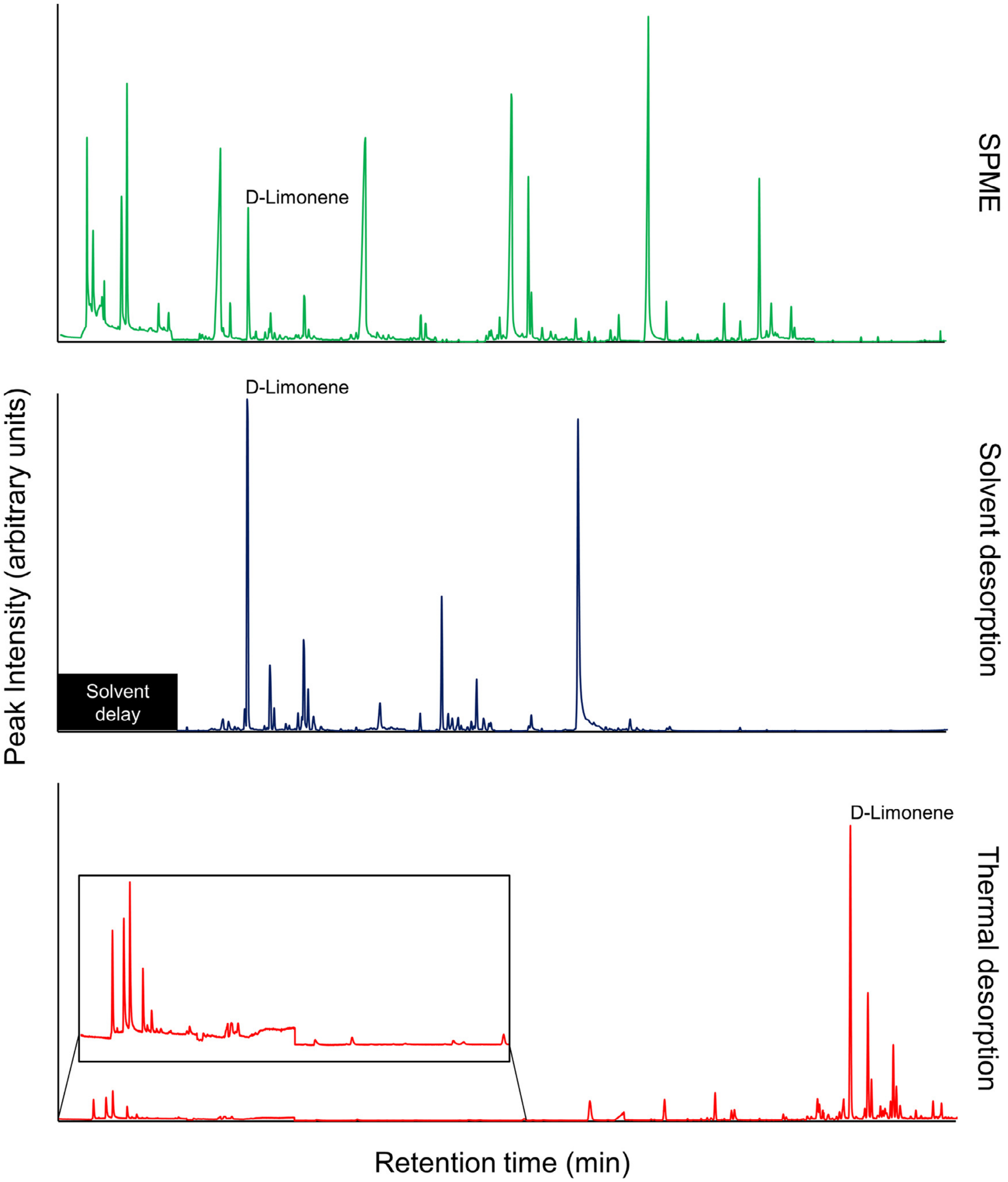

Fig. 4.. Comparison of the chromatograms obtained from SPME (Agilent 6890 GC program), solvent desorption (Agilent 6890 GC program) and thermal desorption (Thermo Scientific Focus GC program) of the agglomerated material.

alkanes, as was the case for the agglomerated material. The potentially odorous constituents are aromatics, linear aldehydes, alcohols, ketones and terpenes. In previous studies on waste plastics, to a large extent the same components were found and reported (Camacho and Karlsson, 2000; Dutra et al., 2011; Fabris et al., 2010).

In Fig. 4 the chromatograms of the agglomerated material are presented measured via the different techniques. SPME is a very accessible technique, in the sense that the sampled fibre can be analysed on basic GC instruments. The sampling itself is straightforward and only takes minutes to execute. With SPME a wide range of components can be detected and qualified. However, this technique did not produce repeatable results and furthermore misses the most volatile components due to competition effects. This means that SPME cannot be used for the quantitative measurement of volatiles in complex plastic mixtures. Kotowska et al. (2012) already concluded in their research of (semi-) volatiles emitted from municipal sewage sludge, that HS-SPME is capable of the sampling of a wide spectrum of VOCs. However, active concentration of the components on sorbents and traps should be considered to obtain a quantitative method.

Capturing the volatile compounds on activated charcoal followed by solvent desorption and GC/MS analysis resulted in repeatable measurements. The desorption by means of a solvent also makes this technique widely applicable in laboratories with basic GC equipment. The main disadvantage of this method is the solvent itself. First of all, the used solvent CS_2 is harmful to human health. The use of a solvent complicates the qualitative determination via a mass spectrometer. A pre-screening with techniques such as SPME would be necessary. The solvent desorption also causes a dilution of the analytes. As a result, this may require a longer sampling time and volume compared to the thermal desorption technique. More importantly, it has negative impact

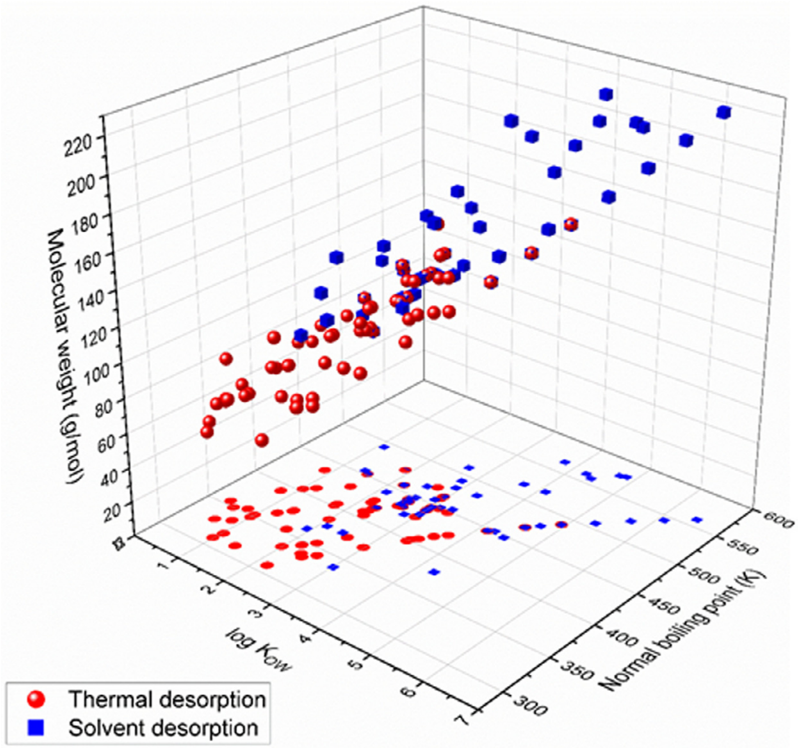

Fig. 5.. Overview of the components detectable by thermal and solvent desorption, in function of log K$_{OW}$, boiling point and molecular weight.

Table 3.
Overview of the investigated sampling techniques: SPME, Thermal desorption and Solvent desorption.

Sampling	Semi-quantitative analysis	Mean RSD (%)	Remarks and limitations
SPME	No	-	+ Good for a fast qualitative description +Applicable to most GC/MS systems - Quantitative analysis very difficult - Addition of internal standard difficult
Thermal desorption	Yes	7.2[a] / 13.4[b]	+ No solvent required + Good response for the more volatile components - More expensive equipment - Less sensitive for high molecular weight components
Solvent desorption	Yes	13.0[a] / 14.5[b]	+ Applicable to most GC/MS systems + Good response for the less volatile components - Solvent: harmful + masks more low volatile components

[a] Mean RSD calculated for the results obtained for Waste stream 2 and Agglomerated material.

[b] Mean RSD calculated for the results obtained for the three waste streams: Waste stream 1, Waste stream 2 and Agglomerated material.

on the qualitative aspects. From Fig. 4, it is clear that there is a loss of both, light and more heavy volatile components. The more volatile compounds are masked due to the set solvent delay in the analysis method. Some higher molecular weight substances are not detected due to limitations in solvent solubility.

The use of a method in which the contaminants are concentrated on a sorbent, and then thermally desorbed, prevents the need for a solvent. Thermal desorption is a clean technique that does not involve dilution of the analytes. Thermal desorption also lends itself well to qualify unknown components via their mass spectra. Headspace sampling with Tenax-TA tubes proved to be a method to execute semi-quantitative measurements. Fig. 4 shows that the majority of the measured compounds has a lower boiling point than D-Limonene. Higher molecular weight pollutants are therefore not measured. Also, more complicated and costly equipment is needed for the GC measurements.

Both semi-quantitative methods are thus complementary in the full screening of the headspace of complex plastic waste streams. SPME proves itself a reliable technique to qualitatively screen the components present in heterogeneous plastic waste.

3.3. Towards a holistic measurement of odour removal in plastic waste recycling processes

This research aims at finding a robust technique for sampling and measuring volatiles and semi-volatiles present in plastic waste streams. Combining the two purge and trap techniques makes it accessible to measure a broad range of these contaminants in a semi-quantitative way. These semi-quantitative methods can be used on complex and variable plastic waste streams, where a direct quantitative method falls short. Developing a direct measurement of the concentration is extremely difficult due to the lack of a proper blank matrix. Direct methods are also not recommended to be applied in measurements of the same sample material before and after a washing treatment. In addition, the spiking of standards on heterogeneous solid matrices is problematic because of the unknown adsorption and surface characteristics of waste plastic films. Odorant components are known to migrate into the plastic material (Charara et al., 1992; Nielsen and Olafsson, 1995; Strangl et al., 2018). Both methods, solvent desorption and thermal desorption are easily extended towards more components.

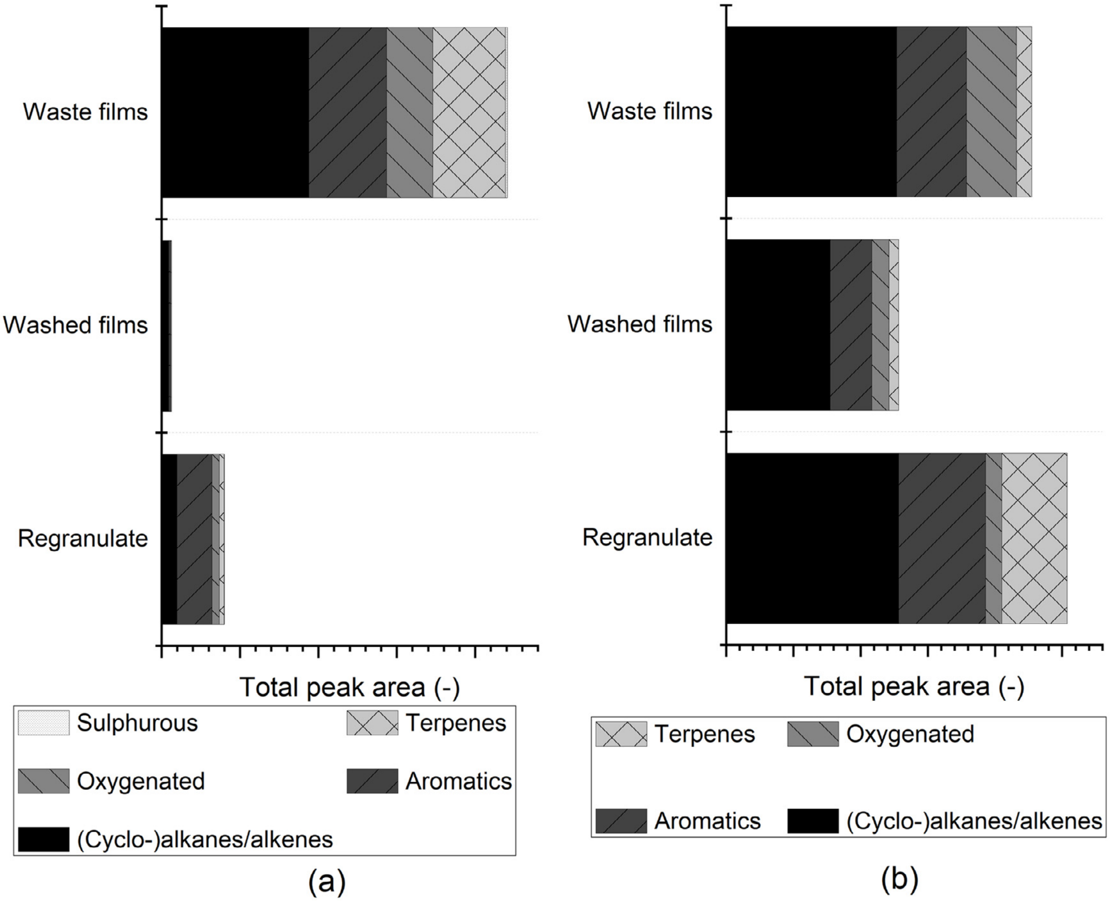

Fig. 6.. Headspace composition of Waste films, Washed films and Regranulated material: (a) Thermal desorption sampling (b) Solvent desorption sampling.

This is a necessity as other waste streams can feature a completely different headspace composition. All the identified components in this study are presented in a 3D scatter plot with as axes log K_{OW}, boiling point (T_b) and molecular weight (M_w) (Fig. 5).

These properties are important to evaluate and optimize washing procedures, as the washing process should be effective to remove a whole range of odour constituents having a wide range of physicochemical properties. Log K_{OW} can give an indication of the required polarity of the washing fluid, which is capable of removing most of the contaminants. In this study, the log K_{OW} of the odour components is estimated by atomic contributions (Wildman and Crippen, 1999). In addition to the polar character, the volatility of the components is also important for the odorous load of the waste streams. In this study, boiling point is used as a proxy, which is also relevant for the potential odour removal in an extruder (with degassing). Furthermore, molecular weight is chosen as a third factor, as it is an important parameter related to diffusion limitations of washing. To assess the final residual odour (type and strength) on a recycled plastic stream, olfactometric detection methods are required, as performed by Strangl et al. (2018, 2017). As can be seen in Fig. 5, our current purge and trap methods are able to detect a whole range of components over different physicochemical properties.

An overview of the investigated techniques within this paper is given in Table 3. The solvent desorption method applied in this research makes it possible to identify and measure compounds ranging in volatility from Styrene (M_W = 104.15 g/mol and T_b = 145°C) to hexadecane (M_W = 226,44 g/mol and T_b = 287°C). Due to the solvent delay time, the solvent desorption technique is not able to measure the low molecular weight compounds. Thermal desorption-GC-MS (TD-GC-MS) was used to measure the more volatile components. TD-GC-MS typically allows to measure the most common VOCs, of which the volatility ranges between acetone (M_W = 58,08 g/mol and T_b = 56°C) and dodecane (M_W = 170,33 g/mol and T_b = 216°C). The CS_2 desorption method extends the range of measurable components, as shown in Fig. 5, to higher molecular weight substances compared to the TD-GC-MS. The more volatile odorous components have a large impact on the odour character of the waste mixtures. However, these are also expected to be removed more easily in washing and degassing processes. Thus it is important to include the higher molecular substances as well, as these can have a scent of their own and these components are often precursors in the formation (by thermo-oxidative degradation) of the more highly odorous volatiles. Evaluation of the log K_{OW} of the detected components, reveals that they tend more towards apolar and even strongly apolar properties. The log K_{OW} values are all above zero, indicating that the components have strong affinity with the polymer matrices. It should be noted, that the Crippen calculation might include deviations thus that the results should be further confirmed.

3.4. *Case study: potentially odour-causing components along the recycling chain*

The used sampling and analytical methods were tested on a plastic waste stream throughout the recycling chain. The particular waste flow is a film fraction that consecutively undergoes a washing step, a drying step and extrusion/regranulation.

Fig. 6a shows that the dirty plastic films contain the most heavily loaded headspace after sampling with Tenax-TA tubes. The decontamination treatment used, which consist of a water wash and drying by hot air, proves to be efficient in the removal of the most volatile components. After extrusion and pelletising, an increase of these

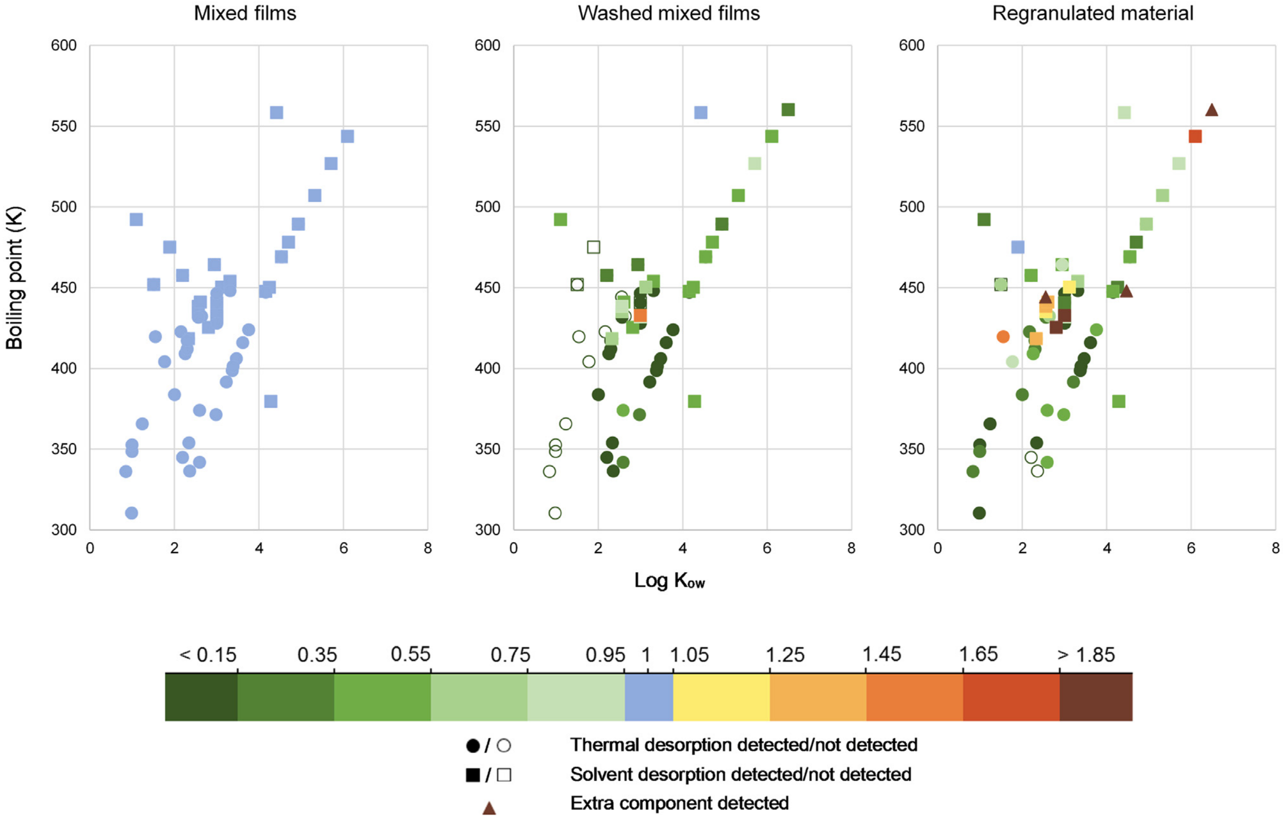

Fig. 7.. Comparison in the components between the case study streams, detected in thermal (●) and solvent (■) desorption sampling. The colour scale shows the removal or addition of components relative to the Mixed films stream.

contaminants is again observed. This can be attributed to the thermal degradation of the plastics. On the other hand, this may also be due to the release of adsorbed components after melting.

From the measurements after solvent desorption sampling, it is clear that the three concerning streams still contain a vast amount of less volatile contaminants (Fig. 6b). The applied washing step is inefficient in the removal of these higher molecular weight and more apolar components. The regranulated material, which has a pungent smell, contains even the highest amounts of these contaminants. This indicates their formation during the high temperatures in the extrusion stage. Besides, this is again an indication that the less volatile pollutants present in the headspace also contribute to the odour profile of the waste streams. It is also possible that these often higher molecular weight components are precursors in the formation of more light volatiles (e.g. aldehydes, acids).

Fig. 7 gives an overview of the components detected with both sampling methods, in which the colour scale indicates the decrease or increase relative to the input mixed film stream. The films after washing and drying treatments show a decrease for nearly all components. Fourteen components were no longer detected in the washed film fraction (isobutyraldehyde, butanal, ethyl acetate, 3-methylbutyraldehyde, dimethylsulfide, hexanal, 2-hexenal, 2-heptanone, benzaldehyde, propylbenzene, octanal, nonanal, beta-pinene, and acetophenone). These compounds include the more polar section (log K_{OW} $<$ 2) of the measured components, which seems logical as the current washing processes are mainly water based. One third of the measured components, generally with log K_{OW} values between 2 and 4, have been removed for more than 85 %. The apolar and more high-boiling components have been removed from the polymer matrix to a lesser extent (ranging from 3 – 80 % decrease). The majority of these compounds (log K_{OW} 1.1 – 5.71 and T_b 101 – 285°C) is still present for more than 35 % of the amount measured on the dirty film fraction. This shows that water is most likely a poor washing medium for the removal of adsorbed potentially odorous contaminants from an apolar polymer matrix.

After extrusion, most of the components removed during the washing step, are again detected. Similar conclusions were made by Strangl et al. (2020), who also found odorants after washing and repelletizing. A doubling of the signal after solvent desorption and an overall six-fold increase in peak area for the thermal desorption sampling support this (Fig. 6). This may indicate that these components are adhered deep inside the solid polymer matrix. And that the diffusion of components from the core of the plastic is not sufficiently fast to remove them via washing. The fact that the vast majority of the compounds are measured in a higher degree compared to the washed films (Fig. 7), also reinforces this assumption. High increases are observed for 2-hexenal (0 to 1.56), 1-methylethyl-benzene (0.43 to 2.30) and pentadecane (0.50 to 1.77). Some oxygenated and aromatic substances are observed in a higher content in comparison with the dirty film fraction. This might imply their formation due to thermo-oxidative degradation during the extrusion process. Bledzki et al. (1999) reported an odour reduction of 37 % after a threefold degasification, but further extrusions lead back to an increase, caused by degradation processes. It is also clear from the graphs that the most apolar and high-boiling components are difficult to remove from the plastic material with current (water based) washing techniques. More intensive washing treatments will be necessary. Deep-cleaning processes (high temperature and vacuum degassing) followed by re-extrusion with melt degassing proved to be efficient for recycled PET (Dutra et al., 2011) and HDPE (Welle, 2005).

4. Conclusion

In this paper, a GC/MS method is developed and applied capable of measuring semi-quantitatively the efficiency of the washing processes of complex plastic waste streams. Three post-consumer waste streams were subjected to a qualitative screening using HS-SPME. Almost all detected components are strongly apolar, and will therefore strongly adhere to the hydrophobic polymer matrix. We have combined two dynamic sampling methods to cover the wide range of components. Active sampling on activated charcoal tubes followed by CS_2 desorption, resulted in the detection of 30 components most often having a volatility lower than D-Limonene. In order to analyse the more volatile compounds, a thermal desorption technique using Tenax-TA sorbent enrichment tubes was explored. Across the three waste samples, 52 VOCs were identified. Both purge and trap techniques had acceptable repeatability (RSD general lower than 20 %), and can be used to quantify the efficiency of odour removal in the plastic recycling chain.

In a case study, we followed the odour removal throughout washing, drying and pelletizing. Results show that washing works to a certain extent, especially for the most polar components (log $K_{OW} < 2$). After reprocessing, however, odorous components increase again with a factor 2 (solvent desorption) and 6 (thermal desorption) compared to the washed films. Furthermore some oxygenated and aromatic components are additionally formed due to thermo-oxidative degradation. The presented analytical methods provide essential insight in the removal efficiency of a whole range of components with different polarity and volatility, which is an essential step in the understanding and optimisation of washing procedures. These insights can strongly contribute towards the closed loop recycling of waste plastics.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Ruben Demets: Conceptualization, Methodology, Writing - original draft, Formal analysis. **Martijn Roosen:** Methodology, Investigation, Writing - review & editing. **Lore Vandermeersch:** Investigation. **Kim Ragaert:** Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition. **Christophe Walgraeve:** Methodology, Investigation, Writing - review & editing. **Steven De Meester:** Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2020.104907.

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