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GC/MS Screening of Substances Released from Post-Consumer Recycled HDPE Pellets into 95% Ethanol: Reproducibility and Variation between Production Batches

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Abstract: The use of post-consumer recycled (PCR) plastic materials in sensitive packaging applications, such as for cosmetic products and detergents, requires a clear understanding of the identities and quantities of chemical substances, which they may release into packed products. With many potential sources of and thus different types of potentially releasable substances, a reliable non-targeted screening method is required to assess these materials. Such a method should be readily applicable in industrial practice and provide a realistic estimation of substance release. This investigation focused on the use of gas chromatography/coupled mass spectrometry (GC/MS) to analyze substances, which recycled HDPE (rHDPE) plastic pellets release into 95% ethanol under accelerated testing conditions. The results of the repeated testing of reference samples clearly demonstrated the good reproducibility of the described methodology, with standard deviations of repeated determinations of the total released substance amounts of 6.8–8.1%. The application to several production batches of three commercial rHDPE grades additionally demonstrated that the batch-to-batch variation of substances which rHDPE materials release can be confined to less than 10% of variation of the total detectable substance amount. The described methodology is therefore seen as a pragmatic, repeatable assessment of recycled HDPE plastic batches with a view to substance release.

Keywords: recycled plastic; migration; extraction; packaging; GC/MS; HDPE; product safety

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1. Introduction

Plastics are an important material for the production of many products in the daily lives of consumers, including, importantly, packaging for food but also for consumer goods, such as cosmetic products and detergents. The recycling of common plastic materials [1], including from packaging waste [2], is already well established and has reached a substantial scale. However, most applications for recycled plastics, especially in the case of polyolefins, lie in fields other than packaging, such as, for example, construction products, agricultural products, appliances or automotive components. The limited uptake of recycled plastics in packaging and other contact-sensitive applications stems, among other factors, from specific regulatory and safety requirements which apply to such applications and the resulting need for a detailed understanding and control of the chemical purity of (plastic) materials used in these applications [3–5].

The use of plastics, including recycled plastics, in contact with food is in most cases subject to a pre-market approval by the relevant authorities, e.g., the European Food Safety Authority (EFSA) in Europe or the Food and Drug Administration (FDA) in the USA. Regulations (EC) No 1935/2004 [6] and (EU) No 10/2011 [7] provide requirements for all food contact materials in the EU, whereas Regulation (EU) 2022/1616 [8] specifically governs recycled plastics. In the USA, reference is made to Title 21 of the Code of Federal

Regulations [9], as well as the Food Contact Notification program. The FDA has furthermore issued guidance for the use of recycled plastics in food contact [10]. Regulations also exist for cosmetic products (e.g., Regulation (EC) No 1223/2009 [11]), and consumer goods safety regulations exist in a range of jurisdictions. Where no detailed or practical guidance from authorities existed, the CosPaTox [5] consortium and Elipso/FEBEA [4] have released industry guidelines. In all these applications, the propensity of a plastic material to transfer chemical substances into products needs to be understood as part of a safety evaluation.

Virgin plastic materials, obtained from primary sources, are generally evaluated in the form of extraction or migration testing [12], followed by an assessment of the identities and quantities of the extractable or migratable substances via a non-targeted screening method, often gas chromatography coupled with mass spectrometry (GC/MS) [12], augmented by additional targeted analyses, as required by the end application. The evaluation generally includes both intentionally added and non-intentionally added substances [13]. The consistent quality of virgin materials is based on the use of high-purity raw materials (monomers, additives) and is further ensured through good manufacturing practice.

Different to virgin plastics, the purity of recycled plastics may be affected by additional sources of potential contamination, including from thermal degradation, from product residues and from collection and waste handling. This potential for contamination requires specific consideration before recycled materials can be used in contact-sensitive (packaging) applications [1,14,15]. While in recent years, an increasing volume of studies have been published, which analyzed and characterized the purity of recycled plastics [14,16–37], fewer results have been made available regarding the consistency of post-consumer recycled (PCR) plastic materials over time, that is, across several production batches or campaigns, and regarding the differences in such consistency between different sources of recycled plastics. One prior study analyzed multiple batches of a single grade of recycled material from a flexible polyolefin packaging waste fraction [23], a stream typically comprising LDPE, LLDPE and PP. The study focused on potential safety concerns; information regarding the reproducibility of the applied analytical method and the differences between different batches of a recycled material was shown in a correlation diagram but not elaborated on in detail. A study on the decontamination efficiencies of rHDPE from milk bottles [38] provided more detail by describing the dichloromethane extraction testing results of samples from three recyclers. A third study [39] also analyzed the consistency of PP recycling streams but on the basis of an analysis of waste bales rather than of the chemical composition of the recyclates.

The primary aim of the study underlying the present study was the definition, validation and application of a pragmatic method based on an untargeted GC/MS screening, which is suitable for the routine analysis of recycled plastics as part of quality management and quality assurance for users of recycled HDPE in packaging applications. As such, it focuses on sample preparation and analytical technologies that are readily available to industrial users of plastic.

rHDPE was chosen as the investigated material due to its high relevance for contact-sensitive packaging applications for cosmetics and detergents.

The choice of contacting recycled plastic pellets with the solvent was made to provide a pragmatic approach. While cryo-milling the sample would provide a more conservative result, this technique is typically not available in the routine analysis of recycled plastic by its users. It is also noted that with the focus being on HDPE, i.e., a polymer used for rigid packaging, the difference between pellet size and wall thickness of the resulting packaging is not as pronounced as, for example, in (L)LDPE—the pellets used to produce thin blown films.

The choice of 95% ethanol follows the experience that this solvent can represent a wide range of cosmetic products [5], as well as its use as a simulant for food contact safety determinations [7]. The 95% ethanol provides results, which are not as overestimated as extraction solvents, such as dichloromethane, and at the same time covers a wider range of filling goods than the 50% ethanol, which may not sufficiently represent apolar/lipophilic

filling goods. This approach is in line with the recently published guidance provided by the CosPaTox consortium [5].

The choice of seven days of contact time was made with a view to operational efficiency. It was supported by additional testing performed during the development of the method, which provided clear evidence that longer contact times only marginally increased the amount of substance transfer for the recycled plastic sample into the simulant. As the aim was to demonstrate the repeatability of the experimental method and study the consistency between different batches, the representativeness of the chosen conditions for a specific actual packaging use case and shelf life was not investigated.

The high ratio of sample mass to simulant (higher than in real-world packaging uses) was chosen to represent an estimate of the upper range migration that can be expected in real packaging applications.

The choice of a non-targeted screening method, rather than a targeted analysis, was made, as a screening method able to detect and identify a multitude of chemical substances in a semi-quantitative fashion was considered to provide a more comprehensive picture of the composition and the variability of recycled plastic materials. While a targeted analysis may provide more precise results or a lower limit of detection, it would not reveal the appearance or a change in the quantity of substances which it does not target. A screening method covers a very large number of substances, allowing the analysis of reproducibility and sample variability to be performed on a large dataset rather than only on a low number of target analytes. The specific choice of GC/MS as the analytical technique, as well as the choice of simulant, follows established practice in the testing of virgin food contact plastics, especially with a view to non-intentionally present substances [13] and recent industry guidance [5].

A secondary aim of the study was to provide an understanding of the typical batch-to-batch variability of recycled HDPE plastic materials from different sources and whether these can be detected with the developed method. While a direct comparison of the peak areas of the total ion chromatograms would have been possible, the measurement results were instead quantified using an internal standard to provide an indication of the quantities of substances present.

The aim of this study did not include providing an evaluation of the 'quality' or the safety of the studied materials nor did it include a comparison between recycled and virgin HDPE plastics. The authors acknowledge that for a formal safety assessment of a recycled plastic, additional analysis may be required, such as specific targeted analyses with a lower limit of detection than GC/MS can provide or the analysis of inorganic substances.

Furthermore, as in practical use during the qualification of recycled plastics, detailed information on the recycling process is not typically available to the recyclate user, the study was performed in a recycling-technology-agnostic manner.

2. Results

2.1. Identities and Quantities of Released Substances

For each of the three recycled HDPE materials, many peaks were found in the respective chromatograms, indicating that a multitude of substances had been released into the simulant. Many small peaks were not present in every chromatogram but appeared only occasionally. In contrast, peaks of larger magnitude were generally present in most or all batches, and replicates and were typically identifiable.

Each analyzed sample exhibited on average 140 $\pm$ 23 (rHDPE-A1), 170 $\pm$ 28 (rHDPE-A2) or 130 $\pm$ 35 (rHDPE-B1) peaks, out of which on average 62–65% could be identified. The identified substances were grouped by their chemical structure into alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS) in plastics. The group of NIAS comprised substances that are not intentionally present in rHDPE plastic materials, such as fragrance compounds, phthalates, salicylates and UV blockers, and which likely originate, as do some fatty acid esters, from the prior filling goods of the HDPE packaging that was recycled to produce

the rHDPE materials that were tested in this study. Unidentified substances were all placed into a single group ('unidentified').

All reported quantifications of substances are relative to the mass of recycled plastic material. In practice, i.e., if such materials are used as packaging, the resulting concentrations of substances in the packaged product can be expected to be substantially lower, following the weight ratio of packaging to product.

As can be seen in the results for the reference samples (Figure 1, left), the released quantities of substances of the groups FAE, IAS/NIAS and unidentified substances differed between the three rHDPE materials, whereas the amounts of alkanes (ALK) were comparable across the three materials. As the total amount of unidentified substances was generally low, the difference in total amount of substances released between the three recycled materials was therefore driven mainly by differences in groups FAE and IAS/NIAS. However, Figure 1 (right) also shows that the total number of substances detected for the three recycled materials was very comparable.

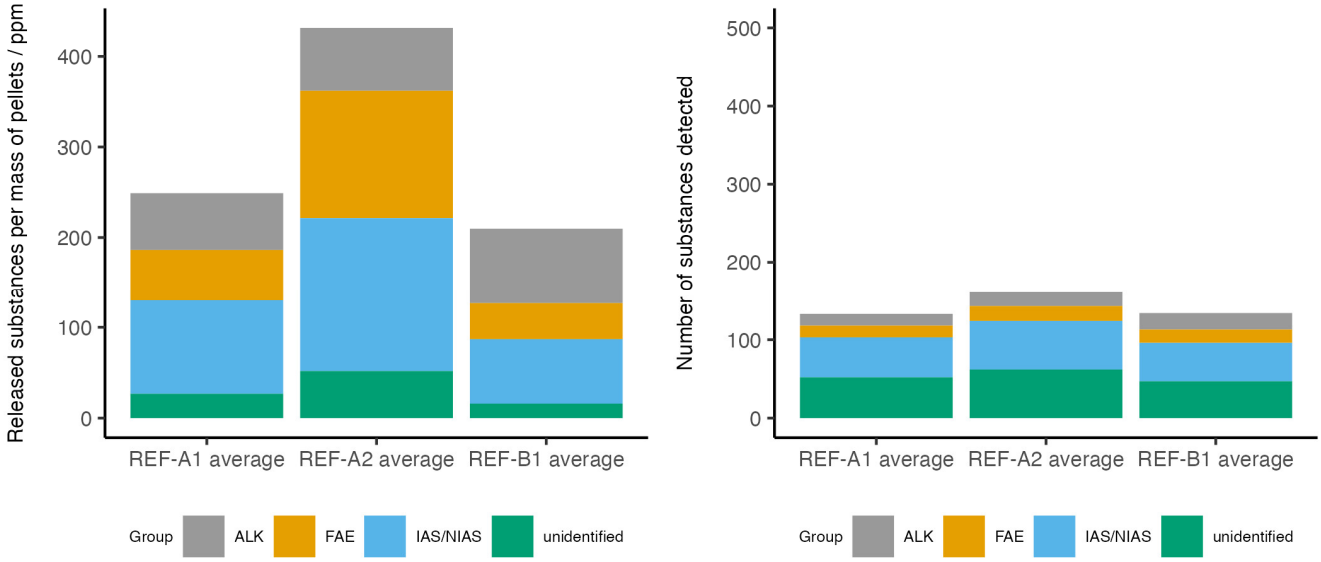


Figure 1. Comparison of the average concentrations (**left**) and the number (**right**) of substances released in the measurements of the reference sample for the materials rHDPE-A1, rHDPE-A2 and rHDPE-B1 by substance group. The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

A comparison of the concentrations of substances released per group (Figure 1, left) with the number of substances released per group (Figure 1, right) illustrates that unidentified substances, though numerous, were generally of low concentration.

2.2. Reproducibility of Results

The reproducibility of the quantification of substances released into the simulant was studied in the form of a repeated measurement of the three reference samples over the course of the full timeframe of the study. Each reference sample was tested at least 5 times, with three full replications performed each time. The results for REF-A1 are illustrated in Figure 2 (see Figures A1 and A2 for REF-A2 and REF-B1).

Neither a large random variation nor trends over time were observed. No substantial difference in variation was observed between the replicates compared to the variation between the different times of testing. The standard deviation of the total quantity of substances detected over all tests on the reference samples was low, at 6.8% for REF-A1, 7.8% for REF-A2 and 8.1% for REF-B1.

While the results remained consistent for each reference, clear differences could be seen between the different references. The good stability of the results obtained for each in-

dividual reference confirms that the differences in the results obtained for the three recycled materials are related to the materials being different in composition, as discussed in the following section.

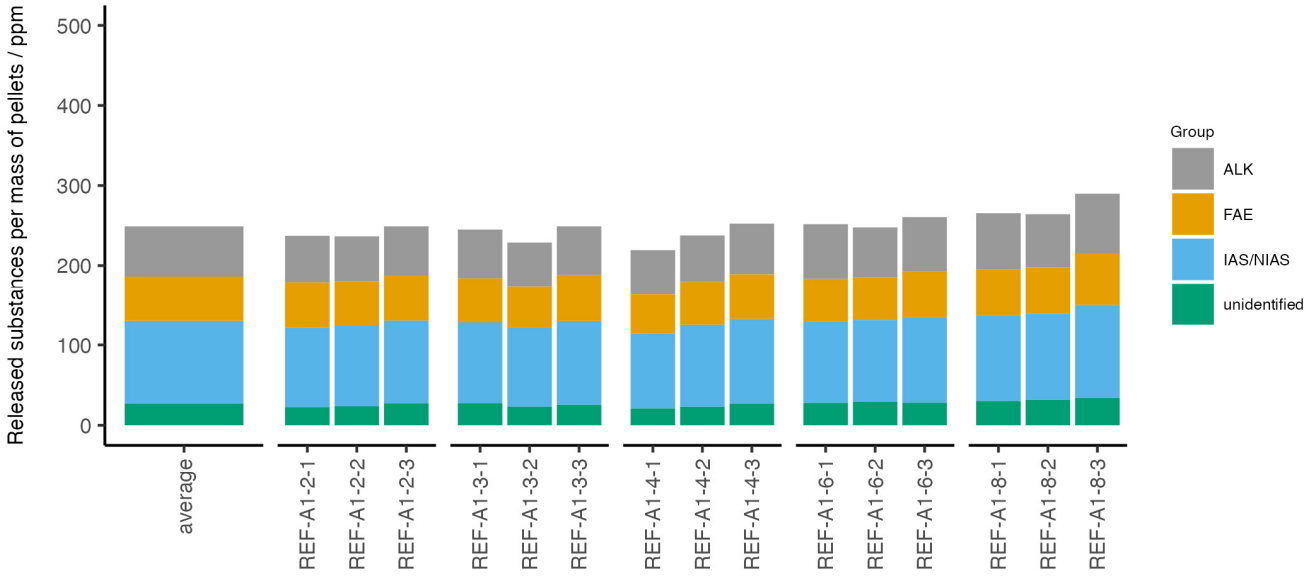


Figure 2. Reproducibility of GC/MS results between repeated measurements of the REF-A1 reference material (the first number represents the week of testing; the second number is the number of the replicate). The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

An evaluation (performed only for materials rHDPE-A1 and rHDPE-A2, as the number of analyses for rHDPE-B1 was too low to support a proper statistical evaluation) of the qualitative detection (detected/not detected) of identifiable substances across replicates provides further indications of the consistency of the method, as well as the samples. The majority of times (103 out of 135 total substances for rHDPE-A1, i.e., 76% of substances, and 108 out of 152 total substances for rHDPE-A2, i.e., 71% of substances), identifiable substances were found consistently in every replicate or none of the replicates of the reference, including the repetitive testing of the reference at different weeks. Cases where the detection results for a substance were inconsistent across the replicates were typically related to the respective substance concentrations being close to the limit of detection of the method. While the number of substances for which each production batch measurement was fully consistent across its replicates was about half of the total (70 substances out of 135 total substances for rHPDE-A1 and 84 substances out of 152 total substances for rHPDE-A2), in most cases, the inconsistency was limited to a small number of batches for which not all replicates agreed. On average, both for rHDPE-A1 and for rHDPE-A2, 89% of batches provided consistent detection results for a given substance across their three replicates.

2.3. Results for Different Production Batches of Recycled HDPE Materials

The test results for the different production batches of each recycled HDPE material are shown in Figures 3–5. For each batch, the replicates showed good consistency, as already noted above and also observed in reference materials' tests. One exception was replicate B-3 of rHDPE-B1 (Figure 5, and the results for bumetrizole in Figures A3–A5), which appeared as an outlier; a specific cause could not be established. The standard deviation of the total quantity of substances detected was found to be 8.3% for rHDPE-A1, 13.0% for rHDPE-A2 and 30.5% for rHPDE-B1 across all batches and replicates, noticeably higher than the 6.8%, 7.8% and 8.1%, respectively, for the variation of the multiple measurements of their reference batches. The higher variation between the results of different production batches,

with the variation between replicates of one production batch remaining comparable to the results obtained for the reference material, confirms that this variation can be understood to result from actual differences in the composition between the different production batches. These differences were small for rHDPE-A1, larger for rHDPE-A2 and pronounced for rHDPE-B1, suggesting a difference in the consistency over time between these three grades of recycled plastic.

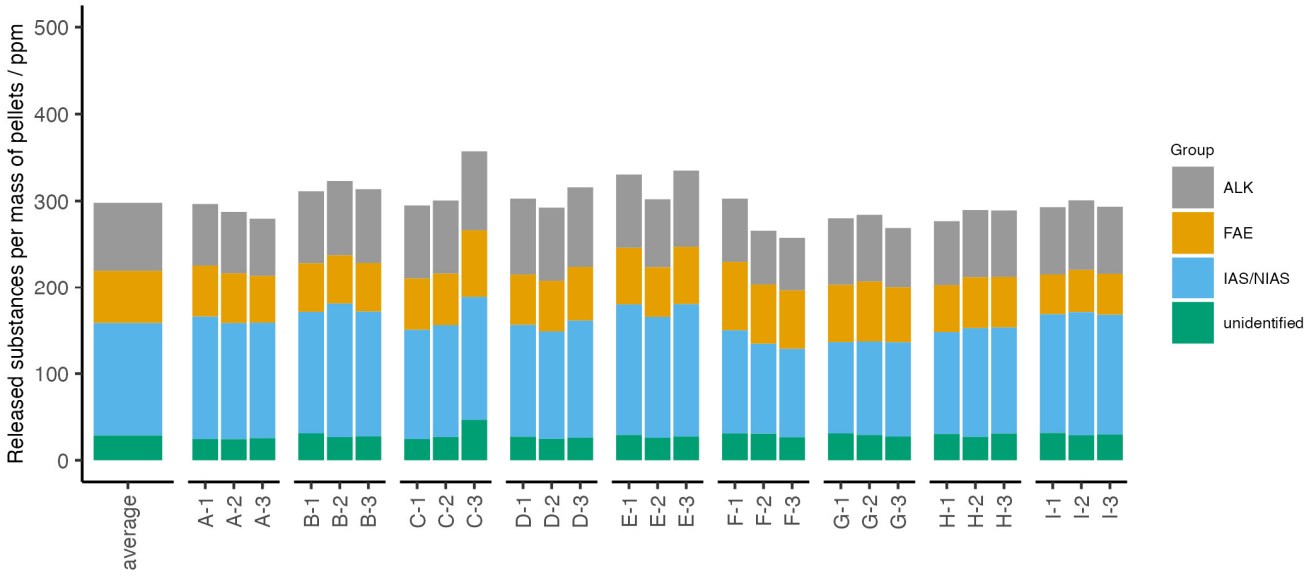


Figure 3. GC/MS results for nine production batches (A–I) of rHDPE-A1, measured in triplicate and grouped by substance class. The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

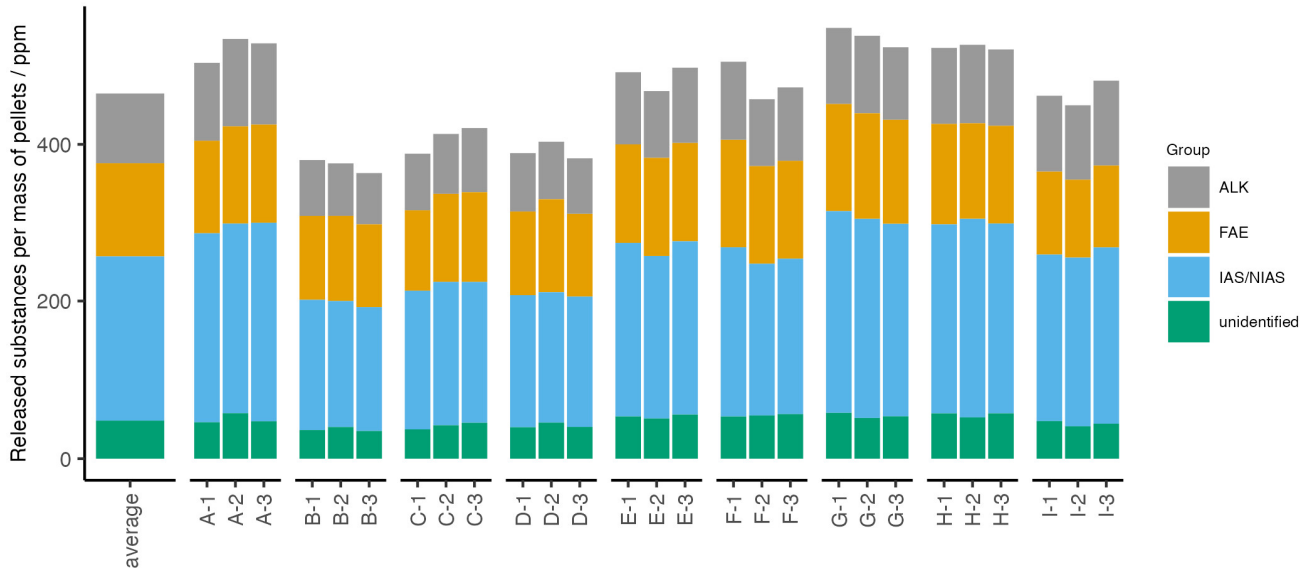


Figure 4. GC/MS results for nine production batches (A–I) of rHDPE-A2, measured in triplicate and grouped by substance class. The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

When performing the same comparisons on the level of selected individual substances rather than on groups of substances, a similar picture emerged (Figures A3–A5), again indicating a very good reproducibility of the method (small variation between replicates) and the ability to distinguish between smaller or larger variations between production batches when comparing rHPDE-A1 with rHDPE-A2 and rHDPE-A3. Substances were selected to include two substances from the same group (alkanes) but which occurred at very different concentrations (octadecane being found in the range of 10–15 ppm in all three materials compared to tetradecane, only found in the range of 1.0–1.5 ppm in rHPDE-A1), as well as from a different group of substances and with a much more polar structure (bumetrizole).

An analysis of the standard deviation for each substance across all replicates of all analyzed production batches confirmed well-controlled standard deviations, considering the low analyte concentrations (Figures A6 and A7). This analysis was performed only for materials rHDPE-A1 and rHDPE-A2, as the number of analyses for rHDPE-B1 was too low to support a proper evaluation.

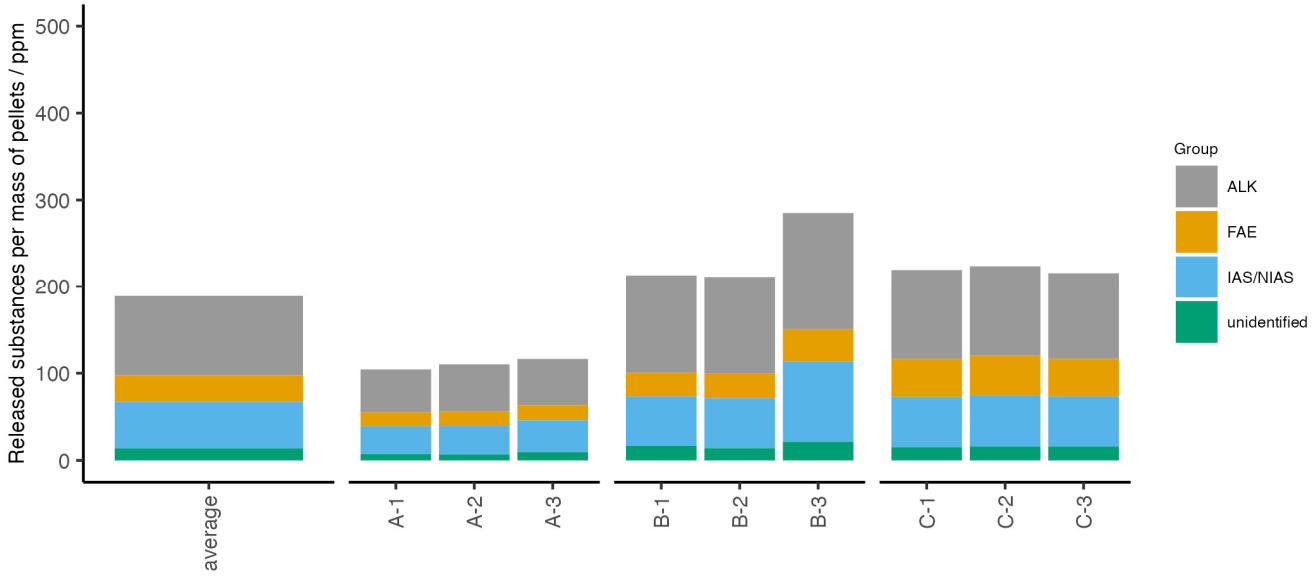


Figure 5. GC/MS results for four production batches (A–C) of rHDPE-B1, measured in triplicate and grouped by substance class. The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

3. Discussion

3.1. Reproducibility of Results

The results of the repeated testing of the reference sample for each material (Section 2.2) were very comparable for individual substances, for substance groups, as well as for the total sum of substances detected. The low variation between the results suggests that the described method of contacting pellets of recycled plastic material with the defined simulant and analyzing the release of substances into the simulant via GC/MS provides stable and reproducible results. These results confirm that the release of substances into the simulant is very consistent for the described methodology.

The good reproducibility of the results supports the intended use of the described method for the intended comparison of different production batches of a given recycled plastic material in order to study its release of substances and its variability over time.

Additionally, the consistent results found for the reference samples over time suggest that these rHDPE materials themselves are stable, that is, they are not subject to noticeable ageing. This suggests that there is no need to test a batch of rHDPE material immediately after production or before use and that keeping the retained samples of older product batches allows for reliable testing at a later time, if required.

3.2. Variability between PCR Material Batches from the Same Source

The three different materials exhibited different variability between their different production batches. While rHPDE-A1 and rHPDE-A2 proved rather consistent, rHDPE-B1 showed substantially higher variability between production batches. While the number of tested production batches, and thereby, the number of samples, was lower than for rHDPE-A1 and rHDPE-A2, the variability in the quantity of detected substances between batches reached more than 100% (Figure 5) for rHDPE-B1, while most of its replicates (Figure 5) as well as all of its reference batch measurements (Figure A2) retained a similar deviation to rHDPE-A1 and rHDPE-A2. Considering the consistency of results in the reference batch measurements for this material and the good agreement between the replicates for each of the tested batches, this variation can with good confidence be attributed to a variation in the composition of the different production batches of this material.

These results therefore demonstrate the potential of the method described in this paper for the purposes of understanding the consistency of a recycled plastic material over multiple batches of production. Such an understanding of variability may also serve the creation of quality assurance and control plans, an important aspect of the quality management of recycled plastics.

3.3. Comparison of Different PCR Materials

As the goals of the present study were to validate an experimental method (Sections 3.1 and 3.2) and to study the variability in the composition of typical recycled plastic materials over different production batches (Section 3.3), the following comparison between the three different PCR materials focuses on conclusions of a general nature rather than discussing the identified substances or their implications for the acceptability of these materials for a given use. Also, no comparison was undertaken regarding the 'quality' of the three rHDPE materials included in this study.

It can be noted that the released quantities of alkanes (ALK) were very comparable between the three materials, whereas the quantities of substances from the other groups (FAE, NIAS) differed substantially. This finding may be explained by considering that alkanes are most likely to originate from (r)HDPE itself, whereas the other groups of substances are most likely to originate from filling goods contained in HDPE packaging that was recycled to produce the recycled HDPE materials or from contaminations that were present in the waste stream. As filling goods and contaminants may differ substantially in their composition from substances present in virgin HDPE plastic materials, and as different recyclers may process different mixes of input materials, a larger variation in the quantities of filling-good-related substances compared to HDPE-related substances is entirely plausible.

At the same time, as visualized in Figure 6, the chromatograms of samples of rHDPE-A1, rHDPE-A2 and rHDPE-B1 show substantial similarities, with essentially all larger peaks, and thus substances, being present in all three chromatograms. The differences between these materials can be understood to be mainly in different quantities of the same released substances, rather than differences in the identity of substances. This result suggests that monitoring of the consistency of rHDPE materials may be focused on the recurring substances (for use in specifically regulated or sensitive applications, attention may still need to be paid to the smaller or less regularly occurring substances in addition to the overall monitoring of consistency across batches).

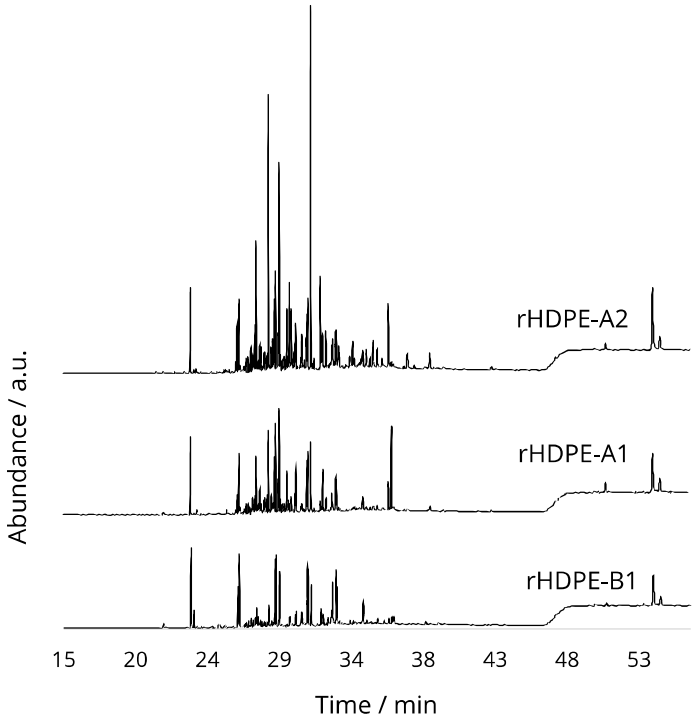


Figure 6. Comparison of representative chromatograms of select samples of rHDPE-A1, rHDPE-A2 and rHDPE-B1 (a.u.: arbitrary units; all chromatograms produced to the same scale but offset for clarity of presentation).

3.4. Limitations of the Methodology

The results presented in this paper provide strong support for the suitability of the described method for testing the release of substances from pellet samples of recycled plastics in an industrial setting, and they demonstrate that a good level of consistency in the composition of rHDPE production batches can be achieved. At the same time, the described methodology has four important limitations that will be briefly discussed here. (1.) Certain substances cannot be assumed to transfer readily into the chosen simulant, ethanol, due to lack of solubility. Performing additional testing with different simulants, chosen to be a good solvent for the substances of interest, may be considered to augment the results where required. (2.) The analytical method of GC/MS cannot detect all chemical substances, in particular not inorganic substances and non-volatile substances (while GC/MS is not able to detect all organic contaminants or elemental contamination, the occurrence of or a change in such contamination is, however, likely to be accompanied by changes, which are detectable via GC/MS. As such, the described method may still reveal changes in composition, even though not all changes in composition may be revealed). GC/MS screenings may therefore be combined with other (targeted) analytical methods to obtain a comprehensive assessment of a plastic material. (3.) Close to the limit of detection, the quality of mass spectra may no longer be sufficient for a reliable structural assignment. This can lead to an increased chance of substances at very low concentrations remaining unidentified. (4.) The described method is semi-quantitative in nature. If an exact quantification of a specific substance is required, for example, for regulatory reasons, a targeted analytical technique may need to be employed.

4. Materials and Methods

4.1. Samples

The three PCR materials investigated in this study were all commercial post-consumer recycled HDPE (rHDPE) pellets obtained from two different European producers. The input materials for recycling were collected from European countries. Pellets were uniform

in size, and approximately 110 pellets were contained in 3 g of the sample. The two materials obtained from producer A were designated rHDPE-A1, rHDPE-A2 (representative sampling from a batch size of 25 tons for both materials), and the one material obtained from producer B was designated rHDPE-B1 (representative sampling from a batch size of 100 tons). Samples of different batches of each material were collected over a span of about three months and sequentially labeled as A. . .I for the samples of each origin. Since the focus of this study was not on the identification of seasonality of recyclate properties, the sampling was allowed to start at different times for the three materials. Samples were collected for rHPDE-A1 during week 1 (A, B), week 2 (C, D), week 3 (E, F), week 5 (G) and week 7 (H, I). For rHPDE-A2, collection was performed during week 1 (A), week 2 (B), week 4 (C, D), week 6 (E, F), week 8 (G, H) and week 9 (I). Samples of rHPDE-B1 were collected only during week 1 (A), week 2 (B) and week 3 (C). An overview is also provided in Table A1.

In addition to these samples, a single reference batch ('REF-A1', 'REF-A2', 'REF-B1') of each recycled HDPE source was included in the testing program to allow for the characterization of the inherent variation in the testing methodology and for operator effects.

4.2. Reagents, Internal Standards

Ethanol (absolute, pro analysis) was purchased from Merck Darmstadt, Germany (article 1.00983.2511). 4,4′-difluorobiphenyl (DFBP) and C_7–C_{30} saturated alkanes in hexane (certified reference grade) were purchased from Sigma-Aldrich, a part of Merck Darmstadt, Germany (articles D102407 and 49451-U). Methanol and tetrahydrofuran (THF) of chromatography grade were purchased from Supelco, a product range of Merck Darmstadt, Germany (articles 1.06035.1000 and 1.08101.1000). Purified water was prepared in-house using an Elga PURELAB flex 3 system made by Elga Celle, Germany..

The simulant used in this study was prepared by diluting absolute ethanol to 95% (*v*/*v*) with purified water and adding DFBP as an internal standard at a concentration of 12.85 mg/L.

The alkane standard for the determination of retention indices was prepared by diluting the certified C_7–C_{30} saturated alkanes reference (containing 1000 µg/mL of each component) in a ratio of 1:5 (*v*/*v*) with tetrahydrofuran (used as received) by diluting the 1 mL of the standard with 4 mL of tetrahydrofuran (used as received). No precise dilution of the alkane standard was undertaken, as the use in providing a retention index reference scale is not dependent on the exact concentration of the standard.

4.3. Equipment

The GC/MS system used was an Agilent 7890 GC with a 5977 MSD mass spectrometer detector made by Agilent, Waldbronn, Germany, utilizing a Restek Rxi-5Sil MS, column (30 m × 0.25 mm id, 0.5 µm df) produced by Restek, Bad Homburg vor der Höhe, Germany.

The test tubes used for the immersion of recycled plastic samples in the simulant were 16 × 100 mm Duran glass tubes (VWR, Darmstadt, Germany art. 391-0145). The included black screw caps (PP) were not used; instead, red screw caps GL18 made of PBT with PTFE coated seals (VWR, Darmstadt, Germany art. 201-0001) were used. The heating block used was a Liebisch, Bielefeld, Germany Thermobil type TM-130-56 equipped with a monoblock MHB-S-26-16. The pipette for the addition of simulant to the test material was a 10 mL Dispensette S Organic from Brand. Other equipment used was generic laboratory equipment.

4.4. Release of Substances into the Simulant

An amount of 3.00 g ± 0.05 g of the sample in the form of pellets was weighed into a screw cap glass tube, and 3.00 mL ± 0.07 mL of the simulant was added. The tube was closed with a screw cap and placed in the metal block thermostat for seven days at a set temperature of 60 °C. After this time, the tube was removed from the block and allowed

to cool to room temperature. After a short shaking of the tube, most of the simulant was pipetted into a GC sample vial. The simulant, now containing the released substances, was not subjected to concentration steps or addition of further standards before injection into the GC/MS instrument. As described in Section 2.2, the prepared simulant already contained the internal standards. The choice to add the standards before contact with the sample was made based on an estimation of the relative magnitudes of potential errors that may be introduced. Specifically, the error introduced by possible absorption of an internal standard contained in the simulant into the sample was seen as lower than potential dosing errors in the alternative approach of adding the standard just before GC/MS analysis. A pre-study (Figure A8) confirmed that the absorption of the chosen internal standard DFBP into the sample is negligible under the described conditions of contact.

Each production batch sample was tested in full triplicate: three sets of pellets from each reference/sample were placed in contact with the simulant, as described above, and the simulant of each replicate was then subjected to separate GC/MS analysis, as described below. For each week of testing, the reference sample was tested once, also in full triplicate, alongside the samples of that week. Where multiple samples were received from the same source in a single week, only one reference run was conducted.

4.5. GC/MS Analysis Method

The settings of the GC/MS instrument were chosen as follows. Injector temperature program: 40 °C, hold for 0.1 min; ramp of 12 °C/s until 280 °C, hold for 5 min. Injector split: 10 mL/min. Solvent delay: 4 min. Carrier gas: helium, 1.0 mL/min. Oven temperature program: 40 °C, hold for 2 min; 5 °C/min until 100 °C; 7 °C/min until 150 °C; 10 °C/min until 280 °C, hold for 12 min; 80 °C/min until 320 °C, hold for 15 min. Transfer line temperature: 270 °C. The mass spectrometer was operated in the scanning mode from 35 to 550 amu (range chosen to cover the widest range of substances). The instrument's software was loaded with commercial mass spectral libraries (including the NIST database), as well as a custom substance reference database, which included mass spectral and retention index information. For substances intentionally used in cosmetic products and packaging but not contained in commercial mass spectral databases, the database was populated mainly with data from our own measurements of authentic substance samples.

To verify that the retention index (RI) values generated by the instrument were reproducible, the alkane standard was measured at the beginning of each series of testing. The retention indices (RI) are linked to the retention time of each alkane. The retention time of each substance may change if chromatography conditions change (i.e., replacement of the column, change in temperature program or gas flow). The obtained RI values were compared with their reference values to confirm the stability of the analytical technique regarding the obtained retention indices.

The chromatograms obtained from the simulant that had been in contact with recycled plastic material samples were evaluated qualitatively in the form of the identification of substances using the retention index (Kovats retention indices based on interpolation between adjacent n-alkanes in the alkane standard; as the alkane standard and the samples were all measured with the same temperature program and GC/MS settings, no conversion of the retention index between the three sets of data was performed) and the mass spectrum. The threshold of acceptance of a structural assignment was set as confidence greater than 50% in the mass spectral match, as assigned by the instrument's software, combined with a match of the retention index within ±10 units. A semi-quantitative analysis via single-point calibration using the internal standard was also performed. Peaks for which the chemical structure could not be identified unambiguously were reported as 'unidentified'. A cut-off was set at 1% of the peak area of the internal standard, corresponding to a concentration of an analyte in the simulant of 0.13 mg analyte/kg simulant. The signal-to-noise ratio at the cut-off point was generally between two and five. Due to the semi-quantitative and substance-specific nature of the MS detection method, an exact limit of detection

(LoD) or limit of quantification (LoQ) was not established for each substance; instead, the above-defined cut-off was used.

A report was generated for each sample (see Tables S1 and S2 for examples), stating for each peak/substance the retention time, the retention index, the identified structure (where identification was possible), the corresponding CAS number and the concentration, expressed as mg per kg of recycled material pellets. For all samples and references, each replicate was analyzed separately. An averaging or combination of replicates was not performed; replicates were considered separately unless otherwise indicated below. Where a single replicate in a measurement of a reference sample or a production batch sample deviated by substantially more than the standard deviation, as determined from all reference measurements, the replicate was considered an outlier.

5. Conclusions

The obtained results demonstrate the suitability of the described test method for reproducibly assessing the release of substances from pellet samples of recycled plastics. Replicates, which were obtained from the repetition of all steps of the methodology on the same reference sample, yielded very comparable results, with a small standard deviation, confirming the reproducibility of the method itself. The same good reproducibility was found in the three replicates tested for several production batches of three rHDPE materials.

When comparing the results between different production batches of each rHDPE material, the identity and quantity of substances they released into the simulant exhibited limited variation for two materials and a larger variation for the third material, demonstrating that the described method allows for the detection of such differences in consistency between different recycled plastic material sources. These results also suggest that, with suitable quality control in recycling, the release of substances from recycled HDPE materials, and thus by proxy, their composition, can be confined to a very reasonable batch-to-batch variance.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/recycling9050101/s1, Table S1: Results of the repeated measurement of reference sample REF-A1, Table S2: Results of the repeated measurement of reference sample REF-A2.

Author Contributions: Conceptualization, H.G.-B.; methodology, M.B. and J.-P.V.; validation, M.B. and J.-P.V.; formal analysis, D.B.; investigation, M.B. and J.-P.V.; resources, H.G.-B.; data curation, H.G.-B.; writing—original draft preparation, D.B.; writing—review and editing, H.G.-B.; visualization, D.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article or the Supplementary Material.

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Conflicts of Interest: Authors Melanie Brandt, Jens-Peter Vietzke and Heiner Gers-Barlag were employed by the company Beiersdorf AG. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The Beiersdorf AG had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Appendix A

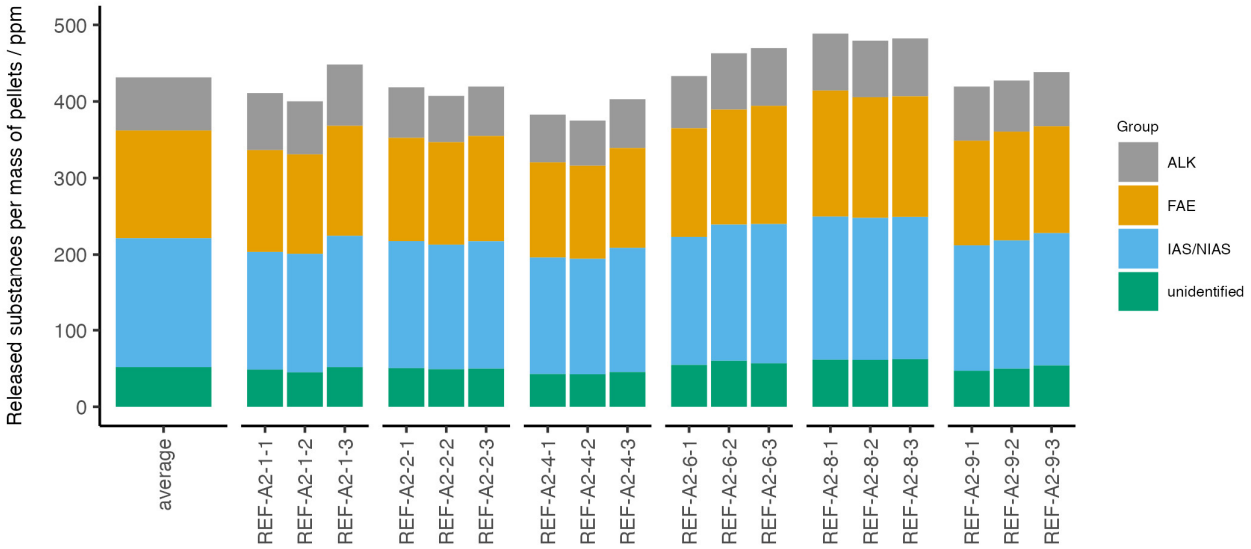


Figure A1. Reproducibility of GC/MS results between repeated measurements of the REF-A2 reference material (the first number represents the week of testing; the second number is the number of the replicate). The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

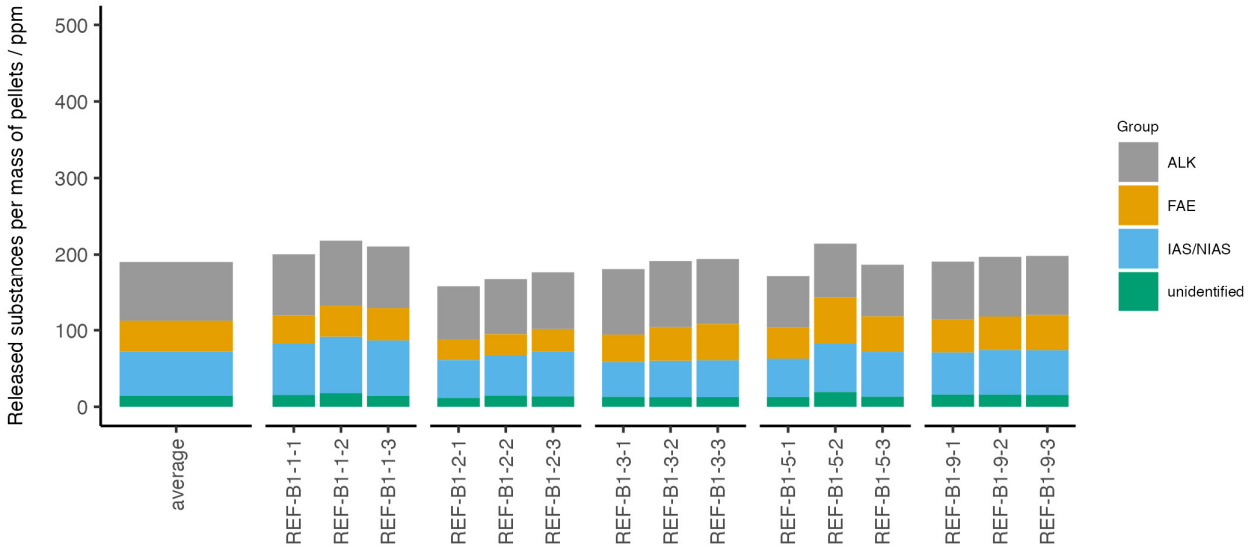


Figure A2. Reproducibility of GC/MS results between repeated measurements of the REF-B1 reference material (the first number represents the week of testing; the second number is the number of the replicate). The grouping represents alkanes (ALK), fatty acids, fatty acid esters and alcohols (FAE), and other intentionally or non-intentionally added substances (IAS/NIAS).

Appendix B

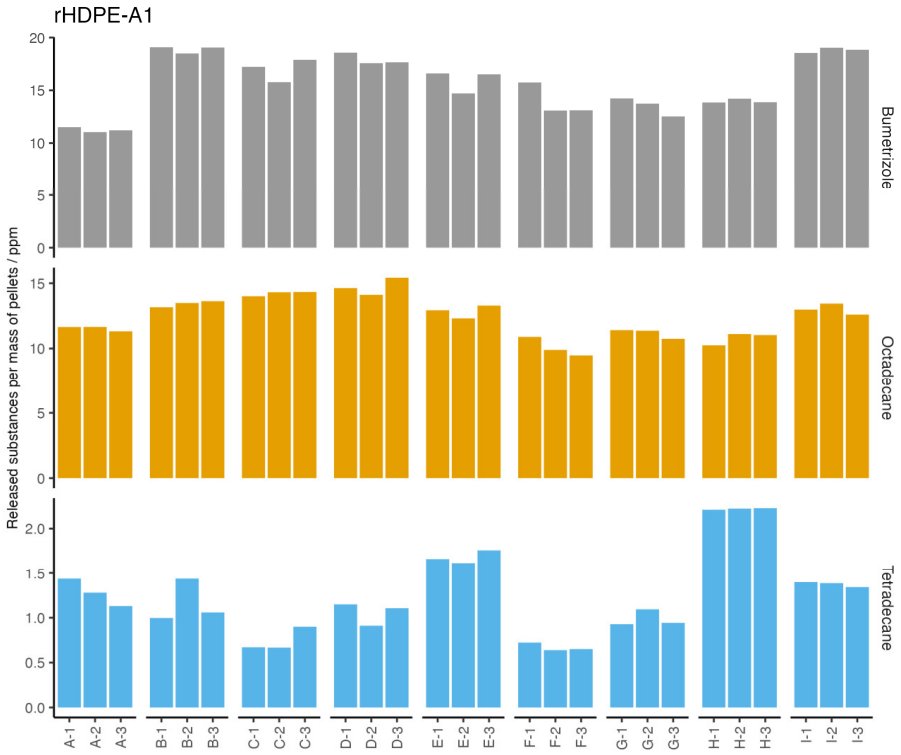


Figure A3. GC/MS results for select individual substances across all batches (A up to I) of rHDPE-A1.

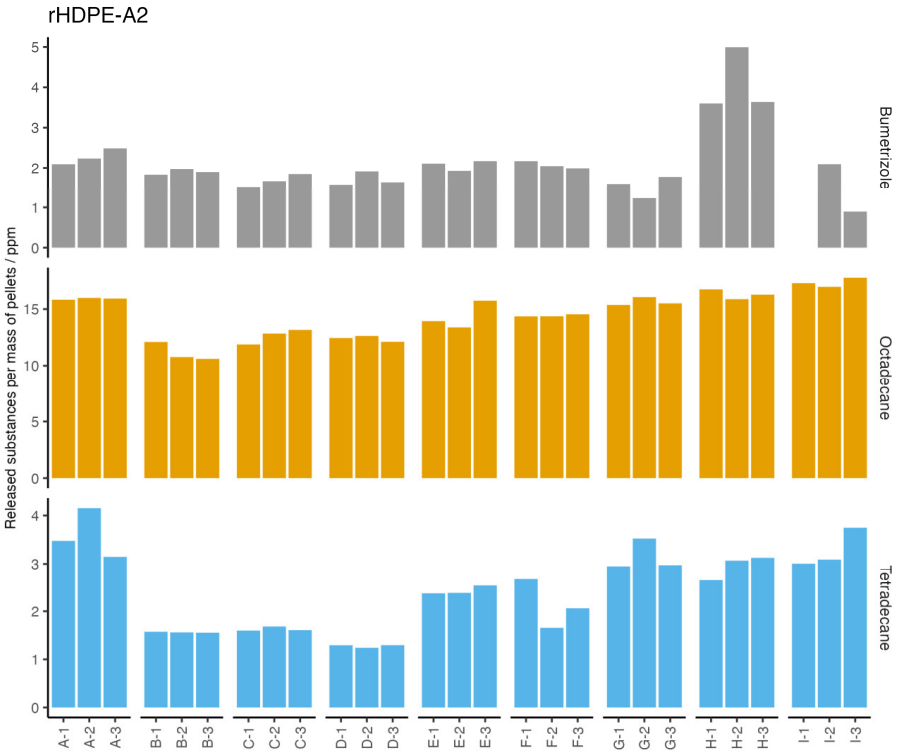


Figure A4. GC/MS results for select individual substances across all batches (A up to I) of rHDPE-A2.

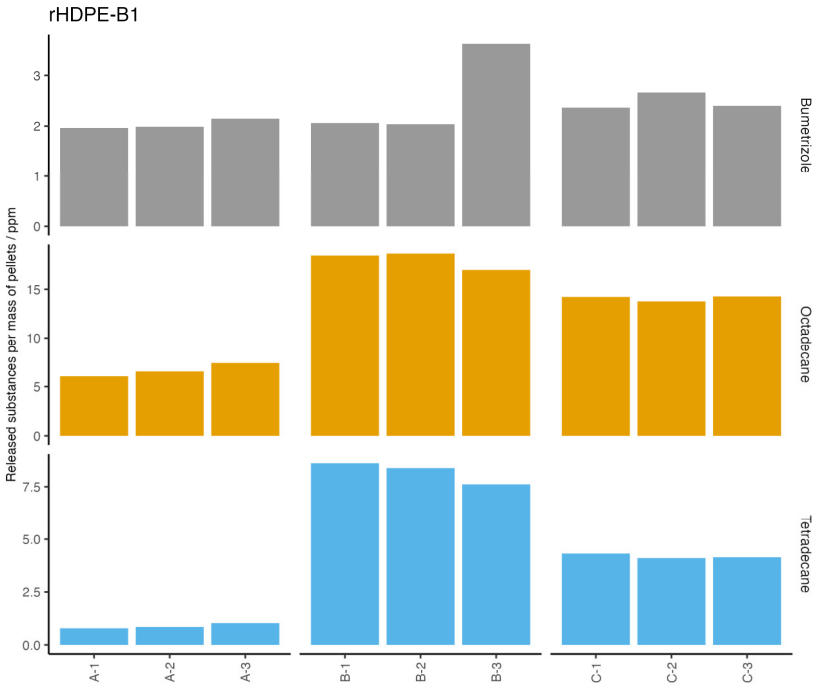


Figure A5. GC/MS results for select individual substances across all batches (A up to C) of rHDPE-B1.

Appendix C

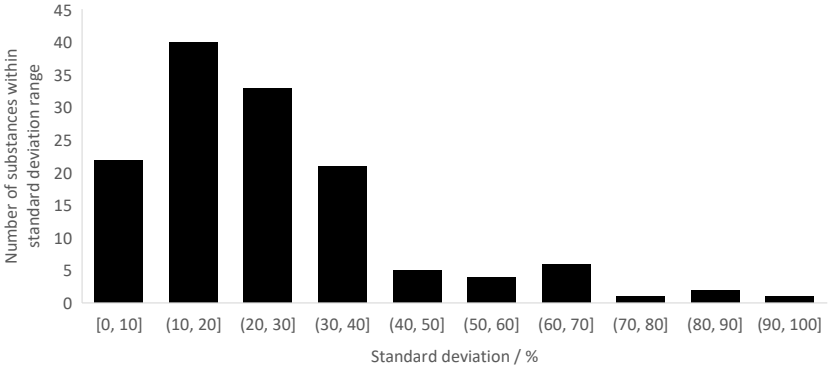


Figure A6. Analysis of the distribution of the standard deviation of the quantification results for each identified substance across all analyses of production batches of sample rHDPE-A1 (replicates were averaged before the analysis).

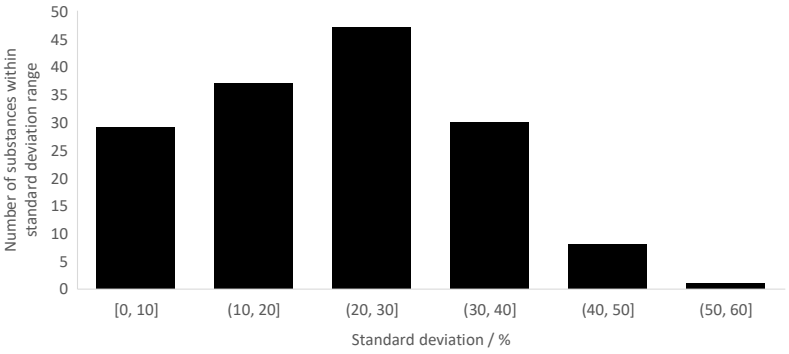


Figure A7. Analysis of the distribution of the standard deviation of the quantification results for each identified substance across all analyses of production batches of sample rHDPE-A2 (replicates were averaged before the analysis).

Appendix D

Table A1. Overview of samples included in this study.

Time of Sampling	PCR Material Production Batches		
	rHDPE-A1	rHDPE-A2	rHPDE-B1
Week 1	A, B	A	A
Week 2	C, D	B	B
Week 3	E, F		C
Week 4		C, D	
Week 5	G		
Week 6		E, F	
Week 7	H, I		
Week 8		G, H	
Week 9		I	

Appendix E

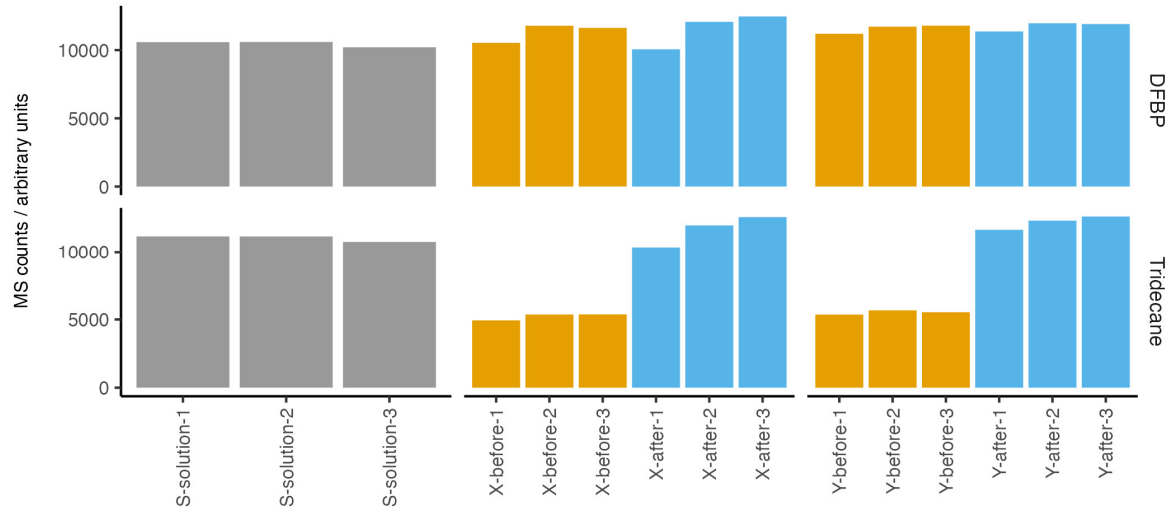


Figure A8. Results of the pre-study related to the potential absorption of internal standard into the pellet sample. A solution of two internal standards at equal concentration in 95% ethanol was used as a reference (S). Two rHDPE pellet samples (X, Y) were stored for seven days at 60 °C in 95% ethanol with the internal standard added from stock solution before or after the incubation time. Three replicates (1–3) were performed for each case. The mass spectrometer counts for the chromatographic peak related to the internal standards are reported in the graph.

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