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RESEARCH ARTICLE

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Effect of recycled content and rPET quality on the properties of PET bottles, part II: Migration

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Polyethylene terephthalate (PET) bottles were produced from three types of recycled PET (rPET) with four levels of recycled content. The migration of substances from these bottles to water was studied. Several migrated substances were detected. The migrated amounts of acetaldehyde and ethylene glycol complied with the limits given in the food contact material (FCM) legislation. Migration of 2-methyl-1,3-dioxolane was below the limit of 10 $\mu g \cdot L^{-1}$, which is conventionally applied for non-intentionally added substances (NIAS) not classified as 'carcinogenic', 'mutagenic' or 'toxic to reproduction' (CMR). Limonene, acetone, butanone and furan were also detected as migrants, of which limonene is a natural fragrant, and the other three are probably residues from solvents used to clean and protect the mould at the small-scale production facility. Finally, benzene and styrene were also found as migrants from rPET. These migrants appear to originate from heat-induced reactions within the PET matrix, which involve contaminants. The formation of benzene in rPET is attributed to polyvinylchloride as contaminant. The migrated amounts of benzene from the PET bottles with recycled content to the water simulant are relatively small (0.03–0.44 $\mu g \cdot L^{-1}$) after 10 days at 40°C. Consequently, the margin of exposure is 3.10^5–8.10^6. Hence, the level of concern for the public health is low, and the migrated amount represents a low priority for risk management. The FCM legislation demands a risk assessment for migrating NIAS. Depending on the underlying data and exposure scenario, different threshold limits in the food can be derived which can still be considered as safe.

KEYWORDS
migration, non-intentionally added substances (NIAS), PET bottles, recycled content

1 | INTRODUCTION

Polyethylene terephthalate (PET) is widely used to produce beverage bottles, packaging trays, blisters, multilayered packaging films, strapping tapes and various nonpackaging applications such as textiles. Its success as packaging material is related to a unique mix of properties: low permeability values for gases, good mechanical properties, highly transparent, highly reflective, relatively easy to process and available at a relative low price. Consequently, it is now the third largest packaging polymer, after polyethylene and polypropylene.[1] Because PET absorbs only limited amounts of molecular contaminants during use, which can also effectively be

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removed afterwards by modern super-clean technologies, for example, based on so-called solid state postcondensation, the recycling of especially PET bottles has developed greatly over the last years.[2,3] In 2016, 1.77 Tg of postconsumer PET bottles were recycled in Europe of the 3.15-Tg PET packages placed on the market.[4] Most of the recycled PET (rPET) was used in packaging applications (38% in trays, 26% in bottles and 11% in strapping) and the remaining 24% in fleece fill.[4]

EU Regulation 282/2008[5] describes the procedure, which recycling companies have to fulfil to get their combination of recycling process and feedstock approved for the production of food-grade rPET. The underlying safety evaluation scheme is a combination of challenge tests with surrogate contaminants on rPET pellets to determine the cleaning efficiency of the recycling process and mathematical modelling of the migration. The central criterion is that the modelled concentration of migrating substances from rPET should never exceed 0.1 $\mu g \cdot kg^{-1}$ of food at the end of the shelf life.[6–8] This combination with modelling was necessary, because the concentration of migrating substances in rPET is often below the detection limit. Many European recycling companies have applied for approval of their combination of process and feedstock; they have received an opinion in favour of authorising the recycling process and are waiting for the EU Commission to publish a list of authorised processes.

Beverage companies that use PET bottles with recycled content (RC) for their products have to prove compliance to the European food contact material (FCM) legislation. In the Netherlands, there are no additional terms in the national law Warenwet with respect to the use of rPET in bottles. In Germany, France, Belgium and Austria, there exist some national laws or recommendations, which are, however, based on typical migration tests for PET or close to the European Food Safety Authority (EFSA) safety criteria. After the publication of the list of authorised processes, these national laws and recommendations will be replaced by the Regulation 282/2008. On European level, all materials and articles used in contact with food must comply with the general requirements of the European Framework Regulation (EC) No 1935/2004.[9] For plastic materials, more specific requirements are laid down in the European Plastics Regulation (EU) No 10/2011. According to the latter regulation, the overall migration limit of 10 $mg \cdot dm^{-2}$ of food contact area has to be obeyed, but this has never been an issue for beverages in PET bottles.[10,11] Additionally, specific migration limits (SMLs) given by the European Plastics Regulation (EU) No 10/2011 have to be fulfilled.[11] Relevant are the SML's for PET monomers and degradation products: acetaldehyde, ethylene glycol, terephthalic acid and isophthalic acid of 6, 30, 7.5 and 5 $mg \cdot L^{-1}$, respectively. Additionally, there is also an SML for the antimony trioxide catalyst of 0.04 $mg \cdot L^{-1}$ (expressed as antimony).[12] Third, the migration of non-intentionally added substances (NIAS) must also be in compliance with the safety requirements of Article 3 of the European Framework Regulation (EC) No 1935/2004.[9] This needs to be assessed in accordance with internationally recognised scientific principles on risk assessment (Article 19 of Regulation [EU] No 10/2011). NIAS for which no dedicated risk assessment is available are often assessed in accordance with the functional barrier principle, according to which non-listed substances shall not be detected in a migration test at a detection limit of 10 $\mu g \cdot kg^{-1}$ provided that they are not classified as 'carcinogenic', 'mutagenic' or 'toxic to reproduction' (CMR) according to Regulation (EC) No 1272/2008[13]; see Article 13 of Regulation (EU) No 10/2011.[12] CMR substances should not intentionally be used. For the risk assessment of non-intentionally added CMR substances, EFSA derived an exposure threshold value for a worst-case scenario of 0.017 $\mu g \cdot L^{-1}$, which can be used as a practical migration limit for genotoxic NIAS for which no specific toxicological data are available.[6] A formal migration limit for genotoxic NIAS does not exist in the EU FCM legislation. Fourth, the rPET applied should be supplied from a PET recycling company that received an EFSA opinion in favour of authorisation.

Because the environmental impacts associated with the mechanical recycling of PET from collected bottles is in general less than the production of new resin from fossil resources,[14,15] the use of rPET in beverage bottles has been encouraged. For example, in the Netherlands, the beverage industry strives to attain a recycling content of at least 37% for large PET bottles in 2018 and 32% for small PET bottles in 2018.[16] From an environmental point of view, a 100% recycling content is optimal, whereas from a quality, food safety and marketing point of view lower recycling contents might be better. This raises the complex question what the optimal level of RC is. The aim of this study is to explore the effect of rPET quality and the level of RC on the migration of substances from PET bottles to bottled water.

2 | MATERIALS AND METHODS

2.1 | Origin of the PET materials, characterisation and production of bottles

PET bottles were made from one type of virgin PET (Indorama RamaPET N180) and three different types of rPET. Type A rPET is originated from a recycling company that processes PET bottles from mono-collection systems as feedstock. Types B and C rPET are originated from a different recycling company that processes co-collected and sorted PET bottles as feedstock.[17] Because of the sensitivity of this quality evaluation for these recycling businesses, their identities are not disclosed.

The elemental composition of the virgin PET pellets and the three chosen rPET pellets was determined according to DIN EN ISO 17294-2 by use of inductively coupled plasma mass spectrometry (ICP-MS) for the metals Cd, Co, Cr, Hg, Mn, Pb, Sb, Ti and Zn. Rhodium and rhenium were used as internal standards. The sample preparation was according to DIN EN 16711-1 (04/2014) by homogenisation and total digestion in the microwave in high-pressure vessels with nitric acid. Additionally, the chlorine concentration was determined for these pellets by microcoulometry according to CEN/TS 15289.

The three chosen types of rPET pellets were mixed with virgin PET pellets in mixing ratios of 0:100%, 25:75%, 50:50%, 75:25% and 100:0% and used to produce PET bottles in a small-scale production facility.[17] The minimal total cycle time was 3.3 min per bottle: injection moulding (33 s at maximally 290°C), reheating (165 s at 110°C) and stretch blow moulding (12 s).

2.2 | Screening of volatile substances in rPET pellets and bottle fragments

Headspace gas chromatography coupled to mass spectroscopy (GC-MS) was performed at Fraunhofer IVV with the use of the following accredited method. The pellets were analysed without grinding, because grinding poses the risk of cross contamination in the mill with substances from previous samples as well as an uncontrolled loss of very volatile substances like acetaldehyde. In order to establish high diffusivity, 1.0 g of the pellets were introduced in a glass vial and equilibrated at 200°C for 1 h. After equilibration, the headspace of the vial was injected on a gas chromatography column with FID detector. The GC was a Perkin Elmer AutoSystem XL. The column was a DB 1–30 m, 0.25 mm i.d. and 0.25 μm film thickness. The temperature programme was 4 min at 50°C followed by a 20°C·min^{-1} of increase up to 320°C at which the temperature was maintained for 15 min. The carriage gas was 50-kPa helium, and the split was 10 ml·min^{-1}. The headspace autosampler was a Perkin Elmer HS 40 XL. The oven temperature was 200°C, the needle temperature was 210°C, the equilibration time was 1 h, and the injection time was 0.02 min. The identification was done by retention time and verified with the coupled mass spectrometer. Quantification was achieved by external standards with calibration curves and at least 5 calibration points per standard. Bottle fragments were studied with the same method. Here, 1.0 g of bottle clippings of roughly 0.5 × 0.5 cm were placed in the glass vial prior to thermal equilibration. Detection limits were approximately 0.1 mg·kg^{-1} for volatile, low molecular substances. To validate this analysis method for volatiles from PET, multiple headspace extractions were conducted. The results were analysed within the theoretical framework for multiple headspace extractions[18]; see Table S7.

2.3 | Screening of medium and nonvolatile substances in rPET pellets and bottle fragments

GC and GC-MS analysis was performed at Fraunhofer IVV with the use of the following accredited method. For each test, 1.0 g of PET material was immersed in 10-ml dichloromethane and stored for 3 days at 40°C. The extracts were decanted from the PET material and analysed by gas chromatography and GC-MS. The gas chromatograph with FID detector was an Agilent 6890 with DB 1–30 m, 0.25 mm i.d. and 0.25 μm film thickness column. The temperature programme was 2 min at 50°C, followed by heating with 10°C·min^{-1} to 340°C and maintaining that temperature for 15 min. The prepressure was 50-kPa hydrogen gas, and the split was 10 ml·min^{-1}. Two internal standards were used: butyl hydroxy-anisole (BHA) and Tinuvin 234. Identification and characterisation were achieved by coupling the headspace chromatography to a mass spectrometer. This gas chromatograph was a Thermoquest SSQ with DB 1 MS–30 m, –0.25 mm i.d. and 0.25 μm film thickness. The temperature programme started at 80°C for 2 min, followed by heating at 10°C·min to 340°C and holding the temperature for 30 min. A full mass scan was made between m/z 40 and 800. The obtained mass spectra were identified by comparing them to the spectra in the National Institute of Standards and Technology (NIST) spectral library. The applied extraction methods followed by gas chromatography is able to determine substances with molecular weights between 150 and about 700 g·mol^{-1}. Additional analysis with high-performance liquid chromatography (HPLC) methods would render more insight in higher molecular migrants with molecular weights above 700 g·mol^{-1}.[19–21] However, these higher molecular weight substances show such a slow diffusion that their contribution to migration is negligible[11] and hence not relevant for this study. Detection limits were approximately 1.0 mg·kg^{-1} for medium volatile substances. To validate this method, the extraction was repeated at longer extraction time and a second extraction, which proved that the extraction was exhaustive; see Table S8.

2.4 | Modelling of the migration

The migration of substances from PET bottles into water was modelled with the measured concentrations in the PET bottle fragments as starting point and diffusion coefficients that were derived from the molecular mass of the migrants.[22] The calculation of the migration was performed using the AKTS SML software version 4.54 (AKTS AG Siders, Switzerland). The programme is using finite element analysis. The mathematical procedure and the main equations are published.[23] The applied surface area to volume ratio was 6 dm^2 to 1 L (EU Cube); the PET bottle wall thickness was assumed to be 300 μm.

2.5 | Measurement of the migration

The bottles were filled with noncarbonated mineral water, closed with standard high-density polyethylene (HDPE) caps and stored for 10 days at 40°C in an acclimatised cell. Subsequently, the contained water was analysed according to the US EPA 524.2 method.[24] In this method, organic volatile compounds are purged from an aqueous sample and trapped in a temporary absorbent, to be subsequently analysed and identified by GC-MS. The GC-MS equipment was from Thermo Scientific, the Purge and Trap assembly from Tekmar. The GC-column was DB-VRX of 20 m, 0.18 mm diameter and 1 μm film thickness. The temperature programme was 3 min at 40°C, followed by heating with 59°C·min^{-1} to 190°C, a holding time of 0.25 s, followed by a further heating with 24°C·min^{-1} to 225°C and maintaining that temperature for 5 min. These measurements were performed in an industrial laboratory, which use glass bottles with

mineral water as a reference standard and have performed this method for more than two decades. During this time period, they have expanded the list of volatile compounds from 86 to 109 on the basis of their experience. In order to obtain an industrial benchmark of migration from PET bottles of three European markets, mineral water packed in PET bottles was purchased in supermarkets and analysed in the same manner; see Table S5. This was a deliberate request of the researchers.

3 | RESULTS

3.1 | Quality of the PET pellets

The level of antimony catalyst varies between 255 and 270 mg·kg^{-1} in the PET pellets (Table S1) and lies within the expected range of 150–300 mg·kg^{-1}.[25–27] Of the other scanned metals, only cobalt is detected at a concentration of 6.5 mg·kg^{-1} for virgin PET and 1.5 mg·kg^{-1} for all types of recycled PET. This is most likely a residue of cobalt catalyst used in the AMOCO process to convert p-xylene in terephthalic acid.[28] Chlorine is hardly present in virgin PET but more profoundly present in Types B and C rPET. Because the chlorine content was determined with microcoulometry and this method is not specific for chlorine, also other halogens such as bromine are likely to be detected. Because virgin PET will always contain some traces of bromine catalyst from the AMOCO process,[28] the real chlorine content of virgin PET is likely to be even lower than the measured value. The major source of chlorine in rPET is likely to be remnants of poly vinyl chloride (PVC) as polymeric contaminant. But the presence of other chlorinated substances cannot be ruled out either.

3.2 | Volatile compounds in the rPET pellets and bottles

In the headspace gas chromatograms of the PET pellets and the cut PET bottle fragments, four clear peaks are identified with retention times below 3.0 min, namely, acetaldehyde, 2-methyl-1,3-dioxolane, benzene and ethylene glycol. The concentrations of these volatiles in the studied PET materials are listed in Table 1. Limonene, a well-known beverage flavour, which is often detected in rPET material, was for all the samples under the detection limit of 40 µg·kg^{-1} and is therefore not listed. It is fairly remarkable that recycled PET materials that have been subjected to super-clean processes still contain volatile compounds, albeit in very low concentrations.

The concentration of acetaldehyde, ethylene glycol and 2-methyl-1,3-dioxolane follows a similar pattern. Their concentrations are relatively low in rPET pellets that underwent super-clean processes with high vacuum solid state condensation but rise after bottles have been produced to fairly stable concentration values. This plateau value in bottles amounts to 12–16 mg·kg^{-1} for acetaldehyde, 4–6 mg·kg^{-1} for ethylene glycol and 1–2 mg·kg^{-1} for 2-methyl-1,3-dioxolane. Because these substances all originate from the elimination of ethylene glycol monomers from PET, a similar vapour pattern is expected. Furthermore, the difference in these concentrations is relatively small between the types of rPET pellets; these concentrations are lowest for Type A rPET and highest for Type C rPET. This small difference disappears after the conversion of the pellets in bottles; then, similar high plateau values are measured. Hence, only for the rPET pellets, there is a weak relation between the quality of the rPET and the concentrations of these volatiles. However, for PET bottles, no clear relationships are found between the quality of the rPET, the RC and the concentration of these volatiles. It is therefore likely that most of these volatiles are formed in a thermal degradation process, in which the exposure time to elevated temperatures is the rate limiting step in the production of these volatiles.

It should be noted that the concentration of acetaldehyde found in the PET bottle fragments is relatively high (11–16 mg·kg^{-1}), although similar high values have been reported in the past prior to the introduction of 2-aminobenzamide as acetaldehyde scavenger in 2005.[29] This relatively high value can be related to the pilot-scale preform and bottle production process, in which PET resin is exposed to elevated temperatures for longer periods of time than in the commercial production process and the fact that no acetaldehyde scavenger was used (see Section 4.1).

The concentration of benzene in the PET materials follows a completely different pattern. Benzene cannot be detected in virgin PET and in Type A rPET pellets (A) and is just detectable in Types B and C rPET pellets. Benzene can also not be detected in bottles made from virgin PET but is present in all bottles with RC. The concentration of benzene rises with the RC. The slope with which the concentration of benzene rises depends strongly on the quality of the rPET. Bottles made from 100% Type A rPET contain 0.2 ± 0.1 mg·kg^{-1}; benzene and bottles made from Types B and C rPET contain 1.8 ± 0.1 mg·kg^{-1} and 1.6 ± 0.1 mg·kg^{-1} of benzene, respectively. The benzene concentrations in bottles made with Type A rPET are both low and close to the detection limit (0.1 mg·kg^{-1}). The clearly found relation between the quality of the rPET, the RC and the benzene concentration suggests that impurities present in rPET are responsible for producing benzene (see Section 4.2).

All gas chromatograms of bottle fragments show peaks at retention times above 3 min. Because these peaks are absent in the chromatograms of all the pellets (virgin and rPET) and present in all the chromatograms of PET bottles, including the one from virgin PET bottles, it was decided that these peaks are artefacts related to the bottle manufacturing process and are ignored in the evaluation of the rPET bottles (see Section 4.1).

To confirm the high levels of acetaldehyde and the presence of benzene in the PET bottles and intermediates, a few measurements with virgin pellet, Type B rPET pellet, preforms and bottles were repeated in a different laboratory with a slightly different GC methodology; see Table S2. These measurements were conducted 3 months after the production of the preforms and the bottles, whereas the results in Tables 1–3 were obtained with bottles within 1–3 weeks after their production. These measurements confirm the high level of acetaldehyde in the preform but not in the

TABLE 1 Concentration of volatile molecular contaminants present in the studied PET pellets (pe) and bottle fragments (bo), ($mg \cdot kg^{-1}$)

Sample	Acetaldehyde	2-methyl-1,3-dioxolane	Benzene	Ethylene glycol
Virgin PET pe	1.8 ± 0.1	0.2 ± 0.1	<0.1	0.8 ± 0.3
Virgin PET bo	14.7 ± 0.2	1.9 ± 0.1	<0.1	4.8 ± 0.1
rPET A pe	0.6 ± 0.1	0.1 ± 0.1	<0.1	0.9 ± 0.1
rPET 25% A bo	13.1 ± 0.6	1.2 ± 0.1	<0.1	5.2 ± 0.1
rPET 50% A bo	13.9 ± 0.2	1.3 ± 0.1	0.1 ± 0.1	4.6 ± 0.1
rPET 75% A bo	13.9 ± 0.9	1.1 ± 0.1	0.2 ± 0.1	4.4 ± 0.1
rPET 100% A bo	12.6 ± 0.2	0.9 ± 0.1	0.2 ± 0.1	4.4 ± 0.1
rPET B pe	1.6 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	1.7 ± 0.1
rPET 25% B bo	14.9 ± 0.5	1.5 ± 0.1	0.6 ± 0.1	5.9 ± 0.1
rPET 50% B bo	15.7 ± 0.3	1.5 ± 0.1	1.0 ± 0.1	5.6 ± 0.1
rPET 75% B bo	15.1 ± 0.8	1.4 ± 0.1	1.4 ± 0.1	5.6 ± 0.1
rPET 100% B bo	16.3 ± 0.2	1.5 ± 0.1	1.8 ± 0.1	6.4 ± 0.1
rPET C pe	5.2 ± 0.1	0.9 ± 0.1	0.1 ± 0.1	2.6 ± 0.1
rPET 25% C bo	13.1 ± 0.6	1.2 ± 0.1	0.5 ± 0.1	5.4 ± 0.1
rPET 50% C bo	12.2 ± 0.4	1.1 ± 0.1	0.9 ± 0.1	5.6 ± 0.1
rPET 75% C bo	11.3 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	5.8 ± 0.1
rPET 100% C bo	13.0 ± 0.1	1.1 ± 0.1	1.6 ± 0.1	6.4 ± 0.1

Note: The type of rPET is denoted with abbreviations A, B and C. The error of these single measurements originated from the area-calculating method.
Abbreviations: PET, polyethylene terephthalate; rPET, recycled PET.

bottle. Most likely, this implies that most of the acetaldehyde is produced during injection moulding, when the material is exposed to the highest temperatures (270–290°C for 33 s) and less during blow moulding of the bottles (maximal 110°C for 165 s). Furthermore, acetaldehyde is lost faster from PET bottles than from preforms by diffusion and evaporation during storage because of the lower wall thickness of the bottles. The measurements also confirm the presence of benzene in the pellets and bottles. The largest increase in benzene concentration was found between the pellets and the preforms, hence during the injection moulding process. During the stretch blow moulding process, the benzene concentration is raised further. This suggests that the process responsible for the production of benzene is thermally activated.

3.3 | Medium and nonvolatile compounds in the rPET pellets

The gas chromatograms of the dichloromethane extracts of the PET pellets and the PET bottle fragments all showed seven or less peaks. The first peak was dismissed as an analytical artefact, because it is also present in the solvent blank. The other six peaks are identified as cyclic dimers and trimers of the PET monomers; see Tables S3 and S4. Cyclic dimers and trimers, as well as higher molecular weight oligomers, are well-known polymerisation side products in PET.[19–21]

The lowest concentration of these cyclic oligomers is found in Type A rPET pellets; the concentration is slightly higher in Type B rPET pellets and the highest in Type C rPET pellets (Table S3). These differences in oligomer concentrations in the pellets are likely to be related to differences in thermal treatment during the production of these rPET pellets. The concentration of these oligomers in all PET bottle fragments is, however, more comparable with the concentration of these oligomers in Type C rPET (Table S4). Furthermore, the concentration of these oligomers in the bottles is not influenced by the RC and the quality of the rPET. Even bottles made from virgin PET showed similar high levels of oligomers. This suggests that these oligomers are formed during the small-scale bottle production process at which the PET material is exposed to elevated temperatures for relatively long periods of time.

3.4 | Measured migration

The experimentally determined concentrations of migrated volatile substances from the PET bottles to the contained water is shown in Table 2. Because the used purging method cannot determine acetaldehyde and ethylene glycol, these are also not listed.

2-methyl-1,3-dioxolane is present in the pellets, bottles and in the food simulant water. The migrated amount corresponds to the initial concentration in the PET bottle. Its concentration is relatively high in virgin PET bottle and in the simulant water it contains, whereas the concentration is slightly lower in PET bottles with RC and in the water they contain. This migrant is the condensation product of ethylene glycol and acetaldehyde, and hence, its concentration depends on the concentration of both precursors. The solid state polycondensation (SSP) process to which rPET pellets are subjected will lower the concentration of acetaldehyde and ethylene glycol in the rPET pellets and hence also of 2-methyl-

1,3-dioxolane. The thermal processing involved with the conversion of pellets in bottles causes renewed thermal degradation and hence raises the concentrations of these migrated substances in the bottles and contained water.

The concentration of limonene (a beverage flavour) is below the detection limit (<40 $\mu g \cdot kg^{-1}$) in the pellets and bottle fragments and is just detected as migrated substance in the contained water (0.01–0.026 $\mu g \cdot L^{-1}$). There was no clear relationship between the RC and the amount of limonene migrated. The type of rPET had a marginal influence on the amount of limonene migrated; it was slightly smaller for Type B in comparison with Types A and C, which could relate to subtle differences in the feedstock and the recycling process.

The concentration of benzene in the contained water is below the detection limit for bottles made with virgin PET. However, for bottles with RC, this concentration varies between 0.03 and 0.44 $\mu g \cdot L^{-1}$. A clear relationship is observed between the type of rPET and the migrated amount and between the RC and the migrated amount. This is further discussed in Section 4.2.

The concentration of styrene in the simulants follows a similar pattern as benzene but at a lower level. This concentration is below the detection limit for bottles with virgin PET and from bottles with Type A rPET, but the concentration of styrene in the aqueous simulant varies between 0.011 and 0.063 $\mu g \cdot L^{-1}$ for bottles with Types B and C rPET. There is a clear relationship between the amount of styrene migrated and the RC for these rPET qualities. Styrene could originate from the thermal degradation of polystyrene, which is present as a polymeric contaminant in lower qualities rPET.

Two commonly used solvents, acetone and butanone, are found as migrants from the PET bottles in the water simulant in low concentrations. For butanone, the determined concentrations vary between below 0.01 and 0.02 $\mu g \cdot L^{-1}$, and for acetone, the concentrations vary between below 0.01 and 0.7 $\mu g \cdot L^{-1}$. Butanone does not migrate in detectable quantities from virgin PET bottles and Type A rPET bottles but does migrate in relatively low quantities from bottles with Types B and C rPET. For acetone, the migrated amounts are higher, but no clear correlations with the type of PET could be found, because acetone even migrates in high quantities from virgin PET bottles. Perhaps these solvents are present in the mould maintenance spray or general purpose cleaning agent. Remarkably, these compounds are not detected in PET pellets and in PET bottle fragments (Table 2). Their apparent absence in the pellets is logical when the mould agent would be the source, whereas for the detection from PET bottle fragments, their concentrations are likely to be below the detection limit.

The last migrant detected is furan. Its concentration varies between 0.05 and 0.13 $\mu g \cdot L^{-1}$ in the water simulant. It is present in both the simulants of virgin PET bottles and of bottles with RC. No clear relation is found with the type of rPET or with the RC. In general, furan is a known pyrolysis product of biomass[30] and is produced in thermally treated food products.[31] Therefore, various organic impurities could be responsible, and its precise origin remains unclear.

3.5 | Modelled migration

The migration of substances from PET bottles to water was also modelled. The required diffusion coefficients for all relevant compounds were predicted with experimentally determined activation energies of diffusion.[22] The model relates the initial concentration of substances in the PET bottle to the concentration of these substances in the contained water in relation to the elapsed time, temperature and volume-to-surface ratio of the bottle. For any substance with a defined migration limit or threshold limit in the food, which can still be

TABLE 2 Concentrations of volatile substances migrated from PET bottles to mineral water during a migration test at 40°C over 10 days, ($\mu g \cdot L^{-1}$)

Bottle	2-methyl-1,3-dioxolane	Benzene	Styrene	2-butanone	Acetone	Furan	Limonene
Glass ref.	ND	ND	ND	ND	ND	ND	ND
Virgin PET	0.55	<0.01	<0.01	<0.01	0.5	0.08	0.020
25% A rPET	0.37	0.037	<0.01	<0.01	<0.01	0.06	0.022
50% A rPET	0.34	0.047	<0.01	<0.01	<0.01	0.05	0.026
75% A rPET	0.25	0.062	<0.01	<0.01	0.3	0.07	0.023
100% A rPET	0.18	0.066	<0.01	0.01	0.3	0.05	0.021
25% B rPET	0.40	0.145	0.011	0.02	0.3	0.10	0.016
50% B rPET	0.34	0.238	0.017	0.02	0.2	0.05	0.020
75% B rPET	0.30	0.284	0.047	0.02	0.7	0.09	<0.01
100% B rPET	0.36	0.438	0.063	0.02	0.2	0.08	0.014
25% C rPET	0.39	0.161	0.013	0.01	<0.01	0.07	0.022
50% C rPET	0.30	0.218	0.040	0.02	0.3	0.13	0.019
75% C rPET	0.28	0.304	0.042	0.02	0.3	0.09	0.020
100% C rPET	0.25	0.388	0.050	0.02	0.1	0.06	0.025

Note: All are single measurements. ND means not detected.
Abbreviations: PET, polyethylene terephthalate; rPET, recycled PET.

TABLE 3 Maximum concentration of substances in the PET bottle wall which corresponds to a migrated amount of 10 μg·L^{-1} after 1 year at 25°C for a 500-ml bottle with a 420-cm^2 surface area and a 300-μm wall thickness

Substance	Molecular weight, (g·mol^{-1})	Molecular volume, (Å^3)	Predicted diffusion coefficient, (cm^2·s^{-1})		Maximum bottle wall concentration, (mg·kg^{-1})	
			From the molecular volume	From the molecular volume −20%	Calculated with normal molecular volume	Calculated with molecular volume −20%
Acetaldehyde	44.1	48.2	$2.11 \cdot 10^{-12}$	$1.75 \cdot 10^{-11}$	0.93	0.35
2-methyl-1,3-dioxolane	88.1	86.8	$7.92 \cdot 10^{-15}$	$6.59 \cdot 10^{-14}$	15.1	5.24
Benzene	78.1	84.0	$1.08 \cdot 10^{-14}$	$9.00 \cdot 10^{-14}$	12.9	4.48
Ethylene glycol	62.1	62.3	$1.85 \cdot 10^{-13}$	$1.54 \cdot 10^{-12}$	3.13	1.09
Cyclic dimer P_2E_2	384.3	323.7	$2.97 \cdot 10^{-20}$	$2.47 \cdot 10^{-19}$	7,760	2,700
Cyclic dimer P_2E_2	384.3	323.7	$2.97 \cdot 10^{-20}$	$2.47 \cdot 10^{-19}$	7,760	2,700
Cyclic dimer P_2E_2	384.3	323.7	$2.97 \cdot 10^{-20}$	$2.47 \cdot 10^{-19}$	7,760	2,700
Cyclic dimer $TP_2E_1D_1$	428.4	366.3	$9.17 \cdot 10^{-21}$	$7.63 \cdot 10^{-20}$	13,900	4,850
Cyclic dimer TP_2D_2	472.5	408.9	$3.23 \cdot 10^{-21}$	$2.68 \cdot 10^{-20}$	23,600	8,200
Cyclic trimer TP_3E_3	576.5	484.6	$6.44 \cdot 10^{-22}$	$5.35 \cdot 10^{-21}$	52,900	18,300

Abbreviations: TP, terephthalic acid; P, either terephthalic acid or isophthalic acid; E, ethylene glycol; D, diethylene glycol.
Abbreviations: PET, polyethylene terephthalate; rPET, recycled PET.

considered as safe, the maximum allowed initial concentration of the substance in the PET bottle resin correlating with this migration limit can be calculated in relation to the elapsed time and experienced temperature. For NIAS not classified as CMR, a threshold limit of 10 μg·L^{-1} can be applied (see Section 4.4). Subsequently, the concentrations of NIAS in the PET samples determined within this study can be compared with these maximum concentrations. In case that the experimentally determined concentrations are below of the predicted calculations, the concentrations in the PET packed beverages are below of the migration threshold limit of 10 μg·L^{-1}. In order to apply a worst-case scenario for the migration, in a second trial, the diffusion coefficients were predicted with an artificially reduced molecular volume by 20%. The migration was calculated for a bottle volume of 1 L with an inner surface area of 600 cm^2 for a storage time of 365 days at room temperature (Figure 1). The solid line in Figure 1 is the prediction from molecular volume. The dashed line can be considered as worst-case prediction with −20% of molecular volume of NIAS. The concentrations given in Figure 1 are calculated for the EU cube. Other surface volume ratios can be considered by use of a surface volume factor. For example, for a PET bottle with 500-ml volume and an inner surface of 4.20 dm^2, the maximum concentrations are a factor of 1.4 lower (f = [4.2 * 1.0]/[6.0 * 0.5] = 1.4). For the experimentally determined substances, the maximum concentrations in a 500-ml bottle that corresponds to a specific migration of 10 μg·L^{-1} after storage for 365 days at 25°C were calculated. These results are given in Table 3.

As a result, from the headspace gas chromatograms, it can be concluded that only acetaldehyde (molecular volume 48 Å^3) and ethylene glycol (62 Å^3) might exceed the migration limit of 10 μg·L^{-1}. However, acetaldehyde and ethylene glycol are both listed in European Regulation 10/2011 with an SML of 6 and 30 mg·L^{-1}, respectively.

Regarding benzene, which is a genotoxic substance, the threshold of 10 μg·L^{-1} is not exceeded. However, in the case of benzene, a much lower threshold limit might be applicable; see Section 4.4.

In order to allow for a comparison between the experimentally determined migration values for benzene (Table 2) and those predicted by the model, the modelling was repeated with same conditions of the experiments (10 days at 40°C). The diffusion coefficient of benzene in PET at 40°C was predicted to be $9.44 \cdot 10^{-14}$·cm^2·s^{-1} based on the molecular volume of benzene and the previously reported procedure.[22] In Table 4, the experimentally determined benzene concentration in bottles made from 100% rPET is related to the modelled concentration of benzene in water and compared with the experimentally determined concentration of migrated benzene. These results are relatively similar, which form additional support for the migration of benzene from the resin to the water. The model slightly overestimates the migration, as was previously reported for small molecules with a molecular volume of less than 200 Å^3.[32]

4 | DISCUSSION

4.1 | Impact of the bottle manufacturing process on the results

Small series (roughly 100 per feedstock) of bottles were produced from different types of rPET with different levels of RC with a small-scale production facility.[17] As a consequence, the residence times in the injection moulding machine and the reheater were substantially longer than what is common in commercial large-scale equipment. Consequently, more molecular contaminants resulting from thermally activated reactions can be expected in bottles produced at the small-scale production facility than in bottles from a commercial large-scale

bottle blowing facility. Indeed, the amount of acetaldehyde in the PET bottles produced in this manner was larger than in most commercially produced bottles.[29,33–35] Additionally, the bottles were produced without acetaldehyde scavenger (2-aminobenzamide).[29] The reaction that is responsible for the production of benzene is also thermally activated, and hence, it would be likely that the concentrations of benzene in both the bottles and the simulant measured in this study are higher than in commercially produced PET bottles and contained products. To estimate the impact of the production method on the migration results, commercially produced mineral waters in PET bottles (with unknown levels of RC) from three different European markets were subjected to the same migration test (Table S5). The comparison with the bottles produced for this study shows that almost all migrants were detected in much higher concentrations in these bottles. The maximally determined benzene concentration in bottles produced for this study was 5.2 times higher than the maximal concentration in a commercial bottled water product. For styrene and furan, the maximal concentrations were 2.7 times higher for the bottles produced in this test as compared with the commercial bottled water products. No precise conclusions can be drawn from this comparison with regard to the influence of the production method on the migration, because relevant information of the commercial bottles (age, RC and type of rPET) is missing. Nevertheless, this comparison makes it likely that the production method causes an overestimation of the amount of volatile compounds produced within PET bottles with RC that migrate to the contained product.

The peaks in the gas chromatograms for volatiles with a retention time of more than 3 min (Paragraph 3.2) were also considered artefacts of the small-scale production method. They are normally absent in commercially produced PET bottles, whereas in our trials, they were present in all PET bottles, also in the bottles which were made from virgin PET. One of the likely sources of contamination is the applied thinner to clean the moulds and the applied mould protect formulation, which is used in this small-scale production machine.

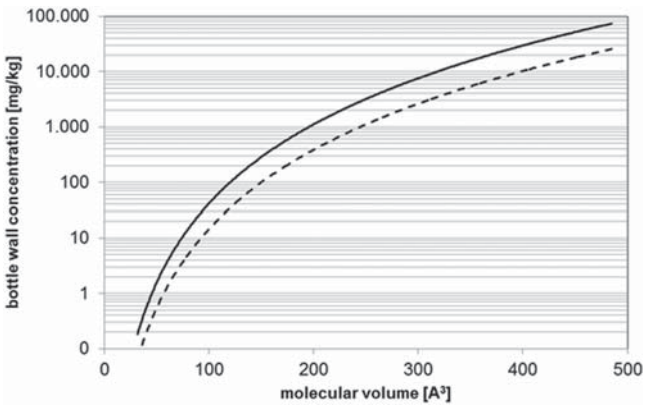


FIGURE 1 Bottle wall concentrations corresponding to a migration of 10 μg·L^{-1} (storage conditions 365 days at 25°C, 1 L packed into 6 dm^2, density of PET: 1.4 g·cm^{-3}, partition coefficient K = 1) of migrants with a varying molecular volumes. Solid line: predicted relationship. Dashed line: worst-case prediction with 20% less molecular volume to the migrant

TABLE 4 Comparison between the modelled migration of benzene from PET bottles to water with the measured migration of benzene to water (stored at 10 days at 40°C)

rPET type	Benzene concentration in rPET bottles with 100% recycled content, (mg·kg^{-1})	Modelled concentration of benzene in water, (μg·L^{-1})	Measured concentration of benzene in water, (μg·L^{-1})
A	0.2	0.08	0.066
B	1.8	0.68	0.438
C	1.6	0.61	0.388

Abbreviations: PET, polyethylene terephthalate; rPET, recycled PET.

Hence, although the small-scale production equipment used did influence the absolute levels of volatile products in the PET bottles and the presence of unknown volatiles with a high retention time, the results of this study should not be used to draw definitive conclusions on exposure and compliance, but rather as a qualitative comparative study on the impact of the quality of rPET and the RC levels on the migration of volatile compounds.

4.2 | Origin of benzene as a NIAS from rPET

All the results on the presence of benzene in PET bottles with RC and the migrated amounts to the contained water in Tables 1, 2 and S2 suggest that the reactions responsible for the formation of benzene in the rPET matrix are dependent on the temperature.

The thermal degradation of PET has been studied previously under various conditions.[36–38] Benzene has been reported as one of the pyrolysis products of PET.[39–41] Various catalysts have been reported to increase the amount of benzene, such as calcium oxide[42] and tetramethyl-ammonium hydroxide and chlorinated substances (1,1,1-trichloroethane and chlorobenzene) that decompose at elevated temperature to hydrochloric acid.[40] This suggests that basic and acid compounds can catalyse the rearrangement of terephthalic groups in benzene and carbon dioxide gas. To our knowledge, strong basic and acid catalysts are not present in virgin PET resin. Only small amounts of phosphoric acid are present in virgin PET to deactivate the antimony trioxide catalyst, giving virgin PET a mild acidic character. In rPET, however, various contaminants can be present. One of the contaminants in rPET that is well known to produce acids is PVC, and it originates from sorting mistakes and packaging components.[43,44] Examples of PVC and poly vinylidene chlorid (PVdC) objects found in sorted PET are PET bottles with PVC labels, PVC blisters, PVC nonpackaging objects, PVC stretch wrap on a PET tray, PVdC-coated PET film for cured meats and PVC-based printing inks. PVC dehydrochlorinates at elevated temperatures to form hydrochloric acid.[45] This acid formed from PVC contaminants is the most likely catalyst that converts PET into benzene when exposed to elevated temperatures.

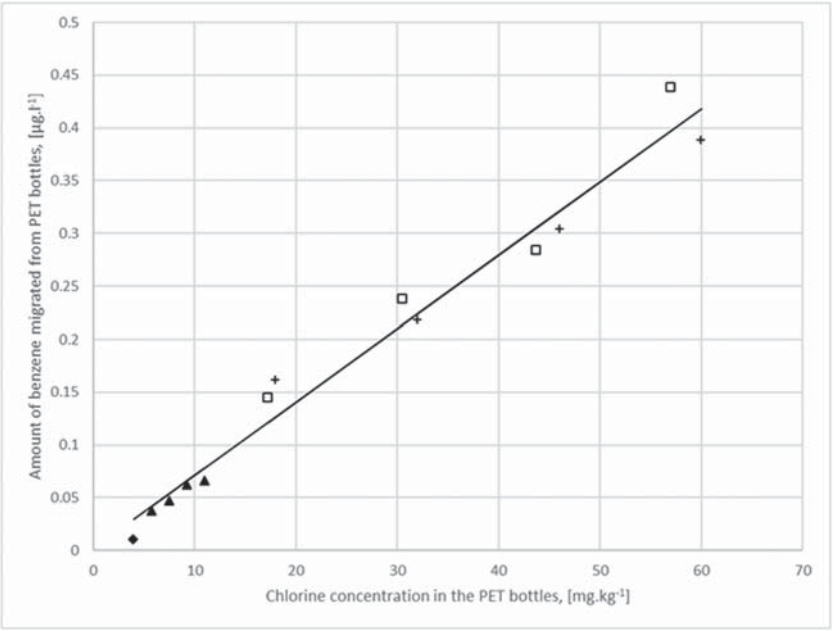


FIGURE 2 Relation between the concentration of chlorine in the polyethylene terephthalate (PET) resin and the measured amount of benzene migrated from the PET bottles to water after 10 days at 40°C. Line is the regression analysis with $r^2 = 0.976$. Symbols: ◆, virgin PET; ▲, rPET A; □, rPET B; and +, rPET C

Alternatively, the PVC present in rPET as polymeric contaminant does not act as a catalyst to decompose PET but rather as a precursor for benzene itself. The prime thermal degradation product of PVC between 200°C and 360°C is namely benzene.[46] It is impossible to resolve the mechanism (catalyst or precursor) with the current data. Dedicated physical chemical research with isotope-enriched PVC and PET could resolve the precise mechanism in the future.

Because it is very difficult to measure the concentration of PVC in PET resin and bottles quantitatively in the 1–1,000 mg·kg^{-1} of concentration range, usually the chlorine content is determined. Therefore, the amount of benzene migrated from the bottles (Table 2) was correlated to the chlorine content of the PET pellet mixture used to make the bottles, to test the assumption that PVC contaminants produce benzene within the PET matrix (Figure 2). The chlorine content of the PET bottles was calculated from the RC and the chlorine contents in the PET resins, (Table S1). The correlation coefficient was 0.97, implying that there is very good correlation between the chlorine content of the PET bottles and the amounts of benzene migrated from the PET bottle (Table S6). This supports the hypothesis that the contaminant PVC present within the rPET matrix is responsible for the production of benzene.

There are, however, several comments to be made to this correlation and hypothesis. First of all, not all the chlorine measured in PET resin will originate from PVC contaminants. The virgin PET will not contain PVC contaminants but still has a chlorine content of 4 mg·kg^{-1} according to microcoulometry. However, this analysis is not very specific for chlorine, and so it is more likely to be caused by traces of bromine catalyst from the AMOCO process.[28]

Also, Type A rPET will most probably only contain small amounts of PVC contaminants (because it uses bottles from deposit refund systems as predominant feedstock, so only few sorting mistakes are likely and almost all the bottles present have been designed for recycling)[47,48] but still has a chlorine content of 11 mg·kg^{-1}. Therefore, there will be different sources of chlorine in PET resin (and possibly other halogens) and whether they all contribute to the formation of benzene is unknown.

Second, other sources of benzene cannot be excluded. Perhaps also, the thermal decomposition of reheat additives (carbon black) and amorphous carbon barrier coatings can also contribute to the formation of benzene. Alternatively, minute quantities of product residues (benzoic acid, juice components, mouth water and detergents) can still be present in rPET resin after SSP treatment in very low quantities and initiate reactions that produce benzene, during the shelf life in very low quantities.

Although there are still unanswered questions regarding the precise origin of benzene and other NIAS in rPET, the current research has already rendered two clear mitigation strategies, reducing the chlorine concentration in the rPET and limiting the exposure time to elevated temperatures during injection moulding and bottle blowing processing to a minimal. The chlorine concentration can most effectively be limited by selecting low-chlorine rPET resins and controlling the RC accordingly.

4.3 | MoE for benzene

The level of concern for public health resulting from exposure to compounds that are both genotoxic and carcinogenic can be assessed with the margin of exposure (MoE) approach.[49,50] The MoE approach is intended for substances that are both genotoxic and carcinogenic, which are found in food products, irrespective of their origin and including FCMs. Hence, it can also be applied to the migration of benzene from PET bottles with RC. In this MoE approach, the benchmark dose that corresponds to the lower confidence limit for an extra tumour incidence of 10% above background

level (BMDL10) is compared with dietary intake estimates. In case the MoE value exceeds 10,000, the exposure is assessed as of low potential concern from a public health point of view and could be considered as a low priority for risk management actions. The BMDL10 for benzene has been reported to amount to 17.6 $mg \cdot kg \cdot bw^{-1} \cdot d^{-1}$.[51] The estimated daily intakes were calculated with the highest determined concentrations of migrated benzene in the water simulants originating from PET bottles made of 100% rPET in three different qualities, which varied between 0.06 and 0.44 $\mu g \cdot L^{-1}$ (Table 2) and two exposure scenario's. In the first scenario, an infant of 5-kg body weight consumes 0.75 $L \cdot day^{-1}$ and in the second scenario an adult of 60-kg body weight consumes 2 $L \cdot day^{-1}$. Consequently, the estimated daily intakes of benzene varied between $2.2 \cdot 10^{-6}$ and $6.6 \cdot 10^{-5} \cdot mg \cdot kg \cdot bw^{-1} \cdot d^{-1}$ and the resulting MoE's varied between $3 \cdot 10^5$ and $8 \cdot 10^6$. Hence, the exposure of benzene migrated from PET bottles with RC to mineral water is of low concern from a public health point of view, might be considered as a low priority for risk management actions and is comparable with the exposure of benzene present in food products.[50]

4.4 | Compliance to the FCM legislation

PET bottles with RC for water and beverages must comply with the requirements of European Regulation No 10/2011 as well as 282/2008.[5,12] According to these two regulations, four criteria must be met: the overall migration limit, the SMLs, the NIAS requirements and the recycling process need to have received an EFSA opinion in favour of authorisation. The overall migration and the specific migration of substances restricted with SMLs were not determined experimentally within this study. However, it has been shown in literature that those limits are generally not exceeded for PET materials.[10,11] In addition, the applied types of rPET originate from companies that operate recycling processes that received an EFSA opinion in favour of authorisation that narrows the assessment to the evaluation of migrating NIAS. NIAS shall be assessed in accordance with internationally recognised scientific principles on risk assessment.[12]

Seven NIAS migrants were detected in the current study: 2-methyl-1,3-dioxolane, benzene, styrene, acetone, butanone, furan and limonene. NIAS that are not classified as CMR according to Annex I, Parts 3.5–3.7 in Regulation (EC) 1272/2008,[13] and for which no toxicological data that could serve as a basis for evaluation are available, are often assessed in accordance with the functional barrier principle, according to which nonlisted substances shall not be detected in a migration test at a detection limit of 10 $\mu g \cdot kg^{-1}$. Of the detected NIAS, four are not classified as CMR substances (2-methyl-1,3-dioxolane, acetone, butanone and limonene), and their concentrations in the mineral water simulants were well below the limit of 10 $\mu g \cdot L^{-1}$.

Three of the detected NIAS are classified as CMR or potentially CMR: benzene, furan and styrene. The maximum detected concentrations during the migration experiment of 10 days at 40°C were 0.44, 0.13 and 0.06 $\mu g \cdot L^{-1}$, respectively. This discussion will further focus on benzene.

As a conservative approach for risk assessment, EFSA has derived a threshold limit for genotoxic substances of 0.017 $\mu g \cdot L^{-1}$ in food, based on a worst-case scenario of an infant of 5-kg bodyweight consuming 0.75 L of water from PET bottles each day and taking into account the Threshold of Toxicological Concern (TTC) of 0.0025 $\mu g \cdot kg \cdot bw^{-1} \cdot day^{-1}$ below which the exposure to an unknown contaminant would have negligible consequences for the human health.[6] For an adult person with a default body weight of 60 kg, a consumption of 1-kg water per day from PET bottles and the TTC of 0.0025 $\mu g \cdot kg \cdot bw^{-1} \cdot day^{-1}$, a threshold limit of 0.15 $\mu g \cdot L^{-1}$ in food can be derived.[6]

However, this TTC approach is only intended for substances where no specific toxicological data are available. In the case of benzene, toxicological evaluations from other fields of application can be referred to for the risk assessment. The World Health Organisation (WHO) has established guidance values for certain chemical constituents in drinking water in their guidelines for drinking water quality.[52] These guideline values represent the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption. For benzene, a guidance value of 10 $\mu g \cdot L^{-1}$ is established. This value represents the concentration in drinking water associated with an upper bound excess lifetime cancer risk of 10^{-5} (one additional case of cancer per 100,000 of the population ingesting drinking water containing the substance at the guideline value for 70 years).[52] These WHO guidelines form the scientific basis for maximum concentrations of certain substances derived for drinking water in the Drinking Water Directive 98/83/EC,[53] which has been implemented into national law in the member states. Beside these guidance values, other parameters such as exposure from other sources than drinking water were also taken into account.[52] Thus, for benzene, a maximum concentration in drinking water of 1 $\mu g \cdot L^{-1}$ has been set in Europe.[53] Although the drinking water directive is not applicable for bottled mineral water[53] and other beverages, the limit specified there can be used as a reference for the risk assessment of bottled water. In Germany, limitations for certain substances in drinking water originating from polymeric materials are laid down in the Federal Environment Agency guidelines.[54] In this guideline, a factor of 20 is applied between legal limits in drinking water and migration limits for FCMs in general. With this consideration, the limit of benzene of 1 $\mu g \cdot L^{-1}$ would correspond to a migration limit of 20 $\mu g \cdot L^{-1}$ for 'normal' FCMs.

Whereas for bottles with higher concentrations of Type B rPET and those with Type C rPET, the migration of benzene is above the limit of 0.15 $\mu g \cdot L^{-1}$ derived for genotoxic substances without specific toxicological data using the very conservative TTC approach, the limit of 20 $\mu g \cdot L^{-1}$ or even the limit of 1 $\mu g \cdot L^{-1}$ for drinking water is respected for all of the investigated PET bottles.

In summary, the Plastics Regulation (EU) No 10/2011 demands a risk assessment for migrating NIAS. Depending on the underlying data and exposure scenario, different threshold limits in the food can be

derived, which can still be considered as safe. Applying the limit that is given for benzene in drinking water in Directive 98/83/EC, all tested bottles can be regarded as food safe. Also, the MoE approach evaluates the migration of benzene from PET bottles with RC as a low concern for the public health and a low priority for risk management actions. The FCM legislation strives to avoid the migration of CMR-NIAS to food products. As the demanded risk assessment leaves a certain room for interpretation depending on the underlying data and exposure scenario, it is difficult to define a maximum content of recycling material in PET bottles that can still be regarded as food safe. However, the As Low As Reasonably Achievable (ALARA) principle is still valid. Hence, food producers have to strive towards ALARA concentrations of CMR-NIAS in food products. For the migration of benzene from PET bottles with RC, this translates in using material with a low-chlorine content, by using high-quality rPET or limiting the use lower qualities rPET. Limiting the use of rPET would be in disagreement with the plastic strategy of the EU. Furthermore, other arguments, such as company policies, colour, haze and bursting strength, can also pose limits on the RC for PET bottles.

5 | CONCLUSIONS

The migration of substances from PET bottles made with different types of rPET and at various levels of RC to mineral water as simulant has been studied. Several well-known migrants (acetaldehyde, ethylene glycol and 2-methyl-1,3-dioxolane) are derived from the ethylene glycol monomer. The extent to which these substances are present in the PET bottles depends on the SSP treatment of the pellets and the residence times in the injection moulding machine and reheater prior to the stretch blow moulding machine. The subsequent migration to water of these substances can be predicted with models and the final concentrations in water comply with the SMLs for acetaldehyde and ethylene glycol and in case of 2-methyl-1,3-dioxolane with the limit of 10 $\mu g \cdot L^{-1}$ which is generally applied for NIAS not classified as CMR. Also, several PET oligomers are present in the PET resins and the PET bottles. Modelling of their migration towards water revealed that their concentrations are also well below the limit of 10 $\mu g \cdot L^{-1}$. Additionally, six different migrated substances are detected. Two solvents (acetone, butanone) that probably derive from the agents used to clean and protect the mould. Also, limonene is detected in very low concentrations, which is a natural compound used in orange based beverages and detergents. Also, furan is detected in very low concentrations in the water contained by both virgin PET bottles and bottles with RC, of which the origin remains unclear. And finally, two other substances are detected in low concentrations: benzene and styrene. Clear relationships are found between the amounts of benzene and styrene migrated to the water and both the type of rPET used and the RC applied. Migration of benzene and styrene from bottles made from virgin PET is not detected. Styrene is likely to originate from the thermal degradation of polystyrene contaminants in the rPET matrix. For benzene, a good correlation is found between the amount of benzene migrated and the chlorine content of the PET pellet mixture used to produce the PET bottle. This evidence suggests that reactions occur within the PET matrix, which produce benzene, and these reactions are promoted by heat and the presence of PVC as contaminant or other chlorine containing substances within the rPET matrix. The final concentration of benzene and styrene in water is extremely low (maximum observed value 0.44 $\mu g \cdot L^{-1}$ for benzene and 0.06 $\mu g \cdot L^{-1}$for styrene). As the residence times in the applied production machines of the small-scale production facility were relatively long, the measured concentrations are likely to be overestimations of the industrial practise. Measurements of these migrants in water within commercially blown PET bottles confirmed that these are lower. The margins of exposure calculated for the migration of benzene varied between 3.10^5 and 8.10^6 and are well above the 10,000 limit. Therefore, this exposure poses a low level of concern from a public health point of view and is considered as a low priority for risk management actions. However, with respect to the FCM legislation, the situation is more complex, because there is no formal limit for NIAS in general or for NIAS classified as CMR. Risk assessments based on internationally recognised scientific principles have to be performed, which can be based on multiple exposure scenarios and hence yield different outcomes. Recommendations for a maximum level of RC for PET bottles can only be made after further risk assessment has been conducted.

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LIST OF ACRONYMS

ALARA As Low As Reasonably Achievable

BMDL10 benchmark dose that corresponds to the lower confidence limit for an extra tumour incidence of 10% above the background level
CMR carcinogenic, mutagenic and or toxic to reproduction
EFSA European Food Safety Authority
FCM food contact material
GC gas chromatography
MoE margin of exposure
NIAS non-intentionally added substance
PET polyethylene terephthalate
PVC poly vinyl chloride
PVdC poly vinylidene chloride
RC recycled content
rPET recycled polyethylene terephthalate
SSP solid state polycondensation
TTC threshold of toxicological concern

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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