



Effect of recycled content and rPET quality on the properties of PET bottles, part III: Modelling of repetitive recycling

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The presence of contaminants in polyethylene terephthalate (PET) bottles and derived materials from the various steps in the recycling loop is studied. Based on these measurements, a model is proposed to generically describe the accumulation of these contaminants within closed-loop recycling schemes for PET bottles. The measured levels of particle contamination and chlorine content of PET bottles, pellets, and intermediate recycling products are used to derive the modelling parameters. Previously determined relations between these measured parameters and critical bottle properties are used to model the effect of the accumulation of the contaminants on the bottle properties. The measurements reveal that the type of collection system influences the accumulation of contaminants in PET bottles greatly. PET bottles in mono-collection systems accumulate less contaminants than PET bottles in co-collection systems do. Therefore, PET bottles within recycling schemes using mono-collection systems can contain more recycled content than those from co-collection systems, without exceeding acceptance limits on critical bottle properties such as haziness, yellowing, and migration.

KEYWORDS

accumulation, contamination, modelling, PET bottles, recycled content

1 | INTRODUCTION

The European Union strives toward a circular economy, of which the recycling of plastic packages forms an important pillar.¹ Of all the postconsumer plastic packaging types, polyethylene terephthalate (PET) bottles are collected and recycled to the largest extent in Europe. In 2016, 1770 kton of postconsumer PET bottles were recycled in Europe of the 3150 kton placed on the market.² Most of the recycled PET was used in packaging trays (670 kton), beverage and nonbeverage bottles (460 kton), strapping (190 kton), and fleece fill (420 kton).² The relative success of PET bottle recycling in Europe can be attributed to multiple factors. The combination of the presence of bottles that have been designed for circularity,

selective collection schemes, and effective mechanical recycling processes renders PET recycled products with few particle and polymeric contaminants.³⁻⁵ Moreover, the subsequent subjecting of the recycled PET's to super-clean technologies also removes most of the molecular contaminants.⁶ This enables the recycling of bottle PET into food packages such as trays and bottles, which is unique amongst the packaging plastics. The evaluation scheme of the European Food Safety Authority (EFSA) for recycling processes intending to produce food-grade rPET contains a precautionary measure that a bottle feedstock should not contain more than 5% PET nonfood packages.⁷ As a consequence, in Europe, beverage PET bottles are widely recycled whereas nonbeverage PET bottles are only recycled to a limited extent.

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PET bottles are collected in various manners in Europe with mono- and co-collection systems. In mono-collection systems, only PET bottles are collected, as it occurs at the deposit-refund systems (DRS) of Denmark, Germany, the Netherlands, Norway, and Sweden and in dedicated separate collection systems in Switzerland. In co-collection systems, the PET bottles are co-collected with other plastic and nonplastic packages and subsequently sorted. These systems vary in collection portfolio from relatively homogeneous to relative heterogeneous. An example of a relative clean co-collection system is the previous Belgian Fost-Plus collection system for only plastic bottles, beverage cartons, and metals. Examples of relative dirty co-collection systems encompass British comingled collection systems which include glass, metals, papers, beverage cartons, and plastic packages and mechanical recovery systems in which plastic packages are recovered from mixed municipal solid waste (MSW). Most co-collection systems have an intermediate level of heterogeneity, such as the German, Dutch, Spanish, and French co-collection systems for plastic packages, beverage cartons, and/or metal packages.

To promote the circular economy, many governments and companies have adopted recycled content (RC) policies. Most Dutch beverage companies use 25% to 50% rPET in their bottles, but some companies produce bottles from 100% rPET.⁸ With the adaptation of higher levels of RCs by the industry, it becomes more important to understand how contaminants accumulate in PET bottles within recycling schemes and how this affects the critical bottle properties. This knowledge will assist stakeholders in selecting RC levels that will assure the overall performance of PET bottles within collection and recycling schemes.

The scientific literature on the accumulation of contaminants within recycled PET bottles is fairly limited. Nevertheless, several more generic studies on accumulation in recycling systems and on contaminants in recycled plastics are available.

The accumulation of contaminants has been modelled for the recycling scheme of paper and board.⁹ Geyer stressed the general point that closed-loop recycling systems are prone to accumulation of contaminants.¹⁰ For postconsumer packaging plastics and PET bottles, accumulation models have not, yet, been reported.

Various molecular contaminants found in recycled plastics have been reported,^{11–16} although their relevance is limited for recycled PET beverage bottles since this material contains much less molecular contaminants than other recycled plastics. Furthermore, most of the volatile molecular contaminants are removed by super-clean technologies during the recycling of the PET bottles.⁶ Nevertheless, these articles render a good understanding of the multitude of contaminants that are present in recycled plastics and these contaminants could potentially end up in recycled PET when insufficiently sorted.

Only a few papers report on the particle and polymeric contamination of recycled plastics.^{4,5,17,18} This is especially relevant for PET bottles since small amounts of particle and/or polymeric contamination in the rPET matrix reduce the optical transparency (haze).^{4,19} Moreover, small amounts of polyvinyl chloride (PVC) and polystyrene (PS) in the PET bottle matrix are held responsible for initiating reactions that result in the formation of undesired molecular contaminants which migrate to the contained beverage.²⁰

Finally, several papers report on the contamination of recycled plastics by metals which can appear both as particle and as more dispersed molecular contamination.^{21,22}

Other scientific contributions have focussed on degradation reactions of recycled PET as a consequence of thermal processing.^{23–26} Three types of thermal degradation in PET are discerned: chain scission reactions, cross-linking reactions, and thermo-oxidative yellowing reactions. In the current practise of PET bottle recycling, the chain-scission reactions are considered to be less important since the drop in molecular weights by thermal processing is usually compensated by the super-clean technologies which restore the chain lengths. However, polymeric contaminants such as PVC, PS, polypropylene (PP), and ethylene vinyl alcohol (EVOH) are known to retard the restoration of chain lengths in the SSP-process.⁴ Also, chain extenders are occasionally used to restore the chain length. Thermally activated cross-linking reactions have been reported²³ but are difficult to determine in a rPET matrix in a nondestructive manner. Also, the yellowing of PET has been described as thermo-oxidative reactions involving the diethyl glycol co-monomers in PET, the hydroxylation of the terephthalic rings, and the introduction of more carbonyl groups which result in more conjugated aromatic moieties in the PET polymer backbone.^{26–28}

Two previous papers have described the impact of RC and rPET quality on two critical properties of PET bottles: the migration of volatile compounds and the optical properties.^{19,20} In these papers, correlations were found between two core parameters of rPET (chlorine content and particle contamination) and the two abovementioned critical bottle properties. A clear relationship was found between the migration of volatile compounds and chlorine content of rPET.²⁰ Also, a clear relationship was found between the particle contamination and the optical properties haze and colour parameter b^* .¹⁹

This paper has two objectives. First, it aims to model and predict the accumulation of contaminants (particles and chlorine) in rPET depending on the type of collection and recycling system used, the applied RC, and the amount of times the PET material has been recycled with an approach that is based on mathematical modelling and measurements. Second, it aims to translate these modelled levels of contaminants into critical properties of PET bottles such as optical parameters (haze, colour) and migration parameters with the correlations found in two previous papers.

In order to achieve these objectives, this paper proposes a new approach to model the accumulation of contaminants within PET bottle collection and recycling systems and to relate these to critical bottle properties. In this paper, measured data of three types of collection and recycling systems are used as case study data to model the accumulation and its effects. The model is inherently a simplified representation of a more complex reality with usually mixed feedstock input at varying levels. Nevertheless, it renders insight in the processes that control the accumulation of contaminants in rPET, offer mitigation opportunities, and predict the effect of this accumulation on the critical bottle properties. And, therefore, this model will clarify the implications of RC policies and collection methods on the critical properties of PET bottles after repetitive recycling in PET bottle collection and recycling systems.

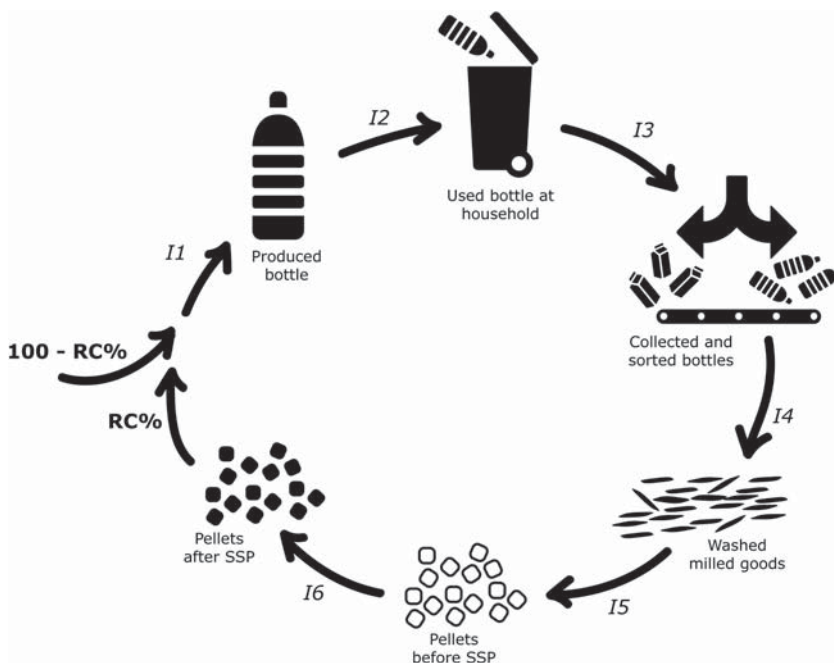


FIGURE 1 Increments in contamination during one recycling loop for polyethylene terephthalate (PET) bottles

2 | MATERIALS AND METHODS

2.1 | Origin of samples

The recycling loop for PET beverage bottles was analysed in six different process steps (Figure 1) at which contaminants can be added. The first step (*I1*) is bottle production and encompasses the injection moulding of a mixture of virgin PET pellets and rPET pellets into preforms, reheating, and stretch-blow moulding of the preforms to freshly produced bottles. The second step (*I2*) is the use of the bottles, from filling and closing in the beverage industry, distribution, retail, storage in house, consumption in house, and discarding the bottles in household waste bins. The third step (*I3*) encompasses collection and sorting, starts with postconsumer discarded bottles at the households and ends at either counted bottle products for deposit systems (*I3a*) or sorted bottle products for separate collection (*I3b*) and recovery systems (*I3c*). The fourth step (*I4*) is the mechanical recycling into washed milled goods, which are further processed into pellets (*I5*) and the subsequent SSP treatment of these pellets (*I6*). Measurements were performed on bottles, washed milled goods, and pellet to describe the recycling loops and provide core parameters to model repetitive PET bottle recycling.

Four types of relatively common PET beverage bottles were studied at the three stages of the production and recycling chain in which the PET is present as bottles (steps *I1* to *I3*): from pellets, to freshly produced bottles, to postconsumer bottles at households, and finally to postconsumer bottles at either counting centres or sorting facilities, see Table S1. Four common types of bottles were chosen to facilitate their retrieval from sorted products and waste streams. The chosen bottles were easily recognized by their brand name and product type, which are treated anonymously. For some bottles, the exact product type would differ for the different bottles analysed, as sub-product varieties are on the market, for example, different flavours of a similar

drink. This could not be avoided, as it was time-consuming to retrieve sufficient bottles from all parts of the recycling system. One of the notable differences was bottle B1 at the deposit system; this bottle was a different sub-product variety compared with the other samples of bottle B1. Samples of the virgin pellets, rPET pellets, and the freshly produced bottles were obtained from the beverage industries. Samples of postconsumer PET bottles were obtained directly from various households. Samples of PET bottles from the deposit system were obtained from a counting centre of the Stichting Retourverpakking Nederland (SRN) deposit refund system. Samples of PET bottles from the separate collection and recovery systems were obtained from two sorting facilities: one sorting facility that only sorts Dutch postconsumer packaging waste that was separately collected and one sorting facility that only sorts Dutch postconsumer packaging waste that was mechanically recovered.

From step 4 on, the materials are milled and thus the individual bottles types could not be traced. Three PET recycling companies provided samples of washed milled goods, pellets before the SSP-treatment, and pellets after the SSP-treatment from their process, see Table S3. These samples are used to analyse steps *I4* to *I6* of the recycling loop.

2.2 | Measurements

Two types of measurements were performed on the samples of the pellets and the PET bottle fragments: particles in solution measurement for particle contamination and micro-coulometry for chlorine content. The method for the particles in solution measurement is explained in paper 1.¹⁹ In short a PET sample is dissolved and this solution is passed through a narrow tube with an automatic camera which makes 10000 images per sample. The counted particles are reported as the amount of recorded particles per 10000 images. Hence, the unit is PPTI. The bottles that are retrieved from households and from sorted products

and/or counted products were first cleaned thoroughly for attached dirt, by washing with soap and water. Fragments from all bottles were further processed and analysed as described in paper I. The chlorine content was determined by micro-coulometry, as explained in paper II.²⁰ The chlorine concentration is expressed in mg of chlorine per kilogram of PET material (mg.kg^{-1}).

2.3 | The model

2.3.1 | Increments in particle contamination

Data on the level of contamination at each process step (paragraph 2.1) was first collected to derive the increments in contamination per process steps, see Table S1. These contamination increments were analysed first to determine the structure of the model for repetitive PET bottles recycling.

For the first two process steps, the variations in the average incremental values of particle counts were larger between different bottle types than the average increments themselves (*I1* and *I2*). Hence, these separate increments fall within the range of uncertainty and cannot be used in the model. The increments in the collection and sorting step from separate collection and recovery (*I3b* and *I3c*) are higher than the uncertainty; thus, particles are added to the rPET during these steps. Also, the increment for recovery from MSW (*I3c*) is higher than the increment for separate collection of recyclables (*I3b*). This suggests that the collection portfolio affects the amount of contaminants that are taken up by the PET bottles during collection and sorting. For the bottles from the deposit system (*I3a*), this increment cannot be easily determined due to the large uncertainty in the measured values. A minor increase is observed for bottle B2 and the decrease in particles for bottle B1 is considered an outlier, as this bottle was obtained from a different sub-product variety as discussed in paragraph 2.1. Hence, the increase in this process step (*I3a*) is probably small. However, an increase in particles is observed throughout the whole process. This increase in particles is clearly larger for the collection systems in which PET bottles were collected together with other materials (co-collection), such as separate collection and recovery from MSW, than for the deposit system (mono-collection).

The incremental values in particle contamination for the fourth step (*I4*) cannot be derived from the collected data, since individual PET bottles cannot be followed in an industrial recycling process to washed milled goods as material from different feedstock is mixed. However, the amount of particles in the washed milled goods of PET material from mainly the deposit system, see Table S4 can be compared with the amount of particles in the counted product from the deposit system in Table S1. Although recycling companies often mix small amounts of co-collected bottles with mono-collected bottles, the increment in particle count for only mono-collection systems is likely to be slightly lower. The small increase in particles that is observed for this process step (*I4*) can therefore potentially be attributed to this mixing of co-collected bottles. Additionally, the data indicates that the level of particle contamination does not decrease during the washing process. Hence, particle and polymeric contaminants

which originate from the use, collection, and sorting steps (*I2-I3*) are effectively not removed by washing.

To determine the increment in particle contamination between the washed milled good and pellets (*I5* and *I6*) the washed milled goods and pellets of two deposit systems were analysed, see Table S4. It is clear that the amount of particles in the PET materials increases during these process steps. This increase is small compared with the increase in particles in the collection and sorting steps for the co-collection systems.

2.3.2 | Increments in chlorine content

Since the migration of volatile compounds relates directly to the chlorine concentration of the rPET pellet, there was no need to study the increments for each step in the recycling chain.²⁰ In contrast to the particle contamination, only one increment per recycling loop has to be defined for the chlorine concentration of the pellets. Therefore, the chlorine content of various types of rPET pellet from different origins and various types of virgin pellets were analysed (see also paragraph 3.1.3). Also, for the chlorine content, clear differences in concentrations were observed for rPET made from bottles from mono-collection systems in comparison with rPET made from bottles from co-collection systems, see Table S3. This resulted in different increment values in chlorine content for these different collection systems.

2.3.3 | The model structure

The mechanically recovered and the separately collected PET bottles (co-collection of PET bottles) clearly accumulate more particle contamination and chlorine concentration than the PET bottles from the deposit system (mono-collection of PET bottles). The lower levels of particle contamination in recycled PET from deposit systems is in agreement with previously published results.^{4,5} Hence, one of the most critical factors describing the quality of rPET pellet is formed by the collection system of the PET bottles since the collection system largely defines the polymeric and particle contaminants that are introduced in the rPET resin. Also, the collection portfolio affects the amount of contaminants that adhere to the PET bottles during collection and sorting and can be mixed in the resin during mechanical recycling.

This resulted in an approach to model the repetitive recycling of PET bottles with only one increment per recycling loop for particles and one for chlorine. The size of this increment is determined by the analyses of rPET bottles and pellets from different collection systems (which is further elaborated in paragraph 3.1) and it is different for three types of collection systems: mono-collection of PET bottles, co-collection type A, with a low amount of contaminant uptake, and co-collection type B, with a high amount contaminant uptake.

To model the repetitive recycling of PET bottles, the critical assumption was made that the increment factor in particle counts and chlorine content are independent of the amounts present from previous recycling loops. In other words, the increase of particles and chlorine in a recycling loop is determined by the nature of the loop and not the history of the (r)PET material.

2.3.4 | Mathematical equations for particles and chlorine content

The accumulation of contaminants within bottle recycling schemes was modelled in EXCEL with equation 1. This equation is used for determining the amount of particles and the chlorine concentration in the rPET after every recycling loop. As the same equation is used for both types of contaminants, the model is further explained only for the amount of particles.

For every recycling loop j the amount of particles present in the PET matrix (AP_j^{PET}) can be described as the sum of two contributions. The first contribution is the amount of particles present in the recycled PET of the previous recycling loop $j-1$ to which the increase in particles of the recycling loop ($\Delta AP_{recycling\ process}^{PET}$) is added multiplied by the recycled content (RC). The second contribution is the amount of particles present in the virgin PET (AP_{virgin}^{PET}) multiplied by the factor 100% minus the RC, see equation 1.

$$AP_j^{PET} = \left(AP_{j-1}^{PET} + \Delta AP_{recycling\ process}^{PET} \right) \times RC + AP_{virgin}^{PET} \times (100\% - RC). \quad (1)$$

This equation describes an asymptotic function for the amount of contaminants in the rPET matrix, for all levels of RC except 100%. At the asymptote, the amount of particles (AP_j^{PET}) is equal to the amount of particles at the previous recycling loop (AP_{j-1}^{PET}). Hence, the asymptotic accumulation value ($AP_{asymptote}^{PET}$) can be derived by rearranging equation 1 to obtain equation (2).

$$AP_{asymptote}^{PET} = AP_{virgin}^{PET} + \frac{RC}{(100\% - RC)} \times \Delta AP_{recycling\ process}^{PET}. \quad (2)$$

2.3.5 | Mathematical equations for critical properties of rPET bottles

In the two previous papers,^{19,20} linear relationships were found between the amount of particle contaminants and several critical properties of the PET bottles, such as haze, L^* colour value and b^* colour value, and between the chlorine content and migration values. The applied linear correlation functions are listed in Table S5. These are linear relations between the measured variable of the PET bottles (AP_j^{PET}) and a critical PET bottle property (CP_j^{PET}), such as Haze and b^* , see equation 3. The slope (b) and intercept (a) of the linear relationship are determined by experimental research. The same type of equation

can be expressed for the correlation between chlorine content and migration values.^{19,20} The correlation functions between the amount of particles and the critical properties of the PET bottles and the chlorine concentration and the amount of migrated volatiles from PET bottles to contained water after 10 days at 40°C is also given in Table S5.

$$CP_j^{PET} = a + b \times AP_j^{PET}. \quad (3)$$

Therefore, the corresponding asymptotic value for the critical bottle properties ($CP_{asymptote}^{PET}$) can be derived by merging equations (2) and (3) to obtain equation 4.

$$CP_{asymptote}^{PET} = a + \left(AP_{virgin}^{PET} + \frac{RC}{(100\% - RC)} \times \Delta AP_{recycling\ process}^{PET} \right) \times b. \quad (4)$$

2.3.6 | Mathematical equations for calculating the limit of RC

The RC which corresponds to a limit in a critical property (RC_{limit}) can be calculated by rearranging equation (2) and entering the amount of particle that corresponds to the acceptance limit for the critical property as the asymptotic value for the amount of particles, which results in equation 5.

$$RC_{limit} = \frac{AP_{asymptote}^{PET} - AP_{virgin}^{PET}}{AP_{asymptote}^{PET} + \Delta AP_{recycling\ process}^{PET} - AP_{virgin}^{PET}} = \frac{CP_{asymptote}^{PET} - AP_{virgin}^{PET} \times b - a}{CP_{asymptote}^{PET} + \left(\Delta AP_{recycling\ process}^{PET} - AP_{virgin}^{PET} \right) \times b - a}. \quad (5)$$

3 | RESULTS

3.1 | Increments per recycling loop

3.1.1 | The parameters for virgin PET

The average amount of particles in virgin PET pellet equalled 330 ± 100 PPTI, and the chlorine concentration of virgin PET was roughly 2 ± 1 mg.kg⁻¹. The latter value was probably an overestimation due to the lack of specificity for chlorine of the measurement method. Nevertheless, both the amount of particles and the chlorine concentration of virgin PET were low in comparison with the studied rPET, see Table S3. Based on these numbers, the parameter for virgin PET were estimated to be 300 PPTI and 2 mg.kg⁻¹ chlorine content, see Table 1.

TABLE 1 The applied model parameters for the virgin PET and the incremental factors for different collection and recycling systems of PET bottles

	Incremental Factors for One Recycling Loop			
	Virgin	Mono-collection	Co-collection A	Co-collection B
Amount of particles (PPTI)	300	12 500	22 000	70 000
Chlorine concentration (mg.Kg ⁻¹)	2	10	35	60

Abbreviation: PET, polyethylene terephthalate.

3.1.2 | The increment in particle contamination for PET in different collection systems

The amount of particles found in rPET pellet varied between 7000 and 100 000 PPTI, see Table S3. The collection system was found to have a major impact on this parameter, see paragraph 2.2. The recycled PET pellets made from bottles that were retrieved with mono-collection systems had clearly lower amounts of particles than those retrieved with co-collection systems, $20\,000 \pm 8000$ and $80\,000 \pm 21000$ PPTI, respectively. However, most of these rPET pellets are produced from mixed inputs (both PET bottles from mono- and co-collection systems), and thus the increment cannot precisely be determined for single collection systems. Moreover, the mixed PET bottle feedstock contains a mixture of PET bottles with unknown levels of RC. Therefore, the difference between the values for the rPET pellets and the values for the virgin pellets are only approximations of the incremental values for one recycling loop and are likely to be overestimations.

The data supports the decision to determine the particle increment of one recycling loop for the different collection systems, see Table S1 and S3. The estimated amounts of particles taken up by one recycling loop ($\Delta AP_{recycling\ process}^{PET}$) for the different collection systems are listed in Table 1.

PET bottles in mono-collection systems are expected to accumulate some particles during production and use of the bottles (*I1* to *I3*). Bottle 1 took up roughly 7000 PPTI (the measured amount of particles in the counted bottle of this type is considered an outlier [see chapter 2: method] and ignored) and bottle 2 took up roughly 5000 PPTI. These PET bottles are expected to take up roughly 6500 PPTI in the mechanical recycling process (*I4* to *I6*), see Table S4 and paragraph 2.2.1. And hence, the PET material in a closed-loop mono-collection and recycling system gains roughly 12 500 PPTI per recycling loop.

For co-collection systems, the largest gains in particle contamination of the PET material occur at the collection and sorting process steps (*I3*). PET bottles in co-collection systems can take up between 12 000 and 60 000 PPTI during that single step in the recycling process. Moreover, PET bottles will further gather roughly 3000 PPTI during the production process and the use phase of the bottles (steps *I1* and *I2*), see Table S2. It is assumed that the amount of particles added during the mechanical recycling process for co-collection PET bottles is similar to the mono-collected PET bottles, and thus 6500 PPTI. Consequently, the estimated increment per recycling loop ($\Delta AP_{recycling\ process}^{PET}$) is 22 000 PPTI for co-collection type A systems and 70 000 PPTI for co-collection type B systems.

3.1.3 | The increment of chlorine content in rPET for different collection systems

The chlorine concentration in the studied samples of virgin PET pellets varied between less than 1 and 4 mg.kg^{-1} and between 8 and 104 mg.kg^{-1} for rPET pellets, see Table S3. The differences between those values were used to determine the incremental value in chlorine

concentration per recycling loop ($\Delta C_{recycling\ process}^{PET}$) for the three different collection systems. For mono-collection, the lowest values for chlorine in rPET were found (resp. 8 and 11 mg.kg^{-1}); these materials originated both from deposit refund systems within the European Union. For co-collection type A, the increment was based on the chlorine concentration that was measured for a rPET that was made with a mix of PET bottles from mono- and co-collection systems. For co-collection system type B, the highest amounts of chlorine content were averaged from the rPET pellets that were produced for bottle production. The rPET pellets for nonfood application were not included in this analysis. Based on these numbers, the increments in chlorine concentration per recycling loop were estimated to be 10 mg.kg^{-1} for mono-collection, 35 mg.kg^{-1} for co-collection type A, and 60 mg.kg^{-1} for co-collection type B (see Table 1).

3.2 | Modelling repetitive recycling

Repetitive closed-loop recycling was modelled with parameters from Table 1 and the equations 1 to 5 and gave asymptotic curves for all RCs except 100%. In Figure 2, a typical example is shown for the accumulation of particles in a mono-collection system for PET bottles. The curves were all similar both for particle contamination and chlorine concentration, and for the different types of collection systems, only the asymptotic values vary with the RC and the collection system. This is also valid for the critical properties of PET bottles in a recycling system. The values for the critical properties that correspond to the asymptotic values for particle contamination and chlorine concentration are listed in Table 2. These critical parameters increase in a nonlinear, near-exponential manner with the RCs, as is evident from the reciprocal function in equation (2) and the calculated results in Table 2.

3.3 | Limits of RC

There are no legal acceptance limits for the critical bottle properties, and hence all companies can select other limits. In Table 3, two typical limits are shown for the three technical parameters as examples of limits which could be selected by individual companies. Companies often have procurement specifications which are based on the optical properties of 3-mm-thick plates, which were approximated in parameters for PET bottle walls. To the best of our knowledge, major PET buyers have limits on benzene and limonene in rPET. However, not all companies do have set migration limits for benzene from rPET, yet. Therefore, two optional limits were chosen that were proposed in paper II.²⁰ The RC limits of both recycling systems that correspond to these acceptance limits for the critical bottle properties are listed in Table 3. These results make it very clear that mono-collection systems allow for larger RCs to be used in closed-loop recycling systems than co-collection systems. The limiting values for the RCs vary between 51% and 90% for mono-collection systems and between 16% and 80% for co-collection systems and are hence roughly in the same range as the currently applied levels of RC (predominantly 25%-

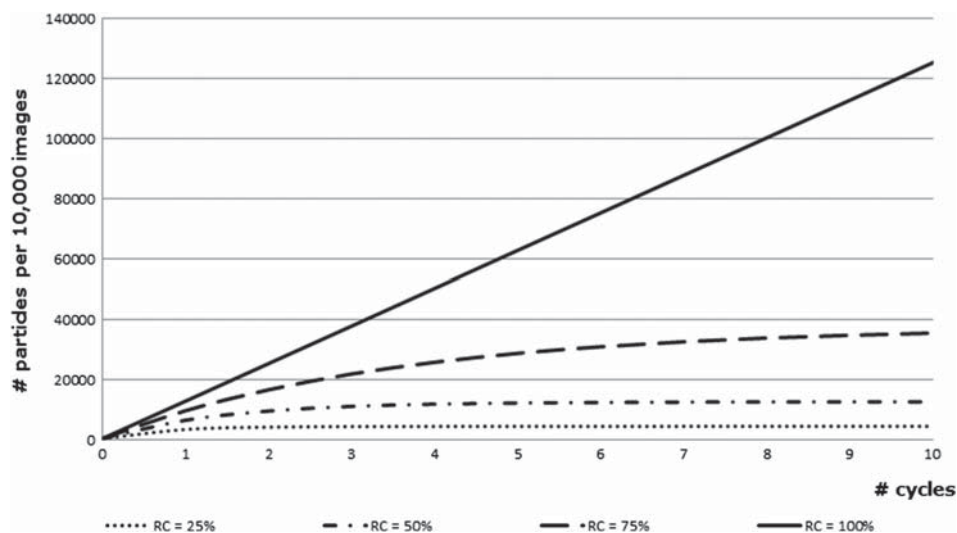


FIGURE 2 Exemplary accumulation curves for the particle contamination of polyethylene terephthalate (PET) bottles within a monocollection system with different levels of recycled content

TABLE 2 Asymptotic values for three critical parameters of PET bottles in closed-loop recycling systems, depending on the recycled content and the type of collection system

RC	Mono-Collection			Co-Collection A			Co-Collection B		
	Haze [%]	b ^a	Migration ^a	Haze [%]	b ^a	Migration ^a	Haze [%]	b ^a	Migration ^a
10%	1	2	0.0	1	2	0.0	1	3	0.1
20%	1	2	0.1	1	2	0.1	2	3	0.1
30%	1	2	0.1	2	3	0.1	4	3	0.2
40%	1	3	0.1	2	3	0.2	6	4	0.3
50%	2	3	0.1	3	3	0.3	8	5	0.4
60%	3	3	0.1	4	3	0.4	12	6	0.6
70%	4	3	0.2	6	4	0.6	19	8	1.0
80%	6	4	0.3	10	5	1.0	31	12	1.7
90%	13	6	0.6	22	9	2.2	70	24	3.8

Abbreviations: PET, polyethylene terephthalate; RC, recycled content.

^aMigration value for benzene from PET bottles with recycled content to contained water after 10 days at 40°C, [$\mu\text{g}\cdot\text{l}^{-1}$].

TABLE 3 The approximated maximum acceptable recycled contents at which the critical threshold values are reached for the three critical parameters of PET bottles in closed-loop recycling systems

Property	RC _{limit}				RC _{limit}			
	Limit 1	Mono-collec-tion	Co-collec-tion A	Co-collec-tion B	Limit 2	Mono-collec-tion	Co-collec-tion A	Co-collec-tion B
Haze	2	51%	37%	16%	3	64%	50%	24%
b*	3	62%	48%	22%	6	89%	83%	60%
Benzene migrated from PET bottles to water [$\mu\text{g}\cdot\text{l}^{-1}$] after 10 d at 40°C	0.15	66%	36%	24%	1.0	93%	80%	70%

Abbreviations: PET, polyethylene terephthalate; RC, recycled content.

50%). The maximal levels of RC vary largely with the acceptance limits for the critical properties, which are not aligned within industry and thus company specific.

4 | DISCUSSION

4.1 | Origin of particles and chlorine in recycled systems for PET bottles

The two largest increments in particle contamination in PET bottle recycling schemes occur during the steps of collection and of the mechanical recycling (paragraph 2.1.1). The increments that occur during collection (I3) are not fully understood yet. The bottles that are retrieved from sorted products and/or counted products from co-collection have substantially higher particle contamination levels than the same type of bottles retrieved from consumers directly or from the mono-collection system. The bottles are cleaned thoroughly for attached dirt, cut into fragments, and cleaned again in the laboratory before analyses. Hence, this particle contamination cannot be attached dirt or other superficial material but really must be material that is already embedded in the PET matrix itself. It is expected that mechanical handling causes dirt and other materials to be scratched into the polymer, as more scratches were observed in the co-collected bottles as compared with the bottles from households and the mono-collection system. The levels of attached dirt of PET bottles in sorted products originating from co-collection systems are usually larger than those from mono-collection systems.⁴ Additionally, the bottles from co-collection were pressed into a bale with other materials and the bottles from households and the mono-collection system were not. Combined with the higher levels of moisture and dirt, this mechanical handling may have caused dirt and other materials to be scratched into the polymer. However, more research is needed to understand this phenomenon better.

The most likely sources of particle contaminants during steps I4 to I6 are sorting faults (other objects than PET-bottles), packaging components (labels, caps, closures, etc), and attached dirt. In a mono-collection system, the counting or sorting mistakes will be negligible and most PET bottles present will be designed for recycling. Hence, only limited amounts of incompletely removed packaging components and attached dirt will be mixed in the recycled PET material of mono-collection systems for PET bottles to form particle contamination. This contrasts with separate collection systems and other co-collection systems, in which the sorted PET bottle products still contain sorting faults (5%-10%), packaging components of bottles that were not designed for recycling and attached dirt.⁴ Hence, the recycled PET of co-collection systems could contain even higher levels of particle contamination as is currently modelled, as the increment I4 to I6 was based on data from the mono-collection system (paragraph 2.1.1).

The chemical nature of this particle contamination for mono-collected PET bottles is likely to be attached dirt (both organic beverage residues and grime) and incompletely removed packaging components (PP from labels, PE from caps and closure rings, hot melt glue,

printing ink). This is in agreement with opinions of representatives of PET bottle recycling facilities. They claim that mono-collected PET bottles need to be rinsed first with large amounts of water in order to obtain highly transparent rPET material as a first step in the mechanical recycling process, hence prior to milling. It is their experience that direct milling causes more dirt to be trapped in the rPET material that cannot be removed during the washing and rinsing steps.

The chemical nature of this particle contamination for co-collected PET bottles is much wider, since also PET bottles (food and nonfood) that have not been designed-for-recycling are present and also substantial amounts of sorting faults. The PET bottles that aren't designed-for-recycling will bring in POM, ABS, Silicon rubber, PVC labels, PS labels, and paper labels as particular contaminants into the rPET material. The sorting faults in sorted PET bottle products can introduce multiple contaminants in the rPET material, such as paper fibres, metals, glass particles, and multiple other polymers such as PS and PVC.^{4,18}

In pioneer studies with the particles in solution measurement for fibre applications, the presence of solid particles (insoluble particles) in PET was attributed to physical and chemical processes inside the polymer matrix, such as catalyst or additives precipitation, heavy branching resulting in gel like particles, agglomeration of degraded polymer particles or additives, or environmental dirt like dust and sand.²⁹

Berg et al have previously reported that a part of the greying of recycled PET occurs as a consequence of the chemical reduction of the antimony trioxide catalyst to black particles of elementary antimony when PET is treated at elevated temperatures above 235°C.³⁰ This relates to the increments I5 and I6 in this study. For rPET made from mono-collected PET bottles, the increments I5 and I6 are indeed relatively important in comparison with I1, I2, I3, and I4 and this chemical reduction process might indeed be responsible for a large fraction of the observed particle contamination. However, this particle contamination might also originate from dirt and foreign polymers being blended into the PET matrix. For rPET made from co-collected PET bottles, the increments I5 and I6 are less important and the largest share in increase in particle contamination occur at I3 and I4. Most of the greying of this quality of rPET can be attributed to the contamination processes of dirt and foreign polymers as described above and only to limited extent to the chemical reduction process.

The origin of chlorine in the PET bottle recycling schemes is likely to be PVC and PVdC as polymeric contaminants originating both from faulty sorted products (PVC blisters, PVC stretch wrap, PVC nonpackaging plastics, laminated flexibles with PVdC) and packaging components (PVC labels, PVC-based printing inks). Other optional sources of chlorine include food and product residues. The measured data supports the hypothesis that the origin of the chlorine could be sorting mistakes and packaging components, see Table S3. An alternative origin for chlorine as product residues appears to be refuted by the measured data since the chlorine content of the washed milled good was low in comparison with the chlorine content of the produced pellets from these washed milled goods. For the same reasons

as discussed above, PET bottles in a mono-collection system will accumulate less chlorine during a recycling loop in comparison with PET bottles in a co-collection system.

4.2 | Justification of the central assumption and data uncertainty

The chosen approach to study the repetitive recycling of PET bottles is a combination of measurements and modelling. In a pure empirical approach, it would be difficult to mimic the uptake of contaminants at households, in collection carriers, and sorting facilities in a laboratory. Moreover, it would be highly laborious to process sufficiently large amounts of PET bottles multiple times to gain insights in the uptake of contaminants during repetitive recycling at various levels of RC. The chosen approach has the great benefit that any combination of RC, quality of rPET applied can be tested with straight-forward mathematical equations. The weakness of the chosen approach is that it relies on the central assumption that the increment in particle contamination and chlorine content is equal for each recycling loop. There are three facts that make this assumption plausible: (a) the contaminants originate from sources outside the recycling system, (b) the contaminant levels of the PET bottles are relatively low, and (c) there is no interaction foreseen between the contaminants present in the PET bottle and the contaminant that are added to the material during the recycling loop. Therefore, the contamination processes are physical and chemical processes, which in turn are determined by the designs of the PET bottles, the collection methods, sorting processes, and the recycling processes in the recycling loop. Hence, although these contamination processes are dependent on many variables in the recycling loop, they are nevertheless independent of the history of the PET material itself.

The model was validated by comparing the modelled amounts of contaminants with the amounts of contaminants found in rPET materials on the market. The rPET material that is currently on the market generally has gone through at least one recycling loop and will consist of some material from previous loops as well. The modelling result of the amount of particles between loops 1 and 2 should thus correspond with the amount of particles found in rPET. In Table S6, this comparison is shown. The modelled results for PPTI after one recycling loop is slightly lower than the measured PPTI for both the material from a mono-collection as for the co-collection system type B. No reference material for co-collection system type A was analysed, as this material is typically added in small amounts to the PET material from mono-collection systems. However, this brief comparison shows that the modelling results are in the same range of the measured PPTI levels, which validates the model.

A concern for this model-based approach is formed by the large uncertainty in the key data, especially in the increments in contamination per recycling loop. Both the particle contamination and the chlorine content of rPET samples show large variations between similar samples. Only the data for virgin PET show a small variation. The large variation in this data for rPET pellets and bottle samples is reminiscent

of the large variation in the contamination process itself. One small PVC flake amongst ten thousands of PET flakes will still cause a meaningful impact on the quality of rPET. These large variations are intrinsic to the studied phenomenon, and hence, the predicted levels of contamination for individual recycling loops are indicative values. The predicted asymptotic values, however, are much more likely to represent the real contamination levels one would encounter in imaginary closed-loop recycling systems in which each use, collection, and recycling loop would be executed similarly. Furthermore, the validation of the model shows that although the key data has a substantial uncertainty, still the model successfully predicts amounts of particle contamination in rPET materials on the market.

Many different PET bottle recycling systems are currently operational in Europe, which can be qualified by their collection system (mono-collection or different executions of co-collection systems), the average level of RC in the collected bottles (RC), and the applications of the produced rPET. In this paper, closed-loop recycling systems are investigated that apply only the rPET that is produced from their own bottles. Although such recycling schemes exist, most operational recycling schemes in Europe have mixed feedstock and mixed applications. Obviously, the accumulation of contaminants in these mixed closed-loop systems will be more complex, since the increments in contaminants can vary for each recycling loop, since for each new loop different shares of rPET pellets with different contaminant levels will be used. Nevertheless, the accumulation of contaminants in these mixed closed-loop recycling systems will follow similar patterns but will be more prone to variations. However, it is likely that the repetitive use of average incremental values in the model will reduce the level of the uncertainty in the final asymptotic value of a recycling system.

4.3 | Implications for the circular economy

For every recycling system, the applicability of the material inside the loop can only be maintained by controlling the concentrations of the critical contaminants. In recycling systems for PET bottles, the critical contaminants are chlorine and particle contamination. Most of these contaminants flow into the recycling system during the use and sorting steps (I2-I3). And, these contaminants are both difficult to remove during the recycling step (I4). Therefore, the quality is currently controlled by accepting low levels of RC and relative large outflows of contaminated material out of the recycling system for bottles to other applications with higher tolerance levels.

Mono-collection systems accumulate the least critical contaminants during the recycling loop and hence allow for the largest RCs: 30% to 90% depending on the acceptance limits. Co-collection systems accumulate much more contaminants during the recycling loop and hence allow for much smaller RCs. Co-collection systems with a narrow collection portfolio allow for 10% to 80% of RC and co-collection systems with a broader collection portfolio allow for 5% to 60% RC, depending on the acceptance limits.

The use of 100% RC in PET beverage bottles in a completely closed recycling loop should only be attempted in case the critical contaminants can be removed completely. Within the current mechanical recycling processes, this is unfortunately not the case.

During this research, a few samples with high levels of contamination were analysed. These samples were intended for nonfood applications, see Table S3. This outflow of the contaminated materials is an effective manner to maintain the contamination level in a recycling system. Such a cleaning mechanism is obviously only effective in case these highly contaminated articles do not return into the PET bottle recycling system as sorting faults.

In case stakeholders intend to raise the levels of RC for PET bottles from the current common values of 25% to 50% to higher levels, then either more mono-collected material should be used for the PET bottles, or alternative methods to remove the contaminants need to be explored. The former can be achieved by using more rPET from beverage bottles for new beverage bottles and hence less for nonbeverage bottles, trays, strapping, and fleece-fibre-fill, as is now often the case. Another option would be to collect more PET bottles via mono-collection systems.

Alternative methods to remove more contaminants can be found in advanced flake-sorting technologies and in chemical recycling technologies. Although most PET bottle recycling companies already apply flake sorting technologies, it is a dynamic field with much innovations, which could result in purer rPET products. Alternatively, the new depolymerisation technologies that are currently emerging could offer an interesting option for the near future.

For future assessments of PET bottle recycling schemes, it is advisable to include the efforts that need to be performed to remove contaminants from the PET bottle material and to strive for a scenario with the highest environmental impact reduction potential.¹⁰ It is likely that the current partial closed-loop recycling system for PET bottles has a very high environmental impact reduction potential and new targets which raise the RC further might not result in higher environmental impact reduction potentials.

5 | CONCLUSIONS

The contamination of rPET with particles and chlorine has been measured at various locations in the recycling loop for PET beverage bottles. Mono-collection systems were found to accumulate less contaminants in the rPET material than co-collection systems. These increments in contamination levels per recycling loop were used to model the accumulation of these contaminants after multiple recycling loops. Under the condition of a closed recycling system with the same types of virgin PET and rPET as feedstock, the contamination will reach asymptotic values of which the height depends on the RC. Based on the previously determined relationships between the level of these contaminants and several critical bottle properties, the model was used to predict these properties after equilibration depending on the RC and the quality of the feedstock. Maximal levels of RC were calculated depending on the acceptance limits for these critical bottle

properties. As expected, recycling schemes which depend on mono-collection systems can endure higher levels of RC without exceeding acceptance limits for critical bottle properties than recycling schemes which depend on co-collection systems with a narrow collection portfolio and those that depend on co-collection systems with a broad collection portfolio. The maximal levels of RC vary largely with the acceptance limits for the critical properties. With this model, the maximal acceptable levels of RC can be calculated based on the amount of contaminants that accumulate in the rPET material with each recycling loop and the acceptance limits on haziness, yellowing, and migration.

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SUPPORTING INFORMATION

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

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