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# SiO<sub>x</sub> layer as functional barrier for PET bottles towards potential contaminants from post-consumer recycled poly(ethylene terephthalate)

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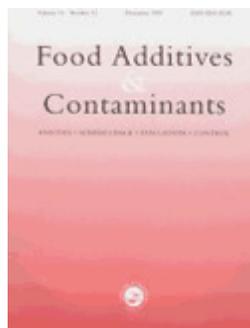
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**SiO<sub>x</sub> layer as functional barrier for PET bottles towards potential contaminants from post-consumer recycled poly(ethylene terephthalate)**

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9 **SiO<sub>x</sub> layer as functional barrier for PET bottles towards potential**  
10 **contaminants from post-consumer recycled poly(ethylene**  
11 **terephthalate)**  
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## Abstract

The barrier effect of a silicon oxide ( $\text{SiO}_x$ ) coating on the inner surface of PET bottles, in terms of the ability to reduce the migration of post-consumer compounds from the PET bottle wall into the food simulants 3% acetic acid and 10% ethanol, was investigated. The barrier effect was examined by artificially introducing model substances (surrogates) into the PET bottle wall to represent a worst case scenario. Test bottles with three different spiking levels up to about  $1000 \text{ mg kg}^{-1}$  per surrogate were blown and coated on the inner surface. The  $\text{SiO}_x$  coated bottles and the non-coated reference bottles were filled with food simulants. From the specific migration of the surrogates with different bottles wall concentrations the maximum concentrations of the surrogates in the bottle wall corresponding to the migration of  $10 \mu\text{g l}^{-1}$  were determined. It was shown that the  $\text{SiO}_x$  coating layer is an efficient barrier towards post-consumer compounds. The maximum bottle wall concentrations of the surrogates corresponding to the migration of  $10 \mu\text{g l}^{-1}$  were in the range of  $200 \text{ mg kg}^{-1}$  for toluene and about  $900 \text{ mg kg}^{-1}$  for benzophenone. Consequently, the  $\text{SiO}_x$  coating allows use of conventionally recycled post-consumer PET flakes (without a super-clean recycling process) for packaging aqueous and low alcoholic foodstuffs (under cold-fill conditions) and prevents the food from migration of unwanted contaminants from post-consumer PET.

**Keywords:-** Functional barrier, PET recycling,  $\text{SiO}_x$  coating, challenge test, food packaging, migration

## Introduction

The use of post-consumer recycled polyethylene terephthalate (PCR PET) in soft drink bottles has been established for a number of years. Post-consumer PET bottles typically are collected with curbside or deposit collections. Subsequently the PET bottles which have been collected are ground and washed. Labels and closures as well as dirt and surface contamination are removed from the PET recyclates. The resulting conventionally recycled PET flakes can be used for non-food packaging applications (e.g. detergent bottles) or fibres. If the recycled PET flakes are to be re-used in food contact applications, further deep-cleansing recycling processes is necessary. Post-consumer substances or compounds from the possible misuse of PET bottles for the storage of e.g. household chemicals which have been absorbed into the PET material may migrate from the recyclate containing bottle into the foodstuff. In case of a too high concentration of the post-consumer compounds in the bottle wall, the migration might pose a health risk for the consumer. Since measurement of bottle wall concentrations for each and every bottle is impossible, so-called challenge tests have been developed in which model chemicals (also named surrogates) are artificially introduced into a recycling process. As a safety parameter or as cleaning efficiency criterion, for these surrogates a migration limit of  $10 \mu\text{g l}^{-1}$  in food from a bottle produced in a challenged recycling process has been generally accepted (FDA 1992, ILSI 1998, BgVV 2000, Franz 2004a, Begley and Hollifield 1993, Franz et al 1998, Franz and Welle 1999, 2002). More recently, the French Food Safety Authority AFFSA has defined  $1.5 \mu\text{g l}^{-1}$  as a target migration limit which should not be exceeded (AFFSA 2006). It is assumed, when taking exposure scenarios also into account, that with these performances a recycling process would remove any unknown contaminant which might be able to migrate and would be capable to produce a recycled PET food contact material which can safely be reused for direct food contact.

In the last decade, several super-clean recycling technologies have been established in industrial or pilot plant scale in several countries (Mueller and Welle 2005). All of these technologies have been shown to be able to reduce the concentration levels of

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6 PET untypical compounds in the PET recycles down to levels which are similar to  
7 the concentrations of technical impurities in virgin PET. The output material of a  
8 super-clean recycling process has therefore a migration potential which is similar to  
9 virgin PET (Franz and Welle 2003). An overview of the different recycling  
10 technologies and food contact application conditions is given on the internet  
11 homepage of the US FDA (FDA 2007).  
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17 Another possibility to prevent the migration of unwanted post-consumer compounds  
18 into PET bottled foodstuffs is the use of appropriate functional barriers. A functional  
19 barrier is defined as a package construction or barrier layer which limits the extent of  
20 migration of a component from the package to the food or food simulant in amounts  
21 below an accepted value threshold or migration limit of no concern. However, it  
22 should be noted that a functional barrier is not necessarily an absolute barrier but a  
23 function of the given food packaging application. The migration kinetics of a  
24 functional barrier system is in general characterized by an initial time lag phase  
25 followed by a much less steeper migration curve line compared to the functional  
26 barrier free package (Feigenbaum et al. 2005, Dole et al. 2006). The lag time is  
27 defined as the time which a substance needs to cross a functional barrier package  
28 construction and to reach the food contact surface. Typically the lag time is  
29 responsible, that during the shelf life of the product the migration limit is not  
30 exceeded. In the special case of PET bottles or sheets, an outside and inner layer of  
31 virgin PET acts as a functional barrier. In the core layer of such a multi-layer  
32 structure conventionally recycled PET is located in a certain amount. The virgin layer  
33 on the inner side with contact to the foodstuff can reduce the migration into the  
34 foodstuff to levels under the general accepted migration limit of  $10 \mu\text{g l}^{-1}$  (Franz et al.  
35 1996, Welle and Franz 2006). In comparison to conventional monolayer PET bottles,  
36 the manufacturing of multilayer PET bottles is more expensive. Another problem is  
37 that the virgin layer might be contaminated with post-consumer compounds by in-situ  
38 diffusion during bottle manufacturing with the consequence that the partially  
39 contaminated virgin layer might have then a lower barrier effect (Franz et al. 1997,  
40 Piringer et al. 1998). The use of conventionally recycled PCR PET in the core layer  
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6 of PET multilayer bottles is therefore today not established on a significant industrial  
7 scale in Europe.  
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10 Another functional barrier technology is the application of a silicon oxide ( $\text{SiO}_x$ )  
11 coating on the inner surface of PET bottles. Typically this technology is used to  
12 reduce the permeation of permanent gases like oxygen or carbon dioxide. Therefore  
13  $\text{SiO}_x$  coated PET bottles are on the market for oxygen sensitive foodstuffs like beer  
14 and juices. On the other hand, the  $\text{SiO}_x$  layer reduces not only the permeation of  
15 gases. The functional barrier might also reduce the migration of post-consumer  
16 compounds into the PCR PET bottled foodstuff. If this functional barrier is efficient  
17 enough, then it would present an alternative option to super-clean technologies and  
18 may allow directly the re-use of conventionally recycled PET without further deep-  
19 cleansing of the PCR PET.  
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28 In the literature some studies can be found dealing with the barrier properties of  $\text{SiO}_x$   
29 coatings inside of PET bottles. For instance, a diamond-like carbon (DLC) layer on  
30 PET bottles enhances the gas permeation barrier (Boutroy et al 2006, Yamamoto et  
31 al 2005, Finch et al 1996). In another study the barrier properties of carbon coated  
32 PET against post-consumer contaminants was investigated (Cruz et al. 2006). The  
33 results of this study, however, do not reflect the barrier properties potential of  $\text{SiO}_x$   
34 layers which, in our opinion, might be due to the laboratory coating scale character of  
35 the investigated samples. In a study with a  $\text{SiO}_x$  coated PET film Dimitroulas et al  
36 (2004) found that the barrier against the chemical substance methylethyl ketone  
37 increases by a factor of 7-8 at room temperature.  
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47 The objective of this study was to investigate and to evaluate the barrier effect of a  
48 market scale commercially available  $\text{SiO}_x$  coating process. The barrier effect was  
49 examined by artificially introducing model substances (surrogates) into the bottle wall  
50 in a worst case scenario. The surrogates were chosen according to the principles  
51 recommended by American and European Guidelines (FDA 1992, FDA 2006, ILSI  
52 1998, BgVV 2000, Franz et al. 2004a). After the contamination, the spiked PET  
53 bottles were industrially coated with a  $\text{SiO}_x$  layer. The specific migration of the  
54 surrogates into food simulants from the bottle wall through the  $\text{SiO}_x$  barrier layer was  
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6 measured. The difference between the specific migration from the coated and non-  
7 coated test bottles represents the barrier effect of the SiO<sub>x</sub> coating layer towards the  
8 applied surrogates. In order to establish a basis for an extrapolation from the worst  
9 case scenario of the challenge test to more realistic concentrations of possible  
10 contaminants, the PET test bottles were spiked with three different contamination  
11 levels (low, medium, high).  
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## 17 18 Materials and Methods

### 19 20 21 22 *Selection of Surrogates*

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24 The barrier properties of the SiO<sub>x</sub> coating was determined by introducing chemicals  
25 (surrogates) into the bottle wall of PET test bottles. The applied surrogates are in  
26 compliance with the four categories of organic compounds: high volatile and polar,  
27 high volatile and non-polar, low volatile and polar, low volatile and non-polar. The  
28 following model compounds were used for the migration tests: toluene,  
29 chlorobenzene, phenyl cyclohexane, benzophenone and methyl stearate.  
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### 38 39 40 *Spiking of the Test bottles*

41 Batches of 1.1 kg of dried PET resin were weighed into glass jars. For the desired  
42 amount of preforms several batches were prepared in parallel. Subsequently the  
43 target weight of each of the chemicals were added to each of the jars. The jars were  
44 tightly sealed and shaken to disperse the chemical mixture onto the surface of the  
45 dried PET pellets. The sealed jars were stored at 38 °C for 7 days. Each day, the jars  
46 were shaken to thoroughly mix the resin and chemicals. At the end of the seven days  
47 storage time, the material was removed from the storage environment and be kept  
48 sealed until it is injection molded into 24.5 g preforms. From the preforms 0.3 l PET  
49 bottles were blown. Subsequently one part of the bottles was coated with the  
50 investigated SiO<sub>x</sub> coating process whereas the other part of the (non-coated) bottles  
51 was used as reference. The concentrations of each surrogate and contamination  
52 level were determined in the coated as well as in the non-coated reference bottles.  
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### *Coating of the test bottles*

The coating film is deposited on the surface of PET bottles using a plasma impulse chemical vapour deposition (PICVD) process. Starting substances for the SiO<sub>x</sub> coating are hexamethyl disiloxane (HMDSO) and hexamethyl disilazane (HMDSN). The barrier coating is a quartz-like surface with almost the stoichiometric composition of SiO<sub>2</sub>. The maximum average thickness of the barrier layer is about 100 nm. The SiO<sub>x</sub> coating is approved by the American health authority FDA under food contact substance notification FCN 329.

### *Migration testing*

The specific migration of the surrogates was measured into the food simulants 3% (w/v) acetic acid and 10% (v/v) ethanol. Due to the fact that the SiO<sub>x</sub> coating might be sensitive towards high pH values, 5 g citric acid per 300 ml was dissolved in the ethanolic food simulant. For migration testing, the bottles were filled with the food simulants (two bottles for each bottle type and food simulant) and stored for 10 d at 40 °C. The bottles were sealed with HDPE closures with an aluminum film on the contact surface in order to prevent sorption of the surrogates into the closures. For the food simulant 10% ethanol a migration kinetic was established. 50 ml aliquots of the food simulant were drawn after 3 d, 6 d, 10 d, 20 d and 30 d. The bottles were refilled after drawing the 50 ml aliquots with the same amount of simulant. The reduction of the concentration of the surrogates by the refilling with food simulants was considered.

### *Determination of the bottle wall concentrations of the surrogates*

The PET test bottles were cut in small pieces of approximately 0.5 x 0.5 cm. 1.0 g of each PET sample was placed in a 5 ml glass vial. 1.0 ml 1,1,1,3,3,3-hexafluoro-*iso*-propanol (HFIP) was given to the PET material and stored for 1 d at 60 °C in order to swell the PET matrix. Then 2.0 ml *iso*-propanol was added for 1 d at 60 °C to extract the swollen matrix. The extract was decanted from the polymer and stored for 4 h at

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6 4 °C. Then it was decanted again from the precipitate and analyzed by GC/FID.  
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8 Quantification was achieved by external calibration using the standard addition  
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10 method. Gas chromatograph: HP 5890II, column: SE 10 - 30 m - 0.32 mm i.d. -  
11 0.32 µm film thickness, temperature program: 40 °C (5 min), rate 15 °C min<sup>-1</sup>, 240 °C  
12 (15 min), pressure: 50 kPa hydrogen, split: 10 ml min<sup>-1</sup>.  
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17 *Determination of the surrogate concentration in migration solutions by purge and trap*  
18 *gas chromatography*  
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22 The concentration of the volatile and medium volatile surrogates toluene,  
23 chlorobenzene, phenyl cyclohexane in the food simulants was determined using  
24 purge and trap gas chromatography (p&t GC) with flame ionisation detection (FID).  
25 Sample preparation: a) Acetic acid: 5 ml of the 3% acetic acid migration solution was  
26 neutralised with 1 ml of 20% caustic soda (NaOH) solution in water. Subsequently  
27 the solution was analysed by purge and trap gas chromatography (FID). b) 10%  
28 ethanol: 10 ml of the 10% ethanol migration solution was analysed by purge and trap  
29 gas chromatography (FID). Method: Gas Chromatograph: Carlo Erba 5300 Mega,  
30 column: ZB 624, length 60 m, inner diameter 0.32 mm, film thickness 1.8 µm, carrier  
31 gas: 120 kPa helium, Temperature program: 35 °C (6 min), rate 5 °C min<sup>-1</sup>, 90 °C  
32 (0 min) rate 10 °C min<sup>-1</sup>, 260 °C (15 min). Purge and trap conditions (PTA 3000):  
33 sample temperature 40 °C, purge time: 20 min, purge flow 20 ml min<sup>-1</sup>, trap  
34 temperature: -65 °C, desorption temperature 200 °C, desorption time 7 min, water  
35 trap MWT, Tenax<sup>®</sup> trap. Quantification was achieved by external calibration using  
36 standard solutions of the surrogates.  
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51 *Determination of the surrogate concentrations in migration solutions by GC/MS (SIM)*  
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54 The 3% acetic acid and 10% ethanol migration solutions were extracted three times  
55 with *n*-hexane (20 ml of food simulant with 8 ml, 5 ml and 5 ml of *n*-hexane).  
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57 Subsequently the concentrations of methyl stearate was determined using GC/MS in  
58 the selective ion mode (SIM). The mass fragment  $m/z = 74$  was used for  
59 quantification.  $m/z = 87$  was used as qualification ion. GC/MS System: Shimadzu QP  
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6 5000, column: DB VRX - 30 m - 0.32 mm i.D. - 1.8  $\mu\text{m}$  film thickness, temperature  
7 program: 40  $^{\circ}\text{C}$  (5 min), rate 15  $^{\circ}\text{C min}^{-1}$ , 250  $^{\circ}\text{C}$  (15 min), pressure: 64 kPa  
8 hydrogen, splitless, interface temperature: 260  $^{\circ}\text{C}$ , Injector temperature: 250  $^{\circ}\text{C}$ .  
9 Quantification was achieved by external calibration using standard solutions of the  
10 surrogates.  
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#### 15 16 17 *Determination of the benzophenone concentrations in migration solutions by HPLC* 18 *(UV)* 19

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21 The migration solutions were analysed by HPLC (UV). HPLC equipment: Dionex,  
22 column: Phenomenex, Synergi Fusion RP 150 $\times$ 2.0 mm, 4  $\mu\text{m}$  particle size, guard  
23 column, mobile phase: 60% acetonitrile and 40% water, isocratic elution, flow rate:  
24 0.3 ml  $\text{min}^{-1}$ , oven temperature: 25  $^{\circ}\text{C}$ , detection at 254 nm, injection volume: 10  $\mu\text{l}$ .  
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#### 31 *Detection Limits* 32

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34 The detection limits were determined according to DIN 32645. The detection limits of  
35 the applied methods for the determination of the surrogates in the different food  
36 simulants are given in Table 1.  
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40 Place here Table 1  
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## 43 Results and Discussion 44

#### 45 46 47 48 *Spiking Levels of Test Bottles* 49

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51 The concentration of the surrogates in the bottle wall was analysed after  
52 manufacturing of the spiked bottles as well as after coating. The concentrations are  
53 measured by extraction of the PET bottle wall with HFIP/*iso*-propanol and gas  
54 chromatographic analysis. The results are summarised in Table 2 (mean value from  
55 three individual bottles). The contamination levels are slightly higher for the medium  
56 and low volatile substances (phenyl cyclohexane, benzophenone, methyl stearate)  
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6 than for volatile substances like the solvents toluene and chlorobenzene. During  
7 preform and bottle manufacturing of the test bottles, the concentration of the high  
8 volatile substances are reduced due to vaporisation.  
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11 Place here Table 2  
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### 13 14 15 16 *Specific migration testing* 17

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19 The specific migration testing was performed using three different detection  
20 methods. Volatile surrogates were quantitatively determined using a purge and trap  
21 gas chromatographic method. The method shows detection limits and a good  
22 linearity of the calibrations curves. However, the method is limited to the volatile  
23 toluene, chlorobenzene and phenyl cyclohexane only. For benzophenone an  
24 HPLC/UV method was applied. In the case of methyl stearate, the analytical  
25 detection in the migration solutions at detection limits below  $10 \mu\text{g l}^{-1}$  failed due to  
26 interferences and analytical artefacts. The applied gas chromatographic separation  
27 with mass spectrometric determination in the single ion mode (GC MS (SIM)) was  
28 not sensitive enough for the determination of methyl stearate in the  $10 \mu\text{g l}^{-1}$  range.  
29 Therefore the results of methyl stearate were not used for the evaluation of the  
30 maximum bottle wall concentrations. However, the concentrations of methyl stearate  
31 in the migration solutions after storage for 10 d at  $40^\circ\text{C}$  was below the analytical  
32 detection limit of  $13.0 \mu\text{g l}^{-1}$  (3% acetic acid) and  $25.4 \mu\text{g l}^{-1}$  (10% ethanol). The  
33 results of the specific migration testing for toluene and chlorobenzene with the  
34 contact conditions 10 d at  $40^\circ\text{C}$  into 3% acetic acid and 10% ethanol are given in  
35 Table 3. For toluene and chlorobenzene the experimental migration kinetics follows  
36 the prediction by changing the bottle wall concentration ( $C_{P,0}$ ). The concentration of  
37 phenyl cyclohexane in migration simulants after storage for 10 d at  $40^\circ\text{C}$  are for all  
38 investigated bottle wall concentrations (coated and non-coated) below the analytical  
39 detection limits of  $0.9 \mu\text{g l}^{-1}$  and  $1.1 \mu\text{g l}^{-1}$ , respectively. For benzophenone only the  
40 bottles with the highest concentrations were measured. The migration was below the  
41 analytical detection limit of  $8.8 \mu\text{g l}^{-1}$ .  
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Place here Table 3

### *Migration kinetics into 10% ethanol*

For the high level spiked test bottles (non-coated and coated) a migration kinetics was established up to a storage time of 30 d at 40 °C. Table 4 summarizes the results of the migration kinetics for toluene, chlorobenzene, phenyl cyclohexane and benzophenone in 10% ethanol. As a result the surrogates toluene and chlorobenzene follow this linear correlation (Figure 1) between the square root of time and the migration for the non-coated as well as for the SiO<sub>x</sub> coated test bottle which indicates that the migration follows Fick's law. For phenyl cyclohexane and for benzophenone, the concentrations in the migration solutions are too low for a correlation.

Place here Table 4

Place here Figure 1

### *Maximum concentrations of surrogates in the bottle wall*

For the evaluation of food law compliance of the PCR PET containing and SiO<sub>x</sub> coated PET bottles a maximum migration of 10 µg l<sup>-1</sup> into food simulants at 40 °C was applied. It should be noted that this 10 µg l<sup>-1</sup> migration limit is not an officially by EU Directives recognised threshold of no concern for potential contaminants from PCR plastics (see introduction). The maximum acceptable concentrations of surrogates in the bottle wall, which corresponds to a 10 µg l<sup>-1</sup> migration value in the investigated 300 ml bottle, can be calculated from the correlation between the bottle wall concentration and the resulting specific migration into the investigated food simulants due to the fact that according to migration theory the bottle wall concentration correlates linear with the concentration in food simulant for a specific migrant. Such a correlation after storage for 10 d at 40 °C was established for the surrogates toluene and chlorobenzene for the non-coated test bottles (Table 3). From the slope of the linear correlation the maximum concentration could be estimated directly. The intercept was not taken into account. For phenyl cyclohexane and benzophenone as well as for toluene and chlorobenzene in the SiO<sub>x</sub> coated

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6 bottles, the concentrations in the migration solutions were below  $10 \mu\text{g l}^{-1}$  even at the  
7 highest bottle wall concentrations. The estimated maximum acceptable  
8 concentrations in PET material which correlate with a  $10 \mu\text{g l}^{-1}$  migration limit in food  
9 simulants are summarised in Table 5. In the cases of a migration below the analytical  
10 detection limits, the highest concentration level in the spiked test bottles was used as  
11 maximum acceptable bottle wall concentration. For the  $\text{SiO}_x$  coated bottles the  
12 maximum concentrations in the bottle wall are much higher due to the additional  
13 barrier effect in comparison to the non-coated reference bottle.  
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## 24 Conclusions

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27 From analytical screening tests on PET recyclate samples taken from the market, it  
28 has been shown, that the concentrations of foreign compounds in production  
29 batches of conventionally recycled PCR PET do not exceed a concentration level of  
30 about  $50 \text{ mg kg}^{-1}$  for any individual post-consumer compounds (Franz et al 2003,  
31 Franz et al 2004b). Chemical compounds, which are introduced into the bottle wall  
32 by misuse of PET bottles for the storage of e.g. household chemicals have high  
33 levels in the individual bottle. However, due to the rarity of this event and due to the  
34 dilution of the contaminated PET flakes during washing with non-contaminated  
35 flakes, the average residual concentration of chemical compounds from misuse are  
36 more likely to be  $<10 \text{ mg kg}^{-1}$  (Franz et al 2004b). Therefore, the artificially  
37 established initial concentrations used in this study and especially at the high spiking  
38 level would be far above any relevant concentrations of post-consumer compounds  
39 occurring in practice and would represent a worst-case scenario for the input-  
40 material.  
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52 From the ratios of the slopes of the migration kinetics (concentration in food simulant  
53 versus square root of time) the barrier effect for the  $\text{SiO}_x$  coating layer for reducing  
54 the migration of toluene and chlorobenzene in 10% ethanol was determined to 37  
55 and 29, respectively. Therefore, the data shows the  $\text{SiO}_x$  layer significantly reduces  
56 migration. It can be assumed, that the barrier effects for other surrogates or post-  
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6 consumer compounds are in a similar range. The migration tests were performed on  
7 a 0.3 l bottle with a surface of about 280 cm<sup>2</sup>. Due to the more favourable  
8 surface/volume ratios of larger bottles, the estimated maximum levels given in Table  
9 8 can be considered as worse case. Therefore the maximum levels of possible  
10 contaminants in the bottle wall will increase with increasing bottle size (increasing  
11 surface/volume ratio).  
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17 The experimental data from this study demonstrate that SiO<sub>x</sub> coated PET bottles  
18 produced from the contaminated test batch would be in accordance with the 10 µg l<sup>-1</sup>  
19 migration limit as long as the estimated maximum concentrations given in Table 8  
20 are not exceeded. The maximum bottle wall concentrations of the surrogates are in  
21 the range of 200 mg kg<sup>-1</sup> (toluene) and about 900 mg kg<sup>-1</sup> (benzophenone).  
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26 Therefore the investigated SiO<sub>x</sub> coating layer is an efficient functional barrier towards  
27 recycle typical compounds. Consequently, this SiO<sub>x</sub> coating layer would allow the  
28 use of conventionally recycled post-consumer PET flakes without super-clean  
29 recycling processes for packaging aqueous and low alcoholic foodstuffs under cold-  
30 fill conditions and prevent the food from migration of unwanted contaminants from  
31 post-consumer PET. In addition, it should be noted that the drawn conclusions  
32 implicate the worst case assumption that 100% post-consumer recycle is used for  
33 PET bottle manufacturing.  
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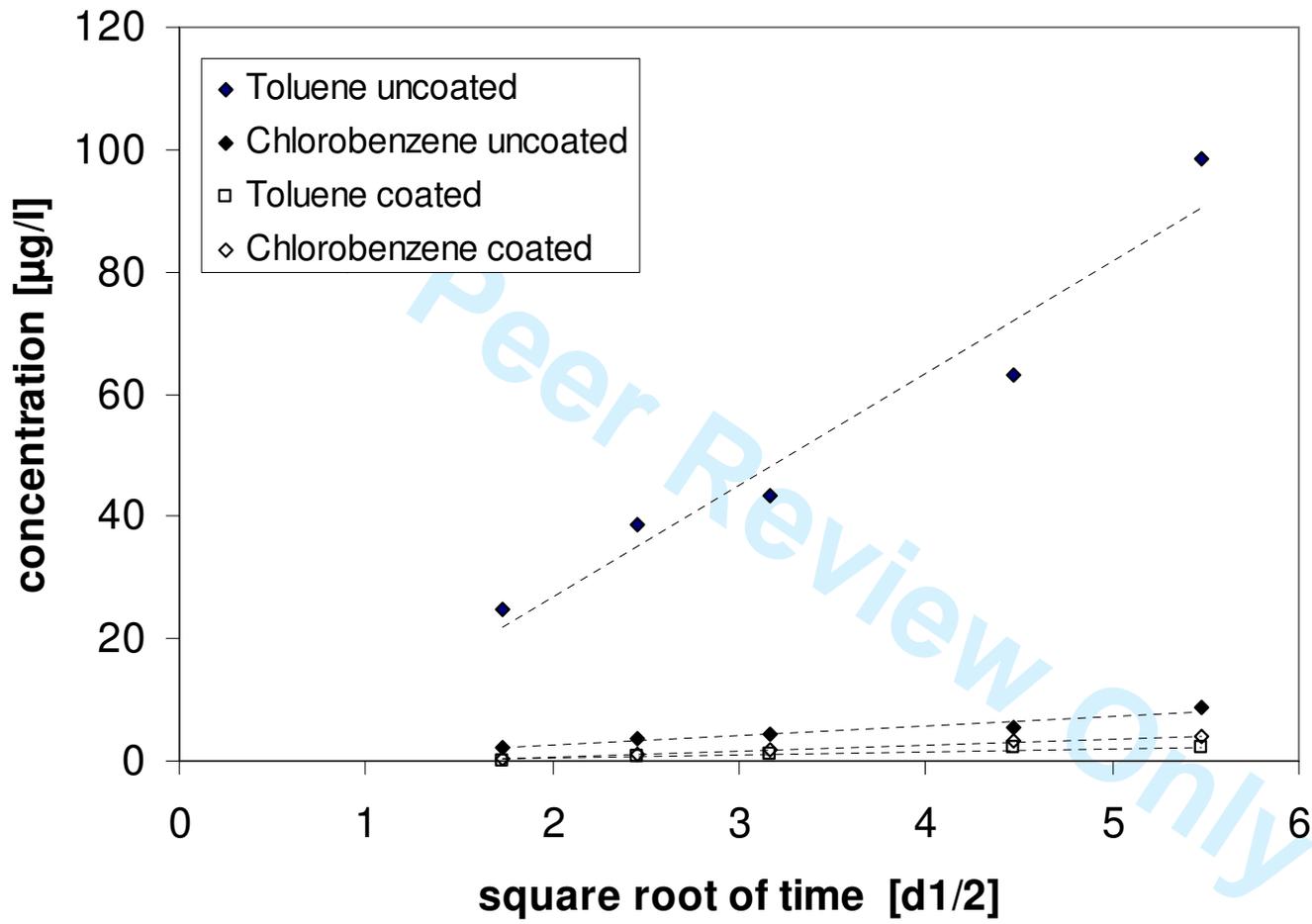


Figure 1: Migration kinetics of toluene and chlorobenzene into 10% ethanol at 40 °C (high level bottles)

Table 1: Detection limits of the applied model compounds in food simulants

Surrogate	Detection limit [ $\mu\text{g l}^{-1}$ ] (method)				
	Toluene (p&t GC)	Chlorobenzene (p&t GC)	Phenyl cyclohexane (p&t GC)	Benzophenone (HPLC/UV)	Methyl stearate (GC MS SIM)
3% Acetic acid	1.0	0.7	1.1	8.8	13.0
10% Ethanol	0.4	0.3	0.9	8.8	25.4

Table 2: Concentration of the surrogates in the bottle wall of the spiked PET bottles determined after extraction with HFIP/*iso*-propanol (mean values of the concentrations and standard deviation from three individual bottles)

Test bottle type	Concentration [ppm]				
	Toluene	Chlorobenzene	Phenyl cyclohexane	Benzophenone	Methyl stearate
low level, non-coated	17.6 ±0.6	26.2 ±0.5	35.3 ±1.0	91.4 ±2.4	107.0 ±2.9
low level, coated	18.7 ±0.3	26.1 ±0.4	32.2 ±0.4	88.9 ±0.7	104.6 ±1.0
medium level, non-coated	70.6 ±0.6	101.3 ±0.8	261.7 ±1.7	394.3 ±3.2	400.9 ±3.0
medium level, coated	57.0 ±0.1	87.6 ±0.3	240.9 ±1.6	396.1 ±2.7	412.5 ±3.4
high level, non-coated	297.5 ±1.2	357.8 ±1.5	782.3 ±1.4	973.9 ±3.5	1029.1 ±16.3
high level, coated	203.6 ±1.5	249.5 ±1.8	601.3 ±4.9	882.5 ±7.7	904.1 ±11.5

Table 3: Concentration of toluene and chlorobenzene in migration simulants after storage for 10 d at 40 °C determined by purge and trap gas chromatography

Simulant	Migrant	bottle type	concentration in food simulant [ $\mu\text{g l}^{-1}$ ]			slope	Intercept	Correlation coefficient $R^2$
			low level	medium level	high level			
3% acetic acid	Toluene	non-coated	1.4	2.3	14.5	0.0489	-0.2170	0.9862
10% ethanol	Toluene	non-coated	2.3	8.6	43.4	0.1488	-1.0284	0.9987
3% acetic acid	Chlorobenzene	non-coated	3.2	5.7	32.6	0.0928	-1.1818	0.9803
10% ethanol	Chlorobenzene	non-coated	4.5	17.1	65.4	0.1848	-0.9022	0.9996
3% acetic acid	Toluene	coated	<1.0	<1.0	<1.0	/	/	/
10% ethanol	Toluene	coated	<0.4	<0.4	1.1	/	/	/
3% acetic acid	Chlorobenzene	coated	<0.7	<0.7	<0.7	/	/	/
10% ethanol	Chlorobenzene	coated	<0.3	0.3	1.7	0.0086	-0.4875	/

Table 4: Results of the migration kinetics of the model compounds from the test bottles into 10% ethanol at 40 °C

storage time [d]	concentration [ $\mu\text{g l}^{-1}$ ] (bottle wall concentration [ppm])							
	Toluene		Chlorobenzene		Phenyl cyclohexane		Benzophenone	
	non coated (297.5 $\pm$ 1.2)	SiO <sub>x</sub> coated (203.6 $\pm$ 1.5)	non coated (357.8 $\pm$ 1.5)	SiO <sub>x</sub> coated (249.5 $\pm$ 1.8)	non coated (782.3 $\pm$ 1.4)	SiO <sub>x</sub> coated (601.3 $\pm$ 4.9)	non coated (973.9 $\pm$ 3.5)	SiO <sub>x</sub> coated (882.5 $\pm$ 7.7)
3	24.7	<0.4	32.7	0.3	<0.9	<0.9	not determined	not determined
6	38.6	0.7	53.8	1.1	<0.9	<0.9	not determined	not determined
10	43.4	1.1	65.4	1.7	<0.9	<0.9	<8.8	<8.8
20	63.0	2.1	99.0	3.2	<0.9	<0.9	14.8	<8.8
30	98.5	2.1	146.4	4.0	1.6	<0.9	21.2	<8.8

Table 5: Estimated maximum concentrations [ppm] of the investigated model compounds in the bottle wall of the test bottles corresponding to a migration of  $10 \mu\text{g l}^{-1}$  in food simulant (contact conditions: 10 d at 40 °C)

Surrogate	Estimated maximum concentrations [ppm] in the bottle wall			
	non-coated bottle		SiO <sub>x</sub> coated bottle	
	3% acetic acid	10% ethanol	3% acetic acid	10% ethanol
Toluene	204	67	>204	>204
Chlorobenzene	108	54	>250	>250
Phenyl cyclohexane	>782	>782	>601	>601
Benzophenone	>974	>974	>883	>883