Release of bisphenol A from polycarbonate baby bottles: mechanisms of formation and investigation of worst case scenarios

Sandra Biedermann-Brem . Koni Grob . Per Fjeldal

Abstract The question was further investigated whether there could be conditions resulting in contamination of beverages in polycarbonate bottles for babies with bisphenol A (BPA) at concentrations causing the tolerable daily intake (TDI) to be approached or exceeded. It is a follow up of previous work showing increased release of BPA after extended use of the bottles. Migration in the proper sense was low, but larger amounts of BPA were observed from degradation of the polycarbonate. Since there are no standardized testing conditions to determine release by degradation of the polymer, worst case scenarios were investigated. Alkali washing solutions at concentrations typical for dishwashers contained BPA in concentrations little above 100 µg/l. In reality they are diluted in the general washing liquid and finally poured out. Drying was the most critical step, particularly after inadequate rinsing of bottles, when alkali detergent was "baked" to the bottle wall at elevated temperature. BPA thus formed is transferred into the beverage, but is unlikely to exceed 10 µg/l. The highest transfer into the beverage (up to about 500 µg/l) could occur when the bottle is positioned in the dishwasher at such inclination that detergent solution does not fully run off and is poorly rinsed, but this scenario is unlikely to often occur. In conclusion, even rather extreme scenarios do not result in BPA contamination near to the level corresponding to the TDI.

Key words Baby bottles . Polycarbonate . Bisphenol A . Detergents . Migration . Release by degradation

Introduction

In 2003, Brede et al. [1] showed that migration of bisphenol A (BPA) from polycarbonate bottles into hot water was in the order of 0.2 µg/l when the bottles were new and increased to 6-8 µg/l after repeated washing. The highest values reached 16 µg/l (200 ml filling). These results were intriguing, since they did not conform with usual migration behavior, where a decrease is observed after continued use. They triggered questions about the origin, the reasons for the increase and whether even higher, possibly critical concentrations could be reached under certain unidentified conditions of use. It also arose suspicion that the previous work reported in literature, all showing migration to be negligible, may not have taken into account all possible scenarios. If the presence of BPA does not result from migration of residual BPA from the polymer, only an investigation of the mechanism of its release and an investigation of the worst case situations enables to give a final answer on the safety of these bottles.

In 2006, the European Food Safety Authority (EFSA) concluded on weak estrogenic activity with reproductive and development toxicity [2] and set a tolerable daily intake (TDI) for BPA of 0.05 mg/kg body weight (bw). This confirmed the specific migration limit (SML) of 3

S. Biedermann . K. Grob (✉)
Official Food Control Authority of the Canton of Zürich
P.O. Box
CH-8032 Zurich, Switzerland
e-mail: Konrad.Grob@klzh.ch
Tel.: +41-43-244-71-31
Fax: +41-43-244-71-01

P. Fjeldal
Norwegian Food Safety Authority, Head Office
PB 383, NO-2381 Brumunddal, Norway

mg/kg food in Directive 2002/72/EC. In-between, in 2002, the EU Scientific Committee on Food (SCF) reacted to new findings by lowering the TDI to 0.01 mg/kg bw as a precautionary temporary measure, but with the later data this reduction was considered unnecessary. Presently the SML is still at 0.5 mg/kg (Directive 2004/19EC).

The usually applied conversion of a TDI to an SML assumes 60 kg body weight and a consumption of food contaminated with the substance in question of 1 kg/d (for a TDI of 0.05 mg/kg bw resulting in the SML of 3 mg/kg). These assumptions are inadequate for babies and small children, since their food consumption per body weight is substantially higher. With a daily consumption of 800 ml from baby bottles and a body weight of 4 kg, the TDI is reached with a BPA concentration of 250 µg/l.

Literature reports release of BPA from polycarbonate baby bottles far below this concentration. For instance, Krishnan et al. [3] estimated release into water after autoclaving in the range of a few µg/l. Mountfort et al. [4] subjected bottles to treatment as used in domestic practice, immersing them in alkaline hypochlorite and washing them in dishwashers at 65 °C using detergent solutions with a pH as high as 10.3. Twenty cycles of each process were performed. Using an analytical method with a detection limit of 30 µg/kg, no BPA was detected in prepared baby beverage or the rinsing solutions. Kawamura et al. [5] found BPA release from a range of polycarbonate products to be low and not affected by microwave heating. Data on low BPA release were also reported by Sun et al. [6], concluding that "polycarbonate baby bottles should be rinsed thoroughly before put into the first use". Wong et al. [7] used conventional simulating migration testing to show that exposure of babies is below the TDI even at worst case conditions and with exaggerated assumptions.

In view of the strong interest in the public, particularly parents concerned about their babies, and the puzzling results published by Brede et al. [1], the subject was picked up again to further check conditions which could release BPA in relevant amounts. Conventional migration testing, as provided by EU legislation (based on Directive 82/711 and amendments) is designed for the transfer of substances already existing in the polymer. Previous work and particularly the increased release of the BPA after repeated use observed by Brede et al. [1] indicated, however, that BPA is not migrating from the bulk of the polymer, but released by chemical attack and, hence, that such standard testing is inadequate.

Testing to ensure safety has to take into consideration worst case conditions, but these first need to be explored by investigating the background of the release. The key question of the work presented here was whether there could be types of uses, unfortunate selections of conditions or a failure in the washing procedure which resulted in a release of BPA approaching or exceeding the TDI.

Experimental

Materials

Baby bottles from four producers were tested: Baby bottle 1 was from Bambino MSAM, Stockholm (250 ml), bottle 2 from Dr. Brown's, Handi-Craft, St. Louis, USA (240 ml), bottle 3 from Avent, Suffolk, UK (260 ml), bottle 4 from NUK, MAPA, Zeven, Germany (250 ml), all bought in Norway.

A laboratory dish washer model DR 300E and a drier Model WA 400 RT from Renggli (Rotkreuz, Switzerland) were used for the normal washing cycles. The detergents were (i) the laboratory product neodisher A8 (Dr. Weigert, Hamburg, Germany), containing “more than 20 % sodium hydroxide, polycarboxylates, chlorine-based bleaching agents, silicates, carbonates, sulfates and 15-30 % phosphate”, with a recommended dosage of 2-5 g/l, and (ii) Sun Tabs (Unilever, Zug, Switzerland), a detergent widely used in households.

HPLC involved an instrument SpectraSystem P4000 (Thermo Separation Products, San Jose, USA) with a fluorescence detector FP-920 from Jasco (Tokyo, Japan). GC-MS was performed with a gas chromatograph Trace Ultra equipped with an on-column injector and an ion trap mass spectrometer Polaris Q (both Thermo Fisher, Milan, Italy).

2,2-Bis-(4-hydroxyphenyl) propane (Bisphenol A; BPA; ~97 %), bis-(4-hydroxyphenyl) methane (bisphenol F; bpF; ≥98 %) and 1-propanol (J&J Brand) were from Fluka (Buchs, Switzerland). Methyl tert. butyl ether (MTBE) and hexane from Brenntag Schweizerhall

(Basel, Switzerland) were redistilled. Methanol (HPLC) was from Baker (Deventer, The Netherlands).

Testing methods

To determine the small molecular weight material present in an internal surface layer of the bottles, bottles were shortly washed under running water, dried with tissue paper and shaken with 10 ml MTBE for 1 min. The amount of material dissolved into the MTBE was determined gravimetrically. BPA in this solution was determined by HPLC with fluorescence detection, other components by GC-MS.

For many experiments, washing cycles were simulated by the following procedure: 100 ml of a detergent solution normally containing 5 g/l detergent in tap water were filled into the bottle and the bottle mounted to a rotary evaporator in order to rotate it in a water bath at 80 °C for 1 h. The inclination of the bottle was adjusted such that the whole internal surface was in contact with the detergent solution. The solution was poured into a glass flask for analysis. With or without rinsing with tap water, the bottle was dried in an oven for drying dishes at 90 °C during 30 min.

In order to determine the amount of detergent solution or water adhering to the internal surface of the bottle (related to wettability of the bottle surface), bottles were tared before simulated washing and weighed again after pouring out the detergent solution.

To determine the amount of BPA formed during the drying process, the dried bottles were extracted by manual shaking with usually 20 ml water at ambient temperature during 30 s.

Uptake of BPA from the bottles into aqueous solutions at various pHs was determined by fillings with 50-100 ml liquid and rotating in a water bath at 80 °C for 1 h as described above to contact the entire internal surface.

The formation of BPA upon evaporation of different detergent solutions on the bottle wall was tested with straight bottles laid horizontally between two objects preventing rolling sidewise. 10 ml of liquid was introduced, forming a stripe on the side wall. The water was evaporated in a GC oven at 90 °C during 2 h. The stripe was extracted with 20 ml water during 3 min, leaving the bottle in the same position. Sometimes the bottle was extracted another time with 20 ml water or 10 ml MTBE. Subsequent experiments were performed after rinsing the whole bottle under running warm water and drying with a towel.

Analysis of BPA in aqueous phases by RPLC

To 10 ml of detergent solution neutralized with 10 % HCl as well as aqueous solutions or extracts, p/p-bisphenol F (bpF) was added as internal standard at 5-20 µg/l (50-200 µl of a 1 µg/ml solution). 200-500 µl were injected into reversed phase HPLC. A 250 x 4.5 mm i.d. column packed with Spherisorb ODS-2, 5 µm (Grom, Herrenberg-Kayh, Germany) was used with isocratic elution involving 65 % methanol/water at 1 ml/min. The bisphenols were detected by fluorescence at 225/295 nm. The detection limit was at 0.01 µg/l (S/N=5), the measuring uncertainty below 20 %.

BPA was unstable in solution of the laboratory detergent neodisher A8: concentrations decreased by a factor of two in a few hours. In solutions of the household detergent Sun Tabs it was stable for more than a day.

Results

A first remark: since the amount of BPA entering the beverage is not determined by a partitioning/equilibration process, but by the amount formed on the surface of the internal bottle wall (see below), the BPA concentration in the beverage or test liquid depends on the volume introduced: with a smaller volume, the concentration is correspondingly higher. As a reasonable worst case it was assumed that the bottles (of about 250 ml internal volume) would be filled with 100 ml beverage. Hence amounts of BPA found in extracts were recalculated into concentrations for 100 ml fillings.

Extracts from new bottles

A first subject of interest concerned the BPA and other low molecular mass components present in the surface layer of a new bottle, i.e. potentially migrating from the polymer into the beverage. Bottles were extracted by shaking with 10 ml MTBE for 1 min. The MTBE dissolved about 1 mg of material, corresponding to the removal of a layer of roughly 50 nm thickness. The same kind of extraction was repeated after 30 washing cycles in the laboratory washer and drier.

Table 1 shows the amounts of BPA determined in the MTBE extract. For all four brands of bottles tested, the results were below 1 µg/l (referring to a 100 ml filling), i.e. considered negligible compared to the 250 µg/l meeting the TDI according to the estimations proposed in the Introduction. The results reasonably agree with the 4-140 mg/kg of BPA found in the polymer [4,7]: 0.1 µg/l in a 100 ml filling corresponds to 10 ng or a 10 mg/kg concentration in the 1 mg polymer dissolved by MTBE.

Since MTBE extracted/dissolved a rather thick layer of polycarbonate, more than a beverage could extract, it was concluded that there was no relevant contribution of BPA from the polymer. Firstly, this confirms previous work in literature that migration in the proper sense cannot result in BPA concentrations in the beverage which could be of health concern. Secondly it indicates that the extraction properties of the beverage filled into the bottle are not important (there is little to extract) and, therefore, that standard migration testing is inadequate in this case. BPA primarily originates from degradation of the polycarbonate.

Table 1 also shows that there was no significant difference in the BPA content in the surface layer of the new bottles and of those having passed 30 washing and drying cycles in the machine. Further, the whole surface layer contained less BPA than Brede et al. [1] determined in the water extract after a series of washing cycles, once again indicating that most BPA is released by degradation of the polymer.

Table 1 MTBE extracts from bottles of four brands, new (after rinsing with water) as well as after 30 washing cycles (µg/l referring to 100 ml filling)

Bottle brand	New bottle	After 30 washing cycles
1	0.16	0.17
2	0.22	0.24
3	0.21	0.19
4	0.38	0.32

The major peak in the GC-MS chromatogram of the MTBE extract corresponded to Irgafos 168 and its oxidation product (approximately double of BPA concentration). Minor amounts (2-10 times less than BPA) were found of the compounds listed in Table 2 with their main fragments in the mass spectra. They consisted of carbonates of BPA, phenol and tert. butyl phenol. Further, some tert. butyl phenol was found. The amounts determined in the surface layer suggested a migration below the threshold of toxicological concern [8,9]. Extracts from bottles used for experiments contained even less of these components, confirming that BPA is the only substance to be investigated.

Table 2 Components in the MTBE extract from a new bottle of brand 1 together with their molecular mass (MMass) and the predominant electron impact (EI) ionization fragments. Phe, phenol; t-BuPhe, tert. butyl phenol.

	MMass	Fragments: m/z (%)
Phe-C=O-Phe	214	141, 39 (65 %), 51 (50), 77 (50), 170 (50), 214 (50), 115 (25)
BPA-C=O-Phe	348	333, 213 (35), 119 (20), 348 (20), 77 (15), 181 (15), 289 (10)
Phe-C=O-BPA-C=O-Phe	468	453, 289 (30), 333 (30), 77 (20), 195 (15), 179 (10), 409 (10), 468 (10)
t-BuPhe-C=O-BPA-C=O-t-BuPhe	580	565, 251 (30), 521 (30), 135 (25), 345 (25), 91 (20), 389 (20), 477 (15), 580 (15)

Extraction of BPA with water

Two extreme cycles of treatment served to investigate the extractability of BPA formed by alkali attack of the polycarbonate. After several experiments, a bottle of brand 1 was extracted twice with MTBE. The BPA concentrations calculated for a 100 ml filling, 1 and 0.5 µg/l (Fig. 1), showed that there were no relevant residues from previous experiments. Then a harsh washing cycle was simulated to obtain strong BPA formation, using a solution containing 2 % laboratory detergent A8 (4 times the recommended dosage). After heating to 80 °C for 1 h (Experimental), the detergent solution was poured out and the bottle dried at without prior rinsing. The extract with 100 ml water (shaking during 30 s at ambient temperature) contained 690 µg/l BPA. A second extract performed immediately afterwards contained 21 µl/l BPA and the following two MTBE extracts (after drying with tissue paper) 4 and 1 µg/l, respectively. A second cycle involving washing with 5 % detergent A8 followed by same drying, again without prior rinsing, resulted in 1580 µg/l BPA in the first water extract. In the second it dropped to 60 µg/l and in the following two MTBE extracts to 60 and 7 µg/l.

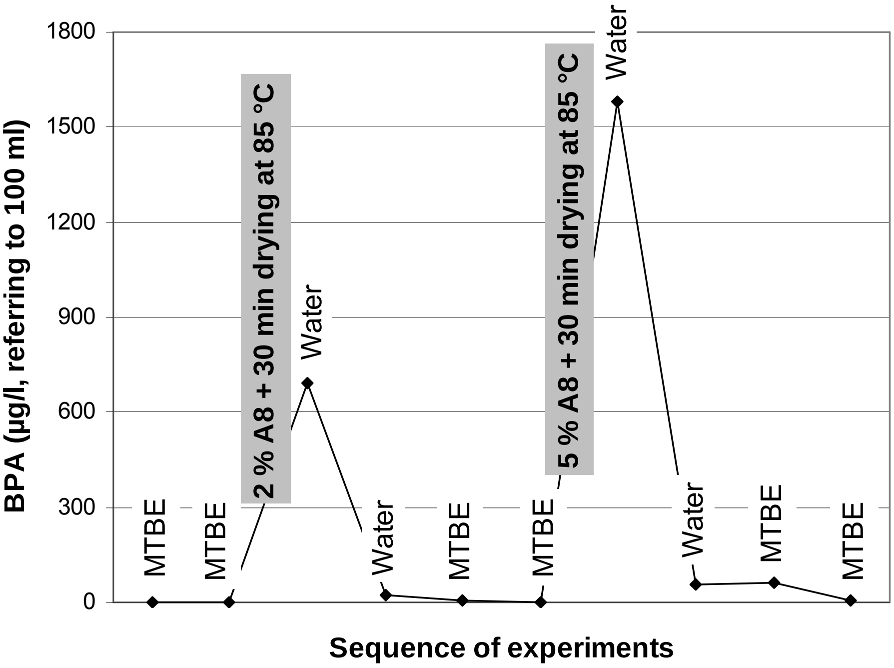

Fig. 1 Sequence of extractions with MTBE or water including two harsh washing cycles with an overdose of the strongly basic laboratory detergent A8 and without rinsing before drying.

It was concluded that, firstly, the BPA formed by a washing/drying cycle can be removed by rinsing with water at ambient temperature, i.e. the BPA is on the surface and does not penetrate the polymer. As even MTBE does not extract relevant additional amounts of BPA, also heating milk or baby formula is not expected to extract more BPA. Secondly, each washing cycle can be considered individually, since the BPA formed is readily removed and leaves behind a polycarbonate releasing little more BPA than a new bottle or one treated by more normal washing cycles. This means that a given bottle can be used for many experiments.

BPA release by aqueous media of various pH

The formation of BPA from the polycarbonate by attack of various aqueous media was tested at 80 °C for 1 h using 100 ml of liquid. As concluded from the above experiment, transfer into the aqueous medium is immediate and complete. Using plain tap water with an (initial) pH of 6, 20 µg/l BPA was formed in a new bottle of brand 1 (Table 3). In another bottle of the same brand, which had been used for more than 10 mostly heavy cycles (including those in Fig. 1), only 12 µg/l BPA was formed, showing no sign that intense use of the bottle would increase BPA formation when tested in this way.

Table 3 BPA (µg/l, related to a 100 ml filling) in aqueous media containing the salts listed in the first column, after heating at 80 °C during 1 h

Aqueous phase	pH	BPA (µg/l, 100 ml) New bottle	Used bottle
Plain water	6	20	12
3 % citric acid	2	1.3	2
3 % phosphate/acetate	8	6	3
3 % sodium bicarbonate	9	25	9
1 % sodium carbonate	11	1640	570
0.1 % sodium hydroxide	12	1010	350

The experiments were continued with the same two bottles (after thorough rinsing with warm tap water), in the sequence shown in Table 3. With an acidified medium (3 % citric acid), BPA formation was approximately 10 times lower (1-2 µg/l), and also a 3 % phosphate/acetate buffer at pH 8 produced substantially less. With 3 % sodium bicarbonate, clearly beyond a hard water, BPA release remained similar to normal tap water. A 1 % sodium carbonate solution, however, caused 1640 µg/l BPA to be formed in the new bottle and about a third of this in the used bottle. A ten times more dilute hydroxide solution resulted in somewhat less BPA. This experiment confirmed that substantial amounts of BPA are liberated only in strongly alkali media – an alkalinity exceeding that in real foods.

Comparison of the four brands of bottles

The above experiment with the 3 % bicarbonate solution was repeated for the four brands of baby bottles tested, for each comparing a new bottle (after rinsing with water) with one having passed 30 washing cycles in the dishwasher. Each experiment was repeated using the same bottle. Differences between the bottles of the four manufacturers were small. The 30 washing cycles decreased BPA formation substantially (by a factor 5), i.e. the increase with use found by Brede et al. [1] could again not be explained in this way.

Table 4 BPA (µg/l, related to a 100 ml filling) in a 3 % sodium bicarbonate solution heated at 80 °C for 1 h in bottles of the 4 brands: two consecutive experiments (1 and 2) performed with new bottles and bottles having passed 30 washing cycles

Bottle	New bottles		30 wash cycles	
brand	1	2	1	2
1	25		8.4	3.5
2	20	24	4.5	2.2
3	12	18	1.7	1.6
4	6	13	2.3	2.4

Critical steps of the washing cycle

Subsequent experiments headed for the critical steps in the washing cycles and the conditions required that relevant amounts of BPA be released into a beverage. Detergents used in washing machines tend to be strongly alkali (in contrast to those used for manual cleaning). Usually the BPA formed on the internal and external surface of the bottles is diluted in a large volume of washing liquid. At the end of the washing process, the amount of BPA-containing detergent solution remaining in the flask in the form of layers or droplets wetting the internal wall is 100-800 mg (determined as described in the Experimental; some data shown below). Then the bottle is rinsed and dried, which means that the water is evaporated from the droplets or layers adhering to the bottle wall and salts (primarily carbonates in non-deionized water) are baked on the wall at temperatures close to 100 °C.

Table 5 shows amounts of BPA formed during washing/drying cycles performed with a bottle of brand 1. As BPA was unstable in the laboratory detergent neodisher A8 and the household detergent (Sun Tabs) formed little BPA, half of the hydroxide contained in neodisher A8, i.e. 10 %, was added to the detergent Sun Tabs. Further, this detergent was applied at a modest over-dose (10 g/l) to yield more significant results.

The experiment in line 1 involved the complete cycle in simulation. The BPA concentration in the resulting 100 ml detergent solution (DS) was 160 µg/l. After rinsing with tap water and drying, the first water extract of the bottle contained 0.3 µg/l BPA, the second 0.02 µg/l. The experiment in line 2 focused on what happens if the bottle is not rinsed before drying. The BPA concentration in the detergent solution at the end of washing was similar to line 1 (130 µg/l). Pouring out without shaking left 110 mg BPA-containing detergent solution in the bottle (last column), contributing 0.12 µg/l BPA to 100 ml filling. However, after drying, 6 µg/l BPA were measured in the 100 ml water extract, nearly all of which must have been formed during the drying process, i.e. by the attack of the alkali baked onto the polycarbonate.

Table 5 BPA formed in a strongly alkali detergent solution (DS) and by drying with or without rinsing the detergent solution from the bottle (brand 1)

		BPA (µg/l, 100 ml)			DS left
	Process	DS	Bottle extract after drying		in bottle
			1st extract	2nd extract	(mg)
1	Washed/rinsed/dried	160	0.3	0.02	
2	Washed/dried	130	6	0.4	110
3	Rinsed with DS/dried		4.2	0.5	270
4	Rinsed with DS/rinsed/dried		0.6	0.1	

In line 3, the bottle was just shortly rinsed with detergent solution at ambient temperature, i.e. no BPA was formed during washing, and dried again without prior rinsing. BPA in the extract amounted to 4.2 µg/l, which confirms that drying is the relevant step. As a control, rinsing with detergent solution followed by rinsing with water and drying yielded little BPA (line 4).

These experiments were performed with 100 ml detergent solution and rotating the bottle. With 250 ml detergent solution filling the bottle and without rotation, the result calculated back to the 100 ml filling was the same (150 µg/l), i.e. there was no mechanical contribution to the leaching process.

A worst case scenario would be a bottle fallen over in the dishwasher or positioned such that the detergent solution is not fully running off, combined with failing rinsing. To be realistic, if that much liquid remains in the bottle that the water is not evaporated during the drying stage, the problem is noticed and the bottle probably rinsed manually. However, with a smaller volume, the drying may reach completeness and the problem remain undetected. Such a scenario was simulated with bottles of brand 2 (straight side wall) positioned horizontally on the side wall. 10 ml of detergent solution or other aqueous media were introduced and evaporated during 2 h at 90 °C. The water evaporated from a stripe with a surface area of about 30 cm^2 and left behind a surface with well visible white precipitate. This stripe was extracted with water.

With neodisher A8 at the recommended dosage, 680 µg/l BPA was determined (Table 6). Related to the 10 ml solution introduced, the BPA concentration reached 6800 µg/l, which is far above that found in the washing solution (Table 5) and suggests that the increasing detergent concentration during drying strongly accelerates the attack on the polycarbonate. Interestingly, even with the substantially less alkali Sun Tabs, a large amount of BPA was generated (line 2).

Table 6 BPA (µg/l, related to a 100 ml filling) formed in bottles of brand 2 laid horizontally, evaporating 10 ml of the aqueous media listed to dryness at 90 °C during 2 h

Liquid dried on	BPA

	bottle wall	(µg/l)
1	5 g/l neodisher A8	680
2	5 g/l Sun Tabs	420
3	10 g/l Handy	9
4	Tap water	6
5	Hard water 43 °fH	8
6	1 g/l $NaHCO_3$	52

The same experiment was used to assess the aggressivity during drying of other media. With 10 g/l of an alkali-free liquid detergent for manual dishwashing (Handy, MIFA, Frenkendorf, Switzerland), little more BPA was formed than with tap water (lines 3 and 4). Evaporation of 10 ml tap water formed about 10 times more BPA than that of the much smaller amount after pouring out the rinsing liquid (Table 5, lines 1 and 4). Hard water (43 °fH) generated somewhat more BPA than laboratory tap water (about 25 °fH). The addition of 1 g/l sodium bicarbonate strongly increased BPA formation, presumably owing to the increase of the pH upon release of carbon dioxide.

Effect of repeated washing

The above experiments did not explain the increase of the BPA concentrations with aging of the bottle described by Brede et al. [1]. In particular, a first hypothesis that attack by alkali would fragment the macromolecules and increase the BPA release by more terminal groups of the polymer chains being available could not be substantiated (Tables 3 and 4). Further investigations focused on the drying of the bottle, as it was found to be the most relevant step of the washing cycle. The amount of liquid drying onto the bottle wall was found to be an important parameter (see above). It depends on how efficiently the liquid is removed and on the wettability of the internal bottle wall.

After heating at 80 °C in bottle 1, the detergent solution (5 g/l neodisher A8) was either poured out, shaken out or wiped out by tissue paper, leaving 105, 23 or <2 mg liquid, respectively, in the bottle (Table 7). Without rinsing with water, the bottle was dried at 90 °C for 30 min. The BPA in the water extracts indeed reflected the amount of detergent solution baked to the bottle wall.

Table 7 The amount of detergent solution (DS) remaining on the bottle wall before drying (mg) influencing the BPA concentration in the extract (µg/l referring to 100 ml)

Removal of detergent solution	DS (mg)	BPA (µg/l)
Poured out	105	2.7
Shaken out	23	0.7
Dried with paper	<2	0.3

The enhanced wettability of the internal bottle wall after aging by 30 washing cycles was evidenced by the amount of liquid retained after pouring out the detergent solution in equal manner. A new bottle each of the 4 brands was tested by two cycles of simulated washing followed by drying without rinsing, using 5 g/l Sun Tabs as detergent. The amount of detergent solution adhering to the internal bottle wall varied between 45 and 220 mg (Table 8), the BPA extracted after drying between 0.1 and 1 µg/l. After the 30 washing cycles, 420-820 mg liquid was retained (increase by a factor of 4.7) and the BPA formation increased to 0.9-7 µg/l (by a factor of 8.7). Also the visual aspect changed: in the new bottle, the liquid formed droplets of various sizes, whereas after 30 washings a large part of the slightly turbid wall was covered by a liquid film.

Table 8. Amount of detergent solution (DS) retained on the bottle wall after pouring out and the amount of BPA extracted after drying; two cycles each for new bottles of the 4 brands and bottles after 30 washing cycles

Bottle brand	New bottle				After 30 washing cycles			
	1st cycle		2nd cycle		1st cycle		2nd cycle	
	DS (mg)	BPA (µg/l)	DS (mg)	BPA (µg/l)	DS (mg)	BPA (µg/l)	DS (mg)	BPA (µg/l)
1	175	0.8	210	1	590	5.8	820	7
2	90	0.1	220	0.3	710	3.5	560	1
3	45	0.2	110	0.1	560	1.3	610	1.3
4	120	0.13	75	0.05	420	0.9	650	2.6

These results lend themselves to explain the observations of Brede et al.: the release of BPA increased by a factor of almost 9 after 30 washing cycles (against a factor of 30-40), and also the amounts determined for the new and the aged bottles were similar to those reported by Brede et al., provided the bottles were not rinsed before drying.

Enhanced wettability could also result from grating the internal bottle wall with sharp tools. However, experiments using a new bottle and weighing the amount of retained washing liquid did not provide significant differences. This is not really a surprise: grating of the polycarbonate does not liberate BPA as such, nor does it as efficiently enhance wettability as do repeated washing cycles.

Conclusions

Firstly the results highlight a general point: current standard methods for testing food contact materials focus on migration, i.e. the transfer of components present in the material into the packed food. They neglect chemical liberation of compounds, such as the release of BPA from polycarbonate. Such release must be tested by investigation of the mechanism involved and the search for the worst case situation. The difficulty is in finding the relevant situation.

In this particular case, investigations aimed at answering the question whether there could be a risk that babies are exposed to BPA from polycarbonate bottles in amounts exceeding the TDI, if not during normal use, then with unusual and perhaps unfortunate conditions and practices. Therefore the tests described above were driven to a point to result in relevant BPA formation. Detergent concentrations were at the upper bound of those usually applied and often with an alkalinity exceeding that of the household detergents usually used. Even rather improbable conditions and scenarios were tested.

The results can be summarized in the following points. A concentration of 250 µg/l in the beverage, potentially resulting in an exposure at the TDI, served as reference.

1. As previously shown, the amount of BPA contained in the polycarbonate is so small that BPA migration in the proper sense is below 1 µg/l; also liquids with a strong extraction power do not extract much BPA.
2. Relevant amounts of BPA may be formed upon degradation of the polycarbonate, but alkalinity in foods and beverages to produce BPA at more than 50 µg/l in a 100 ml filling is beyond sensory tolerance (Table 3).
3. Using strongly alkali detergents, the washing liquid may liberate up to around 200 µg/l BPA when remaining in the bottle. The amount of BPA entering a beverage after pouring out the washing liquid without rinsing the bottle reached 1 µg/l if 500 mg of solution were left in the bottle and diluted in 100 ml beverage. However, in dishwashers, where such detergents may be in use, this liquid is diluted in the rest of the washing liquid and causes the potential transfer to be even lower.
4. The most relevant step is drying: BPA is formed and transferred into the beverage when alkali aqueous solutions are “baked” onto the polycarbonate during the drying process, as it occurs when the washing liquid is poured out, but rinsing with water fails. However, the BPA still amounted to less than 10 µg/l when referred to a 100 ml filling (Table 8).
5. The scenario with the highest transfer of BPA into the beverage involves a slanted position of the bottle in the dishwasher, hindering the detergent solution to run off and rinsing before drying: upon evaporating around 10 ml alkali detergent solution onto the bottle wall, some 500 µg/l BPA was formed related to a 100 ml filling (Table 6). However, this scenario seems unlikely to frequently occur.

6. The finding by Brede et al. [1] that BPA release increases with aging of the bottle can be explained by the increased amount of liquid remaining on the bottle surface at the end of the washing process: enhanced wettability of a roughened surface results in more liquid evaporating from a larger part of the surface, which leaves more carbonates behind attacking the polycarbonate.

With this understanding of the mechanisms of BPA formation and transfer into beverages it seems possible to confirm that even under extreme conditions and scenarios the amount of BPA released from polycarbonate baby bottles is clearly below the TDI for babies. In particular it can be ruled out that the observed increase of BPA release with aging of the bottle may extend to levels which could be of health concern.

References

1. Brede C, Fjeldal P, Skjevrak I, Herikstad H (2003) Food Addit Contam 20:684-689
2. EFSA (2006). Opinion of the Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food on question number EFSA-Q-2005-100, adopted on 29 November 2006.
3 Krishnan AV, Stathis P, Permuth SF, Tokes L., Feldmann D (1993) Endocrinology 132:2279-2286
4 Mountfort KA, Kelly J, Jickells SM, Castle L (1997) Food Addit Contam 14:737-740
5 Kawamura Y, Koyama Y, Takeda Y, Yamada T (2000) J Food Hyg Soc Japan 99:206-212
6 Sun Y, Wada M, Al-Dirbashi O, Kuroda N, Nakazawa H, Nakashima K (2000) J Chromatogr B 749:49-56
7 Wong KO, Leo LW, Seah HL (2005) Food Addit Contam 22:280-288
8. Begley TH (1997) Food Addit Contam 14:545-553
9. Kroes R, Galli C, Munro I, Schilter B, Tran L-A, Walker R, Würtzen G (2000) Food Chem Tox 38:255-312