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Concentrations and Profiles of Bisphenol A and Other Bisphenol Analogues in Foodstuffs from the United States and Their Implications for Human Exposure

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Ⓢ *Supporting Information*

ABSTRACT: As the concern over the safety of bisphenol A (BPA) continues to grow, this compound is gradually being replaced, in industrial applications, with compounds such as bisphenol F (BPF) and bisphenol S (BPS). Occurrence of bisphenols, including BPA and BPS, has been reported in paper products and in environmental matrices. Information on the occurrence of bisphenols, other than BPA, in foodstuffs, however, is scarce. In this study, several bisphenol analogues, including BPA, BPF, and BPS, were analyzed in foodstuffs (N = 267) collected from Albany, NY, USA, using high-performance liquid chromatography−tandem mass spectrometry (HPLC-MS/MS). Foodstuffs were divided into nine categories of beverages, dairy products, fats and oils, fish and seafood, cereals, meat and meat products, fruits, vegetables, and "others". Bisphenols were found in the majority (75%) of the food samples, and the total concentrations of bisphenols (ΣBPs: sum of eight bisphenols) were in the range of below the limit of quantification (LOQ) to 1130 ng/g fresh weight, with an overall mean value of 4.38 ng/g. The highest overall mean concentration of ΣBPs was found in the "others" category, which included condiments (preserved, ready-to-serve foods). A sample of mustard (dressing) and ginger, placed in the category of vegetables, contained the highest concentrations of 1130 ng/g for bisphenol F (BPF) and 237 ng/g for bisphenol P (BPP). Concentrations of BPs in beverages (mean = 0.341 ng/g) and fruits (0.698 ng/g) were low. The predominant bisphenol analogues found in foodstuffs were BPA and BPF, which accounted for 42 and 17% of the total BP concentrations, respectively. Canned foods contained higher concentrations of individual and total bisphenols in comparison to foods sold in glass, paper, or plastic containers. On the basis of measured concentrations and daily ingestion rates of foods, the daily dietary intakes of bisphenols (calculated from the mean concentration) were estimated to be 243, 142, 117, 63.6, and 58.6 ng/kg body weight (bw)/day for toddlers, infants, children, teenagers, and adults, respectively.

KEYWORDS: *bisphenols, BPA, foodstuff, occurrence, dietary exposure assessment*

INTRODUCTION

Bisphenols are a class of chemicals with two hydroxyphenyl functionalities and include several analogues such as bisphenol A [BPA; 2,2-bis(4-hydroxyphenyl)propane], bisphenol S (BPS; 4,4′-sulfonyldiphenol), bisphenol F (BPF; 4,4′-dihydroxydiphenylmethane), bisphenol AF [BPAF; 4,4′-(hexafluoroisopropylidene)diphenol], and bisphenol B [BPB; 2,2-bis(4-hydroxyphenyl)butane]. Among several of the bisphenol analogues that are in commerce, BPA has been the most widely studied. BPA is a high production volume chemical and is widely used as the chemical building block in the manufacture of polycarbonate plastics, the epoxy resins used in food can linings, and dental fillings and sealants.[1−3] Due to its widespread human exposure and toxicity, BPA has drawn considerable attention by regulatory organizations and the general public in recent years.[1,3] Restrictions on the use of BPA in certain consumer products have been suggested.[4−6] For example, the U.S. Food and Drug Administration (FDA) banned the use of BPA in baby bottles and children's drinking cups in July 2012.[4] BPA also has been prohibited from manufacture, sale, or distribution in some consumer products, such as reusable food or beverage containers, infant formula containers, and thermal receipt paper, by several states in the United States since 2009.[5] The European Commission restricted the use of BPA in plastic infant feeding bottles in January 2011.[6] The bisphenol analogues, such as BPS, BPF, and BPB, were developed as alternatives to BPA and replaced BPA for use in epoxy resins, plastics, thermal papers, and food can linings.[7−10]

A few studies have reported the occurrence of BPA in foods.[11−13] BPA was detected in 63 of 105 (detection rate = 60%) fresh foods as well as canned and plastic container-wrapped foods from the United States at concentrations ranging from <0.20 (LOQ) to 65.0 ng/g wet weight (ww); BPA concentrations were not associated with the type of food or packaging material.[11] A Canadian total diet study reported that BPA was found in 36% of 154 composite food samples at concentrations ranging from <0.14 to 106 ng/g ww and that canned foods contained the highest concentrations.[12] A more recent U.S. study indicated that high concentrations of BPA were frequently found in canned foods (91%), and the

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concentrations were in the range of <2–730 ng/g ww.[13] Bisphenol analogues other than BPA were rarely reported in foodstuffs. BPB was reported to occur in 9 of 42 (21%) tomato samples packaged in cans from Italy at concentrations ranging from <2.3 to 85.7 ng/g ww.[14] BPB also was detected in 15 of 30 canned beverages from Portugal at concentrations ranging from <7.0 to 170 ng/L.[15] BPS was found in canned foods from Spain on the order of a few tens to hundreds of nanograms per gram concentrations.[16]

Human exposure to BPA that leaches from packaging or storage containers into foods and beverages is a great public health concern, due to the endocrine-disrupting potentials of this compound. Migration of BPA from polycarbonate drinking and baby bottles into water and foods has been well documented.[17−20] Migration of BPA from metallic can epoxy coatings into various food items also has been reported.[21−24] The European Commission has established a migration limit of 600 μg/kg for BPA in food or food simulators from plastic materials and articles intended to come in contact with foodstuffs.[25] Given the similarity in the structure of various bisphenol analogues, migration of BPB, BPF, and BPS from polycarbonate bottles and metallic can coatings into foods is expected.[14,16]

To date, little information is available on the exposure of humans to bisphenols other than BPA through dietary sources in the United States. Thus, the objectives of this study were (1) to determine concentrations of BPA and several bisphenol analogues, including BPF and BPS, in a wide range of food items collected from Albany, NY; (2) to compare composition profiles of bisphenol analogues in different categories of food; and (3) to assess human dietary exposure to bisphenols on the basis of measured concentrations and daily ingestion rates of various food items.

■ MATERIALS AND METHODS

Sample Collection. A total of 267 food samples were randomly collected from several retail grocery stores in Albany, NY, USA, in 2008, 2011, and 2012. Most of the food samples were of U.S. origin. Food samples were divided into nine categories: (1) beverages (bottled water/soft drinks/fruit juice/beer/wine); (2) dairy products (milk/infant formula/cheese/yogurt/ice cream); (3) fats and oils (cooking oil/salad oil); (4) fish and seafood (freshwater and marine fish/shrimp/crab/clam); (5) cereals and cereal products (bread/rice/noodle/wheat flour/pasta/pie/pizza/cookie/cake/corn products); (6) meat and meat products (chicken/turkey/beef/pork/lamb/ham/sausage); (7) fruits (apple/pear/pineapple/peach/grape/banana/raisin); (8) vegetables (potato/tomato/carrot/mushroom/soybean/onion/broccoli/cabbage/celery/cucumber); and (9) others (soup/egg/barbecue sauce/tomato paste/pancake syrup). The categories of fruits and vegetables include both fresh and canned products. Further details of the food items analyzed are presented in Table S1 (Supporting Information). All samples were stored frozen (−20 °C) until analysis.

Standards, Reagents, and Materials. All chemicals used in this study were of analytical grade. The standards of bisphenol analogues, including BPA (97%), BPAF (97%), bisphenol AP [BPAP; 4,4′-(1-phenylethylidene)bisphenol; 99%], BPF (98%), bisphenol P [BPP; 4,4′-(1,4-phenylenediisopropylidene)bisphenol; 99%], BPS (98%), and bisphenol Z [BPZ; 4,4′-cyclohexylidenebisphenol; 98%] were purchased from Sigma-Aldrich (St. Louis, MO, USA). BPB (98%) was purchased from TCI America (Portland, OR, USA). $^{13}C_{12}$-Labeled BPA (99%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Formic acid (98.2%) was purchased from Sigma-Aldrich. All organic solvents (HPLC grade) were purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Solid phase extraction (SPE) cartridges, including Strata NH_2 cartridges (200 mg/3 cm^3) and Oasis MCX cartridges (60 mg/3 cm^3), were purchased from Phenomenex (Torrance, CA, USA) and Waters (Milford, MA, USA), respectively. Milli-Q water was provided through an ultrapure water system (Barnstead International, Dubuque, IA, USA). The standard stock solutions (1 mg/mL) of all target analytes and internal standard ($^{13}C_{12}$-BPA) were prepared in methanol. All stock solutions were stored at −20 °C. The working solutions were prepared by serially diluting the stock solutions with methanol before use.

Sample Preparation. For the purpose of extraction, food samples were divided into four broad categories: solid foods, oils, beverages, and dairy products. Extraction of four categories of foods is described below.

Solid Foods. Solid food samples were homogenized in a stainless steel Sorvall Omni-Mixer (Dupont, Newtown, CT, USA) and freeze-dried in a FreeZone 6 Freeze-Dry System (LABCONCO Corp., Kansas City, MO, USA). The stainless steel mixer was thoroughly cleaned (using detergents and solvents) after homogenization of each food sample to avoid cross-contamination between samples. Approximately 1.0−3.0 g of the solid food samples were weighed into a 15 mL polypropylene conical tube (PP tube) and spiked with 20 ng of the internal standard ($^{13}C_{12}$-BPA). Extraction was performed twice with acetonitrile (6 mL each) by shaking in an orbital shaker (Eberbach, Ann Arbor, MI, USA) at 250 oscillations/min for 60 min.[13,26] The sample mixture was centrifuged at 4500*g* for 5 min (Eppendorf 5804, Hamburg, Germany), and the extract was combined. The combined extract was evaporated to near dryness under a nitrogen stream and redissolved in 2 mL of 10% dichloromethane/hexane (v/v). The purification of the extract was accomplished by use of a RapidTrace SPE workstation (Caliper Life Sciences, Inc., Hopkinton, MA, USA). The extract was transferred to a Strata NH_2 cartridge, which was previously conditioned with 5 mL of 80% methanol/acetone (v/v) and 5 mL of hexane. The cartridge was washed with 5 mL of hexane, and the target analytes were eluted with 5 mL of 80% methanol/acetone (v/v). The eluate was evaporated, and the final volume was adjusted to 0.5 mL with methanol. The oil samples were extracted similarly to the method described for the solid food samples, except that the oil samples were not freeze-dried.

Beverages. Approximately 5 g of the beverage samples were weighed, spiked with $^{13}C_{12}$-BPA, and extracted twice with ethyl acetate (6 mL each) by shaking for 60 min. The extract was combined, evaporated to near dryness, and redissolved in 2 mL of 10% dichloromethane/hexane (v/v). The extract was purified by passage through a Strata NH_2 cartridge, as described above.

Dairy Products. Dairy products were extracted by following a method described previously, with some modifications.[27] Approximately 3 g of the samples were spiked with $^{13}C_{12}$-BPA and extracted with ∼6 mL of acetonitrile (sample/acetonitrile = 1:2, v/v) by shaking for 60 min. The mixture was centrifuged at 4500*g* for 15 min, and the supernatant was collected and evaporated to ∼4 mL. The extract was diluted to 10 mL with 0.2% formic acid (pH 2.5) and transferred to an Oasis MCX cartridge, which was previously preconditioned with 5 mL of methanol and 5 mL of water. Fifteen milliliters of 25% methanol/water (v/v) and 5 mL of water were used to wash the cartridge. Target analytes were eluted with 5 mL of methanol, which was evaporated to 0.5 mL.[28]

Chemical Analysis. A Shimadzu Prominence series LC-20AD system (Shimadzu USA, Canby, OR, USA), coupled with an Applied Biosystems API 3200 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS; Applied Biosystems, Foster City, CA, USA), was used for analysis. Chromatographic separation was achieved by use of a Betasil C18 column (2.1 × 100 mm, 5 μm; Thermo Electron Corp., Waltham, MA, USA), which was connected to a Javelin guard column (Betasil C18, 2.1 × 20 mm, 5 μm; Thermo Electron Corp.). The injection volume was 10 μL, and the mobile phase flow rate was 300 μL/min. The mobile phase comprises methanol and water. The proportion of methanol was linearly increased from 15 to 50% within 3 min, held for 2 min, increased to 90% within 5 min, held for 2 min, then increased to 99% within 1 min, held for 2 min, reverted to 15%, and held for 5 min (Table S2 in the Supporting Information). The MS/MS was operated in electrospray negative ionization multiple-

Table 1. Concentrations (ng/g Fresh Weight) of Bisphenol Analogues in Different Categories of Food Items Collected from Albany, NY

	BPA	BPAF	BPAP	BPB	BPF	BPP	BPS	BPZ	ΣBPs
Beverages (n = 31)									
mean	0.235	0.006	0.005	0.013	0.025	0.025	0.007	0.025	0.341
95th percentile	1.84	0.009	0.005	0.013	0.025	0.013	0.005	0.025	1.93
frequency (%)	12.9	6.45	0	0	0	3.23	3.23	0	25.8
Dairy Products (n = 29)									
mean	2.55	0.028	0.185	0.014	0.134	0.013	0.040	0.025	2.99
95th percentile	16.3	0.073	1.01	0.013	0.791	0.013	0.020	0.025	16.8
frequency (%)	48.28	10.3	31.0	3.45	17.2	0	13.8	0	75.9
Fats and Oils (n = 5)									
mean	1.90	0.006	0.005	0.013	0.255	0.013	0.005	0.025	2.23
95th percentile	6.27	0.010	0.005	0.013	0.606	0.013	0.005	0.025	6.94
frequency (%)	80.0	20.0	0	0	60.0	0	0	0	100
Fish and Seafood (n = 23)									
mean	3.23	0.010	0.007	0.013	4.63	0.013	0.021	0.025	7.95
95th percentile	9.55	0.005	0.015	0.013	23.0	0.013	0.081	0.025	45.4
frequency (%)	73.9	4.35	21.7	0	17.4	0	26.1	0	91.3
Cereals and Cereal Products (n = 48)									
mean	0.605	0.005	0.013	0.017	0.079	0.130	0.013	0.025	0.887
95th percentile	2.32	0.005	0.015	0.049	0.025	0.013	0.036	0.025	2.57
frequency (%)	56.3	2.08	8.33	12.5	2.08	4.17	14.6	0	70.8
Meat and Meat Products (n = 51)									
mean	0.852	0.014	0.049	0.013	1.34	0.353	0.609	0.026	3.25
95th percentile	3.29	0.017	0.021	0.013	3.30	0.013	0.780	0.025	21.0
frequency (%)	76.5	7.84	11.8	0	7.84	3.92	43.1	1.96	88.2
Fruits Including Canned Fruits (n = 20)									
mean	0.532	0.021	0.061	0.013	0.025	0.013	0.009	0.025	0.698
95th percentile	2.06	0.074	0.069	0.013	0.025	0.013	0.023	0.025	2.17
frequency (%)	45.0	30.0	10.0	0	0	0	25.0	0	75.0
Vegetables Including Canned Vegetables (n = 45)									
mean	8.99	0.009	0.124	0.013	1.00	0.473	0.018	0.076	10.7
95th percentile	47.9	0.042	0.028	0.013	1.19	0.013	0.057	0.273	48.9
frequency (%)	66.7	15.6	6.67	0	17.8	4.44	22.2	11.1	80.0
Others (n = 15)									
mean	9.97	0.012	0.013	0.013	1.21	0.562	0.005	0.025	11.8
95th percentile	48.0	0.043	0.041	0.013	5.52	3.67	0.007	0.025	53.3
frequency (%)	53.3	20.0	6.67	0	13.3	13.3	6.67	0	86.7
All (n = 267)									
mean	3.00	0.012	0.059	0.013	0.929	0.207	0.130	0.034	4.38
95th percentile	9.17	0.024	0.072	0.013	0.735	0.013	0.076	0.025	21.0
frequency (%)	56.9	10.5	11.2	2.62	10.1	3.37	20.9	2.25	74.5

reaction monitoring (MRM) mode, and the MRM transitions are shown in Table S3 (Supporting Information). The MS/MS parameters were optimized by infusion of individual analytes into the mass spectrometer through a flow injection system and are summarized in Table S4 (Supporting Information). Nitrogen was used as both a curtain and a collision gas. Representative total ion chromatograms of a standard mixture and a matrix-spiked sample, showing chromatographic resolution of the target compounds analyzed by HPLC-MS/MS, are shown in Figure S1 (Supporting Information).

Quality Assurance and Quality Control (QA/QC). With every batch of 60 samples analyzed, procedural blanks (n = 3), spiked blanks (n = 3), and matrix spikes (n = 4) were analyzed. Trace levels of BPA (~0.06 ng/g), BPF (~0.05 ng/g), and BPS (~0.02 ng/g) were found in procedural blanks. The concentrations measured in food samples were subtracted from mean values found in procedural blanks for each batch of analysis. The average recoveries of bisphenols (20 ng each) spiked into procedural blanks were in the range of 61–109%, and those (20 ng each) spiked into four broad categories of foods were in the range of 73–106% for solid foods, 78–122% for beverages, 62–120% for oils, and 66–126% for dairy products (Table S5 in the Supporting Information). Several randomly selected samples (n = 4 for each batch) were analyzed in duplicate, and the coefficient variation between the concentrations was <15% for all target compounds. The limits of quantitation (LOQs) were 0.01 ng/g for BPA, BPAF, BPAP, and BPS, 0.025 ng/g for BPB and BPP, and 0.05 ng/g for BPF and BPZ. The LOQs were calculated from the value of the lowest acceptable calibration standard and a nominal sample weight of 1.0 g. Quantification of analytes was performed using regression equations (regression coefficient, r > 0.99) generated from a 10-point calibration standard at concentrations ranging from 0.01 to 100 ng/mL, and the concentrations determined in samples were corrected for the recoveries of the internal standard ($^{13}C_{12}$-BPA). A midpoint calibration standard and a pure solvent (methanol) were injected after every 10 sample injections to monitor for the drift in instrumental response and carry-over of analytes between samples.

Data Analysis. Correlations between bisphenol analogues were tested with Pearson correlation analysis. Concentration differences between food groups were tested with one-way ANOVA. Statistical analysis was performed with SPSS 17.0 and Origin 7.5. Prior to extraction, liquid samples were weighed. Moisture contents of solid food samples were determined for the conversion of data from a dry weight to a wet weight basis. All data are presented on a wet weight (or fresh weight) basis. For data analysis, concentrations below the LOQ were assigned a value equal to the LOQ divided by 2 (LOQ/2).

■ RESULTS AND DISCUSSION

Concentrations. Concentrations of eight bisphenol analogues and the sum of their concentrations (ΣBPs) in nine food categories are shown in Table 1. The majority (199 of 267) of the food samples analyzed in this study contained detectable concentrations of bisphenols. ΣBP concentrations in foodstuffs ranged from below the limit of quantitation (<LOQ) to 1130 ng/g fresh weight, with an overall mean value of 4.38 ng/g (Table S6 in the Supporting Information). The highest ΣBP concentrations (mean = 11.8 ng/g; 95th percentile, 53.3 ng/g) were found in foods from the "others" category, which included condiments (ready-to-serve foods); this was followed, in decreasing order, by vegetables (10.7, 48.9 ng/g; with the exclusion of a processed mustard sample and ginger sample), fish and seafood (7.95, 45.4 ng/g), meat and meat products (3.25, 21.0 ng/g), and dairy products (2.99, 16.8 ng/g). The lowest ΣBP concentrations were found in beverages (mean = 0.341 ng/g; 95th percentile, 1.93 ng/g) and fruits (0.698, 2.17 ng/g) (Table 1; Table S6 in the Supporting Information). The concentrations varied widely not only among the nine food categories but also within the categories (Figure S2 in the Supporting Information). The ΣBP concentrations of bisphenols were compared among the food samples collected during the three years (2008, 2011, and 2012) (Table S7 in the Supporting Information), and no statistically significant difference was found ($p > 0.05$, one-way ANOVA).

BPA was frequently found in fats and oils (detection frequency = 80%), fish and seafood (74%), meat and meat products (76%), and vegetables (67%). The foods in the "others" category contained the highest overall mean concentration of BPA (mean = 9.97 ng/g; range, <0.01−133 ng/g), which was comparable to the concentrations found for vegetables (including canned) (8.99, <0.01−146 ng/g), fish and seafood (3.23, <0.01−47.4 ng/g), and dairy products (2.55, <0.01−20.8) but 1 order of magnitude higher than the concentrations found for beverages (0.235, <0.01−3.41) and fruits (0.532, <0.01−6.52) (Table 1; Table S6 in the Supporting Information; $p < 0.05$). The highest concentration of BPA (146 ng/g) was found in a canned green bean sample (processed sample) in the vegetables category. Notable concentrations of BPA also were found in samples of egg (133 ng/g) in the "others" category, a canned clam (47.4 ng/g) in the fish and seafood category, and soy based infant formula (20.8 ng/g) in the dairy products category.

BPF was detected in various food items (10% detection rate). The category of vegetables (including canned) contained the highest overall mean concentration of BPF (mean = 26.0 ng/g), followed by fish and seafood (4.63 ng/g) and meat and meat products (1.34 ng/g). The highest concentration of 1130 ng/g of BPF was found in a mustard dressing, which was placed in the vegetables category. This product was packaged in a polycarbonate plastic container. The elevated concentration of BPF found in this sample increased the overall mean value for the vegetables category. With the exclusion of this sample, the mean concentration of BPF in vegetables was 1.00 ng/g, which was lower than the concentrations found for fish and seafood or meat and meat products (Table 1; Table S6 in the Supporting Information). The mustard dressing sample also contributed to a relatively high mean concentration of BPF for the entire sample set (5.15 versus 0.929 ng/g after the exclusion of this sample). BPS was more frequently detected in food samples than was BPF (21 versus 10% for the entire sample set). However, the concentrations of BPS were, in general, 1−2 orders of magnitude lower than the concentrations of BPA and BPF (Table 1; Table S6 in the Supporting Information; $p < 0.01$).

The percentage composition of individual bisphenols to ΣBP concentrations is shown in Figure 1. In general, BPA was the predominant analogue, representing, on average, from 31 ± 37% (mean ± SD; for fruits) to 63 ± 34% (for fats and oils) of ΣBP concentrations in foods, with the exception of beverages, for which the percentage of BPF (22 ± 8%) was higher than that of BPA (15 ± 28%). BPF was the second major bisphenol analogue overall and accounted for 17 ± 21% of ΣBP concentrations. The contributions of BPS, BPAF, and BPAP to ΣBP concentrations were <10% each (Figure 1). It should be noted that the predominance of censored data (concentration below the LOQ was substituted with a value of LOQ/2) skewed the percentage distributions of BPB, BPP, BPZ, BPS, BPAF, and BPAP in ΣBP concentrations (Figure 1). The detection frequencies of BPB, BPP, and BPZ (all <5%) in foods were much lower than those for other bisphenol analogues (Table 1). Relationships among the concentrations of several bisphenol analogues in food samples were tested with Pearson correlation analysis (Table 2). The outlier values were excluded from this analysis. Due to the low detection frequency (all <5%; Table 1), the 0−95th percentile values for concentrations of BPB, BPP, and BPZ were similar and, therefore, these three bisphenols were excluded from the data set. Significant positive correlations existed among the concentrations of BPA, BPAF, BPAP, BPF, and BPS in foods [Pearson correlation coefficient (r) = 0.815−0.984, $p < 0.01$; Table 2].

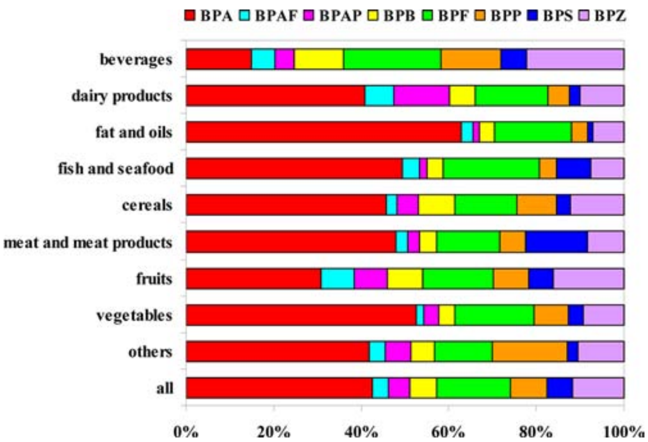

Figure 1. Composition profiles of bisphenol analogues in foodstuffs collected from Albany, NY. Cereals include cereals and cereal products; vegetables and fruits include canned products.

Comparisons of Bisphenol Analogues among Foodstuffs Sold in Different Types of Packaging Materials. BPA can be leached from packaging materials, including metallic cans and plastics, into food.[17−24] The food samples analyzed in this study were grouped into four types on the basis of packaging materials, namely, cans, glass, paper, and plastic, and the concentrations of bisphenols among the four categories were compared. The mean concentrations of BPA (mean =

Table 2. Pearson Correlations among Concentrations of Bisphenol Analogues Measured in Foodstuffs from the United States[a]

	BPA	BPAF	BPAP	BPF	BPS	ΣBPs
BPA	1					
BPAF	0.888**	1				
BPAP	0.847**	0.936**	1			
BPF	0.877**	0.984**	0.921**	1		
BPS	0.954**	0.875**	0.815**	0.876**	1	
ΣBPs	0.987**	0.938**	0.893**	0.922**	0.964**	1

[a]** indicates the correlation is significant at the 0.01 level (two-tailed).

15.1; range, <0.01−146 ng/g) in canned foods were significantly higher than the concentrations in food samples sold in glass (0.641, <0.01−4.16 ng/g), paper (0.838, <0.01−2.37 ng/g), or plastic (0.950, <0.01−20.8 ng/g) containers (Figure 2; $p < 0.05$). No significant differences were found among the four groups for concentrations of bisphenols other than BPA ($p > 0.05$). The canned foods contained higher concentrations of ΣBPs (mean ± SD = 20.8 ± 33.0 ng/g) than did food samples sold in glass (0.765 ± 1.12 ng/g), paper (1.03 ± 0.851 ng/g), or plastic containers (1.38 ± 3.33 ng/g, excluding an outlier value of 1130 ng/g) (Figure 2; $p < 0.05$).

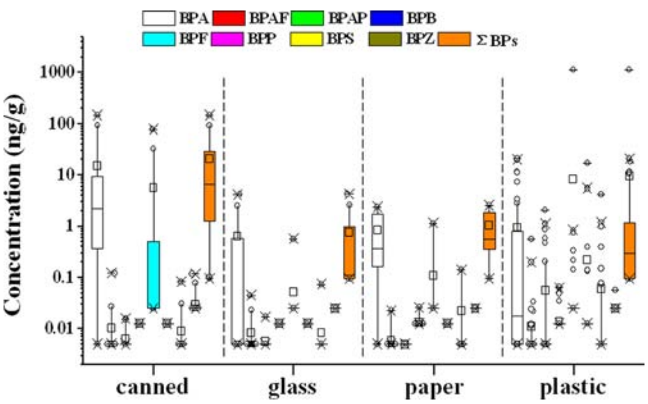

Figure 2. Individual and total concentrations of bisphenols in food samples sold in different packaging materials. The box plot shows 5th (lower whisker), 25th (bottom edge of the box), 75th (top edge of the box), and 95th (upper whisker) percentiles. The low and upper stars represent 1st and 99th percentiles, respectively. The arithmetic mean and median concentrations are given as the open square and the line within the box, respectively. The dots are outliers.

Large variations in BPA concentrations were found in canned foods analyzed in this study, similar to those reported in earlier studies (Table 3).[11,13,14,26,29−37] BPA concentrations (range, <0.01−146 ng/g) determined in canned foods in our study were higher than those reported for canned food samples from Ottawa, Canada (2.27−10.2 ng/g),[29] and Murcia, Spain (<0.008−0.014 ng/g),[36] but similar to those reported for food samples from Dallas, TX, USA (<0.2−65 ng/g dry weight),[11] Naples, Italy (<3.7−115.3 ng/g),[14] Suwon, Korea (<3−136 ng/g),[33] and Oporto, Portugal (<0.2−99.9 ng/g).[34] BPA concentrations found in canned foods in our study were lower than those reported for samples from Washington, DC, and Maryland, USA (<2−730 ng/g),[13] Ottawa, Canada (<0.6−534 ng/g),[26] Miyazaki (11−206 ng/g)[31] and Chiba (<0.3−235.4 ng/g),[32] Japan and Leatherhead, UK (<2−380 ng/g).[37] Such variation in BPA concentrations in canned foods is probably due to the differences in the composition of epoxy can coatings and in the leaching rates of BPA into food products (depending on, e.g., pH, temperature, and duration of storage).[13]

Human Dietary Exposure. Dietary intakes of bisphenols were calculated for different age groups of the general population by multiplying the measured concentrations of bisphenols by the average daily ingestion rates of the corresponding food item by each age group. The total intakes of bisphenols were calculated by summing the intakes from all food categories, as shown in eq 1

$$EDI = \Sigma C_i \times FIR_i \quad (1)$$

Table 3. Concentrations of BPA (ng/g Wet Weight) in Canned Foods Collected from the United States in Comparison with Those Reported for Other Countries

location	n[a]	sampling year	LOQ[b]	mean	range	detection frequency (%)	ref
Dallas, TX, USA	93	2010	0.2	–[c]	<0.2−65[d]	63	11
Washington, DC, and Maryland, USA	78	2011	2	–	<2−730	91	13
Albany, NY, USA	31	2008, 2011, 2012	0.01	15.1	<0.01−146	87	this study
Ottawa, ON, Canada	21	2007	0.5	5.12	2.27−10.2	100	29
Ottawa, ON, Canada	72	2007	0.045	0.57	0.032−4.5[e]	96	30
Ottawa, ON, Canada	78	2009	0.6	72	<0.6−534	99	26
Naples, Italy	42	2008	3.7	38.7	<3.7−115	52	14
Miyazaki, Japan	26	2002	3	42	11−206	100	31
Chiba, Japan	38	2007	0.3	–	<0.3−235	87	32
Suwon, Korea	61	2009	3	–	<3−136	64	33
Oporto metropolitan area, Portugal	47	2012	0.2	19.1	<0.2−99.9	83	34
Barcelona, Spain	11	2009	0.05	–	<0.05−0.607[e]	64	35
Murcia, Spain	20	2012	0.008	–	<0.008−0.014	80	36
Leatherhead, UK	62	2000	2	–	<2−380	61	37

[a]n = number of samples. [b]LOQ = limit of quantification. [c]Not available. [d]ng/g dry weight. [e]Canned beverages (ng/mL).

Table 4. Estimated Daily Dietary Intakes (EDI, ng/kg bw/day) of Bisphenol Analogues for Various Age Groups in the United States

	BPA	BPAF	BPAP	BPB	BPF	BPP	BPS	BPZ	ΣBPs
Mean									
infants (<1 year)	114	0.847	3.27	1.07	12.9	5.61	1.72	2.34	142
toddlers (1−<6 years)	195	1.52	8.43	1.19	22.3	7.47	4.34	2.55	243
children (6−<11 years)	91.2	0.629	3.28	0.596	12.7	4.41	2.49	1.31	117
teenagers (11−<21 years)	48.6	0.312	1.55	0.332	7.68	2.70	1.60	0.748	63.6
adults (≥21 years)	44.6	0.275	1.20	0.346	7.46	2.65	1.31	0.799	58.6
95th Percentile									
infants (<1 year)	630	2.04	11.2	1.16	32.1	7.11	1.97	3.32	682
toddlers (1−<6 years)	1110	3.89	38.3	1.35	70.2	8.84	4.74	3.78	1230
children (6−<11 years)	504	1.55	13.6	0.723	36.1	4.11	2.98	2.04	582
teenagers (11−<21 years)	266	0.740	5.84	0.403	20.5	2.07	1.98	1.20	316
adults (≥21 years)	243	0.639	3.75	0.406	19.7	1.74	1.66	1.30	289

where EDI (ng/kg bw/day) is the estimated daily intake, C (ng/g) is the bisphenol concentration in food samples (mean and 95th percentile values were used to represent average and high exposure scenarios, respectively), and FIR (g/kg bw/day) is the daily food ingestion rate, which was obtained from the U.S. Environmental Protection Agency's (EPA) *Exposure Factors Handbook* and the U.S. Census Bureau.[38,39] For the estimation of EDIs, we stratified the population into five age groups as infants (<1 year), toddlers (1−<6 years), children (6−<11 years), teenagers (11−<21 years), and adults (≥21 years), according to the EPA's *Exposure Factors Handbook*.[38] The details of parameters used in the EDI calculation are summarized in Table S8 (Supporting Information).

Daily dietary intakes of individual and total bisphenols for various age groups are shown in Table 4. An outlier value (1130 ng/g) for BPF and an outlier value (237 ng/g) for BPP, in the vegetable category, were excluded in the calculation of EDIs (Supporting Information, Table S6). The highest mean values for daily intakes of ΣBPs were found for toddlers (243 ng/kg bw/day). This was followed, in decreasing order, by infants (142 ng/kg bw/day), children (117 ng/kg bw/day), teenagers (63.6 ng/kg bw/day), and adults (58.6 ng/kg bw/day) (Table 4).

Among bisphenol analogues, BPA accounted for the majority (∼80%) of the total exposures for each age group, followed by BPF (∼10%). The contributions of other bisphenols to total BP exposures were minor (∼10%). The EDI values of BPA determined in this study (Table 4) were comparable to or somewhat lower than those reported earlier.[40−43] At a joint meeting of the 2010 Food and Agriculture Organization (FAO) and World Health Organization (WHO), experts estimated dietary intake values of BPA at 10−2400, 200−700, and 400−1400 ng/kg bw/day for infants, children, and adults, respectively.[40] The Scientific Committee of European Commission estimated dietary intake values of BPA at 800−1600, 1200, and 110−370 ng/kg bw/day for infants, children, and adults, respectively.[41] It should be noted that the daily dietary intakes estimated in our study can be an underestimate of actual exposures because several food items were not included in the analysis (e.g., fast food, candies, breast milk). Infants can be exposed to such additional sources including breast milk.[44] The dietary exposure to BPA estimated in our study was 2−4 orders of magnitude lower than the current oral reference dose of 50 μg/kg bw/day recommended by the EPA and the European Food Safety Authority.[44,45]

In summary, the concentrations and profiles of several bisphenol analogues, including BPA, BPF, and BPF, were determined in foodstuffs collected from Albany, NY, USA. The majority (75%) of the food samples contained detectable concentrations of bisphenols, and the total concentrations ranged from 0.10 to 1130 ng/g fresh weight, with an overall mean value of 4.38 ng/g. Canned vegetables, fish and seafood, meat and meat products, and dairy products contained notable concentrations of ΣBPs. BPA and BPF were the predominant analogues, accounting for, on average, 42 and 17%, respectively, of the total bisphenol concentrations. Canned foods contained relatively higher concentrations of individual and total bisphenols in comparison with foods sold in glass, paper, and plastic containers. The mean daily dietary intakes of bisphenols (calculated from the mean concentration) were estimated at 117 ng/kg bw/day for children and 58.6 ng/kg bw/day for adults in the United States.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text (eight tables and two figures). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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