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Widespread Occurrence of Bisphenol A in Daily Clothes and Its High Exposure Risk in Humans

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Supporting Information

ABSTRACT: Bisphenol A (BPA) is an important endocrine disrupting chemical. Although high levels of BPA in some new clothes have been reported, the occurrence of bisphenol chemicals including BPA in daily clothes is still unknown, and the human exposure to BPA in clothes has not been well assessed. In this study, used/washed clothes were collected from residents' wardrobes and the concentrations of BPA and its analogues were detected. BPA was present in all the used clothes at concentrations ranging from <3.30 to 471 ng/g (median: 34.2 ng/g; mean ± SD: 57.5 ± 93.6 ng/g), while bisphenol S was also detected in 29% of the samples. Although higher average concentration (88.4 ± 289 ng/g) and maximum concentration (1823 ng/g) of BPA were found in the new clothes, the median concentration of BPA in the used clothes (34.2 ng/g) was even higher than that in the new clothes (17.7 ng/g). Cross contamination of BPA during laundering was identified by a simulated laundry experiment, which explained the homogenizing tendency of bisphenol contaminants in the used clothes. An estimated dermal exposure dose of 52.1 ng/kg BW/d was obtained for BPA exposure in children from the highly polluted sweaty clothes (with BPA concentration of 199 ng/g). This indicates a relatively high exposure risk in humans. Compared to other exposure routes, the contribution of dermal exposure dose of BPA from the daily clothes should not be neglected.

1. INTRODUCTION

Bisphenol A (BPA) [4,4′-(propane-2,2-diyl)diphenol, CAS 80−05−7] is a chemical that is produced in large quantities for use primarily in the manufacturing of polycarbonate plastics and epoxy resins. Due to its widespread usage, BPA is present in various environmental media, including surface water,[1,2] soil,[1,2] air,[1,2] and dust.[3,4] The estrogenic activity of BPA has been reported since 1938.[5] After that, it has also been pointed out that low dose BPA exposure can cause a wide range of adverse effects on animals during their development and adulthood.[6] Furthermore, the potential association of BPA exposure with alterations in hormone levels, impairments of ovary and uterine functions, and reductions in sperm quality has been reported in some epidemiological studies.[7,8] In addition to BPA, bisphenol analogues (e.g., bisphenol F (BPF) and bisphenol S (BPS)) also display estrogenic properties and other adverse effects.[9,10]

Dietary intake has been commonly considered as the most important pathway for human exposure to BPA.[11,12] However, the contamination of BPA in foodstuff and beverages is mainly due to the release from polycarbonate bottles and food cans coated with epoxy resins,[11,13] which indicates a doubtful exposure route to the general population, especially for those who rarely consume canned food. In addition, BPA in food packaging accounts for merely 5% of the total BPA consumption.[16] Therefore, other important exposure routes, e.g., dermal exposure,[14,15] need to be investigated.

The occurrence of bisphenol chemicals, including BPA and BPS, has been reported in clothes bought from stores in the U.S.A. and indicated that some new clothing with relatively high concentrations might result in high dermal exposure risk to BPA.[14] Compared with new clothes, humans have more frequent contact with used/washed clothes in daily life. However, the occurrence of BPA in daily clothes and the potential migration and redistribution of BPA during laundering are still unknown. To address these questions, used and freshly laundered clothes were collected from the wardrobes of several Chinese families, and the concentrations of BPA, BPS, BPF, bisphenol AF (BPAF), bisphenol AP (BPAP), bisphenol Z (BPZ), and 4,4′-thiodiphenol (TDP) were measured and compared with those in new clothes. In addition, simulated laundering experiments and a sweat leaching experiment were conducted, and the dermal exposure to BPA via clothing was estimated.

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2. MATERIALS AND METHODS

2.1. Chemicals and Reagents. Analytical standards of BPA (97%), 4,4′-sulfonyldiphenol (bisphenol S, BPS, 98%), 2,2-bis(4-hydroxyphenyl) hexafluoropropane (bisphenol AF, BPAF, 97%), 4,4′-(1-phenylethylidene)bisphenol (bisphenol AP, BPAP, 99%), 4,4′-dihydroxydiphenylmethane (bisphenol F, BPF, 98%), 1,1-bis(4-hydroxyphenyl)cyclohexane (bisphenol Z, BPZ, 98%), and 4,4′-thiodiphenol (TDP, 97%) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). Stable isotope-labeled standard, $^{13}C_{12}$-BPA (≥99%) was purchased from Cambridge Isotope Laboratories (MA, U.S.A.). Chromatographic grade methanol, ethyl acetate was purchased from ANPEL Laboratory Technologies Inc. (Shanghai, China). L-Histidine monohydrochloride monohydrate ($C_6H_9O_2N_3{\cdot}HCl{\cdot}H_2O$, ≥ 98%) was purchased from TCI (Shanghai, China).

2.2. Sample Collection. In total, 93 garments, including 49 pieces of used clothing and 44 pieces of new clothes were collected. The used clothes were randomly obtained from 38 families' wardrobes in 3 different cities of China, while the new ones were purchased from online retailers and local stores in Tianjin, China. According to the material, the clothes ($n = 93$) were divided into three categories: cotton and cotton blended ($n = 42$), synthetic/artificial fiber ($n = 29$), and unknown material (referring to those whose tags were blurred or missing, $n = 22$). The details of the textiles are shown in Table S1 in the Supporting Information (SI).

2.3. Sample Pretreatment. Square pieces of cloth (10 × 10 cm^2) were randomly cut from the collected textile samples by avoiding printing and laces, and then weighed accurately to calculate the area density (mg/cm^2). After that, approximately 1.0 g portions of textiles were weighed, placed in 50 mL conical glass flasks and then spiked with 50 ng of $^{13}C_{12}$-BPA. Subsequently, 20 mL of ethyl acetate was added, and the flasks were sealed with aluminum foil. After 30 min of ultrasonic extraction at room temperature (25 ± 2 °C), 10 mL of mixed solution were transferred to a 15 mL polypropylene (PP) tube and then centrifuged at 1700*g* for 5 min. The supernatant was evaporated to near dryness under a gentle stream of nitrogen and reconstituted with 2 mL methanol, and then subjected to vortex mixture and filtered with a 0.22-μm nylon filter prior to the analysis of high-performance liquid chromatograph coupled with triple quadrupole mass spectrometer (HPLC-MS/MS).

The concentrations of bisphenols in the laundry wastewater obtained in the laundering experiment were determined by liquid−liquid extraction. More details were shown in Text S1 in the SI.

2.4. Simulated Laundry Experiments. To evaluate the cross contamination of BPA during the laundry process, different simulated laundry experiments were designed. On the basis of the detected BPA concentrations, two garments with high BPA concentrations were selected as "source clothes", while eight garments with low BPA concentrations were selected as "receptor clothes" (see details in Table S1 in the SI). In the simulated laundry experiment without detergent, five pieces of cloth (approximately 15 × 15 cm^2 for each, including one "source" and four "receptors") cut from the selected clothes were put in a glass beaker, and then 1200 mL of water was added. The beaker was shaken at 180 r/min in an orbital shaker for 1 h, and then dewatered by extrusion and eventually drip-dried at room temperature in a desiccator. Similarly, the laundry experiment with detergent was conducted. One "source" and four "receptors" were laundered together in 1200 mL of solution containing 1.0 g/L of laundry detergent, referring to the situation in real life. Concentrations of bisphenols in cloth after laundering and in the laundry wastewater were determined. On the basis of the detected concentrations in the "sources", "receptors", and laundry wastewater, a mass balance of >93% was obtained for the systems (Table S2).

To further investigate the continuous release of BPA and assess the efficiency of cross contamination among the clothes during washing, a multiple-round laundering experiment was conducted by using cloth from one "source clothes" (i.e., source M1) and 4 "receptor clothes" which contain different proportions of cotton (i.e., receptor M1, M2, M3, and M4 as shown in Table S1). After the first round of laundering, approximately 1.0 g of cloth was cut off from each dried cloth sample; then five pieces of cloth (i.e., source M1 and receptor M1, M2, M3, and M4) were immersed in another 3 L of water, and then shaken for one more hour and dried before next round of laundering. This laundering procedure was repeated five times. After the last laundering round, the concentrations of the target analytes in cloth were analyzed.

2.5. Simulated Sweat Leaching Experiment. A simulated sweat leaching experiment was performed to evaluate the dermal exposure to BPA from sweaty clothes. The artificial sweat was prepared according to the International Standard Organization (ISO105-E04−2008E), with the detailed formula shown in Table S3. Solid phase extraction (SPE) cartridges, Oasis HLB cartridges (500 mg/6 cc; Waters, Milford, MA) were used as the receiving phase for the compounds leached from cloth. A detailed flow diagram of the leaching experiment is presented in Figure S1. In a sweating scenario, assuming that (i) perspiration lasts for 2 h everyday[17,18] with a sweat rate of 1.5 L/h,[19,20] (ii) the leached out contaminants from clothes are constantly penetrating into and absorbed by skin, and (iii) a mean body surface area of Chinese adults is 1.63 m^2 (Table S4). Three milliliters of artificial sweat was used to leach BPA from a piece of cloth of 16 cm^2 (4 × 4 cm^2). The cloth squares were separately cut from three used clothes, of which BPA concentrations ranked either the 50th or 95th percentile among all the used clothes. The cut cloth was placed in a SPE cartridge preconditioned with 10 mL methanol and 10 mL water, and then soaked in 3 mL of artificial sweat for 2 h. After the artificial sweat was loaded slowly and drained downward naturally from the cartridge, the sweaty cloth was removed upward with tweezers. Subsequently, the SPE cartridge was dried with a gentle nitrogen flow and then eluted by 15 mL of methanol. The eluate was spiked with $^{13}C_{12}$-BPA (20 ng) and concentrated to 2 mL by nitrogen and analyzed by HPLC-MS/MS.

2.6. Chemical Analysis. An Agilent 1260 HPLC coupled with Agilent G6460C triple quadrupole mass spectrometer (Agilent Technologies, CA, U.S.A.) was applied for the measurement of bisphenols. Ten microliters of final solution were injected onto a Boltimate C18 column (100 × 2.1 mm^2, 2.7 μm, Welch Materials, Inc., Shanghai, China). Detailed information about chromatographic separation can be found in our previous study,[21] and the specific MS parameters are listed in Table S5.

2.7. Quality Assurance and Quality Control. Among the target bisphenols, no compounds except BPA and BPS were detected in the clothes. Therefore, only BPA and BPS were discussed in this study. The textiles containing the lowest

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level of target BPA and BPS were used to check the method recoveries for the spiked BPA and BPS. Four replicates were performed, and the average recoveries of analytes were 81.48 ± 19.7% (for BPA) and 109.71 ± 6.56% (for BPS). The procedural blanks of BPA ($n = 3$) during the sample extraction process were less than 5% of the detected BPA concentrations in the samples, and the blank was deducted from the detected BPA concentrations when calculating the BPA pollution in clothes. No BPS and other bisphenol analogues were detected in the blanks. In addition, no detectable bisphenols were found in the water, laundry detergent, and artificial sweat used in the simulated laundry experiments and the sweat leaching experiment. The limits of quantitation (LOQs) and limits of detection (LODs) were 3.33 ng/g and 1.00 ng/g for BPA and 0.53 ng/g and 0.16 ng/g for BPS, based on signal-to-noise ratios (S/N) of 10:1 and 3:1, respectively. A midpoint calibration standard and solvent blank were injected after every 10−15 samples as a check for instrumental drift and crossover between samples, respectively.

2.8. Data Analysis. Quantification was performed by an isotope-dilution method using the responses of the corresponding internal standards. The calibration curves were linear over a concentration range of 0.2 ng/mL to 200 ng/mL for BPA and BPS. Statistical analyses were performed with the statistics software package SPSS v.22.0. The investigated data followed a normal distribution after logarithmic transformation, and a one-way analysis of variance (ANOVA) or Student's t test was used to assess the differences between groups.

3. RESULTS AND DISCUSSION

3.1. Bisphenols in Textiles. BPA and BPS were detected in the collected textile samples ($n = 93$), with detection frequencies of 99% and 43%, respectively (Table 1). BPA

Table 1. Concentrations (ng/g) of BPA and BPS[a] in New or Used Textiles

	DR[b] (%)	median	mean ± SD[c]	CV[d]	range
collected textiles ($n = 93$)					
BPA	99	26.9	72.1 ± 209	2.90	<3.30−1823
BPS	43	7.38	44.0 ± 109	2.48	<0.53−536
used clothes ($n = 49$)					
BPA	100	34.2	57.5 ± 93.6	1.63	<3.30−471
BPS	29	5.67	14.6 ± 21.8	1.50	<0.53−80.3
new clothes ($n = 44$)					
BPA	98	17.7	88.4 ± 289	3.27	<3.30−1823
BPS	59	12.3	59.9 ± 133	2.22	<0.53−536
new textiles[e] ($n = 77$)					
BPA	82	10.7	*366 ± 1690*	4.62	*<2.21−13300*
BPS	53	1.02	*15.0 ± 58.9*	3.93	*<0.74−394*

[a]Nondetects of BPS were not included in the calculation of median, mean ± SD and CV. [b]Detection rate. [c]LOQ/$\sqrt{2}$ was used for detects with concentration lower than LOQ when calculating mean values. [d]Coefficient of variance, calculated as the standard deviation divided by the mean (STDEV/mean). [e]Data cited from the reference.[12]

dominated in the two bisphenols, with a median concentration of 26.9 ng/g. In the textile samples with detectable BPS (26 new clothes and 14 used clothes), a median concentration of 7.38 ng/g was found for BPS. When the clothes were divided into three groups according to the material composition, different levels of bisphenols can also be observed. For the cotton textiles ($n = 42$), including 100% cotton and cotton blend textiles, the geometric mean (GM) concentration of bisphenols (BPA + BPS) was calculated as 21.0 ng/g (Figure 1a). A much higher GM concentration (64.6 ng/g) was

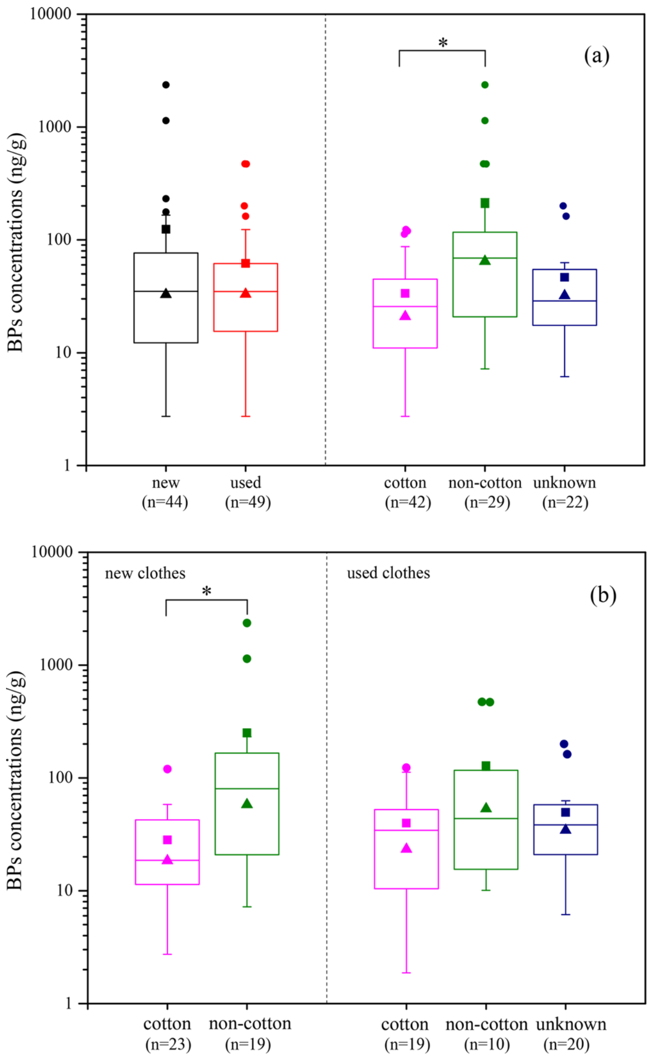

Figure 1. Distribution of bisphenols (BPs = BPA + BPS) in different clothes samples (a), as well as distribution of bisphenols in the new or used clothes samples classified by cloth material (b). Whiskers represent the maximum and minimum in each subgroup of data except outliers. Solid circle: outliers (1.5 times interquartile range); Solid square: mean values; Solid triangle: geometric mean. Statistical significance was set at $p < 0.05$.

obtained for bisphenols in the noncotton textiles ($n = 29$), while noncotton in the present study contains synthetic materials (e.g., polyester, nylon, and Spandex) and artificial materials (e.g., regenerated cellulose fiber). For example, very high concentrations of bisphenols (1823 ng/g for BPA and 536 ng/g for BPS) were found in the new textile made of polyester and Spandex.

In the new clothes ($n = 44$), the median concentration of BPA was detected to be 17.7 ng/g. A widespread occurrence of bisphenols in the new textiles collected in the U.S.A. has been reported,[14] with a median concentration of 10.7 ng/g for BPA (Table 1). Unexpectedly, a higher median concentration of BPA, 34.2 ng/g, was observed in the used clothes ($n = 49$), although the mean (57.5 ng/g) and maximum (471 ng/g)

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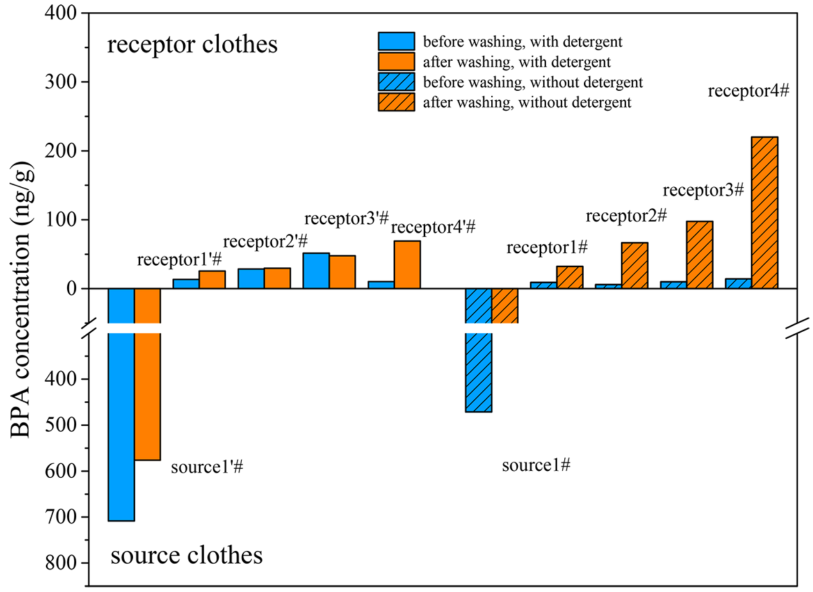

Figure 2. BPA concentrations in the "receptor clothes" and "source clothes" before and after the single round laundering.

concentrations were lower than those of the new clothes (Table 1). This indicates a different data dispersion of BPA concentrations in the used and new textiles. Coefficients of variance (CVs) can represent data dispersion. The CV value of the BPA concentrations in used clothes was 1.63, which was much lower than the CVs of BPA in new clothes in the present study (CV = 3.27) and in new textiles in the U.S.A. (CV = 4.62).[14]

Material composition has been found an important factor affecting the concentrations of bisphenols in the new textiles collected from the U.S.A.[14] However, although the overall concentration of BPA and BPS (i.e., bisphenols concentration) in the new clothes made of synthetic/artificial fiber was significantly higher than that in the new cotton-containing clothes, material-related differences of the bisphenols concentration in the 49 used clothes were not as obvious as those found in the new clothes (Figure 1b). The occurrence of bisphenols in the new clothes may be due to the usage of bisphenols-containing materials used in textile industries. In addition, BPA contamination might also be present in the polymer fibers produced by recycled plastics. The lower impact of materials on the bisphenols concentration in used clothes may be due to the redistribution of these contaminants during laundering, which will be further discussed later. When the used clothes were classified according to the users' age, namely babies (0−2 yrs, n = 25), children (2−18 yrs, n = 13), and adults (>18 yrs, n = 11), the bisphenols concentration in the clothes of babies (GM: 23.6 ng/g) was slightly lower than that of children (GM: 41.9 ng/g) and adults (GM: 50.6 ng/g) (Figure S2). Similarly, the bisphenols concentration in new baby clothes (GM: 15.4 ng/g) was lower than those in the clothes of children (GM: 44.1 ng/g) and adults (GM: 39.3 ng/g). Consequently, the lower bisphenols concentration in used baby clothes may relate to the low original level of bisphenols in new baby clothes and the fact that the baby clothes were usually washed separately, which reduced the cross contamination potential.

3.2. Cross Contamination of BPA in Textiles during Simulated Laundering.

As mentioned above, BPA was frequently detected in used clothes, with a median concentration even higher than that in the new clothes. In addition, the lower CVs and lower material impact on the bisphenols concentrations found in used clothes indicate a homogenizing tendency of bisphenol contaminants in the used textiles. This suggests the potential secondary contamination of used clothes.

In the simulated washing experiment without laundry detergent, the concentrations of BPA in four "receptor clothes" with low initial concentrations (e.g., receptor 1, 2, 3, and 4) increased by two to 15 times after the simulated washing, while the BPA concentration in the "source clothes" with high initial concentrations (e.g., source 1) decreased by 42% (Figure 2). On the basis of the mass balance analysis (Table S2), 76% of the BPA released from "source clothes" transferred to the "receptor clothes". Although similar low initial BPA concentrations (<20 ng/g) were present in the receptor clothes, after the simulated washing, varied increases in the BPA concentration in the cloth of receptor clothes were observed. In receptor 1, a cloth made of 100% nylon, the BPA concentration increased to 32.2 ng/g, while that in receptor 2 (89% polyester + 11% Spandex) was 66.7 ng/g. In comparison, cotton-containing fabrics are more susceptible to BPA in the mix-washing experiment. For example, in receptor 3 and 4, which contain 90−100% cotton, the BPA concentration significantly increased to 97.6 and 220 ng/g, respectively (Figure 2). This indicates different interception ability of cloth materials to BPA (log K_{OW} of 3.32). For chemicals with log K_{OW} of 2−4, significantly higher sorption ability of cotton cloth compared to that of polyester cloth during laundering has been reported.[22]

The application of laundry detergent decreased the BPA cross contamination. For example, in the group of cloth washed with detergent, the increase of BPA in receptors (receptor 1′, 2′, and 4′) was much lower than that found when washed with pure water, and even decreasing BPA concentration was found in receptor 3′ (Figure 2). This can be explained by the fact that the presence of detergent enhances the solubility of BPA in water phase, thus reducing its sorption of clothes. According to the varied BPA concentrations in cloth before and after laundering (Table S2), approximately 54% of

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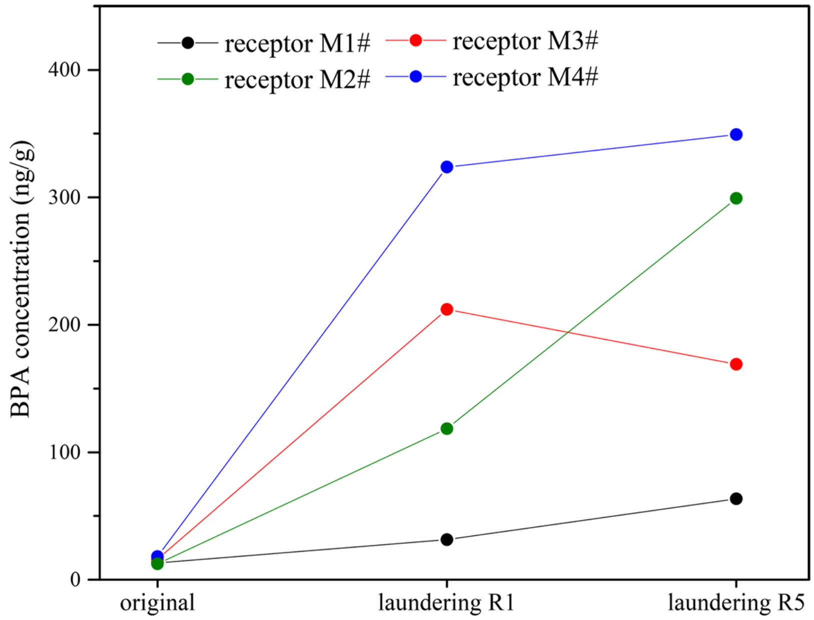

Figure 3. Concentrations of BPA in four "receptor clothes" before and after the multiple round laundering. "Laundering R1" and "laundering R5" indicates the first and fifth round of laundering, respectively.

Table 2. Migration Rate of BPA from Sweaty Clothes and the Estimated Daily Dermal Exposure from Clothes (EXP_{cloth})

BPA in clothes[a]	MR[b] ($ng/cm^2/d$)	$EXP_{sweaty\ cloth}$ (ng/kg BW/d)[c]			EXP_{daily} (ng/kg BW/d)[d]		
		toddlers	children	adults	toddlers	children	adults
median (34.2 ng/g)	0.049	9.34/2.03	8.27/1.80	6.07/1.32	0.009	0.008	0.006
high (123 ng/g)	0.136	25.9/5.64	23.0/4.99	16.9/3.67	0.033	0.029	0.022
high (199 ng/g)	0.308	58.8/12.8	52.1/11.3	38.3/8.32	0.137	0.121	0.089

[a]The clothes with initial BPA concentrations of the median and 95th levels in the used clothes was selected. [b]MR = $^{mass_{BPA}}/_{clotharea}$, where $mass_{BPA}$ (ng/d) was the mass of detected BPA per day leached from the used clothes; cloth area was 16 cm^2 in this experiment. [c]$EXP_{sweaty\ cloth}$ was calculated according to eq 1, while BW values of 16.3 kg (for toddlers of 3 years old), 25.7 kg (for children of 7 years old), and 60.5 kg (for adults of 20−24 years old) were used here, with details shown in Table S4 in the SI; The absorption rates of 46% and 10% were applied respectively in the calculation of $EXP_{sweaty\ cloth}$; [d]EXP_{daily} was calculated according to eq 2.

the BPA released from "source clothes" transferred to the "receptor clothes". This indicates that the cross-contamination of BPA in rinsing process without detergents may be more serious than that in washing with detergents.

Repeated washing can result in further increase in BPA concentration in clothes. As shown in Figure 3, obvious increases in the BPA concentration after the fifth round of laundering were present in receptor M2 and receptor M1. The BPA concentration in receptor M4 changed slightly compared with that found after the first round of laundering. A decrease of BPA concentration was found in receptor M3, indicating that after multiple rounds of laundering, the transformation of receptor M3 from "receptor" to "source of contamination" occurred. It should be noted that potential contamination of BPA from washing machines to clothes might also be present, since many inner gallbladders of machines are made of PC-ABS (polycarbonate-acrylonitrile butadiene styrene) plastics. Moreover, the occurrence of BPA in indoor air and dust has been frequently reported.[23−25] In daily life, migration of BPA between clothes and the surrounding environment can also affect the BPA concentrations in clothes, while a similar phenomenon has been observed for phthalates,[26−28] polychlorinated biphenyls,[29] flame retardant,s[22,30] and other species.[31]

3.3. Human Exposure Assessment for BPA in Clothes.

A simulated sweat leaching experiment was performed to evaluate the dermal exposure to BPA under sweating condition. Three used garments ranking the 50th (34.2 ng/g) and 95th percentile (123 and 199 ng/g) among all the used clothes were selected due to their BPA concentrations. The migration of BPA from clothes to epidermis was estimated by using the artificial sweat.[32] The amount of BPA leached out of the 16 cm^2 of cloth was 0.8−4.9 ng, indicating a BPA migration rate of 0.05−0.31 ng/cm^2-cloth/d (Table 2).

According to previous studies,[14,33,34] the daily dermal exposure dose of BPA from the sweaty clothes (EXP_{cloth}, ng/kg BW/d) was estimated using eq 1:

$$EXP_{sweatycloth} = \frac{MR \times SA \times F'_{pen}}{BW} \quad (1)$$

where MR represents the simulated migration rate from textiles to epidermis ($ng/cm^2/d$), SA represents the skin contact surface area (using values shown in Table S4, cm^2), F'_{pen} represents the penetration rate of BPA into skin (10% or 46%),[35,36] BW represents the average body weight of Chinese, with the detailed average BWs of different age groups shown in Table S4. Because of the great difference of the reported F'_{pen} values, both of low F'_{pen} of 10%[36] and high F'_{pen} of 46%[37] were applied to estimate the dermal exposure to BPA. When high

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F'_{pen} was applied, the estimated dermal exposure dose of BPA from the sweaty clothes ($EXP_{sweaty\ cloth}$) ranged from 9.34 to 58.8 ng/kg BW/d for toddlers, from 8.27 to 52.1 ng/kg BW/d for children and from 6.07 to 38.3 ng/kg BW/d for adults; when low F'_{pen} was applied, the estimated dermal exposure dose of BPA from the sweaty clothes ($EXP_{sweaty\ cloth}$) was in the range of 2.03−12.8 ng/kg BW/d for toddlers, 1.80−11.3 ng/kg BW/d for children and 1.32−8.32 ng/kg BW/d for adults (Table 2).

The daily dermal exposure dose of BPA from dry clothes was estimated according to eq 2:

$$EXP_{daily} = \frac{C \times D \times SA \times F_{mig} \times F_{pen} \times T \times N}{BW} \quad (2)$$

where F_{mig} is the migration rate of BPA to the skin per day (0.005 1/d), F_{pen} is the penetration rate of BPA into body (0.01, unitless), T is the contact duration between textiles and skin (assumed to be 1 d), and N is the mean number of events per day (assumed to be 1 1/d).[14] D was the area density of the used clothes measured in this study. Concentrations of BPA (C) in the three used garments selected in the simulated sweat leaching experiment were also applied. The daily dermal exposure dose of BPA from dry clothes was estimated as 0.009−0.137, 0.008−0.121, and 0.006−0.089 ng/kg BW/day for Chinese toddlers, children, and adults, respectively, which were 3 orders of magnitude lower than those estimated from the sweaty clothes. However, it should be noted that this estimation does not consider the contribution of indirect contact of clothing and skin. Although the transport of semivolatile organic compounds (SVOCs) from clothing to skin through direct contact is much faster than that from the air gap (between clothing and skin) to skin,[38] the Fickian diffusion from clothing to skin through the air gap may also contribute to BPA's exposure, which can be further estimated if the appropriate parameters can be obtained.[39]

According to the urinary BPA concentrations in the U.S.A. and Chinese adults, the estimated daily intake (EDI) of BPA was approximately 34 ng/kg BW/day, while similar value (30.76 ng/kg BW/day) was obtained for the global EDI in adults.[37] Dietary exposure was commonly considered as the major route for human's exposure to BPA.[11] However, relatively high concentrations of BPA were only detected in canned food, and the daily dietary intake (EXP_{diet}) of BPA for adults based on canned food were estimated to be 400−1400 (by JECFA),[40] 1500 (by SCF),[41] and 185 ng/kg BW/d (by FDA).[42] There is a huge difference between the canned food consumption of different populations.[43] For example, the average annual consumption of canned food is 92 kg for Americans, 56 kg for Europeans, and only 6 kg for Chinese.[44] However, although canned food consumption of Americans is greatly higher than that of Chinese, little difference in the EDI between U.S.A. and Chinese adults, as mentioned above, are present.[37] This indicates that there are other important exposure routes to BPA. When both canned and noncanned food were considered, mean EXP_{diet} of BPA was estimated 52−81 ng/kg BW/d (for Canadians)[13] and 43 ng/kg BW/d (for Chinese).[45] In comparison, for Chinese adults, the $EXP_{sweaty\ cloth}$ from sweaty clothes obtained in this study was 1.32−38.3 ng/kg BW/d, which was comparable to the EXP_{diet} (43 ng/kg BW/d) and EDI levels (about 30 ng/kg BW/d) (Figure 4). Compared to EXP_{diet} and $EXP_{sweaty\ cloth}$, the contribution of other exposure routes, including that from air inhalation,[37] drinking tap water,[37] and contacting dust,[23] personal care products,[46] and paper products,[47] is much lower (Figure 4).

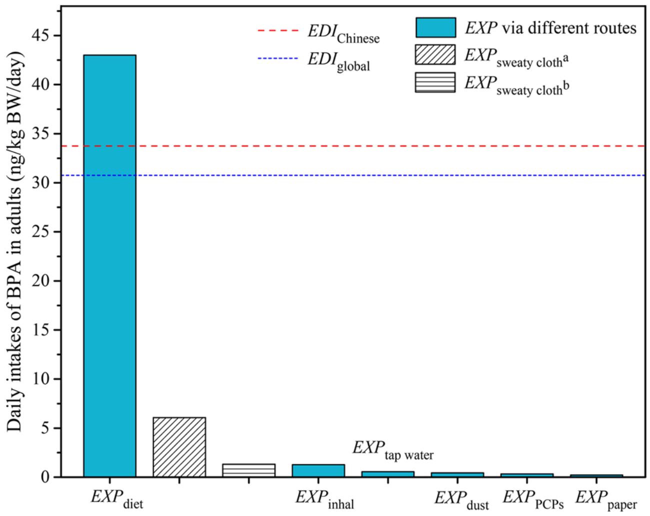

Figure 4. Daily intakes of BPA in adults via different external exposure routes (EXP) and those calculated based on the urinary concentrations (EDI). BPA Daily intakes from diet (EXP_{diet}), inhalation (EXP_{inhal}), tap water ($EXP_{tap\ water}$), dust (EXP_{dust}), personal care products (EXP_{PCPs}), and paper products (EXP_{paper}) were cited from refs 43, 37, 37, 23, 44, and 45, respectively. EDI values were cited from ref 37. Upper corner mark a or b indicate the estimated dermal exposure doses from daily clothes, which were calculated based on the absorption rate of 46% or 10%, respectively.

According to the study, the widespread occurrence of BPA is present in our daily clothes. In general, laundry cannot remove BPA efficiently but cause cross contamination in clothes. Children with higher ratio of body skin area to body weight might face greater exposure risk, especially for BPA released from the sweaty clothes. As the prohibition of BPA use in food-related products has been issued continuously, human exposure to BPA via dermal contact with clothes may become more important, especially in the sweating scenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02090.

Additional information as noted in the text; detailed information on clothes samples, description of the experimental process and the important instrument parameters, different concentrations of bisphenols in clothes of different age groups, and the coefficients used in human exposure estimation (PDF)

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