

Transfer of bisphenol A from thermal printer paper to the skin

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Abstract Of 13 thermal printing papers analyzed, 11 contained 8–17 g/kg bisphenol A (BPA). When taking hold of a receipt consisting of thermal printing paper for 5 s, roughly 1 µg BPA (0.2–6 µg) was transferred to the forefinger and the middle finger if the skin was rather dry and about ten times more if these fingers were wet or very greasy. This amount transferred to dry skin was neither significantly increased when taking hold of the paper at up to 10 sites, nor reduced when BPA-free paper was contacted afterwards. After 60–90 min, BPA applied to the skin as a solution in ethanol was only partially or no longer at all extractable with ethanol, whereas BPA transferred to the skin by holding thermal printer paper remained largely extractable after 2 h. This suggests that penetration of the skin depends on the conditions. Extractability experiments did not enable us to conclude whether BPA passes through the skin, but indicated that it can enter the skin to such a depth that it can no longer be washed off. If this BPA ends up in the human metabolism, exposure of a person repeatedly touching thermal printer paper for 10 h/day, such as at a cash register, could reach 71 µg/day, which is 42 times less than the present tolerable daily intake (TDI). However, if more than just the finger pads contact the BPA-containing paper or a hand cream enhances permeability of the skin, this margin might be smaller.

Keywords Thermal printer receipt · Skin contact · Exposure to bisphenol A · Skin permeability

Introduction

Bisphenol A (BPA) is the subject of hot debates regarding “low dose” toxicological effects [1–3], i.e., effects at doses clearly below the present tolerable daily intake (TDI) of 0.05 µg/kg body weight [4, 5]. If such effects were proven to be pertinent for human health, exposure to sources so far considered minor might become relevant. Dermal exposure to BPA from thermal printer paper might be such a source.

Thermal printer paper includes the printing ink covering the whole surface on the side to be printed. The colorant consists of a leuco dye, i.e., a molecule that can adopt two forms, one of which is colorless. On printing, a thermal head causes the components to melt and react with each other, causing the dye to become dark. Thermal printing papers are regularly used at workplaces like laboratories with recorders using such paper or at cash registers of shops.

Kietzmann et al. [6] demonstrated the percutaneous absorption of deuterated BPA by bovine udders, though without concluding a quantitative uptake. Kaddar et al. [7] determined the cutaneous penetration of BPA into and through pig skin in a Franz diffusion cell. After 10 h, 5.4% of the applied dose (unknown amount in physiological serum) was found on the epidermis, 8.8% in the dermis, and 0.7% in the receptor fluid (totally 14.9%). The experimentation was stopped after 10 h, “as this is the maximal BPA exposure time for workers” (a statement to be questioned, since BPA remaining on the skin after the work may continue to migrate into the skin).

This communication presents data on the transfer of BPA from thermal printer paper to the skin of fingers under

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various conditions. Some experiments on the uptake by the skin involved the skin of the fingers actually contacting thermal printer paper under conditions as realistic as possible. They provided data for a worst-case scenario, but were not adequate to investigate the extent of uptake into the human metabolism.

Materials and methods

Samples of thermal printing papers consisted of receipts from various shops and paper of recorders for chromatographic instruments. Thermal printing paper was identified by its ability to turn dark upon heating. Ethanol absolute, HPLC-grade methanol, and HPLC-grade acetonitrile were from Baker (Deventer, NL).

BPA was extracted from thermal paper (100 mg) by immersion in 10 ml methanol overnight at 60 °C. Extracts were diluted 1:1,000 in 10% methanol/water. BPA transferred to fingers was recovered by moving fingers in 10 ml ethanol for 30 s. After each experiment, fingers were washed with warm water and soap to extract ethanol. The skin was dried by a towel and for at least several minutes in the air before the next experiment was started.

Ethanol extracts were diluted 1:10 with deionized water. BPA was analyzed as described in [8]. Briefly, 500 µl diluted extract was injected into a 250×4.6-mm-i.d. column packed with Spherisorb ODS-2, 5 µm. BPA was eluted with a gradient of 50 to 100% acetonitrile (1 ml/min). Fluorescence was detected at 226/296 nm.

The limit for quantitation was 0.05 µg in 10 ml ethanol. The response was linear from 0.1 to 50 µg/ml ($R^2 \geq 0.994$). Repeated injections ($n=6$) of the same extract (1.2 µg/ml) resulted in a relative standard deviation of 4%. The measuring uncertainty was below 10%.

Results

BPA in thermal printer paper

Table 1 lists BPA concentrations in 13 samples of thermal printer paper (mean of two determinations). In the 11 samples containing BPA, the mean concentration was 13.3 g/kg. Two papers did not contain BPA, indicating that such alternatives are available on the market.

Transfer to the fingers

Recovery of BPA from fingers after touching thermal printing paper was checked by repeated extraction. The paper was firmly held with three fingers for 30 s, with the BPA-containing side contacting the pads of the forefinger

Table 1 BPA concentrations in thermal printing paper

Paper	BPA (g/kg)
Receipt train service	12
Receipt canteen	17
Receipt shop 1	16
Receipt shop 2	11
Receipt shop 3	13
Receipt shop 4	17
Receipt shop 5	8
Receipt shop 6	12
Receipt shop 7	15
Receipt shop 8	<0.0005
Recorder 1	11
Recorder 2	16
Tram ticket	<0.0005

and the middle finger. After moving the fingers in ethanol for 3 s, 2.2 µg BPA was extracted. Immediately afterwards, the same fingers were immersed for an additional 5 s in fresh ethanol, from which 0.9 µg BPA was determined. A third extraction for 22 s yielded 0.3 µg BPA. It was decided to go for an intense extraction by moving the fingers in ethanol during 30 s, which might have included some BPA infiltrated into the surface layer of the skin.

The two sides of the paper released very differing amounts of BPA: contacting the printed side transferred 2.2 µg BPA; that of the rear side 0.2 µg (perhaps contaminated by set-off from the printed side).

Extraction from fingers not previously used for related experiments released less than 0.05 µg BPA. After about 10 experiments including extraction with ethanol, washing with soap and drying, the fingers released traces close to 0.05 µg BPA, presumably from deeper skin layers.

For the experiments on the transfer of BPA from the paper to the fingers, a “standard” was defined, from which individual parameters were varied. The standard involved the BPA-containing side of the thermal printing paper being pressed against the pads of the forefinger and the middle finger by the thumb for 5 s, applying a pressure as needed to pull the paper out of a printer. The skin was slightly greasy (either with natural grease of the skin of the forehead or from briefly touching tissue paper containing some vegetable oil), but not greasy to the extent that it left behind a visible mark on the paper. After each experiment, hands were intensely washed with soap and warm water.

Four repeated experiments with recorder papers 1 and 2, containing 11 and 16 g/kg BPA, respectively (Table 2), transferred 0.3 µg BPA with a relative standard deviation of

Table 2 BPA transferred to fingers under standard conditions (individual measurements for two fingers; mean per finger)

Paper	BPA content in paper (g/kg)	BPA on two fingers (μg)	Mean/finger (μg)
Recorder 1	11	0.2, 0.3, 0.3, 0.2	0.13
Recorder 2	16	1.2, 0.9, 1.5, 1.1	0.6
Receipt canteen	17	6.0, 5.0	3.3
Receipt shop 4	17	0.7, 1.3	0.5
Receipt shop 7	15	2.0, 2.2	1.1

23% and 1.2 μg BPA with a relative standard deviation of 21%, respectively (which is far beyond the uncertainty of the measurement).

Data on the BPA transfer from five thermal printing papers under standard conditions are shown in Table 2. Amounts of BPA found on the fingers were not directly related to the BPA concentration in the paper, which might be due to differing BPA distribution in the paper surface and varying integrity of the fiber layer containing the BPA. The mean transfer on a single finger was 1.13 μg .

Table 3 shows the influence of the skin properties on the BPA transfer. Compared with the standard (slightly greasy) skin, dry skin resulting from washing with soap and drying for about 5 min picked up somewhat less BPA from recorder paper 2, but no difference was observed for the receipt of shop 4. The BPA transfer was strongly increased for humid fingers (leaving visible humidity on the paper), e.g., with some saliva as commonly applied to better grip paper. After this kind of contact, a whitish stain was visible on the finger, suggesting that a surface layer of the paper disintegrated and was transferred to the skin. With wet skin, softened in warm water and just shaken to remove the excess water, transfer was still higher. Oily fingers (leaving a visible mark on the paper) also increased the transfer to about 10 μg . No whitish stain was observed on the finger pads, suggesting that transfer to oily fingers occurred by extraction of BPA from the paper rather than from dissolved fiber structure.

Table 3 Transfer of BPA to two fingers depending on skin properties (papers according to Table 1; individual measurements)

	BPA on two fingers (μg)	
	Recorder 2	Shop 4
Standard (slightly greasy skin)	1.2, 0.9, 1.5, 1.1	0.7, 1.3
Dry skin after washing and drying	0.7, 0.6	1.0, 0.6
Humid finger	7, 28	
Wet fingers	46, 36	
Oily finger	14, 9	11, 7

Table 4 BPA transfer to two fingers depending on the mode of holding the paper (individual results)

Mode of holding paper	BPA on finger (μg)
Holding 1 s	0.4, 0.3
Holding 5 s, standard	1.2, 0.9, 1.5, 1.1
Low pressure	0.7, 0.2
Pulling paper through fingers	0.6, 0.8
Holding 60 s	1.5, 0.7

Table 4 reports amounts of BPA transferred to the two fingers with standard slightly greasy skin surface, but varying the mode of holding the paper (recorder paper 2). Keeping the paper at standard pressure for only 1 s caused the transfer to be reduced by a factor of about three. Holding it for 5 s at the minimal pressure to prevent it falling resulted in poorly reproduced lower transfer. Perhaps against intuition, pulling the paper through the fingers with standard pressure for 5 s also yielded a smaller transfer, which suggests that abrasion of the surface layer was not relevant for normal skin and transfer was primarily via extraction into the skin. Holding prolonged to 60 s was similar to the standard conditions, which means that the skin was saturated in less than 5 s.

Table 5 reports on the effect of repeated contact with always fresh spots of recorder paper 2. Three or even ten standard contacts did not increase the amount of BPA on the skin, which suggests that equilibrium between the BPA concentration in the paper and the surface layer of the skin was reached. In practice it means that a person working at a cash register and touching a receipt every few minutes does not accumulate more BPA than another person touching such paper much less frequently. The last experiment tested the reverse situation: after a standard contact, a clean paper was contacted (5 s, same pressure) at three different spots, checking whether this would transfer BPA back to paper. Interestingly, the amount of BPA on the finger did not decrease significantly: the BPA seemed to firmly adhere to the skin surface, which in practice means that the person at a cash register is unlikely to transfer substantial amounts of BPA to the food packs or other surfaces. These data suggest

Table 5 BPA transfer during repeated contacts

Number of contacts	BPA on finger (μg)
1 (standard)	1.2, 0.9, 1.5, 1.1
3	1.1, .9
10	1.3, 0.7
1, then 3 with clean paper	1.0, 0.7

that the amount of BPA on the contaminated skin surface remains fairly constant.

Experiments regarding the penetration into or through the skin

Of 10 μg BPA applied to a finger as a solution in ethanol (10 μl , 1 mg/ml), extraction by ethanol shortly after evaporation of the solvent recovered 95%. Recovery 90 min after application, however, was below the detection limit, i.e., corresponded to less than 5% of the amount applied. With a 60-min interval between application and extraction, 10% was recovered. Evaporation of BPA from the skin was ruled out by wrapping aluminum foil tightly around the finger (including extraction of the latter for determining potential transfer from the warm finger to the cooler foil). It is assumed that the BPA which cannot be extracted with ethanol during 30 s can no longer be washed off and either remains in the skin surface until the stratum corneum is removed or migrates into and perhaps through the dermis.

The experiment was repeated by applying 1 μl of a 10 mg/ml BPA solution to the finger pad, i.e., the same amount of BPA in ten times less ethanol, varying the interval between the application and the extraction from 5 to 90 min. After some 15 min only half of the BPA was recovered, but some 40% remained extractable with ethanol even after 1.5 h (Fig. 1; mean values from two experiments). This indicates that ethanol was a vector supporting the penetration of the skin surface.

The next experiment was performed without ethanol: recorder paper 2 was touched with the wet forefinger and middle finger for 5 s. BPA on the forefinger was extracted with ethanol either immediately, or with a delay of 20 or 60 min. Then the hand was washed with soap and cold or hot water, rubbing the contaminated middle finger, and BPA on the middle finger was also extracted with ethanol. The

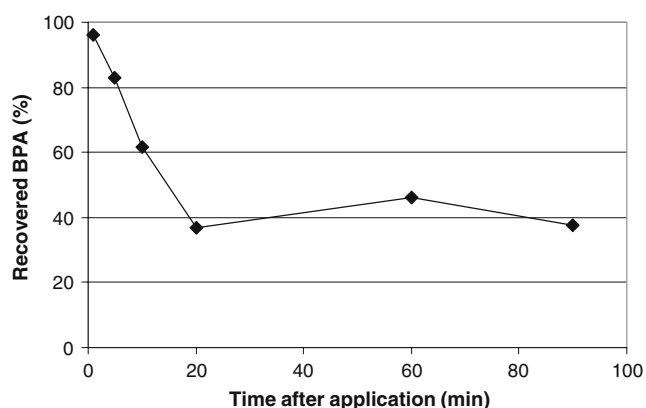


Fig. 1 BPA recovered by extraction of the skin with ethanol after the times shown on the x-axis; 10 μg BPA in 1 μl of ethanol applied to a finger pad

Table 6 BPA transferred onto fingers by wet contact; amounts extractable with ethanol directly or after washing with soap and cold or warm water, either immediately after contacting recorder paper 2 or after waiting 20 or 60 min

Direct extraction (μg)	Washing	Extraction after washing (μg)	Recovered residue in skin (%)
Cold water			
46	Immediately	2.5	5.4
36	After 20 min	3	8.3
44	After 60 min	3.1	7.0
Warm water			
18, 33	Immediately	0.2, 0.4	1.1, 1.2
36, 25	After 20 min	0.1, 0.5	0.3, 2.0
22, 29	After 60 min	0.8, 0.3	3.6, 1.0

recovered amounts of BPA in the left column of Table 6 indicate that the amount of BPA directly extracted with ethanol did not significantly decrease with a delay of up to 60 min (with a high uncertainty resulting from the difficulty in reproducibly transferring a given amount of BPA in this way). After washing with cold water, some 5–8% of the BPA was recovered by ethanol. After washing with warm water, it was clearly less. There was no significant increase in the amount of BPA only recoverable with ethanol after a longer waiting period which would have supported progressive penetration of BPA deeper into the skin. It was concluded that the relatively large amount of BPA transferred to wet fingers remained on the surface and was largely removable by (intense) washing. This might be explained by a large part of the BPA being located in particles which are in only loose contact with the skin.

Similar experiments involved standard dry skin on which no particles seemed to adhere (with a correspondingly lower transfer). In the first experiment, the four fingers of both hands except the thumb were brought into contact with recorder paper 2 using gentle pressure. BPA on the fingers of one hand was immediately extracted with ethanol, BPA of the other 2 h later. The amounts extracted after 2 h were not significantly lower (Table 7; the recovery for the sum of the four fingers was calculated as 88%). This also indicates that BPA—in presumably more intimate skin contact—after touching the paper with dry fingers remained on the skin surface to a far higher proportion than after application in ethanol.

In the second, analogous experiment, the hands were washed with soap and warm water immediately after contacting the paper with the forefinger and the middle finger of both hands, then BPA was individually extracted from each finger with ethanol. None of the fingers released a detectable amount of BPA into ethanol ($<0.05 \mu\text{g}$; Table 8), which means that from the roughly 0.6 μg BPA transferred to a finger in this way (Tables 3

Table 7 BPA transferred onto dry fingers by contacting recorder paper 2; extraction with ethanol immediately afterwards or 2 h later

Extraction	Ethanol extraction of BPA (μg)				
	Forefinger	Middle finger	Ring finger	Little finger	Sum
Immediately	0.6	0.7	1.1	1	3.4
After 2 h	0.6	0.8	1	0.6	3
Recovery (%)					88

and 7), more than 90% was removed by washing. The same procedure was repeated by washing the fingers only 2 h after contacting the paper. Now the ethanol extracted measurable amounts of BPA (mean of $0.17 \mu\text{g}$), i.e., washing only removed 73% of the BPA. This indicates that during the 2 h about $0.17 \mu\text{g}$ BPA migrated into the skin of a finger to such a depth that it was no longer removable by water.

Basically this experiment was not conclusive in as far as the amount of BPA penetrating the skin could have been larger than that detected by ethanol extraction (see experiment with BPA applied with ethanol, where after 90 min the BPA was no longer extractable with ethanol). However, in this experiment the amount no longer extractable by ethanol must have been small, as shown by the high recovery shown in Table 7.

Discussion

On average, holding thermal printing paper transferred $1.13 \mu\text{g}$ BPA to the pad of a finger touching the BPA-containing side. Humid or very greasy skin easily picked up ten times more (maximum $23 \mu\text{g}/\text{finger}$). The highest transfer with wet fingers involves particulate matter, i.e., fibers and particles from the disintegrated paper surface. Such BPA adhering to the skin via particles is rather easily removed by abrasion and it is not in as intimate contact with the skin as when it is dissolved in the skin surface itself.

Touching a paper consecutively at several spots with normal (neither humid nor oily) skin did not increase the transfer, nor did touching BPA-free paper significantly decrease it, suggesting that staff regularly in contact with such paper, e.g., at a register desk, have a fairly constant amount of BPA on the skin all day long. When all ten finger pads occasionally contact thermal printer paper, on average a total of $11 \mu\text{g}$ BPA would be on the skin. This amount can easily be increased by an order of magnitude when a larger surface of the hand gets into contact with the BPA from the paper, e.g., when thermal printer paper is rumbled.

The experiments did not enable us to determine whether or not BPA passes through the skin into the human

metabolism, but they did show that BPA can enter the skin to a depth such that it is no longer removable by washing hands. Such BPA either remains in the skin up to the renewal of the latter or migrates deeper and eventually reaches body fluid. There is ample time for the latter process once BPA can no longer be washed off.

BPA applied to the finger pad with ethanol rapidly entered the skin to such an extent that after about 1 h it was no longer extractable even with ethanol for 30 s. Absorption of BPA transferred from paper was far weaker: after 2 h, most of the BPA could still be washed off. Hence uptake depends on a vector. Hand creams could be such vectors.

Two hours after contacting thermal printer paper with dry skin, 27% of the BPA picked up could no longer be washed off by water, but was still extractable with ethanol. For the given paper this meant a corresponding uptake by the skin of $0.09 \mu\text{g}$ BPA per hour and finger. In a worst-case scenario this amount would finally enter the human metabolism. In a further elaboration of this scenario it could be assumed that all eight fingers and two thumbs of a person pick up BPA in this way. If the thermal printer paper transferring the highest amount of BPA (the receipt from the canteen; Table 2) is touched frequently enough to maintain about $3 \mu\text{g}$ BPA on each finger pad (at least once every few hours), the uptake into the skin via ten digits during a working day of 10 h would be $10 \times 10 \text{ h} \times (27\% \text{ of } 3 \mu\text{g})/2 \text{ h} = 41 \mu\text{g}$. If the hands are not washed before going home, the $30 \mu\text{g}$ BPA left on the ten digits could also be resorbed, increasing the maximum exposure to $71 \mu\text{g}/\text{day}$.

The estimated potential exposure of $71 \mu\text{g}/\text{day}$ for normal skin is 42 times below the $3,000 \mu\text{g}/\text{day}$ that are derived from the present TDI using the normally assumed 60 kg body weight or eight times below the amount which is assumed to be safe by present European specific migration limit (SML of $0.6 \text{ mg}/\text{kg}$; EU-Directive 2002/72). The scenario took into account the highest transfer to the skin from the five thermal printer papers tested, but does not really consider the worst case, such as a contact with a much larger skin surface or the use of hand creams that increase the permeability of the skin. Each of these could increase exposure by a factor of ten.

On the basis of the present TDI, thermal printer paper with BPA can probably be considered safe even for these reasonable worst cases, but it should be reconsidered more

Table 8 BPA extracted with ethanol from fingers after contacting thermal printer paper and washing either immediately or after 2 h

	Extracted BPA ($\mu\text{g}/\text{finger}$)
Immediate extraction	<0.05, <0.05, <0.05, <0.05
Extraction after 2 h	0.2, 0.2, 0.06, 0.2

carefully once “low dose” effects are taken into account for risk assessment: it could cause far higher exposure than known for food.

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