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## BPA and its analogues in thermal papers: an assessment of presence and dermal exposure†

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Thermal papers are a significant source of exposure to bisphenol A (BPA) and other phenolic compounds (PCs), absorbed through the skin *via* dermal contact. This study analyzed thermal paper receipts from various commercial settings in Türkiye to assess BPA and its structural analogs. For both deterministic and probabilistic risk assessments, the estimated daily intake (EDI), hazard quotient (HQ), and hazard index (HI) were calculated for the general population and workers exposed *via* dermal contact from handling thermal receipts. The results showed that BPA and bisphenol S (BPS) were the most frequently detected chemicals (detected in 99% and 100% of samples, respectively) with concentrations ranging from 1.98–1061 µg per g paper and 0.070–210 µg per g paper in thermal paper receipts in Türkiye, respectively. The EDI of PCs based on the mean concentration determined in the samples for the general population ranged between 0.00000184 µg per kg per day and 0.000445 µg per kg per day, whereas it ranged between 0.0000919 µg per kg per day and 0.022 µg per kg per day for occupational exposure of workers. The EDI value based on the mean concentration detected in samples was 0.000445 µg per kg per day and 0.00223 µg per kg per day for the general population and occupational exposure, respectively. Exposure to BPS was lower, resulting in exposure values of 0.000039 µg per kg per day and 0.002 µg per kg per day for the general population and occupational exposure, respectively. Although these mean concentration based exposure levels are below the U.S. EPA reference dose (50 µg per kg per day for BPA), they exceed the more stringent European Food Safety Authority (EFSA) total daily intake (TDI) limits set for BPA (0.0002 µg per kg per day) in some cases, indicating potential health risks. The HQ and HI analyses further underscore the risks, particularly for workers, with HI values surpassing safe thresholds. The study calls for stricter regulations on BPA and its analogs in thermal papers due to the significant risks, even from BPA-free products that use BPS as a substitute.

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### Environmental significance

BP-A and BP-S are widely used to manufacture various consumer products such as thermal papers and sales receipts. BP-S containing products are being marketed as “BPA-free” products since the use of BPS has not been regulated. Considering the increased direct contact of handling thermal receipt papers in daily life, recent discoveries have indicated direct dermal exposure to these chemicals, resulting in their observation in urine due to absorption into skin. Moreover, significantly higher levels of BP-A and BP-S in urine samples due to occupational exposure were reported compared to general exposure. Therefore, the investigation of the transfer of these compounds into the human body is essential.

## 1 Introduction

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane) is a synthetic chemical and is used in polycarbonate plastic and epoxy resin production. It has a wide application area in various

consumer products and industrial applications including plastic bottles, thermal papers, dental resins, sports equipment, and compact disks (CDs)/digital versatile disks (DVDs).<sup>1–3</sup>

In 2009, it was estimated that 2.2 million tons of BPA were produced globally and it is expected that the production will reach 7.3 million tons by the end of 2023.<sup>4</sup> In thermal receipt papers, BPA has been widely used as a color developer. Due to the global restriction and regulations on BPA as a result of recognition of its negative effects on human and environmental health, it has been substituted with alternative chemicals such as bisphenol S (BPS) in thermal receipt papers. However, despite the restrictions, BPA is still in use in various products and applications. Additionally, there is limited research on the

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negative effects of BPS on environmental compartments and human health. A ban has entered into force in the European Union (EU) on January 2, 2020 on the use of BPA in thermal paper stating that the substance cannot legally be placed on the market in thermal paper in a concentration equal to or greater than 0.02% by weight.<sup>5</sup> Hence, it is forecasted that 61% of all thermal paper in the EU is to be based on BPS by 2022. Outside of the EU, Switzerland is the first country to ban BPA and BPS initiating a ban on these chemicals in thermal paper. Several jurisdictions in the US introduced bills to regulate BPA in consumer products, *i.e.* the governor of Illinois signed the HB 2076 bill<sup>6</sup> into law to regulate BPA in thermal paper. Use of BPA is banned in Türkiye for certain applications such as production of polycarbonate materials used in baby feeding;<sup>7,8</sup> however, to the best knowledge of the authors, there are no regulations on BPA or BPS in thermal receipt papers in Türkiye.

The new regulation on BPA has been published by the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) under the Water Framework Directive (WFD) regulation. According to the new regulation, BPA has been added to the priority pollutant list under the WFD;<sup>9</sup> hence, it is the first bisphenol that is listed on the priority pollutant list of the WFD.

The occurrence and levels of BPA and other phenolic compounds (PCs) have been reported in different environmental media: up to 3900  $\mu\text{g kg}^{-1}$  in indoor dust,<sup>10</sup> up to 9730  $\mu\text{g kg}^{-1}$  in dust,<sup>11</sup> up to 39 000  $\mu\text{g kg}^{-1}$  in thermal receipts,<sup>12</sup> up to 898.7  $\text{ng L}^{-1}$  in drinking water,<sup>13</sup> up to 46.31  $\mu\text{g kg}^{-1}$  in sediment, up to 81.39  $\mu\text{g kg}^{-1}$  in sediment organic matter,<sup>14</sup> and up to 2.79  $\mu\text{g L}^{-1}$  in human urine samples.<sup>15</sup>

Due to the widespread use of BPA and its alternatives such as BPS, bisphenol Z (BPZ), bisphenol F (BPF), bisphenol C (BPC), bisphenol AP (BPAP), 2,4-bisphenol S (2,4-BPS), bisphenol E (BPE), bisphenol B (BPB), bisphenol AF (BPAF), and bisphenol P (BPP) in consumer products, the release of PCs into the environment and their subsequent transfer to humans are inevitable. The topic has gained significant public attention in recent years due to these chemicals' adverse health effects,<sup>16</sup> especially significant negative impacts on reproductive abilities as endocrine disruptors even at low concentrations.<sup>3,12,17–20</sup> It has been suggested that BPA may affect human reproductive and other systems by acting like human hormones.<sup>21</sup> In response, BPS has been one of the most widely used BPA replacements introduced by manufacturers to make “BPA-free” products. However, two recent studies reported that BPS is as hormonally active as BPA,<sup>22</sup> and, like BPA, it interferes with the endocrine (hormone) system<sup>23</sup> in ways that may produce harmful effects, such as obesity, cancer and neurological disorders. The study by Qui *et al.*<sup>24</sup> reported that both BPA and BPS alter the normal development of the reproductive system. If these chemicals are ever released into the environment, they eventually enter the human body *via* many pathways like oral ingestion,<sup>25</sup> dermal contact,<sup>26</sup> and inhalation.<sup>25,27</sup>

The main goal of the present study was to determine the levels of PCs including BPA, BPB, BPS, BPZ, BPAF, BPF and BPP in thermal papers, which were randomly collected from supermarkets, general and fast-food restaurants, gas stations, credit

cards and bank machines in Türkiye. Secondly, the current study aims to estimate the daily intake of selected PCs *via* dermal absorption from the handling of thermal papers.

## 2 Materials and methods

### 2.1 Reagents

All solvents were of liquid chromatography grade. PCs including BPA, BPB, BPS, BPZ, BPAF, BPF and BPP were purchased from Accustandard (New Haven, CT, USA). BPA- $d_{16}$  was from Dr Ehrenstorfer GmbH (Augsburg, Germany), while  $^{13}\text{C}_{12}$ -BPA was from Cambridge Isotope Laboratories, Inc (Tewksbury, MA, USA).

### 2.2 Sample collection

A total of 152 thermal receipt papers were collected randomly from commercial settings including banks, supermarkets, cafes, restaurants, gas stations, fast food stores, and health centers, from 8 different cities in Türkiye in 2020. Additionally, a thermal paper certified to be free of BPA was purchased from a supplier and replicate analysis ( $n = 10$ ) was conducted for this sample. The samples were wrapped in pre-baked (at 450 °C) aluminum foil bags and were stored at  $-20$  °C until analysis.

### 2.3 Sample preparation

Extraction of targeted chemicals from the thermal paper samples was carried out according to the method described by Babu *et al.*<sup>28</sup> with a minor revision. Briefly, the thermal paper samples were cut into small pieces using a stainless steel clipper. The clipper was cleaned using acetone before it was used for each sample. The cut pieces were blended, and a sub-sample of approximately 20–30 mg thermal paper was transferred into a 15 ml screw cap glass centrifuge tube. After addition of 522 ng of recovery compound (in acetonitrile) (BPA- $d_{16}$ ), the cap of the tube was closed tightly and samples were kept in the dark for about an hour. 5 ml of acetonitrile was used as the extraction solvent. The sample was vortexed for 60 seconds, the cap of the tube was closed tightly and then it was kept in the dark overnight. The next day, ultrasonic extraction (for 15 minutes) was applied to the sample to extract the targeted chemicals. After extraction, the sample was centrifuged at 4000 rpm for 10 minutes and the aliquot was filtered through a 0.45  $\mu\text{m}$  PTFE syringe filter. A 1 ml aliquot was transferred into an amber GC-vial and spiked with 100 ng of BPA- $^{13}\text{C}_{12}$  immediately prior to analysis as an internal standard.

### 2.4 Instrumental analysis

A Shimadzu 8040 triple quadrupole LC-MS/MS system was used for analysis of PCs. Chromatographic separation was achieved on a Shim-pack FC-ODS (150  $\times$  2 mm, Shimadzu, Kyoto/Japan) column. The injection volume, flow rate in the column and oven temperature were 10  $\mu\text{l}$ , 0.3  $\text{ml min}^{-1}$  and 40 °C, respectively. The mobile phase is composed of 10 mM ammonium acetate in water (A) and acetonitrile (B). The gradient program was set as follows: 0.0–1.0 min; 80% of solvent B, and 1.0–2 min; a linear



gradient to 95% solvent A; 2.0–4.0 min, 95% solvent B; 4.0–4.01 min gradient to 50% solvent B; 5.0 min stop.

The capillary voltage was kept at 4.0 kV and the vaporizer temperature was 350 °C. Detailed information on BPA and other PC precursor ions ( $m/z$ ), product ions ( $m/z$ ) and retention time is given in ESI Table S1.†

## 2.5 Quality assurance and quality control

All glassware was soaked in soapy water overnight prepared using Alconox detergent and then was rinsed first with tap water and then with Milli-Q water. All glassware and metal tools were baked at 450 °C for at least 4 hours before use. All materials were cleaned with acetone/hexane before use to prevent any contamination.

Initially, it was aimed to use a BPA-free certified paper as a material to prepare blanks. However, a noticeable amount of BPA was present in the certified thermal paper; therefore, only solvent blanks were used in the current study. A solvent blank was processed for every 12 samples. None of the targeted PCs were present in blank samples; therefore, the method detection limit (MDL) was accepted to be equal to the instrument detection limit (IDL) for all targeted chemicals. For statistical analysis, if a targeted chemical was <MDL, half of the MDL was used in calculations. In the current study, the variability of the mean value of data is expressed as the standard error (SE).

The IDL values for BPA, -B, -S, -Z, -AF, -F and P were 0.050, 2.93, 0.004, 0.008, 0.003, 1.51, and 0.383  $\mu\text{g g}^{-1}$ , respectively. The recovery ratio of BPA-d<sub>16</sub> was between 71 and 125% with an average value of  $90 \pm 1.16\%$ .

## 2.6 Exposure assessment and risk characterization

**2.6.1 Exposure assessment.** Similar to other chemicals, ingestion, inhalation and dermal contact are the main human exposure pathways to PCs. In this manner, thermal receipt paper appears to be a source of human exposure to BPA and its alternatives *via* dermal transfer, which is particularly relevant for occupational exposure (cashiers) as well as general public exposure. BPA is clearly transferred from thermal paper to the finger pads when they are handled and then it can penetrate the skin and into the bloodstream.<sup>29</sup>

Therefore, in the assessment of exposure to PCs *via* thermal paper receipts, dermal contact is considered the sole human exposure pathway due to the handling behavior of consumers as well as the high levels of PCs in such paper.<sup>11,30,31</sup>

The estimated daily intake (EDI;  $\mu\text{g per day per kg bw}$ ) of PCs was calculated using eqn (1) modified from the equation given by Liao and Kannan:<sup>30</sup>

$$\text{EDI} = \frac{k \times C \times \text{HF} \times \text{HT} \times \text{AF}}{\text{BW} \times 10^9} \quad (1)$$

where  $k$  is the paper-to-skin transfer coefficient ( $21\,522 \text{ ng s}^{-1}$  for all PCs),  $C$  is the concentration of PC determined in thermal paper ( $\mu\text{g per g paper}$ ), and HF is the handling frequency (times per day). HT is the handling duration of receipts (5 s).<sup>1</sup> Studies conducted in other parts of the world have taken into account different rates of HF for occupational exposure and public

exposure pathways. In the current study, a HF value of 150 times per day for occupational exposure<sup>12</sup> and a HF value of 3 times per day for public exposure<sup>12</sup> were used in calculations. A detailed list of parameters and values used in calculations is given in ESI Table S2.†

**2.6.2 Risk characterization.** The numeric values of parameters used in risk characterisation are given in ESI Table S3.† The hazard quotient (HQ) is calculated to evaluate the potential for non-cancer health hazards to occur from exposure to PCs. In the current study, as dermal contact is the sole exposure pathway, HQ was used to evaluate the non-carcinogenic effects of PCs due to their dermal exposure. A  $\text{HQ} < 1$  indicates safety levels, while a  $\text{HQ} > 1$  indicates a potential risk. The HQ value was calculated using eqn (2).

$$\text{HQ} = \frac{\text{EDI}}{\text{RfD}} \quad (2)$$

$\text{RfD}_{\text{dermal}}$  values are still not available for any of the targeted bisphenol compounds, while  $\text{RfD}_{\text{oral}}$  is present only for BPA.<sup>32</sup> The USEPA sets an  $\text{RfD}_{\text{oral}}$  value of BPA at 50  $\mu\text{g per kg bw per day}$  (ref. 32), while the European Food Safety Authority<sup>33</sup> recommends a temporary tolerable  $\text{RfD}$  value of 4  $\mu\text{g per kg bw per day}$  for BPA. However, in 2023, the EFSA has re-evaluated BPA safety and the new TDI was reduced by a factor of 20 000, resulting in a TDI of 0.2  $\text{ng per kg bw per day}$ .<sup>34</sup> Little information is available to calculate the risk assessment of PCs through dermal absorption and it is mainly based on the calculation of EDI values.<sup>12,30</sup> Therefore, in the current study, the oral reference dose ( $\text{RfD}_{\text{oral}}$ ) and temporary tolerable reference dose from the EFSA<sup>34</sup> were used to calculate the  $\text{RfD}_{\text{dermal}}$  values of PCs. In this manner, eqn (3) proposed in ref. 35 was used with a small modification to make the best assumption that could be made to estimate the  $\text{RfD}_{\text{dermal}}$  values for the dermal absorption of the investigated PCs.

$$\text{RfD}_{\text{dermal}} = \text{RfD}_{\text{oral}} \times \text{ABSGI} \quad (3)$$

where  $\text{RfD}_{\text{oral}}$  is 50  $\mu\text{g per kg bw per day}$  for BPA.<sup>36</sup> As  $\text{RfD}_{\text{oral}}$  is not present for other PCs, it is assumed for all other PCs that  $\text{RfD}_{\text{oral}} = \text{temporary tolerable RfD}$  (0.2  $\text{ng per kg bw per day}$ ) set by.<sup>34</sup> ABSGI is the fraction of the contaminant absorbed in the gastrointestinal tract. The ABSGI value is not present for any of the PCs of interest. Gayrard *et al.*<sup>37</sup> found high absorption and bioavailability (70%) of BPA following sublingual administration that was dramatically different than the much lower bioavailability (<1%) of BPA following gavage administration in a parallel experiment. However, these findings are currently being rejected for use in risk assessments by the US Food and Drug Administration (US FDA) as they are not plausible.<sup>38</sup> Based on an *in vitro* OECD TG428 study performed in ref. 39 using BPA in an aqueous solution on non-viable human skin samples, it is estimated that the dermal bioavailability of BPA was around 10%.<sup>40</sup> Gayrard *et al.*<sup>41</sup> reported a systemic bioavailability of 57.4% for BPS in a study conducted to investigate the oral systemic bioavailability of selected bisphenol compounds in pigs. Consequently, in the current study, we assume an ABSGI value of 10% for BPA and other PCs except for BPS (57.4%).



Health risks associated with exposure to multiple PCs are estimated by using the hazard index (HI) (the summation of hazard quotients ( $HQ_k$ ) of individual PCs ( $k$ )), which can be calculated using eqn (4).<sup>42,43</sup>

$$HI = \sum HQ_k \quad (4)$$

A value of  $HI > 1$  indicates that there is a chance of occurrence of non-carcinogenic effects as a result of concurrent exposure to multiple PCs, while the exposed individual is unlikely to experience obvious adverse health effects when  $HI < 1$ .

**2.6.3 Monte Carlo simulation and sensitivity analysis.** In risk quantification, when a single-point value is used for each variable, the probability of uncertainties increases in estimates. Therefore, in order to reduce the probability of error, it is recommended to use a set of numbers in the domain of the variables involved in the calculation of risk. In the current study, for this purpose Monte Carlo simulation is used.<sup>44,45</sup> The user can identify the variables that have the most impact on the outcomes of the risk assessment by applying the sensitivity analysis function of Monte Carlo simulation. In this study, the @Risk program (offered by Lumivero company (Raleigh, NC, USA) in Microsoft Excel) was used for the simulation and sensitivity analysis with 10 000 trails. Sensitivity analysis is an important tool in risk assessment as part of Monte Carlo simulation. This analysis is a technique aimed at determining the impact of specific variables on the results. The variables used in the model were based on previous studies and summarized in ESI Tables S2 and S3.†

### 3 Results and discussion

#### 3.1 PC concentration in thermal paper receipts

Fig. 1 shows a comparison of PC concentrations in thermal paper receipt samples analysed in the current study, while the concentration values of each targeted PC in individual samples are given in ESI Table S4.†

Among the targeted bisphenols, it was found that BPA and BPS were the dominant color developers used in the thermal receipts collected from the Turkish market ( $n = 152$ ) and detected in 99% (1.98–1061  $\mu\text{g per g paper}$ ) and 100% (0.007–210  $\mu\text{g per g paper}$ ) of the analysed samples, respectively. In addition to these two species, BPB, BPZ, BP-F and BPP were also determined but at a lower frequency. Generally, BPA and BPS showed higher concentration levels compared to other PCs detected in the samples (Fig. 1). BPP showed the lowest detection frequency (2.64%,  $n = 4$ ) with a concentration value between 0.011 and 0.018  $\mu\text{g per g paper}$ . BPAF was not present in any of the analysed thermal paper samples. The detection frequency values of PCs are ranked as follows: BPS (100%) > BPA (99.0%) > BPB (80%) > BP-F (57%) > BPZ (43%).

A comparison of detected concentrations in samples was made by grouping the samples based on a designated categorization. The first approach for such categorization was to group the samples based on the manufacturers' brand names. The collected 152 thermal paper receipts were from 10 different brands. The main grouping criterion was based on the presence of three or

more samples from the same paper brand. The no-name brand papers or a sample size of 2 or less were grouped together and the results are given under "Brand f" in ESI Table S5.† The concentration ranges and mean concentration values of detected PCs in samples from different brands studied in the current research are given in ESI Table S5.† The percent contribution of each targeted PC compound to the total PC concentrations detected in each sample was calculated and is shown in ESI Fig. S1.† In most of the samples, BPA was the PC that contributed the most to the total concentration in the brands a, b, c, d, e, f, g and h (% contribution range between 1.7% and 99.7%), followed by BPS (0.1–97.9%) and BPB (1.4–38%). However, in brands i and j, BPS (0.02–98.33%) was the dominant chemical that contributed the most to the total concentration.

The second approach to categorization was grouping the samples based on the manufacturer's notifications of the "presence of BPA" in the thermal receipts. The first group was BPA-free certified paper (hereafter referred to as CTP,  $n = 15$ ), the second group was BPA-free stated thermal paper (not certified by the manufacturer but stated on the back of the paper to be BPA free; hereafter referred to as STP,  $n = 10$ ) and the third group was regular thermal receipt paper (hereafter referred to as RTP,  $n = 142$ ). It is important to note that CTP paper was not included in the total number ( $n = 152$ ) of the analysed samples and it was used to assess the presence of such chemicals in certified material. The average concentration ( $\pm\text{SE}$ ) values of targeted chemicals in CTP, STP and RTP groups are given in Table 1.

Although CTP paper is expected to be completely free of BPA, this chemical was still present in CTP paper samples at a mean concentration of  $34.06 \pm 0.904 \mu\text{g per g paper}$ . The mean concentration of BPA in STP and RTP groups was  $81.5 \pm 52 \mu\text{g per g paper}$  ( $DF = 100\%$ ) and  $374.35 \pm 17.5 \mu\text{g per g paper}$  ( $DF = 99\%$ ), respectively. Although the mean BPA level in the CTP group was approx. 2.4–11 times lower compared to the mean levels detected in STP and RTP groups, the presence of BPA in CTP paper is still an indication that people may still be exposed to BPA even though vendors are aware of its negative effects and have a high level of awareness to use thermal paper certified as BPA free.

As some published data and government documents<sup>46,47</sup> report that BPS is a safer alternative to BPA, it seems that BPA is still the preferred PC compound in thermal receipt papers in Türkiye. Moreover, surprisingly, a sample from the STP group showed the highest BPA concentration (431.5  $\mu\text{g per g paper}$ ) and showed lower levels of BPS (0.09–207.6  $\mu\text{g per g paper}$ ). In addition to BPA and BPS, BPB, BP-F and BPZ were also present in STP and RTP group papers.

The third approach was to group the samples based on service categories and results are shown in ESI Table S6.† Cinema, gas station and fast food receipts showed similar concentrations ( $398.4 \pm 13.5 \mu\text{g per g paper}$ ,  $397.4 \pm 36.6 \mu\text{g per g paper}$ , and  $394 \pm 35.8 \mu\text{g per g paper}$ , respectively), yet these were the highest BPA concentration level compared to other service group samples. Samples from café-restaurant settings showed the lowest mean BPA concentration ( $157.5 \pm 100 \mu\text{g per g paper}$ ). Fuel bills showed the highest mean BPB concentrations ( $42.1 \pm 4.3 \mu\text{g per g paper}$ ) but the average BPB levels in other service groups were similar (from  $15.1 \pm 2 \mu\text{g}$



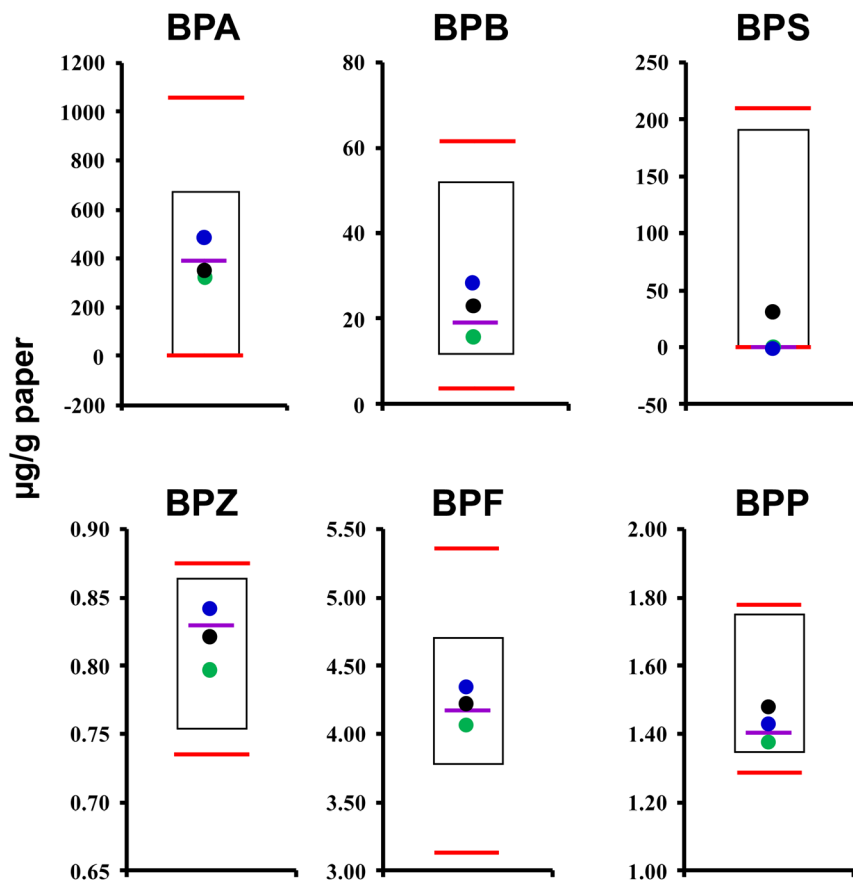


Fig. 1 Concentrations of PCs (top and bottom borders of the boxes represent 5th and 95th percentiles, green and blue circles represent the 25th and 75th percentiles, horizontal red lines show the minimum and maximum values, and black circles and the horizontal purple line represent the mean and median concentrations, respectively).

per g paper to  $29.4 \pm 5.8$   $\mu\text{g}$  per g paper). Health center and supermarket receipts showed similar BPS concentrations ( $67 \pm 66.74$   $\mu\text{g}$  per g paper and  $62.2 \pm 16.4$   $\mu\text{g}$  per g paper, respectively), yet had the highest BPS concentration level compared to other service groups, while samples from gas stations showed the lowest BPS concentration ( $0.22 \pm 0.04$   $\mu\text{g}$  per g paper) level.

A comparison of BPA and BPS levels in thermal receipt papers in Türkiye to the levels reported in other countries is given in Table 2. The results of the current study for BPA and BPS are in the lower end of the reported concentrations worldwide (Table 2). Furthermore, the maximum concentration of BPA determined in the current study is approx. 20 times lower compared to the maximum concentration of BPA reported in a study conducted in Türkiye in 2016 by Yalcin *et al.*<sup>55</sup> However, it is worth mentioning that Yalcin *et al.*<sup>55</sup> analysed only 12 samples, yet the concentration levels reported for such a small sample size would probably not be representative of typical levels in a broader Turkish market.

### 3.2 Risk assessment of BPA and its alternatives in shopping receipts

Occupational exposure to PCs can occur through handling receipts. A study in the United States found that pregnant women employed as cashiers had the highest levels of urinary

BPA concentrations, measuring  $2.8$   $\mu\text{g}$   $\text{g}^{-1}$  (equivalent to  $0.0028$   $\text{mg}$   $\text{g}^{-1}$ ), compared to pregnant women in other professions, such as teachers and industrial workers, who had concentrations of  $1.8$   $\mu\text{g}$   $\text{g}^{-1}$  and  $1.2$   $\mu\text{g}$   $\text{g}^{-1}$ , respectively.<sup>59</sup> This outcome is attributed to the frequent handling of thermal paper found in cash register receipts by women working as cashiers. The Washington Toxics Coalition estimated that an average shopper could transfer around  $30$   $\mu\text{g}$  of BPA to their skin by handling a receipt (rubbing it five times between two fingers and a thumb), based on BPA concentrations detected in thermal paper.<sup>60</sup> The mean daily intake (MDI) of BPS was estimated to be  $12.3$  ng per day for the general population through handling of thermal paper.<sup>61</sup> Additionally, these researchers estimated the MDI of BPA from handling paper currency to be  $0.102$  ng per day for the general population in the United States.<sup>30</sup> To the best of our knowledge, there is one study that has estimated the mean daily intake (MDI) of BPS from handling paper products and currency, as reported in ref. 62. That study determined that the MDI of BPS *via* dermal absorption in adults handling paper products and paper currency was  $12.0$  ng per day for the public. These findings suggest that alternatives to BPA, such as BPS, which share similar physical and chemical properties, are likely to transfer from the surface of thermal paper onto the skin and may potentially be absorbed through the skin or ingested.



Table 1 Levels of bisphenols in CTP, STP and RTP receipt papers<sup>a</sup>

|             | CTP <sup>b</sup> (n = 15) (µg per g paper) | STP <sup>c</sup> (n = 10) (µg per g paper) | RTP <sup>d</sup> (n = 142) (µg per g paper) |
|-------------|--|--|---|
| <b>BPA</b>  |  |  |   |
| Min.        | 37.41                                      | 3.34                                       | 0.0250                                      |
| Max.        | 35.18                                      | 431.5                                      | 1061.1                                      |
| Avg ± SE    | 34.06 ± 0.94                               | 81.5 ± 52                                  | 374.4 ± 17.5                                |
| Median      | 35.1                                       | 4.11                                       | 397.4                                       |
| DF (%)      | 100  | 100  | 99  |
| <b>BPS</b>  |  |  |   |
| Min.        | nd   | 0.09                                       | 0.0705                                      |
| Max.        | nd   | 207.6                                      | 210.3                                       |
| Avg ± SE    | nd   | 154.1 ± 25.8                               | 22.4 ± 5.03                                 |
| Median      | nd   | 191.10                                     | 0.21  |
| DF (%)      | 0  | 100  | 100   |
| <b>BPB</b>  |  |  |   |
| Min.        | nd   | 1.46                                       | 1.46  |
| Max.        | nd   | 15.5                                       | 61.7  |
| Avg ± SE    | nd   | 4.23 ± 1.85                                | 19.8 ± 1.16                                 |
| Median      | nd   | 1.46                                       | 17.5  |
| DF (%)      | 0  | 20   | 84  |
| <b>BP-F</b> |  |  |   |
| Min.        | nd   | 0.75                                       | 0.75  |
| Max.        | nd   | 4.44                                       | 5.74  |
| Avg ± SE    | nd   | 2.45 ± 0.569                               | 2.80 ± 0.146                                |
| Median      | nd   | 2.27                                       | 4   |
| DF (%)      | 0  | 50   | 58  |
| <b>BPZ</b>  |  |  |   |
| Min.        | nd   | 0.003                                      | 0.003                                       |
| Max.        | nd   | 0.86                                       | 0.876                                       |
| Avg ± SE    | nd   | 0.09 ± 0.085                               | 0.37 ± 0.034                                |
| Median      | nd   | 0.003                                      | 0.003                                       |
| DF (%)      | 0  | 10   | 45  |

<sup>a</sup> nd: not detected in the sample. <sup>b</sup> CTP: certified thermal paper. <sup>c</sup> STP: BPA-free stated thermal paper. <sup>d</sup> RTP: regular thermal receipt paper.

Thermal paper can release free PCs upon contact, which may then be absorbed into the skin, leading to exposure during handling and use. Several studies have investigated the release of BPA from POS receipts, showing that BPA can be extracted from the receipts and has the potential to be absorbed into the skin upon contact.<sup>29</sup> It has been reported that approximately 0.17 µg of BPA migrated into the skin two hours after contact, and this amount could not be recovered by washing with water. Experimental conditions have also demonstrated that BPA can penetrate the skin under certain conditions.<sup>63</sup>

**3.2.1 Deterministic calculation.** Section 2.6 provides detailed information about the parameters used for calculating daily bisphenol exposures. EDI values calculated in the current study for PCs detected in samples for general public and occupational exposure of adults *via* dermal contact with thermal receipt papers are given in Table 3. The mean concentrations of BPs in the thermal paper (C) were 357 µg g<sup>-1</sup>, 23.2 µg g<sup>-1</sup>, 31.3 µg g<sup>-1</sup>, 0.821 µg g<sup>-1</sup>, 4.21 µg g<sup>-1</sup> and 1.48 µg g<sup>-1</sup> for BPA, BPB, BPS, BPZ, BP-F and BPP, respectively. The paper-to-skin transfer coefficient was taken as 21 522 ng s<sup>-1</sup> for all PCs.<sup>29</sup> The handling frequency (HF) was determined to be 3

and 150 times per day for public and occupational exposure, respectively.<sup>12</sup> The handling duration of receipts (HT) is 5 s,<sup>31,64</sup> and the absorption fraction of bisphenol compounds by skin (AF) was taken as 27%.<sup>29</sup> Based on these parameters, the daily mean occupational exposures (EDI<sub>occupational</sub>) to BPA, BPB, BPS, BPZ, BPF and BPP from the thermal paper were 2.23 × 10<sup>-2</sup> µg per kg per day, 1.44 × 10<sup>-3</sup> µg per kg per day, 1.95 × 10<sup>-3</sup> µg per kg per day, 5.11 × 10<sup>-5</sup> µg per kg per day, 2.63 × 10<sup>-4</sup> µg per kg per day and 9.19 × 10<sup>-5</sup> µg per kg per day, and the daily mean public exposures (EDI<sub>public</sub>) were 4.45 × 10<sup>-4</sup> µg per kg per day, 2.89 × 10<sup>-5</sup> µg per kg per day, 3.90 × 10<sup>-5</sup> µg per kg per day, 1.02 × 10<sup>-6</sup> µg per kg per day, 5.26 × 10<sup>-6</sup> µg per kg per day and 1.84 × 10<sup>-6</sup> µg per kg per day, respectively (Table 3). According to Table 3, the EDI values were compared with the reference dose established by the USEPA (50 µg per kg per day for BPA)<sup>32</sup> and the TDI set by the EFSA (0.0002 µg per kg per day for other BPs).<sup>34</sup> The results indicate that the calculated EDI values for all bisphenols are well below the reference dose set by the USEPA.<sup>32</sup> However, these values significantly exceed the EFSA's much stricter TDI limit.<sup>34</sup> For instance, the highest mean EDI value for BPA (2.23 × 10<sup>-2</sup> µg per kg per day) exceeded the TDI



**Table 2** Comparison of BPA and BPS levels in thermal receipt papers in Türkiye to the levels reported in other countries

| Country          | Range ( $\mu\text{g per g paper}$ ) |                            | Reference  |
|------------------|-------------------------------------|----------------------------|------------|
|                  | BPA                                 | BPS                        |            |
| Türkiye          | 1.98–1061                           | 0.007–210.28               | This study |
| Korea            | 6165.8–10 353                       | 0.0138–26 200              | 49         |
| Nigeria          | 1500–3160                           | —                          | 1          |
| Brazil           | <170–16 880                         | <30–8933                   | 3          |
| China            | 2770–14 000                         | <1–3                       | 50         |
| France           | <170–20 270                         | <30–12 560                 | 3          |
| Spain            | <170–19 280                         | <30–13 290                 | 3          |
| UK               | 60–63 000                           | —                          | 51         |
| Germany          | 15 000–15 900 <sup>a</sup>          | 13 100–14 700 <sup>a</sup> | 52         |
| Italy            | <4–15 300                           | <0.012–3530                | 53         |
| USA              | 7000–36 000                         | 11 900–26 200              | 54         |
| USA              | 11 500–26 300                       | 15 200–30 100              | 55         |
| Türkiye          | 110–21 650                          | —                          | 48         |
| Brazil           | <LOQ–42 800                         | 11 000–22 000              | 12         |
| Switzerland      | 560–30 400                          | 8300–12 600                | 56         |
| China            | 160–26 750                          | —                          | 57         |
| China            | 2580–14 700                         | —                          | 31         |
| Belgium          | <LOQ–2090                           | —                          | 11         |
| USA (Albany)     | —                                   | 0.0138–22 000 <sup>b</sup> | 58         |
| Other USA cities | —                                   | 0.998–12 000 <sup>b</sup>  | 58         |
| Japan            | —                                   | 0.546–6130                 | 58         |
| Korea            | —                                   | 0.09–11                    | 58         |
| Vietnam          | —                                   | 0.1–0.55                   | 58         |
| Switzerland      | 8000–17 000                         | —                          | 29         |

<sup>a</sup> Range of median values in samples collected in 2015, 2016 and 2017; LOQ: limit of quantitation. <sup>b</sup> Concentration detected in paper currency.

approximately 100 times.<sup>34</sup> However, the EDI values calculated for some bisphenol analogs, such as BPZ and BPP, do not exceed TDI, suggesting a lower risk of exposure to these substances. These findings underscore the need to reassess the potential risks of bisphenol exposure, especially considering the EFSA's more rigorous safety standards. Furthermore, they

highlight the importance of not overlooking health risks, even at low levels of exposure.

EDI values ( $\mu\text{g per kg per day}$ ) calculated in the current study were compared to EDI values detected in previous research (Table 4). To maintain consistency in EDI calculation and comparison of results with each other, BPA and BPS concentrations reported in the previously published literature were employed in eqn (1) along with the same HT, HF and AF parameters used in the calculations of the current study. As seen in Table 4, occupational or public exposure EDI values in Türkiye were lower than EDI values calculated for Nigeria, Brazil, France, Spain, China, Germany, the USA and Switzerland except for the EDI values calculated for some countries including Korea, Japan and Vietnam.<sup>61</sup> In this study, the results obtained for BPA in the case of public exposure were 7.5 times lower than the EDI values determined in Nigeria<sup>1</sup> and 42.5 times lower than a value calculated in another study in Türkiye<sup>55</sup> and Switzerland.<sup>56</sup> The EDI value for public exposure determined for BPS in this study was 325 times lower than that in Switzerland.<sup>56</sup> In the case of occupational exposure, the results obtained for BPA were 6.4 times lower than the EDI values determined in Nigeria,<sup>1</sup> 38.2 times lower than that in Switzerland<sup>56</sup> and 39.1 times lower than that in another study conducted in Türkiye.<sup>55</sup> The EDI value for occupational exposure determined for BPS in this study was 318 times lower than that in Switzerland.<sup>56</sup> The European Food Safety Authority (EFSA) and the U.S. Food and Drug Administration and European Commission Scientific Committee suggested the estimated tolerable intakes of BPA to be 0.0002  $\mu\text{g per kg bw per day}$ , 50  $\mu\text{g per kg bw per day}$ , and 10  $\mu\text{g per kg bw per day}$ , respectively.<sup>34</sup> In this manner, considering an adult with a body weight of 70 kg, it can be concluded that EDI values for public and occupational exposure determined based even on maximum values ( $\text{EDI}_{\text{occupational}}$ :  $6.61 \times 10^{-2} \mu\text{g per kg per day}$  for BPA and  $1.31 \times 10^{-2} \mu\text{g per kg per day}$  for BPS;  $\text{EDI}_{\text{public}}$ :  $1.32 \times 10^{-3} \mu\text{g per kg per day}$  for BPA and  $2.62 \times 10^{-4}$

**Table 3** Estimated daily intake ( $\mu\text{g per kg per day}$ ) values of BPs via dermal exposure from handling thermal receipt papers by the general population and occupationally exposed individuals, in Türkiye

|                                   | BPA                   | BPB                   | BPS                   | BPZ                   | BPF                   | BPP                   |
|-----------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| <b>EDI<sub>occupational</sub></b> |                       |                       |                       |                       |                       |                       |
| Minimum                           | $1.23 \times 10^{-4}$ | $2.27 \times 10^{-4}$ | $4.62 \times 10^{-6}$ | $4.58 \times 10^{-5}$ | $2.20 \times 10^{-4}$ | $8.36 \times 10^{-5}$ |
| Maximum                           | $6.61 \times 10^{-2}$ | $3.84 \times 10^{-3}$ | $1.31 \times 10^{-2}$ | $5.45 \times 10^{-5}$ | $3.58 \times 10^{-4}$ | $1.14 \times 10^{-4}$ |
| Mean                              | $2.23 \times 10^{-2}$ | $1.44 \times 10^{-3}$ | $1.95 \times 10^{-3}$ | $5.11 \times 10^{-5}$ | $2.63 \times 10^{-4}$ | $9.19 \times 10^{-5}$ |
| Median                            | $2.43 \times 10^{-2}$ | $1.19 \times 10^{-3}$ | $1.31 \times 10^{-5}$ | $5.16 \times 10^{-5}$ | $2.60 \times 10^{-4}$ | $8.75 \times 10^{-5}$ |
| 5th percentiles                   | $2.25 \times 10^{-4}$ | $7.49 \times 10^{-4}$ | $5.05 \times 10^{-6}$ | $4.70 \times 10^{-5}$ | $2.35 \times 10^{-4}$ | $8.40 \times 10^{-5}$ |
| 25th percentiles                  | $1.98 \times 10^{-2}$ | $9.49 \times 10^{-4}$ | $8.06 \times 10^{-6}$ | $4.96 \times 10^{-5}$ | $2.53 \times 10^{-4}$ | $8.54 \times 10^{-5}$ |
| 75th percentiles                  | $2.94 \times 10^{-2}$ | $1.70 \times 10^{-3}$ | $2.63 \times 10^{-5}$ | $5.24 \times 10^{-5}$ | $2.70 \times 10^{-4}$ | $8.90 \times 10^{-5}$ |
| 95th percentiles                  | $4.21 \times 10^{-2}$ | $3.24 \times 10^{-3}$ | $1.19 \times 10^{-2}$ | $5.38 \times 10^{-5}$ | $2.94 \times 10^{-4}$ | $1.09 \times 10^{-4}$ |
| <b>EDI<sub>public</sub></b>       |                       |                       |                       |                       |                       |                       |
| Minimum                           | $2.47 \times 10^{-6}$ | $4.55 \times 10^{-6}$ | $9.25 \times 10^{-8}$ | $9.16 \times 10^{-7}$ | $4.39 \times 10^{-6}$ | $1.67 \times 10^{-6}$ |
| Maximum                           | $1.32 \times 10^{-3}$ | $7.68 \times 10^{-5}$ | $2.62 \times 10^{-4}$ | $1.09 \times 10^{-6}$ | $7.16 \times 10^{-6}$ | $2.28 \times 10^{-6}$ |
| Mean                              | $4.45 \times 10^{-4}$ | $2.89 \times 10^{-5}$ | $3.90 \times 10^{-5}$ | $1.02 \times 10^{-6}$ | $5.26 \times 10^{-6}$ | $1.84 \times 10^{-6}$ |
| Median                            | $4.85 \times 10^{-4}$ | $2.39 \times 10^{-5}$ | $2.61 \times 10^{-7}$ | $1.03 \times 10^{-6}$ | $5.20 \times 10^{-6}$ | $1.75 \times 10^{-6}$ |
| 5th percentiles                   | $4.49 \times 10^{-6}$ | $1.50 \times 10^{-5}$ | $1.01 \times 10^{-7}$ | $9.39 \times 10^{-7}$ | $4.71 \times 10^{-6}$ | $1.68 \times 10^{-6}$ |
| 25th percentiles                  | $3.97 \times 10^{-4}$ | $1.90 \times 10^{-5}$ | $1.61 \times 10^{-7}$ | $9.92 \times 10^{-7}$ | $5.06 \times 10^{-6}$ | $1.71 \times 10^{-6}$ |
| 75th percentiles                  | $5.87 \times 10^{-4}$ | $3.41 \times 10^{-5}$ | $5.26 \times 10^{-7}$ | $1.05 \times 10^{-6}$ | $5.39 \times 10^{-6}$ | $1.78 \times 10^{-6}$ |
| 95th percentiles                  | $8.42 \times 10^{-4}$ | $6.48 \times 10^{-5}$ | $2.39 \times 10^{-4}$ | $1.08 \times 10^{-6}$ | $5.87 \times 10^{-6}$ | $2.18 \times 10^{-6}$ |



**Table 4** Comparison of EDI values ( $\mu\text{g}$  per kg per day) to the EDI values calculated using data reported in the literature for other countries, from handling thermal receipt papers by the general population and occupationally exposed individuals<sup>a</sup>

| Country                        | <i>n</i> | <i>C</i> ( $\mu\text{g}$ per g paper) |           | EDI ( $\mu\text{g}$ per day per kg BW)                     |  |          |              | Reference  |
|--------------------------------|----------|---------------------------------------|-----------|--|--|----------|--------------|------------|
|                                |          | BPA                                   | BPS       | BPA  |  | BPS      |              |            |
|                                |          |                                       |           | Public   | Occupational   | Public   | Occupational |            |
| Türkiye                        | 152      | 357**                                 | 31.3**    | 0.000445   | 0.022  | 0.000039 | 0.002        | This study |
| Nigeria                        | 80       | 2270*                                 | —         | 0.003  | 0.141  | —        | —            | 1          |
| Brazil                         | 22       | 13 100*                               | —         | 0.016  | 0.816  | —        | —            | 3          |
| France                         | 47       | 8440*                                 | —         | 0.011  | 0.525  | —        | —            | 3          |
| Spain                          | 43       | 9080*                                 | —         | 0.011  | 0.565  | —        | —            | 3          |
| China                          | 201      | 3610**                                | —         | 0.004  | 0.225  | —        | —            | 50         |
| Germany                        | 311      | 15 900**                              | 147 000** | 0.020  | 0.990  | 0.018    | 0.915        | 52         |
| USA                            | 33       | 19 300**                              | 14 600**  | 0.024  | 1.202  | 0.018    | 0.909        | 54         |
| Türkiye                        | 12       | 13 830**                              | —         | 0.017  | 0.861  | —        | —            | 48         |
| Brazil                         | 190      | 16 300***                             | 16 500*** | 0.020  | 1.015  | 0.021    | 1.027        | 12         |
| Switzerland                    | 100      | 13 500**                              | 10 200**  | 0.017  | 0.841  | 0.013    | 0.635        | 56         |
| China                          | 42       | 9380**                                | —         | 0.012  | 0.584  | —        | —            | 31         |
| Switzerland                    | 13       | 13 300**                              | —         | 0.017  | 0.828  | —        | —            | 29         |
| US, Korea,                     | 103      | 4.8–13 900                            | —         | $5.98 \times 10^{-6}$ <sup>b</sup> to $0.017$ <sup>c</sup> | $3.90 \times 10^{-5}$ <sup>b</sup> to $0.865$ <sup>c</sup> | —        | —            | 61         |
| Japan and Vietnam              |          |                                       |           |  |  |          |              |            |
| Various Countries <sup>d</sup> | 156      | $0.001^e$ – $77.1^f$                  | —         | $1.25 \times 10^{-9}$ to $9.60 \times 10^{-5}$             | $6.23 \times 10^{-8}$ to $4.80 \times 10^{-3}$             | —        | —            | 30         |

<sup>a</sup> \*Median value, \*\*mean value, \*\*\*geometric mean value, and EDI: Estimated Daily Intake ( $\mu\text{g}$  per kg per day). <sup>b</sup> Based on the 5th percentile concentration value. <sup>c</sup> Based on the 95th percentile concentration value. <sup>d</sup> United States, Canada, Czech Republic, Russia, Turkey, Australia, Brazil, Egypt, South Africa, China, India, Japan, Korea, Kuwait, Malaysia, the Philippines, Singapore, Thailand, Vietnam, and United Arab Emirates. <sup>e</sup> Min. value of reported mean concentrations. <sup>f</sup> Max. value of reported mean concentrations.

$\mu\text{g}$  per kg per day for BPS) in the current study for BPA and BPS were far below the limit values set by the U.S. Food and Drug Administration and European Commission Scientific Committee (Table 3). However, the majority of EDI values for BPA and BPS exceed the tolerable daily intake levels set by the EFSA, indicating that these compounds could pose a significant public health risk for both occupational and public exposures. On the other hand, the EDI values for BPZ and BPP remain well within EFSA limits, suggesting a comparatively lower risk associated with these compounds. Overall, these findings highlight the need for closer monitoring of BPA and BPS exposures and a thorough assessment of their potential health risks. Similarly, none of the daily EDI values determined in the studies conducted in the countries listed in Table 4 exceed the daily limit values set by the U.S. Food and Drug Administration and the European Commission Scientific Committee based on a 70 kg adult body weight, although they do exceed the value set by the EFSA.

Hazard Quotient (HQ) and Hazard Index (HI) values calculated in the current study for PCs detected in samples for general public and occupational exposure of adults *via* dermal contact with thermal receipt papers are given in Table 5 and hazard index (HI) values for BPs in thermal receipts are shown in Fig. 2.

HQ values calculated as the ratio of daily exposure to RfD for BPs ranged from  $2.47 \times 10^{-5}$  to 192 and  $4.93 \times 10^{-7}$  to 3.84 for occupational and public exposure, respectively. As seen in Table 5, the HQ values for BPA and BPS are generally well below 1, whereas the HQ values for other bisphenols are consistently

above 1, indicating that there is a potential health risk derived from bisphenols other than BPA, as these HQ values exceed 1. In addition, the cumulative risk assessment (HI) for all BPs was found to be in the range of 28.9–332 and 0.557–6.65 for occupational and public exposure, respectively. For occupational exposure, it was determined that there is significant concern for health risk as the HI exceeds 1, even when considering the minimum values, whereas for public exposure, the HI exceeds 1 only for values other than the minimum (Fig. 2).

**3.2.2 Probabilistic calculation.** The results of the probabilistic risk assessment for occupational and public exposure to BPs through dermal contact with thermal paper are shown in ESI Fig. S2–S5† and 3. The concentration (*C*) of BPs in the thermal paper ranged from  $1.98 \mu\text{g g}^{-1}$  to  $1061 \mu\text{g g}^{-1}$ ,  $3.65 \mu\text{g g}^{-1}$  to  $61.7 \mu\text{g g}^{-1}$ ,  $0.074 \mu\text{g g}^{-1}$  to  $210 \mu\text{g g}^{-1}$ ,  $0.735 \mu\text{g g}^{-1}$  to  $0.875 \mu\text{g g}^{-1}$ ,  $3.53 \mu\text{g g}^{-1}$  to  $5.75 \mu\text{g g}^{-1}$  and  $1.34 \mu\text{g g}^{-1}$  to  $1.83 \mu\text{g g}^{-1}$  for BPA, BPB, BPS, BPZ, BPF and BPP, respectively. The paper-to-skin transfer coefficient (*k*) ranged from 1072 to 21 522  $\text{ng s}^{-1}$  for all PCs.<sup>29,54</sup> The handling frequency (HF) was determined to be 3 and ranged from 96 to 150 times per day for public and occupational exposure, respectively.<sup>12,65</sup> The handling duration of receipts (HT) ranged from 5 to 10 s (ref. 31, 57 and 65) and the absorption fraction of bisphenol compounds by skin (AF) ranged from 2.3 to 46%.<sup>29,39,63</sup> Based on these parameters, the EDI from the thermal paper for occupational exposure to BPA, BPB, BPS, BPZ, BPF and BPP ranged from 0.004 to 16.0, 0.001 to 0.84, 0.0003 to 3.29,  $2.75 \times 10^{-5}$  to 0.0165, 0.0001 to 0.099 and  $5.97 \times 10^{-5}$  to 0.033 for BPA, BPB, BPS, BPB, BPF, and BPP, respectively (ESI Fig. S2†). For public

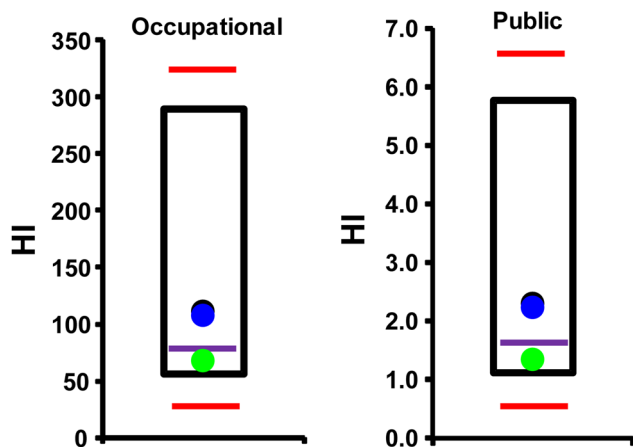


**Table 5** Hazard quotient (HQ) and hazard index (HI) values of BPs via dermal exposure from handling thermal receipt papers by the general population and occupationally exposed individuals, in Türkiye

|                  | HQ <sub>occupational</sub> |      |       |      |      |      | HI <sub>occupational</sub> |
|------------------|----------------------------|------|-------|------|------|------|----------------------------|
|                  | BPA                        | BPB  | BPS   | BPZ  | BPF  | BPP  |                            |
| Minimum          | 0.00002                    | 11.4 | 0.040 | 2.29 | 11.0 | 4.18 | 28.9                       |
| Maximum          | 0.013                      | 192  | 114   | 2.72 | 17.9 | 5.71 | 332                        |
| Mean             | 0.004                      | 72.2 | 17.0  | 2.56 | 13.1 | 4.60 | 109                        |
| Median           | 0.005                      | 59.7 | 0.114 | 2.58 | 13.0 | 4.37 | 79.8                       |
| 5th percentiles  | 0.00004                    | 37.4 | 0.044 | 2.35 | 11.8 | 4.20 | 55.8                       |
| 25th percentiles | 0.004                      | 47.5 | 0.070 | 2.48 | 12.6 | 4.27 | 66.9                       |
| 75th percentiles | 0.006                      | 85.2 | 0.229 | 2.62 | 13.5 | 4.45 | 106                        |
| 95th percentiles | 0.008                      | 162  | 104   | 2.69 | 14.7 | 5.46 | 289                        |

|                  | HQ <sub>public</sub> |      |       |       |       |       | HI <sub>public</sub> |
|------------------|----------------------|------|-------|-------|-------|-------|----------------------|
|                  | BPA                  | BPB  | BPS   | BPZ   | BPF   | BPP   |                      |
| Minimum          | 0.0000005            | 0.23 | 0.001 | 0.046 | 0.220 | 0.084 | 0.577                |
| Maximum          | 0.0003               | 3.84 | 2.28  | 0.054 | 0.358 | 0.114 | 6.65                 |
| Mean             | 0.0001               | 1.44 | 0.340 | 0.051 | 0.263 | 0.092 | 2.19                 |
| Median           | 0.0001               | 1.19 | 0.002 | 0.052 | 0.260 | 0.087 | 1.60                 |
| 5th percentiles  | 0.000001             | 0.75 | 0.001 | 0.047 | 0.235 | 0.084 | 1.12                 |
| 25th percentiles | 0.0001               | 0.95 | 0.001 | 0.050 | 0.253 | 0.085 | 1.34                 |
| 75th percentiles | 0.0001               | 1.70 | 0.005 | 0.052 | 0.270 | 0.089 | 2.12                 |
| 95th percentiles | 0.0002               | 3.24 | 2.08  | 0.054 | 0.294 | 0.109 | 5.78                 |

**Fig. 2** Hazard index (HI) of PCs (top and bottom borders of the boxes represent the 5th and 95th percentiles, green and blue circles represent the 25th and 75th percentiles, horizontal red lines show the minimum and maximum values, and black circles and the horizontal purple line represent the mean and median concentrations, respectively).

exposure to BPA, BPB, BPS, BPB, BPF, and BPP, EDI values ranged from 0.0002 to 0.573,  $3.52 \times 10^{-5}$  to 0.036,  $1.25 \times 10^{-5}$  to 0.117,  $1.04 \times 10^{-6}$  to 0.0006,  $6.58 \times 10^{-6}$  to 0.004 and  $2.37 \times 10^{-6}$  to 0.001, respectively (ESI Fig. S3<sup>†</sup>). The hazard quotient (HQ) values for BPs in receipts are shown in ESI Fig. S4 and S5,<sup>†</sup> while hazard index (HI) values are shown in Fig. 3. For occupational exposure, HQ<sub>occupational</sub> ranged from 0.0006 to 3.55, 27.3 to 47 878, 5.14 to 25 258, 1.19 to 843, 6.70 to 4775 and 2.41 to 1599 for BPA, BPB, BPS, BPZ, BPF and BPP, respectively (ESI

Fig. S4<sup>†</sup>). In contrast, for public exposure, HQ<sub>public</sub> ranged from  $2.47 \times 10^{-5}$  to 0.123, 1.01 to 2018, 0.231 to 937, 0.057 to 29.8, 0.312 to 175 and 0.099 to 57.6 for BPA, BPB, BPS, BPZ, BPF and BPP, respectively (ESI Fig. S5<sup>†</sup>). These findings suggest that certain chemicals, particularly BPB, BPS, and BPF, exhibit high HQ values under both occupational and public exposure scenarios, indicating potential health risks. The wide range of HQ values observed for BPB (occupational: 27.3 to 47 878; public: 1.01 to 2018), BPS (occupational: 5.14 to 25 258; public: 0.231 to 937), and BPF (occupational: 6.70 to 4775; public: 0.312 to 175) points to significant health concerns in both exposure scenarios. Although BPA and BPZ generally show lower HQ values, in some cases, they exceed acceptable levels (HQ < 1), which is notable and requires further investigation. The fact that many HI values exceed 1 in both occupational and public exposure highlights a substantial health risk, emphasizing the necessity for stringent monitoring and the implementation of protective measures across both exposure scenarios. The cumulative risk assessment (HI) for all BPs was found to be in the range of 572 to 50 638 and 26.6 to 2136 for occupational and public exposure, respectively. As a result of probabilistic calculations, 90% of the HI data for occupational exposure were found to be between 2500 and 22 500, and 90% of the HI data for public exposure were found to be between 104 and 914 (Fig. 3). These data suggest that occupational exposure poses a significant health risk, while public exposure levels are also considerable, with both scenarios showing instances where the HI > 1 limit is exceeded. This highlights the need for close monitoring of BP exposure and the implementation of risk management strategies both in the workplace and among the



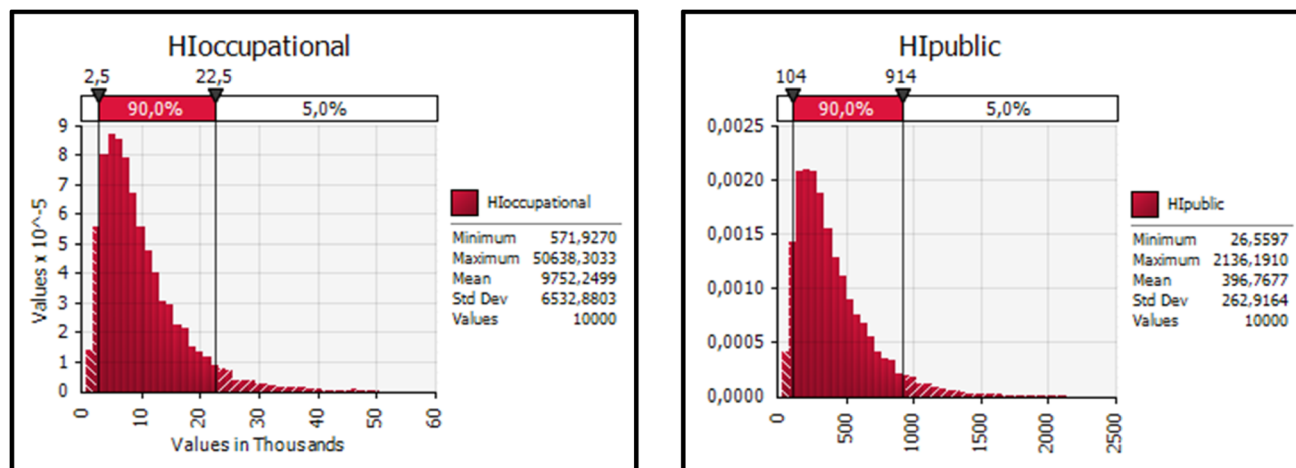


Fig. 3 Hazard index (HI) for BPs in thermal papers.

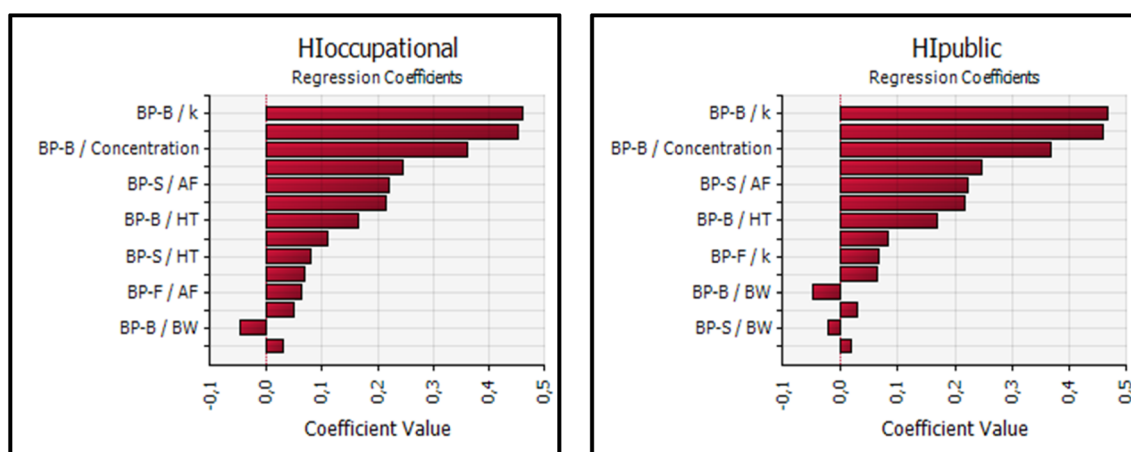


Fig. 4 Sensitivity analysis of the hazard index (HI) for BPs in occupational and public exposure groups.

general population to address the potential health risks associated with these exceedances.

**3.2.3 Sensitivity analysis.** A sensitivity analysis was conducted to determine the most influential variables in risk assessment calculations. ESI Fig. S6–S9† and 4 show the results of sensitivity analysis of EDI, HQ and HI for occupational and public groups exposed to BPs *via* dermal contact with thermal papers. ESI Fig. S6 and S7† show that the most effective parameters for EDI calculations in both occupational and public exposure scenarios are the absorption fraction of bisphenol compounds by skin (AF) and the paper-to-skin transfer coefficient ( $k$ ). These parameters exhibit the highest positive impact on EDI across all bisphenol types, while body weight (BW) consistently shows a minimal negative correlation, indicating that a higher body weight slightly reduces the estimated intake. Similarly, ESI Fig. S8 and S9† reveal that AF and  $k$  are also the dominant parameters in determining HQ values in both occupational and public exposure. Additionally, the concentrations of certain bisphenols, particularly BPB and BPS, significantly contribute to the overall risk assessment. As

observed with EDI, BW has a minor negative impact on HQ values. In Fig. 4, the sensitivity analysis identifies the paper-to-skin transfer coefficient ( $k$ ) and the concentration of BPB as the most effective parameters in calculating the Hazard Index (HI) for both occupational and public groups. These parameters have the highest positive influence on the HI, with BPS and BPF also showing some impact, though to a lesser extent compared to BPB. Therefore, reducing the migration of BPB from thermal papers could be one of the ways to mitigate non-carcinogenic risks. As in the other analyses, BW shows a minimal negative correlation with HI, suggesting that higher body weight may slightly reduce the risk.

These findings underscore the critical role of parameters like AF and  $k$  in the risk assessment of bisphenol exposure. Reducing these factors could effectively lower the associated health risks. The consistent influence of these parameters across both EDI and HQ calculations highlights their importance in developing strategies to manage and mitigate potential health risks in both occupational and public environments.



## 4 Conclusion

To the best of our knowledge, the current research is the first comprehensive study reporting PC concentrations in thermal paper receipts in Türkiye. BPA and BPS were the most frequently used bisphenol varieties in all thermal paper receipts, but BPB, BPZ, BP-F and BPP were also observed in the samples. BPS seems to be the main technical alternative to BPA in Türkiye. The model developed by the European Food Safety Agency (EFSA) estimates a typical daily dermal exposure rate of 0.059 µg per kg bw (ref. 52) for BPA. In the current study, the public and occupational daily exposure rates of BPA (based on the mean concentration value detected in the analysed samples) for a 70 kg body weight adult correspond to  $4.45 \times 10^{-4}$  µg per kg bw and 0.022 µg per kg bw, respectively. Hence, when comparing the results of the current study to the EFSA model, it is observed that public and occupational exposure rates are lower. Nevertheless, further studies are needed to better characterize the occurrence of bisphenols in thermal papers used in Türkiye and to assess the contribution of thermal papers to human exposure to BPA and to its proposed alternatives. Additionally, the presence of higher BPA levels in thermal papers may act as a contamination agent for “BPA” free waste paper during the recycling/reprocessing of paper and paper products.

As in studies conducted in other parts of the world, BPA is still the most common color developer reported in thermal papers in Türkiye, followed by BPS, although its potential toxic effects are already widely known. Data on the occurrence and levels of BPA alternatives other than BPS in the abiotic environment are still scarce; however, such data are essential to understand the environmental fate of these chemicals. While the environmental persistence of BPA is considered very low, on the other hand, the environmental persistence of BPS is considered moderate. The ubiquitous occurrence of BPA and its less toxic analogues such as BPS, BPF and BPAF in the environment poses threats to both humans and wildlife. Several regulatory organizations across the world have established reference doses/safe limits for daily human BPA exposure because of its public health implications. However, different cells and organs may be impacted differently by the same amount of BPA depending on their level of sensitivity. Therefore, the best approach to avoid the toxicity of these chemicals is minimizing exposure to them in daily life.

## Consent to publish

All the authors have given their consent for publishing the manuscript.

## Data availability

All data and materials reported in the article are included in the manuscript and can be found in the ESI file.†

## Author contributions

Conceptualization: Perihan Binnur Kurt-Karakus. Data curation: Perihan Binnur Kurt-Karakus, Merve Özkaleli Akçetin, and

Nebile Daglioğlu. Formal analysis: Merve Özkaleli Akçetin and Perihan Binnur Kurt-Karakus. Investigation: Merve Özkaleli Akçetin, Hatice Kübra Gül, and İsmail Ethem Gören. Methodology: Merve Özkaleli Akçetin, Hatice Kübra Gül, İsmail Ethem Gören, and Nebile Daglioğlu. Supervision: Perihan Binnur Kurt-Karakus and Nebile Daglioğlu. Visualization: Merve Özkaleli Akçetin and Perihan Binnur Kurt-Karakus. Writing – original draft: Merve Özkaleli Akçetin and Perihan Binnur Kurt-Karakus. Writing – review & editing: Perihan Binnur Kurt-Karakus, Nebile Daglioğlu, and Hatice Kübra Gül.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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