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Sanitary pads and diapers contain higher phthalate contents than those in common commercial plastic products

Chan Jin Park^{a,1}, Radwa Barakat^{a,b,1}, Alexander Ulanov^c, Zhong Li^c, Po-Ching Lin^a, Karen Chiu^a, Sherry Zhou^a, Pablo Perez^a, Jungyeon Lee^d, Jodi Flaws^a, and CheMyong Jay Ko^{a,*} ^aDepartment of Comparative Biosciences, College of Veterinary Medicine, University of Illinois at Urbana-Champaign, Urbana, IL 61802, USA

^bDepartment of Toxicology, Faculty of Veterinary Medicine, Benha University, Benha 13518, Egypt ^cMetabolomics Center, University of Illinois at Urbana-Champaign, Urbana, IL 61802, USA ^dTV Chosun Broadcasting, 33, Sejong-daero 21-gil, Jung-gu, Seoul 04519, Korea

1. Introduction

Most women of reproductive age use sanitary pads during their menstrual periods for an average of 1800 days in their lifetime [1]. Similarly, the diaper is a hygiene product that is in direct contact with the external genitalia of infants and toddlers for several months to years [2]. In recent years, synthetic plastic materials have been used as liquid absorbents to improve the functionality and softness of sanitary pads and diapers [3]. However, some of these plastic materials release volatile organic compounds (VOCs) and endocrine-disrupting chemicals [4–6], potentially posing risks to women and children who use them [7–9]. In particular, since VOCs and phthalates are absorbed through the skin [2, 10–13], it is necessary to understand whether household products such as sanitary pads and diapers that contact the skin contain these chemicals. As a result, the safety of sanitary pads or diapers is becoming a world-wide public health concern with growing suspicions that some substances in those products may adversely influence the health of women and children.

In the summer of 2017, South Korean media outlets reported a few newly marketed brands of commercial sanitary pads containing VOCs [14, 15] with a high degree of suspicion that these chemicals might be the causes of menstrual irregularities as some of the consumers experienced after using the particular branded pads [16]. Soon, the issue became a societal concern after the public became aware that sanitary pads in direct contact with the skin around the external genitalia were likely causing menstrual irregularities. The skin of this area tends to be thinner and more absorbent than those of others such as the hands [17]. In response to these concerns and confusions, we decided to undertake an independent small-scale measurement of VOCs and phthalates in commercially available sanitary pads and

Conflicts of interest

^{*}Corresponding author at the Department of Comparative Biosciences, College of Veterinary Medicine, University of Illinois at Urbana-Champaign, Urbana, IL 61802, USA, jayko@illinois.edu (C.J. Ko), Tel.: +1 217 333 9362 (C.J. Ko). ^IThese authors contributed equally to this work.

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diapers sampled from South Korea and other countries. To estimate the risk of the VOCs contained in sanitary pads and diapers, the measured contents from these hygienic products were compared with publicly available measurement data from other consumer products such as beverages, foods, and plastic wares and also with the regulatory guidelines for such products.

We measured VOCs contents primarily because they were reportedly detected in the sanitary diapers and suspected to be the causes of menstrual irregularities. VOCs are released from a variety of anthropogenic sources such as cleaning products, paints, solvents, personal care products, and tobacco smoke [18]. Previous studies assessed the exposure level to VOCs by measuring their contents in the air, urine, and water [19, 20]. VOCs increase the risk for neurocognitive impairment, asthma, congenital disability, and cancer [21]. Notably, exposure to methylene chloride, toluene, and xylene are known to negatively affect the development and function of reproductive system [22–25]. However, to date, no study has measured VOC contents in the sanitary pads and diapers or reported their impact on female reproductive function and child health.

We included phthalates in our measurement because studies in animal models indicated that phthalates might disrupt menstrual cycles [26, 27] and that a particular subsets of phthalates such as di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), and benzyl butyl phthalate (BBP) are routinely detected in women [28–30]. Phthalates are widely used plasticizers found in common consumer products such as medical devices, feminine hygiene products, cosmetics, toys and childcare articles [31–33]. They are non-covalently bound to plastics and are easily released from them and absorbed into the body by inhalation, ingestion, and dermal absorption, thus resulting in systemic contact [34]. Exposure to phthalates is known to affect the development and functions of the cardiovascular, reproductive and endocrine systems [27, 35–38].

2. Methods

2.1. Sample preparation

Sanitary pads and diapers were collected from markets in Korea, Japan, Finland, France, Greece, and the United States (Supplementary Table 1). To measure VOC contents, air (750 μ L) was taken from the center of each pack of sanitary pads or diapers using a sample lock syringe (gas-tight) and then injected directly into a gas chromatograph. The procedure was carried out at the University of Illinois Metabolomics Center (http://biotech.illinois.edu/metabolomics).

To measure phthalate contents, a single pad or diaper from each pack was weighed before sample collection. Samples of one square centimeter (1 cm^2) were collected using clean scissors from four different locations of each pad or diaper (Figure 1). They were weighed together and placed in a 20 mL glass vial. Then, 6 mL of 80% methanol (v/v) was added to the vial and kept on a rocker for 15 minutes for extraction. Next, 1 mL was transferred from the vial to a new 2 mL glass vial. The samples were analyzed by LC/MS/MS at the University of Illinois Metabolomics Center.

2.2. Measurement of VOCs by GC/MS

The VOC contents were measured by using a GC/MS system (Agilent Inc., CA, USA) consisting of an Agilent 7890B gas chromatograph and an Agilent 5977A MSD. Separation was performed on a ZB-624 (30 m × 0.32 mm I.D. and 1.4 μ m film thickness) capillary column (Phenomenex, CA, USA). The inlet, MSD interface, and ion source temperatures for the GC/MS system were adjusted to the following, respectively: 1800°C, –230°C, and 230°C. An aliquot of 750 μ L air/gas was injected with a gastight syringe (Hamilton, HV, USA) in a split-less mode (9mL/min @ 2min). The helium carrier gas was kept at a constant flow rate of 1.1 mL/min. The temperature was programmed to 5 min isothermal heating at 40°C followed by a temperature increase of 20°C/min until it reached 200°C. The mass spectrometer was operated in positive electron impact mode (EI) at 69.9 eV ionization energy at m/z 33–300 scan range. Mass spectra were recorded in a combined scan/SIM mode. For a SIM mode, m/z fragments were tracked: 84 (methylene chloride), 92 (toluene) and 106 (xylenes). Target peaks were evaluated using the Mass Hunter Quantitative Analysis B.08.00 (Agilent Inc., CA, USA) software. Target peaks indicate the chemical-specific peaks in presented histogram (Figure 2).

2.3. Measurement of phthalates by LC/MS/MS

Samples were analyzed with the 5500 QTRAP LC/MS/MS system (Sciex, Framingham, MA), and Software Analyst 1.6.2 was used for data acquisition and analysis. The 1200 series HPLC system (Agilent Technologies, Santa Clara, CA) includes a degasser, an auto-sampler, and a binary pump. The LC separation was performed on a C6-phenyl Phenomenex column $(2 \times 100 \text{ mm}, 3\mu\text{m})$ with mobile phase A (0.1% formic acid in water) and mobile phase B (0.1% formic acid in acetonitrile). The flow rate was 0.25 mL/min. The linear gradient was: 0–1min, 90% A; 10–16min, 0% A; 17–21min, 90% A. The auto-sampler was set at 10°C, and the injection volume was 10µL. Mass spectra were acquired under both positive (ion spray voltage was +5500 V) and negative (ion spray voltage was -4500 V) electrospray ionization (ESI). The source temperature was 450°C. The curtain gas, ion source gas 1, and ion source gas 2 were 32, 65, and 55, respectively. Multiple reaction monitoring (MRM) was used for quantitation: in the positive ESI, DBP m/z 279.2 --> m/z 149.0; DEP m/z 223.1 --> m/z 149.0; DEHP m/z 391.4 --> m/z 149.0, and BBP m/z 313.1 --> m/z 149.0 (Figure 2).

2.4. Quantitation of measurements

For quantification of VOC contents, 1 mL of each standard was placed into a sealed glass vial and vaporized under room temperature with the following dilutions using a gas tight syringe: an aliquot of 25 μ L was taken with gas-tight syringe from the stock vapor and transferred into another sealed vial. The glass vial volume was measured before dilution, and concentrations in each vial were measured in parts per billion (ppb). Sample concentrations were calculated based on a calibration curve obtained from standard dilutions (concentration/peak area). Methylene chloride, toluene, and xylenes were confirmed by certified standards (Fisher Scientific International, Inc., NH, USA) and quantified using 518 ppb, 6.7 ppb, 0.09 ppb, 0.0011 ppb standard mixture dilutions. In the quantitative analysis, the limit of quantitation is 0.001 ppb for each VOC. The actual VOC concentration in samples were presented as respective calculated value/volume of collected air samples. The

data were expressed by average \pm SEM (standard error mean, pbb, n=3–5, numbers of packs per brand). The concentrations of phthalates were calculated using the LC/MS/MS data and were expressed by average \pm SEM (standard error mean, ppb, n=3–5, numbers of packs per brand). The quantitation limit is 0.1 ppb (0.1 ng/mL) for DBP/DEHP/DEP and 0.05 ppb (0.05 ng/mL) for BBP. Certified Standards for each phthalate were purchased from Sigma-Aldrich (St. Louis, MO). The actual phthalate concentration in samples were presented as respective calculated value/weight of excised samples. The concentrations were used to calculate the total content per pad or diaper.

2.5. Statistical analysis

The data were analyzed using the statistical software package SPSS. Average concentrations of each VOC and phthalates were calculated from all sanitary pad or diaper products. To determine if the average VOC or phthalates content of each product was significantly higher than the product average, Student's t-tests were performed between the overall average of each VOC or phthalates and average VOC or phthalate content of each product. Statistical significance was assigned as p 0.05 and marked as (*). The data are expressed as mean \pm SEM.

3. Results

3.1. VOC contents in sanitary pads

The levels of methylene chloride, toluene, and xylene were measured in the air of the sanitary pad and diaper packages (Table 1). The GC/MS analysis detected methylene chloride in two sanitary pad packages: Brand-2 (0.028 ppb) and -6 (0.008 ppb). The package of Brand-2 contained significantly higher (p<0.01) methylene chloride than the average of all products tested. Toluene was detected in packages from nine brands, except Brand-10 and -11. The packages of Brand-3 (5.230 ppb) and -4 (5.471 ppb) contained significantly higher concentration of toluene (p<0.01) than the average of all products. Xylene was detected in all of the sanitary pad packages. In Brand-11, m-xylene and o-xylene were not detected. The highest concentrations of m-xylene (0.192 ppb) and p-xylene (0.278 ppb) were found in Brand-2. Brand-2 (0.263 ppb), Brand-3 (0.276 ppb), and Brand-4 (0.287 ppb) contained the highest concentration of o-xylene among the sanitary pad packages. The Brand-2 package contained significantly higher (p<0.01) m-xylene and p-xylene than the average of all products.

3.2. VOC contents in commercial diapers

In the diaper packages, methylene chloride was not detected by GC/MS analysis, but all contained toluene and xylene as determined by the GC/MS measurement (Table 2). Brand-A (0.397 ppb) had the highest concentration of toluene. The highest concentrations of xylene, including m-, p-, and o-xylene, were measured in Brand-C (0.013, 0.014, and 0.021 ppb, respectively).

3.3. Phthalate content in commercial sanitary pads

Phthalate (DBP, DEHP, DEP, and BBP) concentrations were measured in 11 different brands of sanitary pads (Table 3). BBP was not detected in any of sanitary pads tested. However,

every sanitary pad contained DBP (52.1-7,820.4 ppb) and DEHP (5.5-197.4 ppb). The highest concentration of DBP was measured in Brand-1 (7,820.4 ppb) (p<0.01). While DEHP concentration was lower than DBP concentration in each sample measured, Brand-1 (134.5 ppb) and Brand-4 (197.4 ppb) contained significantly higher concentration than the average of all sanitary pads examined (p<0.05, p<0.01; respectively). The highest concentration of DEP was found in Brand-6 (134.3 ppb), which was significantly higher than average of all sanitary pads examined (p<0.03). DEP was not detected in Brand-2, -5, -10, and -11. Brand-10 and Brand-11 had the lowest total phthalate concentrations.

3.4. Phthalate contents in commercial diapers

Phthalate (DBP, DEHP, DEP, and BBP) concentrations were measured in four different diaper brands (Table 4). BBP was not detected in any diapers. However, every diaper contained DBP (13.4–1,609.7 ppb) and DEHP (12.6–62.8 ppb). Brand C had the highest concentration of DBP (1,609.7 ppb) while Brand-D had the highest concentration of DEHP (62.8 ppb). DEP was found only in Brand-C (0.8 ppb) and Brand-D (2.9 ppb).

4. Discussion

This study found that a majority of sanitary pads or diapers surveyed in this study contained both VOCs and phthalates with varying amounts measured among them. The packages of Brand-3 and -4 sanitary pads contained the highest total VOC concentration (5.676 ppb and 5.956 ppb, respectively) (Table 1), and Brand-1 sanitary pads contained the highest total phthalate concentration (8,014.9 ppb) (Table 3). In the following, the amount of VOCs and phthalates measured in the sanitary pads and diapers are compared with previously reported contents of VOCs (Table 5) and phthalates (Table 6) in other consumer products and their potential impact on health discussed.

Methylene chloride is a VOC that dissolves in a wide range of organic compounds, which makes it a useful solvent. This chemical compound is used in a variety of industrial applications such as adhesives, paints and coating products, pharmaceuticals, and aerosols [39]. A study showed that animals exposed to methylene chloride experienced behavioral alterations and also induced developmental abnormalities in their offspring. This is supported by another finding that methylene chloride can cross the placenta [40]. Studies found methylene chloride in human breast milk, indicating potential postnatal exposure via breast feeding [41]. A recent study showed that prolonged contact with methylene chloride caused chemical burns in the skin [31]. Our measurement revealed that neither sanitary pads nor diapers contained methylene chloride at the level of concern (Tables 1 and 2).

Toluene is a volatile aromatic hydrocarbon that is used mainly in blending motor gasoline but also as a solvent for paints, thinners, adhesives, inks, fabric dyes, and cosmetics [42]. In air samples from packages of sanitary pads, the highest concentration measured was 5.471 ppb (Table 1). This concentration is similar to reported toluene levels in residential indoor air [43] but higher than those measured in the airs of new cars [44] (Table 6). Toluene crosses the placenta and has been detected in amniotic fluid and breast milk [45]. Previous animal studies showed that toluene administered to pregnant females increased fetal mortality, caused developmental defects, and induced neurobehavioral toxicity [42, 46]. In

humans, toluene vapor is rapidly absorbed from the respiratory tract through inhalation and is absorbed via skin [47]. The skin absorption rate of toluene is higher than those of benzene and tetrachloroethylene (perclene) [9]. The absorption rate of toluene in mouse skin was 16.38 mg/cm²/h when they were exposed to 1,000 ppm solvent vapor. The rate of toluene absorption is proportional to its concentration. If human skin is exposed to the measured 5.471 ppb of toluene, the absorption rate will be $0.09 \ \mu g/cm^2/h$ (5.471 ppb/1000 ppm x 16.38 mg/cm²/h x 24 h/day = 2.15 $\mu g/cm^2/day$). Assuming a contact area of skin by a sanitary pad of 250 cm² (25 cm x 10 cm), the skin making a contact with a sanitary pad may absorb as much as 537.7 $\mu g/day$ (2.15 $\mu g/cm^2/day x 250 \text{ cm}^2$). The Reference Dose (RfD) for toluene is 20 $\mu g/kg/day$ [48]. Therefore, if a woman who weighs 70 kg were exposed to such amount, the absorption rate would be 7.7 $\mu g/kg/day$ (537.7 $\mu g/day/70$ kg, predicted daily absorption rate / RfD x 100) (See supplementary Table 2).

Xylene is an aromatic hydrocarbon widely used in manufacturing a variety commercial products including medical devices as a solvent [49]. In air samples from packages of sanitary pads, the highest xylene concentration measured was 0.757 ppb (Table 1), which was much lower than in residential indoor air [43] or new cars [44] (Table 5). In a wholebody inhalation exposure experiment conducted on pregnant Sprague Dawley rats (gestation day 6-20 inclusive, 6 h/day), the no observed/lowest observed adverse effect level (NOAEL and LOAEL) for developmental toxicity was 100 ppm and 500 ppm (o-xylene), respectively [50]. The study also found that VOCs adversely affect the systemic and neuronal development as well. A study with a human cohort showed that in utero exposure to oxylenes (OR=1.42 [1.19-1.70]) or m/p-xylene (OR=1.51 [1.26-1.82]) increased the risk of developing childhood autism [51]. Exposure to xylene occurs via inhalation, ingestion, or eye or skin contact. The main consequences of inhaling xylene vapor are neuropsychological and neurophysiological dysfunction accompanied by as headache, dizziness, nausea, and vomiting [52]. Moreover, frequent or prolonged skin contact with xylene causes irritation, dermatitis, dryness, and skin cracking [53]. In humans, the absorption rate of the liquid form of xylene through the skin is from 4.5 to 9.6 $mg/cm^2/h$, which is about 3 times lower than that of toluene $(14-23 \text{ mg/cm}^2/\text{h})$ [11]. If human skin is exposed to 0.757 ppb of xylene, the absorption rate will be 0.004 μ g/cm²/h (0.757 ppb / 1000 ppm x 16.38 mg/cm²/h / 3, = 0.10 μ g/cm²/day) based on reported studies on xylene absorption rate. Assuming a contact area of skin by a sanitary pad of 250 cm^2 , skin making a contact with a sanitary pad may absorb as much as 24.8 μ g of xylene per day (0.10 μ g/cm²/day x 250 cm²). The RfD for xylene is 2 mg/kg/day [54]. If a woman who weighs 70 kg is exposed to such amount, the predicted daily absorption rate will be 0.35 μ g/kg/day (24.8 μ g/day / 70 kg). Hence, based upon this calculation, she may absorb 0.02% of RfD (predicted daily absorption rate / RfD x 100) (See supplementary Table 2).

The Guideline on Establishment of Test Item in Preparation of Standards and Analytical Methods of Quasi-Drugs of South Korea's Ministry of Food and Drug Safety (MFDS) (2016; http://www.mfds.go.kr/eng/eng/download.do?

boardCode=17840&boardSeq=71866&fileSeq=1) has only four criteria (pigments, acid and alkali, fluorescent whitening agent, and formaldehyde) to determine the safety of sanitary pads. All that is needed to market a diaper is to submit a "conformity" confirmation from the

third inspection agency in Korea. This suggests the possibility of human exposure to other hazardous chemicals contained in sanitary pads and diapers. In August 2017, a company that produced some of the products tested in this study officially announced that their products meet the Oeko-Tex Standard 100, class 1 of Europe (toluene <30 ppb for fabric, xylene <10 ppm for accessories, methylene chloride <1 ppm for accessories) and the VOC content standards for drinking water (toluene <1 ppm, xylene <10 ppm, methylene chloride <5 ppb; National Primary Drinking Water Regulations, EPA) [55]. The VOC concentrations in the sanitary pad and diaper packages (Tables 1 and 2) measured in this study met the above criteria. However, we found that there was a difference in concentration depending on the brands. Of note, Brand-4 sanitary pad package contained a 5,900-fold higher total VOC contents than Brand-11 (Table 1). In diapers, 3- to 63-fold differences of VOC (Table 2) concentrations were seen among the brands. These results show that there is a considerable difference in the concentration of VOCs among the sanitary pad and the diaper products.

Phthalate contents were also vastly different among the brands surveyed (Table 3 and 4). All of the sanitary pads and diapers examined contained DBP (52.1–7,820.4 ppb in sanitary pads, 13.4–1,609.7 ppb in diapers) and DEHP (5.5–197.4 ppb in sanitary pads, 12.6–62.8 ppb in diapers). Sanitary pads from seven brands and diapers from two brands contained DEP (8.1–134.3 ppb in sanitary pads, 0.8–2.9 ppb in diapers). Of note, Brand-1 sanitary pads contained 130-fold higher total phthalate content than Brand-11 (Table 3). The highest concentration of DBP detected in sanitary pads (Table 3) and diapers (Table 4) were 7,820.4 ppb and 1,609.7 ppb, respectively. These concentrations are considerably higher than concentrations detected in package film [56], paper cups [57], and even cereals [58] (Table 6). The highest DEHP concentrations detected in sanitary pads (Table 3) and diapers (Table 4) were 197.4 ppb and 62.8 ppb, respectively; these are higher than the DEHP concentrations in paper cups [57], package film [56], and microwavable boxes [56] (Table 6). Moreover, the highest concentration of DEP measured in a sanitary pad was 134.3 ppb, which is higher than DEP concentrations in condiments [58], plastic cups [56], cereals [58] and many plastic products [56] (Table 6).

Among the phthalates, oral exposure to DBP was reported to decrease maternal weight gain, fetal weight gain, food consumption, and increase miscarriages in rats [59, 60]. Furthermore, prenatal DEHP exposure (20 and 200 µg/kg/day and 500 and 750 mg/kg/day) from gestation day 10.5 until birth increased uterine weight, decreased anogenital distance, disrupted estrous cyclicity, and reduced fertility, which likely resulted from the anti-androgenic effect of DEHP [61, 62]. Exposure to DEHP during fetal development altered follicular recruitment and development, eventually causing premature ovarian failure [34]. In a recent Japanese diaper study, DEHP and DBP were detected in the top sheets and determined to be 600 ppb and 200 ppb, respectively [2]. When taken with our work, which detected DEHP and DBP with a concentration of 12.6-62.8 ppb and 13.4-1,609.7 ppb from an entire layer including top sheet to back sheet, the Japanese study indicates that DEHP is likely concentrated in the top sheet of the diaper, while DBP present in all layers. Low-molecularweight phthalates such as DBP, DEP, and DEHP readily dissolve into lipids in the epidermis of the skin and are taken up by systemic circulation [10]. The testicular development during infancy influence the pubertal onset and normal adult fertility [63]. Because the top sheet of the diaper is in direct contact with the external genitalia of the newborn, phthalates in the top

sheet can be absorbed into the skin and adversely impact the development and function of the reproductive and urinary systems. Compared to other parts of human body, scrotum showed the highest dermal absorption rate for parathion (4 ppm in acetone) with a 5.5-fold and 9.1-fold increased absorption rates when compared to abdominal skin and palm, respectively [64]. Vulvar tissue is more permeable to most of chemicals than other skins due to it is hydrated, thin and extensively vascularized [17]. Due to the high absorbency for chemicals, vaginal tissue is often used as a drug delivery route [65]. Thus, repeated wearing of sanitary pads and diapers makes the tissue vulnerable to toxicants released from the sanitary pads or diapers.

Due to their reproductive toxicity, some of phthalates are classified as Category 1B by European authorities. Particularly, DEHP, DBP, DiBP and BBP are banned from using them in producing toys, baby care products, cosmetics, and medical devices [66, 67]. According to the renewed Directive (EU) 2015/863, contents of four phthalates, DBP, DEHP, BBP, and DIBP, will be restricted to < 0.1% in all electrical and electronic equipment (from 22 July 2019) and medical devices (from 22 July 2021) after the grace periods end [68]. The use of DEHP, BBP, and DBP in toys is already subject to REACH Regulation (EC) No 1907/2006. This regulation limits the total DEHP+DBP+BBP content to be lower than 0.1% (1,000 ppm) and total DINP + DIDP + DNOP content lower than 0.1% in toys and child care products [69]. Obviously, the concentrations of phthalates contained in the sanitary pads and diapers measured in this study were below the European guidelines. However, recent reports showed that environmentally relevant exposure to phthalate $(20-200 \mu g/kg/day)$ induced severer reproductive toxicity and behavioral disorders than exposure to a considerably higher dose (500-750 mg/kg/day) in rodents [70, 71], raising a question if exposure to a low dose is always safer. In our result, sanitary pads containing maximum 7,820.4 ppb (7.82 mg/kg), and each pad of Brand-1 (6.8 g) containing 0.05 mg of DBP. In a previous study using hairless guinea pig, *in vivo* absorption of DBP after dermal application was 62% [12]. According to this, if a woman wore the sanitary pad (Brand-1), daily absorption of DBP will be 0.03 mg (0.05 mg/day x 62%). If a woman who weighs 70 kg is exposed to such amount, the absorption rate will be 0.47 μ g/kg/day (0.03 mg/day / 70 kg, predicted daily absorption rate). The RfD for DBP is 0.1 mg/kg/day [72]. Hence, based upon this calculation, she may absorb 0.47% of RfD (predicted daily absorption rate / RfD x 100) from sanitary pad (See supplementary Table 2).

5. Conclusions

This study found that most of sanitary pads or diapers surveyed contained both VOCs and phthalates. The amounts measured were different among the brands and was below the RfD. However, daily absorption of toluene from sanitary pad reached to the maximum of 38.4% RfD. Given the fact that women are exposed to various chemicals through various routes, consideration should be given to the risks of chemicals that are additionally absorbed from the sanitary pad. This finding raises a concern for the safety of using some of the products and a need for efforts to reduce VOC and phthalate contents. Most of all, the physical location of the exposure site, the high absorption rate of the genitalia for chemicals, and the long-term exposure period demand a thorough investigation on the potential impact of the exposure to VOCs and phthalates. This manuscript is a report of a preliminary investigation,

which calls for future studies into the potential health risk of using sanitary pads and diapers with high VOC or phthalate contents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

BBP	Benzyl butyl phthalate
DBP	Di-n-butyl phthalate
DEHP	Di-2-ethylhexyl phthalate
DEP	Diethyl phthalate
EPA	Environmental Protection Agency
EU	European Union
GC/MS	Gas chromatography-mass spectrometry
LC/MS/MS	Liquid chromatography-tandem mass spectrometry
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RfD	Reference Dose
VOCs	Volatile organic compounds

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Figure 1. Sample preparation for measurement of phthalates from sanitary pads. Samples were collected from four locations (dotted boxes) on the sanitary pad.

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A, Standard GC/MS chromatogram showing the separation pattern of VOCs including methylene chloride, toluene, and xylene. **B-E**, Standard LC/MS/MS ion chromatogram obtained from DEP (**B**), DEHP (**C**), DBP (**D**), and BBP (**E**).

Table 1.

VOC contents (ppb \pm SEM) inside the plastic packages of sanitary pads

Brands	n	Methylene Chloride	Toluene	o-Xylene	m-Xylene	p-Xylene
1	5	BD	0.235 ± 0.059	0.017 ± 0.005	0.012 ± 0.004	0.015 ± 0.005
2	5	$0.028 \pm 0.012^{\ast}$	0.836 ± 0.351	0.263 ± 0.066	$0.192 \pm 0.047 {}^{\ast}$	$0.278 \pm 0.077 {}^{\ast}$
3	5	BD	$5.23 \pm 0.914 {}^{\ast}$	0.276 ± 0.071	0.086 ± 0.025	0.084 ± 0.025
4	5	BD	$5.471 \pm 2.438 \\ ^{\ast}$	0.287 ± 0.101	0.095 ± 0.029	0.103 ± 0.038
5	5	BD	0.427 ± 0.225	0.048 ± 0.019	0.027 ± 0.009	0.034 ± 0.011
6	4	0.008 ± 0.008	0.205 ± 0.069	0.127 ± 0.049	0.09 ± 0.033	0.132 ± 0.048
7	3	BD	0.107 ± 0.014	0.008 ± 0.004	0.002 ± 0.002	0.004 ± 0.002
8	4	BD	0.005 ± 0.003	0.003 ± 0.001	0.001 ± 0.001	0.002 ± 0.001
9	4	BD	0.635 ± 0.365	0.277 ± 0.195	0.136 ± 0.09	0.12 ± 0.081
10	4	BD	BD	0.008 ± 0.003	0.003 ± 0.002	0.003 ± 0.002
11	4	BD	BD	BD	BD	0.001 ± 0.001

 $\overset{*}{}_{\rm significantly}$ different from the average concentration of all sanitary pads

BD, below detection limit (detection limit, 0.001 ppb for each VOCs)

Table 2.

VOC contents (ppb \pm SEM) inside the plastic packages of diapers

Brands	n	Methylene Chloride	Toluene	o-Xylene	m-Xylene	p-Xylene
А	3	BD	0.397 ± 0.187	0.005 ± 0.002	0.003 ± 0.001	0.004 ± 0.001
В	3	BD	0.102 ± 0.023	0.008 ± 0.003	0.002 ± 0.001	0.003 ± 0.001
С	3	BD	0.36 ± 0.112	0.021 ± 0.009	0.013 ± 0.005	0.014 ± 0.005
D	3	BD	0.192 ± 0.048	0.02 ± 0.002	0.009 ± 0.001	0.01 ± 0.001

BD, below detection limit (detection limit, 0.001 ppb for each VOCs)

Table 3.

Phthalate contents (ppb \pm SEM) in the sanitary pads

Brands	n	DBP	DEHP	DEP	BBP
1	5	$7820.4 \pm 2734.6^{\ast}$	134.5 ± 37.7 *	60.0 ± 12.8	BD
2	5	144.9 ± 40.3	51.2 ± 10.0	BD	BD
3	5	1127.8 ± 492.3	34.1 ± 4.4	11.2 ± 6.2	BD
4	5	782.0 ± 149.0	197.4 ± 17.6 *	58.9 ± 47.6	BD
5	5	848.6 ± 364.8	47.8 ± 12.8	BD	BD
6	4	1995.3 ± 1630.3	37.7 ± 11.1	134.3 ± 101.6 *	BD
7	3	2478.6 ± 2216.0	46.9 ± 16.2	8.4 ± 8.4	BD
8	4	629.1 ± 466.2	37.3 ± 9.6	8.1 ± 8.1	BD
9	4	486.0 ± 411.3	11.3 ± 6.9	109.1 ± 42.2	BD
10	4	150.8 ± 66.9	5.5 ± 2.6	BD	BD
11	4	52.1 ± 10.8	9.8 ± 6.4	BD	BD

 * significantly different from the average concentration of all sanitary pads

BD, below detection limit (detection limit, 0.1 ppb for DBP, DEHP, and DEP; 0.05 ppb for BBP)

Table 4.

Phthalate contents (ppb \pm SEM) in the diapers

Number	n	DBP	DEHP	DEP	BBP
Α	3	13.4 ± 5.4	12.6 ± 2.1	BD	BD
В	3	984.5 ± 422.8	30.1 ± 3.3	BD	BD
С	3	1609.7 ± 1516.9	42.2 ± 3.3	0.8 ± 0.8	BD
D	3	1005.8 ± 403.1	62.8 ± 6.7	2.9 ± 0.8	BD

BD, below detection limit (detection limit, 0.1 ppb for DBP, DEHP, and DEP; 0.05 ppb for BBP)

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Table 5.

Occurrence of methylene chloride, toluene, and xylenes in consumer products (units: ppb otherwise indicated)*

Category	Samples	Sample number (n)	Methylene chloride	Toluene	0-xylene	m-xylene	p-xylene	Method	Ref.
Indoor air	Residence indoor air	284	NA	5.33-7.08	0.58-0.76	1.52-2.1	0	GC/MS	[43]
	Newly built house indoor air (< 1 yr)	4	NA	0.80–23.35		3.22-66.55		TD-GC/FID	[73]
	Elementary school indoor air	1	NA	0.6 - 2.2		1.1 - 2.2		GC/MS	[74]
	Scented candles (before lighting)	9	NA	0.01-10.3	0.01-0.01	0.01-0.32	0.01-0.01	TD-GC/MS	[75]
	Scented candles (after lighting)	9	NA	0.01-1.58	0.01-0.01	0.01-0.04	0.01-0.01	TD-GC/MS	[75]
	New cars (leather trim, <4 month)	3	NA	0.08-0.09	Ŋ	ND		GC/MS	[44]
	New cars (fabric trim, <4 month)	3	NA	0.48–0.69	0.88–1.20	1.75–2.5	3	GC/MS	[44]
Drinks	Household drinking water (Taiwan)	131	ND-21.08 ppm	ND-16.77 ppm	NA	NA	NA	GC/MS	[76]
	Household drinking water (Kuwait)	624	NA	ND-490.91		ND-133.58		GC/MS	[77]
	Bottled water (various countries)	71	NA	ND-313.12		ND-117.34		GC/MS	[77]
	Sports beverages (PET bottled)	9	NA	0.27-25.9 ppt	0.11–0.61 ppt	NA	NA	HS/SPME-GC/MS	[78]
Foods	American cheese (USA market)	3–11	NA	17–255	3-4	4–112		GC/MS	[79]
	Cheddar cheese (USA market)	7–13	NA	7–1300	QN	5-43		GCMS	[62]
	Pork bacon (USA market)	1–14	NA	12-230	2	5-25		GC/MS	[62]
	Olive/safflower oil (USA market)	3–7	NA	6-32	6–23	2-110		GC/MS	[79]
	Scrambled eggs (USA market)	2-8	NA	4-100	Ŋ	2-4		GC/MS	[79]
	Fruit-flavored cereal (USA market)	3–6	NA	3-140	ŊŊ	4-7		GC/MS	[79]
	Cereal products (Belgian market)	NA	NA	ND-71.8	ND-3.5	NA	NA	HS-GC/MS	[80]

Category	Samples	Sample number (n)	Methylene chloride	Toluene	o-xylene	m-xylene	p-xylene	Method	Ref.
Plastic	Wrapping Films (PVC polymer)	З	NA	3.70-3.77 ppm	12.90–13.50 ppm	23.51–24.59 ppm	2.16–2.26 ppm	HS/SPME-GC/MS	[81]

* Data were adopted from previous studies.

FID, flame ionization detection; GC, gas chromatography; HS, headspace analysis; MS, mass spectrometry; NA, not available; ND, not detected; SPME, solid phase micro extraction; TD, thermal desorption

Category	Samples	Sample number (n)	DBP (Dibutyl phthalate)	DEHP (Di-ethylhexy phthalate)	DEP (diethyl phthalate)	BBP (Benzyl-butyl phthalate)	Method	Ref.
Consumer products	Baby diapers top sheet	50	0.2 ppm	0.6 ppm	NA	0.1 ppm	GC/MS	[2]
	Adult-use cosmetic products	60	123-62607 ppm	ND	80–36006 ppm	ND	HPLC	[82]
	Baby-care products contained	24	ND	ND	10–274 ppm	ND	HPLC	[82]
	Paper cup	19	12.87–31.48	13.94–15.23	NA	NA	HPLC	[57]
Drinks	Bottled water (Hungary)	3	0.8-6.6	1.7–16.0	NA	0.1 - 6.0	GC/MS	[83]
	Bottled water (Jordan)	14	1.17-13.9	1.15-4.86	NA	NA	HPLC	[84]
	Bottled water (Ireland)	3	0.062-0.068	1.19–1.68	ND	ND	GC/MS	[85]
	plastic water bottle (Ireland)	ю	20.92-71.68 ppm	0.39–1.49 ppm	DN	ND	GC/MS	[85]
Foods	Cereals (Chinese market)	44	12.1–279	62.9–1380	1.40–20.8	0.45-62.9	GC/MS	[58]
	Snacks (Chinese market)	17	3.81–181	63.8–933	1.33 - 8.50	0.63-59.0	GC/MS	[58]
	Beverages (Chinese market)	3	32.8–52.9	72.3–160	6.96–13.9	0.03-0.36	GC/MS	[58]
	Condiments (Chinese market)	7	9.42–101	61.5-400	0.77–90.1	0.30-8.68	GC/MS	[58]
	Seafood (Chinese market)	3	85.8–116	523-1110	2.34-5.13	1.61–8.67	GC/MS	[58]
	Meat products (Chinese market)	4	23.7–6.8	103-400	2.61–22.8	0.52-1.83	GC/MS	[58]
Plastic (ppm)	Reusable plastic cup	S	9.84	119.35	ND	0.44	GC/MS	[56]
	Milk package bag	5	9.84	42.5	ND	0.07	GC/MS	[56]
	Microwavable box	5	1.44	8.72	ND	0.1	GC/MS	[56]
	Package film	5	1.88	27.58	ŊŊ	0.09	GC/MS	[96]
	Disposable cup	5	1.12	2.88	ND	ND	GC/MS	[56]
	Storage box	5	1.18	3.94	ND	ND	GC/MS	[56]

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Table 6.

Occurrence of DBP, DEHP, DEP, and BBP in consumer products (units: ppb otherwise indicated)*

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GC, gas chromatography; MS, mass spectrometry; NA, not available; ND, not detected

* Data were adopted from previous studies.