Risk Assessment of Volatile Organic Compounds in Disposable Sanitary Pads in Nigeria

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ABSTRACT

Risk assessment of volatile organic compounds (VOCs) in selected disposable sanitary pads (DSPs) used in Nigeria was conducted. The risk assessment was performed by deducing the systemic exposure dose (SED) values and comparing them with reference dose (RfD) values. Thirty-four (34) VOCs and their corresponding concentrations in sixty-five (65) DSPs samples were identified using static headspace gas chromatograph coupled to a flame ionization detector (SHS-GC-FID). Out of the 17 VOCs detected in 16 DSPs brands, only three (3) VOCs were common across all brands; namely 1,2-dibromo-3-chloropropane, 1,2-dibromoethane, 1,2-dichloropropane. The VOC detected at the highest concentration was dibromomethane (0.14 mg/g), whereas 1,1-dichloroethene was detected at the lowest concentration (0.01 mg/g). The SED results were above the RfD values for all the VOCs detected. The research findings suggest that the DSPs contained VOCs which are harmful to the user, posing adverse health effects such as menstrual cycle changes, decreased menstruation, uterine disease and cancer. Therefore, there is need for regulatory agencies to enforce the conduct of appropriate tests on DSP prior to their distribution into the Nigerian markets.

Key words: Disposable sanitary pads, volatile organic compounds, risk assessment, SHS-GC-FID.

INTRODUCTION

Disposable sanitary pads are a type of feminine hygiene products used by pubescent and adult women during menstruation and post childbirth. The use of DSPs exposes users to different chemical compounds which include endocrine-disrupting chemicals (EDCs) (dioxin and dioxin like compounds (DLCs), furans, phthalates, bisphenols, parabens, triclocarban, plasticisers) and VOCs (such as benzene, tetrachloromethane, trichloromethane, trichloroethene, tetrachloroethene). This is worrisome as some of the constituents of DSPs may not be listed on the product packaging. To ensure the safety of the DSPs users, regulations concerning the chemical components and their quantities are established. Such regulatory classifications vary between countries and is subject to either mandatory legal enforcement or voluntary manufacturers' control [1,2]. Countries like China, Korea, Japan, Vietnam, Indonesia Bangladesh, India, Nepal and Pakistan [2-5] as well as the EU [3,6] have standards and regulations for DSPs. Within Africa, Burundi, Kenya, Rwanda, South Sudan, Tanzania, Uganda, Ethiopia, Kenya, Malawi, Tanzania, Uganda, South Africa, Zambia, Zimbabwe and Nigeria have standards for DSPs; while Central African Republic and Liberia neither have a standard nor a regulatory body. Standards in Chad, Mali, Gambia, Senegal could not be obtained while Ghana awaits endorsement of a standard [5].

In Nigeria, the National Agency for Food and Drug Administration and Control (NAFDAC) classifies DSPs as medical devices, while the Standard Organisation of Nigeria (SON) is responsible for the maintenance of the standard of manufactured products as well as the development and enforcement of the product and process standards. NAFDAC presently does not conduct any test on the DSP products while SON carries out some chemical tests but not the determination of the VOC content of DSPs. As recently as 2020, Gao *et al*. found that in China, EU and US, fragrances, deodorisers and phthalates incorporated into DSPs lack standards or regulations for their use [7].

VOCs are small molecular chargeless organic compounds of varying lipophilicity that vaporize at room temperature. Lipophilicity is important because the cellular membranes are composed principally of a protein–lipid matrix, and at sufficient concentrations VOCs may diffuse into the cell, dissolve the matrix or extract the fat or lipid components of the membrane [8]. Thus, VOCs cause skin irritations among other problems and it is the vulval tissue and mucosa of the vaginal opening that are in direct contact with the DSPs. Some VOCs are also present as contaminants or by products in bleached fluff pulp during the manufacture of the absorbent core of the DSPs [9]. Compounds like chlorine and chlorine dioxide are used to bleach pulp and they react with the pulp to produce chlorinated organic compounds [9,10]. Others are added as fragrance, adsorbents, moisture barriers, adhesives and binders [11]. DSPs give cause for concern because of the toxicity of the VOCs found in them. Woo *et al*. [12] corroborated this finding in their study which showed that the safety of DSPs was a concern because the materials used in their preparation release VOCs and EDCs which pose potential risks to consumers including developmental and reproductive harm [12,13]. Some of these VOCs include styrene, chloromethane, chloroethane, chloroform, acetone. The health effects of VOCs vary greatly according to the compound, level of exposure and length of exposure [8]. As reviewed by Woo *et al*. [12] pregnancy outcome complications associated with VOCs (such as styrene and p-DCB) to the reproductive organs are premature births, spontaneous abortion, congenital malformation and infertility. Some VOCs detected in DSPs were styrene, chloromethane, chloroethane, chloroform, acetone, which have a range of properties such as carcinogenicity, reproductive intoxicant, neurotoxicity and irritation [14].

Various organizations such as National Latina Institute for Reproductive Health, Colorado Organization for Latina Opportunity and Reproductive Rights, Teens Turning Green and Women Executives Accelerating Change Today (WEACT) for Environmental Justice have strongly expressed the need for consumers to be informed about the ingredients in the DSPs especially as they are used regularly and on the most intimate part of the users anatomy. DSP manufacturers should be held accountable if there are associated health hazards from regular DSP use [14]. These hazards can be determined by conducting a risk assessment; a science-based risk evaluation method for the safe management of materials, which hazard identification, hazard characterisation, exposure assessment, risk characterisation, clinical evaluation and finally post market surveillance [1].

Risk assessment is employed to assess the risk of adverse effects of VOCs on human health and provide acceptable risk levels without any harm. Exposure assessment involves calculating the SED value using parameters such as concentration of VOCs identified in the DSPs, skin absorption rate (%), transfer rate (%), period of exposure (day/30 days), number of pads per day (pad/day) and body weight (kg) [1]. Risk characterisation involved assessing the risk of harm to human health and carcinogenicity of the VOCs using calculated SED values and comparing to exposure and reference values. One output from risk assessment is risk management which involves policy and risk reduction actions. Others include exposure route(s), status evaluation, monitoring of trends, identification of exposed individuals, suspect chemical screening, identifying of contamination source(s), exposure pathways, fate and transport properties [15].

With little information to determine the presence and concentration of VOCs in DSPs. in the African, there is a need to carry out this study. This present study seeks to provide some contribution to fill this gap by performing a risk assessment of volatile organic compounds in disposable sanitary pads sold in Nigeria, as well as providing data to contribute to the United Nations Sustainable Development Goal (SDG) 3 which states that "the number of deaths and illnesses from hazardous chemicals, air, water and soil pollution and contamination will be substantially reduced by 2030". This study aims to perform a risk assessment on volatile organic compounds in disposable sanitary pads sold in selected states in Nigeria. The objectives includ to identify and determine VOCs in DSPs sold in selected states in Nigeria using Static Headspace Gas Chromatograph coupled to a flame ionization detector (SHS-GC-FID), determine the SED values of the VOCs and perform a risk assessment by comparing the calculated SED values to Reference Dose (RfD) values of VOCs in DSPs sold in selected states in Nigeria.

MATERIALS AND METHODS

VOC standard (M-502A-R3-10X) was purchased from AccuStandard, New Haven, CT, USA. A four-point calibration curve was adopted for the quantitative analysis of the VOCs in the DSPs [11]. Standards were prepared by accurately measuring volumes of the VOC standard and made up to 10 mL with water, each in a separate 20 mL SHS vial. Fresh standard solutions were prepared for each run.

Sample Collection and Sample Preparation

DSP samples (65) of similar brand were collected from 4 cities (Kaduna, Lagos, Port Harcourt and Abuja) in Nigeria. DSP samples were prepared according to the procedure employed by Lin et al [11] but modified as the top and back sheets of DSPs were taken apart before 1 g of only the SAP layer was placed into a 20 ml SHS vial. The vials were capped with silicone rubber and PTFE faced septa, using a crimper before they were placed into the Agilent 7697A HS sampler/carousel [9,10].

Instrumentation

A Static Head Space (SHS) Autosampler – Agilent Technologies 7697A attached to an Agilent 6860 GC A DB-624 was fitted with a capillary column coated with 6% cyanopropyl/94% polydimethylsiloxane (30 m × 0.53 mm × 3 µm film thickness) (Agilent Technologies) and coupled to a flame ionisation detector (FID). The injection temperature was 250 °C, split ratio 1:1 injection mode, 1 µL (0.001 mL) injection volume, an injection pressure of 4.227 psi (using nitrogen gas) and the loop temperature was set at 85 °C. The GC oven was set at 35 °C, held for 5 min, increased at a rate of 11 °C/min to 60 °C, then to 220 °C at a rate 22 °C/min. The FID temperature was set to 300 °C, with a H_2:H_2O airflow of 30 mL/min:300 mL/min; helium was used as makeup gas at a flow of 18 mL/min; while the transfer line temperature was set at 120 °C [15].

The VOC identified across the various DSP samples were collated per DSP brand. The results of concentration of individual VOCs from the chromatogram generated using SHS-GC-FID to analyse 1g of DSP, were multiplied by the weight of the pad to generate the concentration of the VOC in mg/pad. These individual values (in mg/pad) were averaged out for the same brands and the values was used to determine SED values.

Exposure Assessment

The effect of SED is experienced at a site different from the point of exposure to VOCs. The point of contact for VOCs in DSPs is often the vulvovaginal epithelial cells; these cells absorb fluids much quicker than other body cells, resulting in higher exposure to VOCs [16]. The VOC concentration in the brands were used to calculate the exposure assessment which involves calculating the SED value using Equation 1 [1,9]:

$$SED\ (mg/kg/day) = \frac{C \times A \times T \times N \times P}{BW} \tag{1}$$

where:

C is concentration of VOC in each DSP (mg/pad).
A is the skin absorption (100%).
T is transfer to the skin (100%).
N is the number of pads (5 pads/day).
P is the period of exposure (7 days).
BW is average body weight of a preteen (43kg).
C was determined by calculating the product of the SHS-GC-FID analysis values (mg/g) with the sanitary pad weight (g/pad).

Statistical Analysis

The data was analysed using Statistical Package for the Social Sciences (SPSS), with the statistical significance set at $p < 0.05$. The average concentration of each VOC was calculated from all DSPs to determine any difference between the VOC across the 16 brands. Results from DSP brands were compared using analysis of variance (ANOVA).

RESULTS AND DISCUSSION

VOC Identification and Concentration

All 65 DSPs analysed in this study contained alkyl VOCs at various concentrations. Figures 1 and 2 show chromatograms, one from each batch of 2 runs.

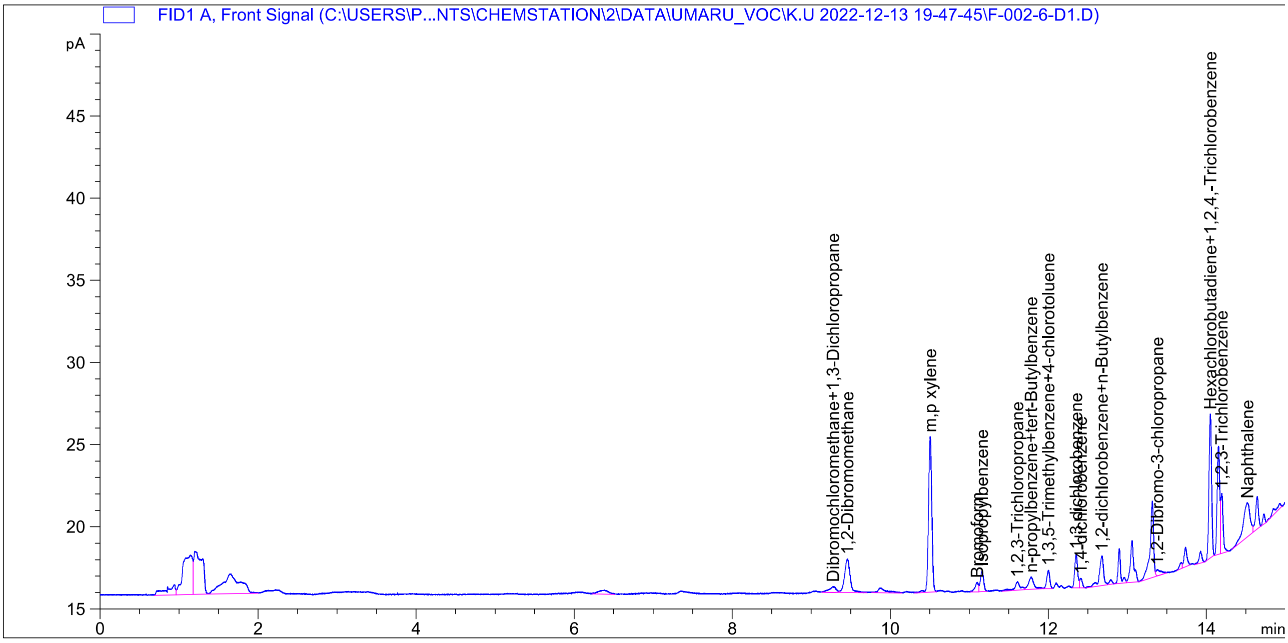

Figure 1: SHS-GC-FID chromatogram showing the VOCs in a DSP sample (Batch 1).

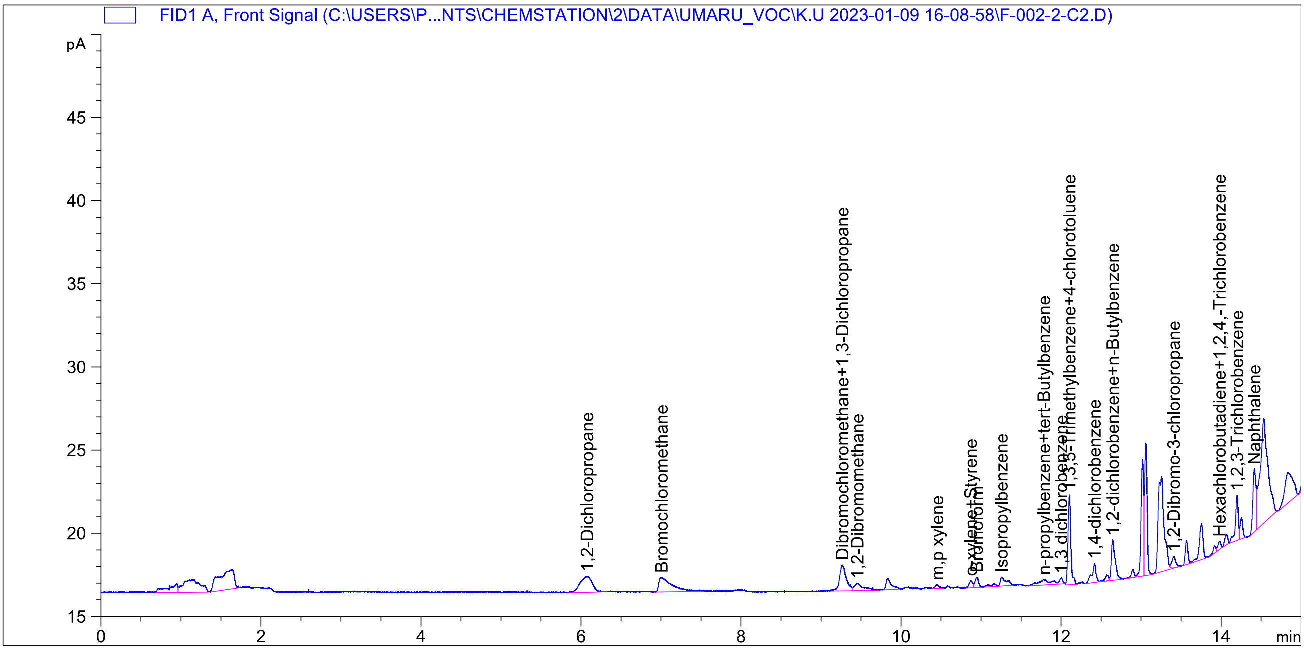

Figure 2: SHS-GC-FID chromatogram showing the VOCs in a DSP sample (Batch 2).

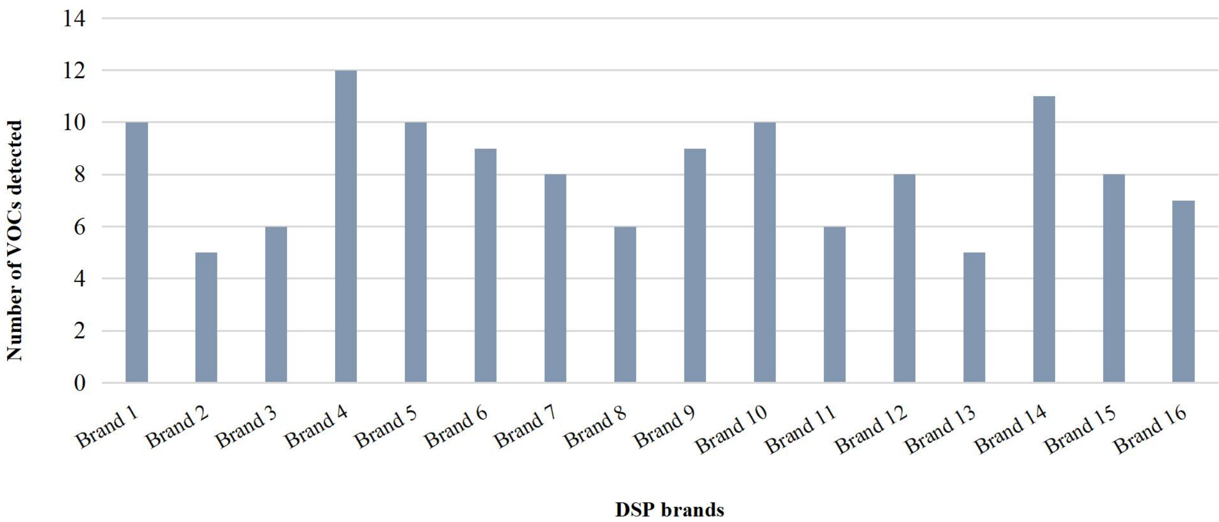

Figure 3: Number of alkyl VOCs detected in each of the DSPs samples.

Figure 3 shows the number of alkyl VOCs detected in each of the DSPs samples. Brand 4 contained the highest number of alkyl VOCs (12) followed closely by Brand 14 with 11 alkyl VOCs and Brands 1, 5 and 10 with 10 alkyl VOCs each. Conversely, brands 2 and 13 contained the lowest number of alkyl VOCs (5).

Table 1 details the alkyl VOCs and the corresponding concentration range of in DSP samples.

Table 1: alkyl VOCs and the corresponding concentration range of in DSP samples.

S/N	VOC	Conc range (µg/g of pad)
1.	1,1-Dichloroethene	1.20
2.	1,1,2-Trichloroethene	1.60 – 7.21
3.	1,1,2,2-Tetrachloroethane	2.98 – 7.96
4.	1,2-Dibromo-3-chloropropane	12.67 – 77.19
5.	1,2-Dibromoethane	4.74 – 32.84
6.	1,2-Dichloropropane	3.56 – 18.20
7.	1,2,3-Trichloropropane	2.10 – 12.52
8.	Bromochloromethane	7.18 – 89.03
9.	*cis*-1,2-Dichloroethene plus 2,2-Dichloropropane	28.08 – 58.85
10.	*cis*-1,3-Dichloropropene	1.48 – 2.56
11.	Dibromochloromethane	3.84 – 20.45
12.	Dibromochloromethane plus 1,3-Dichloropropane	1.23 – 99.58
13.	Dibromomethane	3.19 – 136.84
14.	Dichloromethane	1.96 – 7.45
15.	*trans*-1,3-Dichloropropene	76.40 – 126.39
16.	Tribromomethane	5.67 – 83.08
17.	Trichloroethane	4.29 – 29.66

Six (6) VOCs detected are similar to those detected by Kim *et al*. [9] ; namely 1,2-dibromo-3-chloropropane, 1,2-dichloropropane, 1,2-dibromoethane, 1,1,2-trichloroethene, 1,3-dichloropropane, bromochloromethane, dibromochloromethane and tribromomethane. An isomer of trichloroethane (1,1,2-trichloroethane) and 1,2-dichloroethene (*cis*-1,2-dichloroethene) detected in this study, were detected by Kim *et al*. (2019). Dichloromethane was also detected in DSP samples analysed by Park *et al*. (2019), but as a target VOC. Alkyl VOCs detected by Lin *et al*. (2020) were 12 in number, however, these were target VOCs (tVOCs); non-target VOCs detected were 3-methylhexane, 2-methylhexane and methylcyclohexane.

Dibromomethane and *trans*-1,3-dichloropropene were detected at the highest concentrations at 136.85 µg/g (Brands 12) and 126.394 µg/g and 16.58 µg/g (Brand 9) respectively. VOCs detected by Kim *et al*. (2019) were in lower quantities compared to this study; the highest was 1,1,2- trichloroethane at 14.97 µg/g, followed by 1,2-dichloropropane at 0.35 µg/g and 1,2-dichloroethane at 0.22 µg/g. The three aforementioned VOCs had their lowest values of 4.29 µg/g and 3.56 µg/g respectively, with no detection for 1,2-dichloroethane.

Table 2: Brand with associated lowest and highest VOCs in DSP samples.

Brand	VOC	Lowest conc (µg/pad)	VOC	Highest conc (µg/pad)
Brand 1	*cis*-1,3-Dichloropropene	1.71	1,2-Dibromo-3-chloropropane	77.19
Brand 2	Dibromochloromethane plus 1,3-Dichloropropane	4.87	1,2-Dibromo-3-chloropropane	14.70
Brand 3	1,2,3-Trichloropropane	9.93	1,2-Dibromo-3-chloropropane	37.33
Brand 4	1,1-Dichloroethene	1.20	1,2-Dibromo-3-chloropropane	51.54
Brand 5	1,1,2,2-Tetrachloroethane	3.21	*trans*-1,3-Dichloropropene	76.40
Brand 6	1,1,2-Trichloroethene	1.60	*trans*-1,3-Dichloropropene	96.60
Brand 7	Trichloroethane	5.96	*trans*-1,3-Dichloropropene	107.52
Brand 8	1,1,2,2-Tetrachloroethane	4.18	Bromochloromethane	89.03
Brand 9	1,2-Dibromoethane	5.91	*trans*-1,3-Dichloropropene	126.39
Brand 10	1,1,2-Trichloroethene	2.67	*trans*-1,3-Dichloropropene	104.50
Brand 11	1,2,3-Trichloropropane	6.20	Bromochloromethane	63.64
Brand 12	1,1,2,2-Tetrachloroethane	3.26	Dibromomethane	136.85
Brand 13	Dibromochloromethane plus 1,3-Dichloropropane	1.23	1,2-Dibromo-3-chloropropane	29.25
Brand 14	1,2,3-Trichloropropane	2.10	Dibromomethane	75.76
Brand 15	1,1,2,2-Tetrachloroethane	3.60	Tribromomethane	32.63
Brand 16	1,1,2,2-Tetrachloroethane	2.98	Bromochloromethane	27.31

Table 2 shows the 16 brands of DSP analysed and the lowest and highest VOC detected in each brand. *Trans*-1,3-Dichloropropene was detected as the highest VOC in 5 different brands (Brands 5, 6, 7, 9 and 10). 1,2-Dibromo-3-chloropropane was also detected as the highest VOC in 5 different brands (Brands 1 - 4 and 13). This was followed by bromochloromethane (Brands 8, 11 and 16), tribromomethane (Brand 15) and dibromomethane (Brand 14).

Brands 5, 8, 12, 15 and 16 had 1,1-dichloroethene detected as the VOC with the lowest concentration, while 1,2,3-trichloropropane was detected at the lowest concentration for brands 3, 11 and 14. Despite being manufactured in different countries, these DSP brands show some similarity of lowest and highest VOC detected. This could be as a result of similar manufacturing procedure or starter material. It is noteworthy that only a single brand - Brand 3 - had certifications from NAFDAC, SON and Mandatory Conformity Assessment Programme (MANCAP). Brands 4, 6, 9, 12, 13 and 15 only had NAFDAC registration numbers and none from SON and MANCAP; Brand 16 had certification from NAFDAC and SON with none from MANCAP. Meanwhile Brands 2, 5, 8, 10 and 11 did not have any certifications. Certifications for the other three brands (14, 7, 1) showed inconsistency; for Brand 14, only 2 samples had NAFDAC registration number; Brand 7 - only 1 sample had NAFDAC registration number and - Brand 1, all samples had NAFDAC registration number while half of the samples had SON certification. There was no MANCAP certification for Brands 14, 7 and 1 and no SON certifications for Brands 14 and 7.

Exposure Assessment of VOCs in DSPs

The exposure assessment was carried out by deducing the SED value from DSPs.

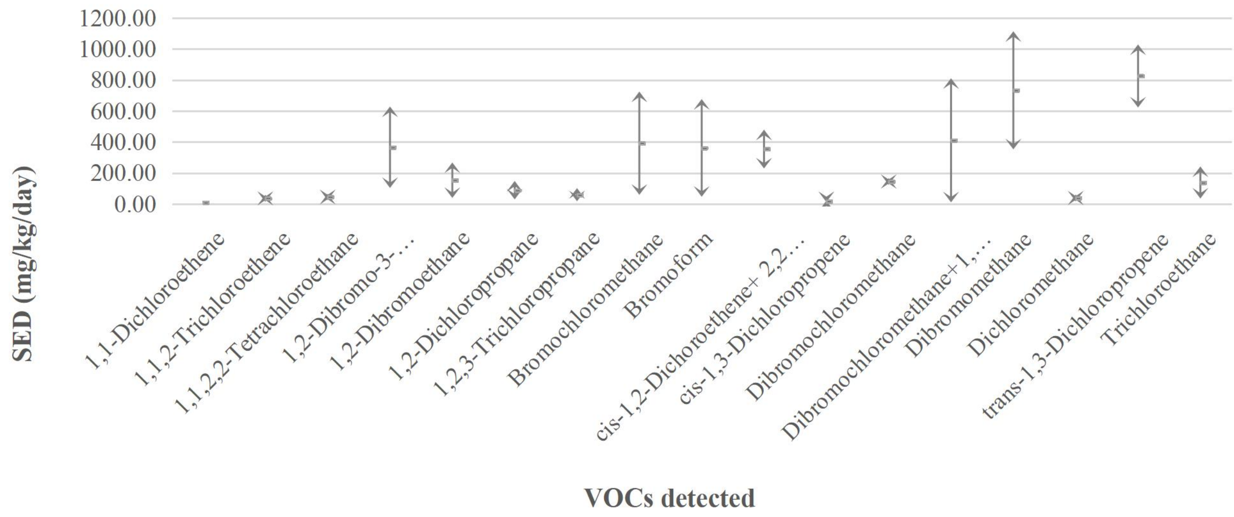

Figure 4: SED values of VOCs detected in DSPs.

SED values showed a range of exposure (Figure 4). The greatest range was observed for Dibromochloromethane and 1,3-dichloropropane, then, dibromomethane; while the lowest exposure was from 1,1-dichloroethene.

Risk Characterisation of VOCs in DSPs

Table 3: Risk Characterisation of the VOCs detected in DSP samples.

S/N	VOC	SED (mg/kg/pad)	RfD (mg/kg/pad)
1.	1,1-Dichloroethene	9.80	0.02
2.	1,1,2-Trichloroethene	13.03 – 58.73	0.0002
3.	1,1,2,2-Tetrachloroethane	24.28 – 64.76	0.0005
4.	1,2-Dibromo-3-chloropropane	103.09 – 628.31	0.0002
5.	1,2-Dibromoethane	38.58 –267.31	0.0001
6.	1,2-Dichloropropane	28.99 – 148.10	0.0005
7.	1,2,3-Trichloropropane	17.08 – 101.88	0.0002
8.	Bromochloromethane	58.48 – 724.70	0.0001
9.	*cis*-1,2-Dichoroethene plus 2,2-Dichloropropane	228.55 – 479.03	0.03 (0.01)
10.	*cis*-1,3-Dichloropropene	12.07 – 20.82	0.034
11.	Dibromochloromethane	122.85 – 166.42	0.0005
12.	Dibromochloromethane plus 1,3-Dichloropropane	10.04 – 810.55	0.0005 (0.0005)
13.	Dibromomethane	351.85 – 1113.89	0.0001
14.	Dichloromethane	15.94 – 60.65	0.06
15.	*trans*-1,3-Dichloropropene	621.88 – 1028.79	0.003
16.	Tribromomethane	46.18 – 676.24	0.0001
17.	Trichloroethane	34.90 – 241.44	0.01

Table 3 details the risk characterisation of the VOCs detected in DSP samples. Risk characterisation entails assessing the extent of harm to human health using calculated SED and RfD values. If the SED is below the RfD, there is no need for concern by regulatory organisations. However, if the SED is above the RfD, then there is the need for the involvement of regulatory organisation. There are a number of adverse health effects as a result of exposure to VOCs. For instance, exposure to 1,1,2,2-tetrachloroethane, 1,2-dibromoethane, 1,2,3-trichloropropane and bromochloromethane from DSPs usage is associated with to hepatoxicity; likewise, 1,2-dibromoethane and bromochloromethane are associated with nephrotoxicity while reproductive toxicity can be experience from exposure to 1,2-dibromo-3-chloropropane and 1,2-dichloropropane [9]. Exposure above RfD by *cis*-1,3-dichloropropene is linked to decrease in body weight, [9]. The results show that all the DSP brands contained VOCs with SED values that are above RfD values. This indicates that users are exposed to VOCs from the DSPs; this exposure is associated with certain harmful effects to the user particularly toxicity to the liver, kidneys, and central nervous system.

Statistical Analysis

The concentration for the three VOCs that all DSP samples have in common (1,2-dibromo-3-chloropropane, 1,2-dibromoethane, 1,2-dichloropropane) was analysed for ANOVA using SPSS with the statistical significance set at $\alpha = 0.05$. The result showed that there was no significant difference between the DSP brands analysed ($p = 0.973$ which is > 0.05). This implies that all the DSPs analysed can pose similar health effects as far as the VOCs are concerned.

CONCLUSION

All the DSPs analysed contained various types and concentrations of VOCs. These results demonstrated that product labels are not an indicator of their VOC content. The users need to be aware of the harm associated with continuous use of these DSP products. There is need for regulatory agencies – NAFDAC, SON AND MANCAP – to develop standards which will enforce the conduct of appropriate tests on DSP prior to their importation and eventual use by the female populace. Such tests are to identify and quantify VOCs in DSPs, then conduct risk assessment of the VOCs to the user. In addition, these agencies should provide regulations regarding the use of chemicals for the production of DSPs, with sanctions placed on the use of those chemicals that have adverse heath effect to the user. Such adverse health effects like hepatoxicity, reproductive toxicity, nephrotoxicity can be exacerbated because certain VOCs are carcinogenic. These include ethylbenzene, styrene, benzene, toluene, xylene and chlorinated VOCs such as dichloromethane and trichloroethane. The information obtained from this research findings may assist in the achievement of the United Nations Sustainable Development Goal (SDG) 3 which aims that the number of deaths and illnesses from hazardous chemicals, air, water pollution, soil pollution and contamination will be substantially reduced by 2030.

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