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The Migration of Phthalate Esters in High Density Polyethylene/Polyethylene Terephthalate Packaged Water At Different Storage and Environmental Conditions in Lagos Metropolis

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Abstract

The demand for potable drinking water is met by production, marketing and consumption of water packaged in polyethylene terephthalate (PET) bottles and high-density polyethylene (HDPE) sachets. This study investigated the effects of temperature and storage time on the concentration of phthalate esters (PAEs) leached into packaged drinking water purchased in Lagos, Nigeria. Water samples were collected from factories as soon as they were produced, stored for 30 days indoors at 23-27 °C and outdoors at 31- 33 °C. Using Liquid-Liquid Extraction, the PAEs were extracted with dichloromethane and quantified with an Agilent 6890 Gas Chromatograph coupled with Flame Ionization detector (GC-FID). Five phthalate esters, namely: dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DnBP), benzyl butyl phthalate (BBP) and di (2-ethylhexyl) phthalate (DEHP) were detected in the packaged waters. The obtained results show an elevation in the concentration of PAEs because of storage time and condition. The range of PAEs was found to be 0.03µg/L to 7.76 µg/L with DEHP being the most frequently detected phthalate in the drinking water samples. The highest concentrations obtained for DEHP was found to be slightly above the United States Environmental Protection Agency (USEPA)), Maximum Contaminant Level (MCL) set for DEHP in drinking water which is 6 µg/L. The results obtained in this study confirmed the possible leaching of PAEs into the drinking water samples from the packaging materials, with concentrations that are dependent on the storage time and the temperature at which the samples were stored. It is recommended that drinking water that is packaged in high density polyethylene or polyethylene terephthalate should not be stored for extended time and efforts should be made to store them at lower temperatures

Keywords*: Leaching; Phthalate Esters; Drinking Water; Polyethylene Terephthalate (PET), Storage*

Introduction

Phthalate esters (PAEs) are a group of chemical compounds widely used as additives in plastics. They are known to improve the flexibility of plastics through weak secondary molecular interactions with polymer chains (Koniecki *et al.*, 2011) and are therefore, used in various products such as packages, films, paints, adhesives, cosmetics, pharmaceuticals, medical devices, and ink for printers. These esters are commonly used as plasticizers to improve the softness and flexibility of plastics. Phthalate plasticizers are not chemically bound to materials; they can leach at a constant rate from plastic products to the environment and consequently, are distributed in the ecosystem (Edjere *et al.,* 2016). Phthalate esters and their metabolites are classified as endocrine disruptors or hormonally active agents and long-term exposure of humans to PAEs can result in different types of adverse effects including such disorders as breast cancer, prostate cancer (Sax, 2010), disorders of androgenic hormone biosynthesis and function (Ceretti *et al.,*2009), thyroid gland disorders (Gupta *et al,*.2010; Ghisari *et al.,*2009), infertility (Cuenca *et al*., 2020), attention deficit hyperactivity disorder (ADHD) (Chopra et *al*., 2013), obesity, liver damage, allergy (Braun *et al*., 2013) and asthma (Shu *et al*., 2013).

According to estimates given by The World Bank in 2019, approximately 60 million Nigerians do not have access to clean water for drinking (press release number: 2021/138/AFR). This has led to significant increase in the demand for packaged water usually in HDPE sachets and PET bottles (WHO, 2014). Lagos State, which is situated in Southwest of Nigeria, is one of the fastest growing metropolises in Africa with an estimated population of twenty-three million people (Population Stat., 2020). Approximately 60% of the population depend on packaged drinking water to meet their daily drinking water needs (Vedachalam *et al.,* 2017). Storage of drinking water outdoors where the temperatures of up to 39 °C by retailers of packaged water in Lagos metropolis have been observed. This has raised concerns about the potential harm to human health from exposure to plasticizers like PAEs, which may leak into the drinking water ingested by the public. Phthalate esters have been widely reported globally in different environmental matrices. For instance, 2290 ng $m^{-3}$for DEP, 3975 ng $m^{-3}$for BBP and 2437ng $m^{-3}$for DEHP were observed in indoor air from the study of 10 newly decorated apartments in Hangzhou, China (Pei *et al.*, 2013). Dibutyl phthalate (DBP), DEHP and Di(n-octyl) phthalate (DnOP) were observed to have contributed more than 90% of the total PAEs detected by Wang *et al.* (2015) in both vegetables and soils. Three PAEs, namely, DEP, dimethyl phthalate (DMP) and DBP were detected in 10 popular brands of PET bottled water in Beijing (Xu *et al*., 2019). In Nigeria, Adeniyi *et al*. (2011), Edjere *et al*. (2016) and Olutana *et al*. (2016) detected and quantified DMP, DEP, DBP, and DEHP in water, sediment, sludge, and fishes from rivers, respectively. High concentrations of DBP were detected were in *T. guineensis*, *C. nigrodigitatus* and African prawn in Lagoons (Adeoguna *et al.,* 2015). The mean concentrations of DMP, DEP and DBP were respectively found to be 1.15 ± 0.28 mg/L, 0.09 ± 0.16 mg/L, and 0.28 ± 0.33 mg/L in drinking water samples collected from street hawkers in Lagos, Nigeria by Dada *et al*. (2018).

Although there have been studies on the concentration of PAEs leached into drinking water, there is a scarcity of studies on the effect of storage conditions and influence of storage time on the migration of PAEs into packaged water. This study, therefore, was aimed at investigating the level of some target PAEs leached into different samples of drinking water packaged in PET/HPDE bottles and sachets in Lagos metropolis, the effect of the storage conditions and the influence of storage time (contact time) on the concentration of PAEs leached.

Materials and Methods

Sample Collection

Twenty samples of HDPE sachet water and twelve PET bottles waters were each purchased from seven manufacturers. Thus, seven brands of HDPE sachet water and PET bottled water were purchased from packaged water manufacturers in different Local Government Areas (LGA) ranging from high income areas to low-income areas in Lagos State, Nigeria. The LGAs are Lagos Mainland, Agege, Amuwo Odofin, Ikeja, Ojo, Eti-Osa and Mushin. The samples were purchased and collected from their factories on the day of production in August 2019.

Four samples of each brand of the HDPE sachet water and PET bottled water were grouped into the following: Group one: Samples to be analysed within 12 hours after purchase; Group two: Samples to be analysed after one month of storage at room temperature (23 °C to 27 ºC), Group three : Samples to be analysed after one month of storage at outdoor temperatures between 31°Cto 33°C. For analyses, the four samples of each brand were made into composite and taken for analysis.

Chemicals and Reagents

Certified traceable EPA standards Phthalate Esters Mix: DMP (99.9%), DEP (99.9%), DBP (97.6%), BBP (98.7%), BEHP (99.7%) in hexane and Phthalate Esters Mix: DMP (99.9%), DEP (97.6%), DBP (99.3%), BBP (99.9%), BEHP (99.7%) in methanol were purchased from Sigma-Aldrich for recovery studies. Analytical grades Butyl benzoate (BB) and sodium chloride were purchased from BDH and Sigma-Aldrich, respectively. Dichloromethane and Methanol (both of which were HPLC grades) and analytical grade Hexane were purchased from Fisher Scientific (Loughborough, UK). Ultrapure water produced by a Milli-Q Integral water purification system (Millipore, USA) was used.

Preparation of Stock and Working Solutions

Stock solution of the Phthalate Esters Mix standards (40 µg/mL) (DMP, DEP, DBP, BBP and DEHP) and internal standard (100 µg/L) Butyl Benzoate (BB) were prepared in hexane as working solutions from which other concentrations were prepared by serial dilution of the stock solution. All solutions were stored in the dark at 4°C prior to use.

Analytical Procedure

An aliquot of 100 mL of the collected water samples was measured into in a 200 mL volumetric flask. One (1) mL of internal standard (42 µg/L) and 1.0 ± 0.05 g of sodium chloride (previously dried at 400°C for 3 hours) were added, and the resulting solution was extracted with 20 mL of dichloromethane (DCM) using a mechanical flask shaker for 20 mins, centrifuged and the extract collected. This was repeated three times. The combined

DCM layers containing the analytes of interest were collected and concentrated to near dryness over anhydrous sodium sulphate. Blanks were also prepared using the same procedure for water samples. The concentrated extracts were reconstituted with 2 mL of DCM (Kanchanamayoon *et al.*, 2012).The reconstituted extract (10 µL of 2 mL) was injected into an Agilent 6890N Gas Chromatograph(GC) coupled with flame ionization detector (FID). The injector and detector temperatures were set at 250°C. The flow rate of the carrier gas (N_2) was set at 10 mL/min. The analytes were separated on a cross-linked methyl silicone HP-5 capillary column having dimensions: 30 m x 0.25 µm x 0.320 mm (supplied by Agilent Technologies, USA) with column head pressure of 10psi. Analysis was done in split mode of 100:1. Analytical quantification was enabled with the use of Agilent GC Chemstation software. Internal standard calibration method was used for quantification of PAEs in the samples. The GC-FID was calibrated using six calibration solutions between 0.5 - 10 µg/L of target phthalate mixture each solution containing 21µg/L of internal standard. Identification of target PAEs were based on retention time as compared to that of the standards (within ± 1.0 min).

Quality Control

All the glass wares used were soaked in 10% nitric acid, washed with detergent then rinsed with deionised water, dried, and sealed with aluminium foil and then stored. Glasswares were further pre-rinsed with acetone prior to use. During sample handling, separating funnels fitted with Teflon stopcocks, glass vials and volumetric flask with Teflon caps and glass syringes were used. Use of plastic materials was completely avoided. Laboratory reagents and instrumental blanks were analysed with each batch of samples (5 samples) as blank to check for possible contamination and interferences. Drift in sensitivity of the GC-FID was checked in between every batch of 5 samples using midpoint calibration standard (4 ppm). Internal standard was used to correct for the loss of analyte during sample preparation. Drinking water samples were analysed in triplicates. Limit of detection (LOD) and limit of quantification (LOQ), accuracy (recovery study), precision (between-run and within-run) and linearity were determined. LOD and LOQ were determined using the formula: LOD = $3.3(S_y/S)$ and LOQ = $10(S_y/S)$ respectively (Shrivastava *et al.*, 2011) where S_y is the standard deviation of y-intercepts of regression lines of the curve and S is the slope of the calibration curve at concentration levels 1.0 - 8.0 µg/L. Recovery studies were conducted at concentration levels 4.0, 6.0 and 10.0 µg/L to check the accuracy of results obtained for DMP, DEP, DBP, BBP and DEHP. Linearity study was also conducted using five concentration levels and repeated five times. Precision (intra-assay) of the method expressed as percentage of relative standard deviation (%RSD) was evaluated by five repetitive analysis of water spiked with DMP, DEP, DBP, BBP and DEHP standards at concentrations 1.0, 2.0 and 4.0 µg/L.

Results and Discussion

A chromatogram of target PAEs standard solution is shown in Figure 1. The retention times (R_T) of 4.33 ± 0.14 for DMP, 4.99 ± 0.11 for DEP, 7.42 ± 0.04 for DBP, 11.55 ± 0.03 for BBP, 13.63 ± 0.02 for DEHP and a total run time of 13.72 minutes were obtained at optimized chromatographic conditions. Lower retention time was reported by Sibali *et al.* (2013) while Kanchanamayoon *et al.* (2012) reported higher retention times of 14.48, 15.76, 18.72, and 24.41 minutes for DMP, DEP, DBP and DEHP, respectively

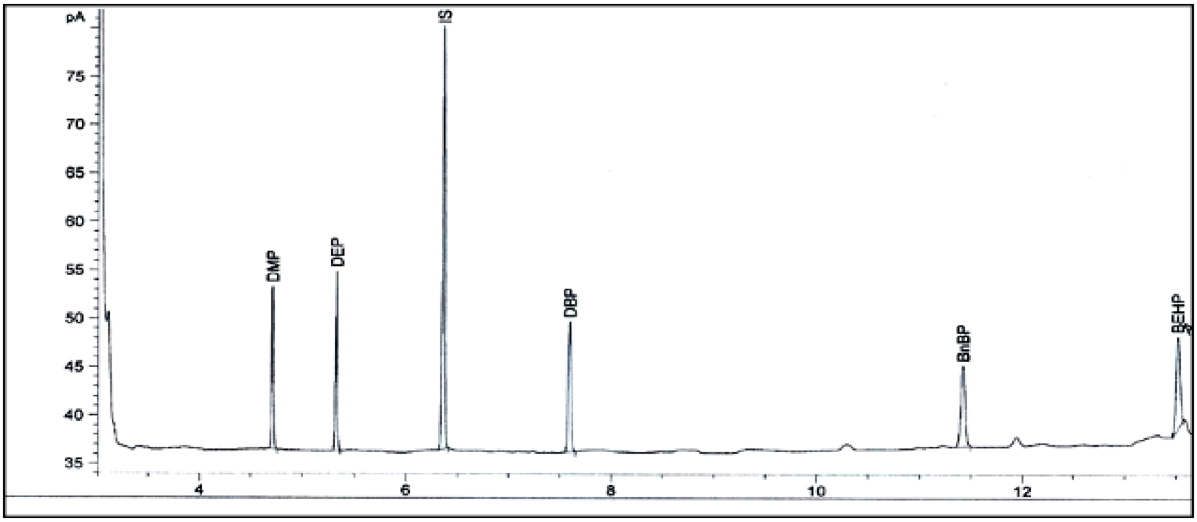

Figure 1: A representative chromatogram of for target PAEs and Internal standard. DMP- Dimethyl Phthalate, DEP – Diethyl Phthalate, IS, n-Benzyl Benzoate, DBP-Dibutyl phthalate, BBP - Benzyl Butyl Phthalate, BEHP - di-2-ethylhexyl phthalate

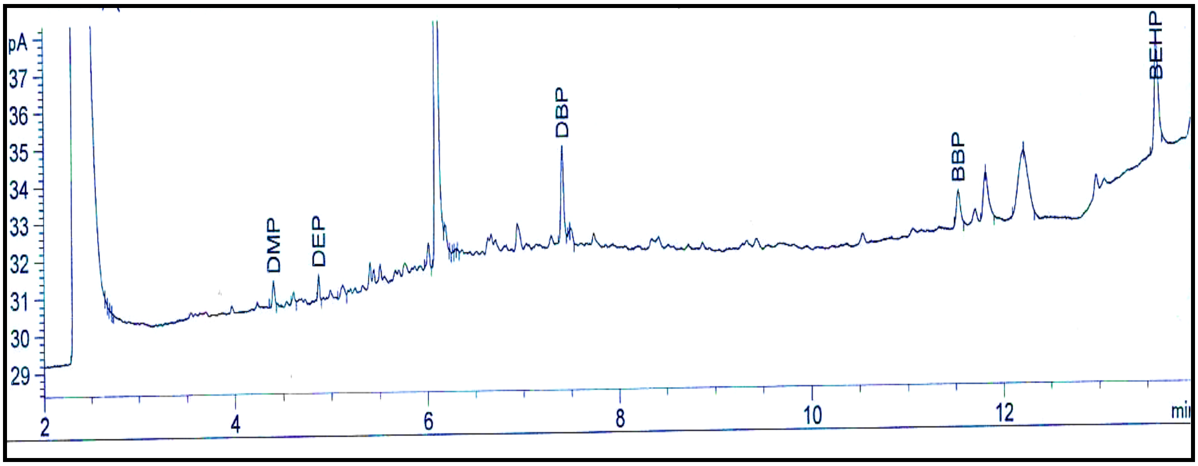

Figure 2: Chromatogram of water sample.

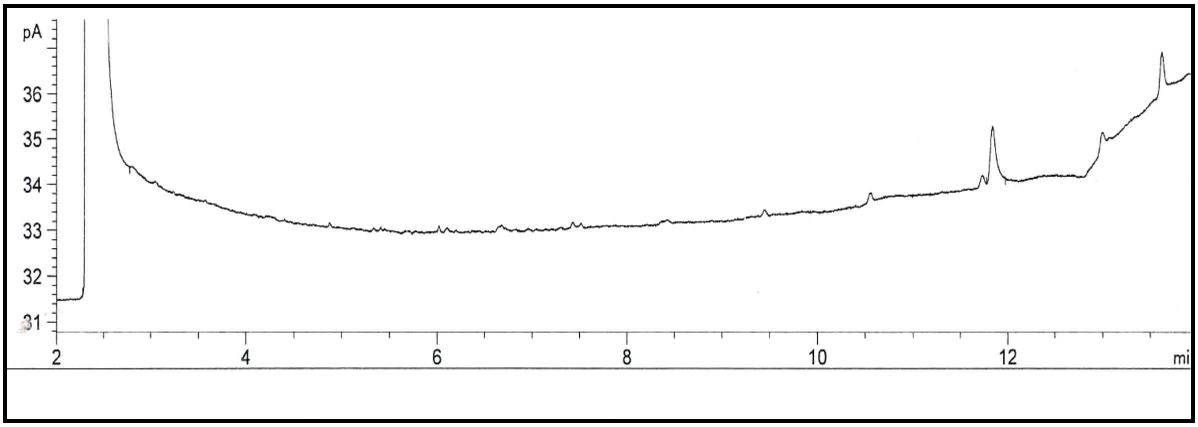

Figure 3: Chromatogram of blank.

Values obtained for LODs of PAEs ranged from 0.001µg/L (DEP) to 0.0930 µg/L (DEHP). LOD for DMP, DEP, DBP and BBP were lower than 0.060 µg/L reported by Sibali *et al,* (2013) in water samples. LODs obtained in this study were like those reported by Fatoki *et al.*, (2010). LOQ values were between 0.022µg/L (DBP) and 0.282 µg/L (DEHP).

Recovery studies from spiked double distilled water (determined in triplicate) yielded means percentage recoveries of 97.98% for DMP, 95.57% for DEP, 97.68% for DBP, 100.76% for BBP and 97.39% for DEHP as shown in Table 1. Percentage recoveries in this study were higher than those obtained by Kanchanamayoon *et al.* (2012). They had values of 87.3% for DBP and 79.17% for DEHP, while Fatoki *et al.* (2009), using SPE method, reported lower recoveries for DMP (82.14±1.32 %) and DEP (89.72 ±0.52 %) for water samples, than those obtained in this study.

Linearity was evaluated and the results are as shown in Table 1. Mean correlation coefficient (R^2) obtained was 0.9960 ± 0.0024. This is an improvement compared to mean correlation coefficients (R^2) of 0.9920 ± 0.0063 and 0.9951 obtained by Zaater e*t al.* (2013) and by Kanchanamayoon *et al.* (2012), respectively.

Precision of the study expressed as relative standard deviation (RSD%, n = 5) varied from 2.31 ± 0.93% (DMP) to 3.72 ± 2.29% (DEHP). This is comparable to the RSD% of 3.62 ± 1.99% reported by *Xu et al.* (2019). Lower results of 1.4 to 2.0% and 1.4 to 2.8% were reported by Yan *et al,* (2010) and Kanchanamayoon *et al.* (2012) respectively. An improvement on RSD was observed in the study as compared to the 7.5% (DMP) and 5.8% (DPB) values reported by Ajdari *et al.* (2018)

Table 1: Result of Linearity-correlation coefficients (R^2), LOD, LOQ, recovery and precisions studies for phthalates in drinking water using GC-FID.

Phthalate	**R^2, n = 5**	**LOD (µg/L) n = 5**	**LOQ (µg/L)**	**Recovery (%) n = 3**			**Precisions(%RSD) n = 5**		
				4.0 µg/L	6.0 µg/L	10.0 µg/L	1.0 µg/L	2.0 µg/L	4.0 µg/L
DMP	0.9958±0.001	0.004	0.120	99.99	92.69	101.25	14.13	3.43	1.64
DEP	0.9976±0.002	0.001	0.002	99.27	87.03	100.42	2.66	1.64	3.45
DBP	0.9974±0.002	0.007	0.022	100.02	103.14	90.30	3.53	2.32	1.08
BBP	0.9943±0.004	0.009	0.022	100.76	89.84	100.40	3.77	2.94	3.32
DEHP	0.9948±0.003	0.093	0.282	93.15	94.78	104.08	6.25	3.12	1.79

The water samples were analysed for phthalates on purchase and under indoor (23 to 27 ºC) and outdoor (31 to 33 ºC) storage conditions. Concentrations of PAEs in water samples from HPDE sachet and PET bottles at the time of purchase are as shown in Table 2. The value of DEP were all less than the LOD (≤ 0.01 µg/L) while values of DMP, DBP, BBP and DEHP ranged from ≤ 0.04 µg/L (LOD) to 1.58 ± 0.07 µg/L, ≤ 0.007 (LOD) to 0.84 ± 0.12 µg/L, ≤ 0.009 µg/L (LOD) to 1.90 ± 0.12 µg/L and ≤ 0.093 µg/L (LOD) to 2.46 ± 0.14 µg/L respectively for PAEs in HPDE sachet water samples. The values of PAEs in PET bottle water samples at purchase were between ≤ 0.007 µg/L (LOD) and 0.471 ± 0.51 µg/L for DBP, ≤ 0.009 µg/L (LOD) to 0.82 ± 0.04 µg/L for BBP and ≤ 0.093 µg/L (LOD) to 4.33 ± 0.03 µg/L for DEHP. DMP and DEP in PET bottle water samples were both below their LOD values of ≤ 0.04 µg/L and ≤ 0.01 µg/L respectively.

Table 2: Concentration of phthalates (µg/L) in different brands of water samples at purchase (± SD, n = 3).

	Water sample	**DMP**	**DEP**	**DBP**	**BBP**	**DEHP**
SPW	A	≤ LOD	≤ LOD	≤ LOD	0.64 ± 0.10	0.39 ± 0.05
	B	1.58 ± 0.07	≤ LOD	≤ LOD	1.90 ± 0.12	1.83 ± 0.03
	C	≤ LOD	≤ LOD	≤ LOD	0.63± 0.02	0.39 ± 0.12
	D	≤ LOD	≤ LOD	0.84 ± 0.12	≤ LOD	1.79 ± 0.08
	E	≤ LOD	≤ LOD	≤ LOD	≤ LOD	≤ LOD
	F	≤ LOD	≤ LOD	≤ LOD	≤ LOD	1.25 ± 0.09
	G	≤ LOD	≤ LOD	≤ LOD	≤ LOD	2.46 ± 0.14
BPW	A	≤ LOD	≤ LOD	≤ LOD	0.03 ± 0.02	0.02 ± 0.12
	B	≤ LOD	≤ LOD	≤ LOD	0.03 ± 0.02	0.13 ± 0.07
	C	≤ LOD	≤ LOD	≤ LOD	0.82 ± 0.04	4.33 ± 0.03
	D	≤ LOD	≤ LOD	0.47 ± 0.05	≤ LOD	1.02 ± 0.37
	E	≤ LOD	≤ LOD	≤ LOD	≤ LOD	0.50 ± 0.14
	F	≤ LOD	≤ LOD	≤ LOD	≤ LOD	≤ LOD
	G	≤ LOD	≤ LOD	≤ LOD	≤ LOD	2.32 ± 0.14

LOD: 0.04 µg/L - DMP, 0.01 µg/L -DEP, 0.007 µg/L - DBP, 0.009 µg/L – BBP and 0.093 µg/L - DEHP. SPW- Sachet Packaged Water, BPW- Bottled packed water. Values: Mean ± SD (n = 3)

Samples in group 2 which are the water samples kept indoor (between 23 and 25° C) for 30 days from purchase were analysed and the results are as shown in Table 3. The concentration of PAEs in sachet water samples varied from ≤ 0.04 µg/L (LOD) to 3.86 ±

0.05 µg/L for DMP, ≤ 0.007 µg/L (LOD) to 0.85 ± 0.10 µg/L for DBP, ≤0.009 µg/L (LOD) to 2.78 ± 0.10 µg/L for BBP and 0.22 ± 0.34 µg/L to 4.35 ± 0.13 µg/L for DEHP while all the values for DEP were found to be below the LOD value ≤ 0.001 µg/L. Comparing Tables 2 and 3, the concentrations of the various PAEs increased (Is the increase statistically significant?). Of note is DEP which was not initially detected in samples at purchase (Table 2) but was present in samples stored indoor for 30 days at a concentration range of 0.46 ± 0.14 µg/L to 0.85 ± 0.10 µg/L. Increased concentration of PAEs was also observed in water from PET bottles stored indoor (23 - 25°C) for 30 days compared to samples analysed at purchase.

Table 3: Concentrations* of phthalates (µg/L) found in different brands of water samples after storage indoors (23-27°C) for one month

	Water sample	DMP	DEP	DBP	BBP	DEHP
SPW	A	≤ LOD	≤ LOD	≤ LOD	0.93±0.02	1.37±0.01
	B	3.86 ± 0.05	≤ LOD	0.46 ± 0.14	2.78±0.10	3.17±0.03
	C	≤ LOD	≤ LOD	≤LOD	2.04±0.02	0.93±0.10
	D	≤ LOD	≤ LOD	0.85 ± 0.10	≤LOD	3.96± 0.12
	E	≤ LOD	≤ LOD	0.63 ± 0.41	≤LOD	2.04±1.01
	F	≤ LOD	≤ LOD	≤ LOD	≤LOD	0.22±0.34
	G	≤ LOD	≤ LOD	≤ LOD	≤LOD	4.35±0.13
BPW	A	≤ LOD	≤ LOD	≤ LOD	0.93±0.07	0.82±0.22
	B	≤ LOD	≤ LOD	≤ LOD	0.86±0.14	0.66±0.03
	C	≤ LOD	≤ LOD	0.95 ± 0.02	2.97±0.12	5.92±0.01
	D	≤ LOD	≤ LOD	0.43 ± 0.51	≤LOD	1.02±0.14
	E	≤ LOD	≤ LOD	≤ LOD	≤LOD	1.09±0.04
	F	≤ LOD	0.78 ± 0.01	0.62 ± 0.04	≤LOD	1.37±0.32
	G	≤ LOD	≤ LOD	≤ LOD	≤LOD	3.62±0.14

LOD: 0.04 µg/L - DMP, 0.01 µg/L -DEP, 0.007 µg/L - DBP, 0.009 µg/L – BBP and 0.093 µg/L - DEHP.SPW- Sachet Packaged Water, BPW- Bottled packed water. *Values: Mean ± SD (n = 3)

Samples in Group 3 which are water samples in HPDE sachets and PET bottles kept outdoor (31 - 33°C) for 30 days. Results of analysis (Table 4) indicated that values of PAEs in the sachet water samples kept outdoor had a range of ≤ 0.04 µg/L (LOD) to 4.5 ± 0.07 µg/L for DMP, ≤ 0.01 µg/L (LOD) to 0.64 ± 0.08 µg/L for DEP, ≤ 0.007 µg/L (LOD) to 2.15 ± 0.14 for DBP, ≤ 0.009 µg/L (LOD) to 3.09 ± 0.12 µg/L for BBP and 0.96 ± 0.01 µg/L to 7.35 ± 0.09 µg/L for DEHP while concentration of PAEs in PET bottle water samples ranged from ≤ 0.04 µg/L (LOD) to 1.25 ± 0.02 for DMP, ≤ 0.01 µg/L (LOD) to 2.84 ± 0.02 µg/L for DEP, ≤ 0.007 µg/L (LOD) to 2.28 ± 0.90 µg/L for DBP, ≤ 0.009 µg/L (LOD) to 1.71 ± 0.07 µg/L for BBP and 0.36 ± 0.10 µg/L to 7.76 ± 1.01 µg/L for DEHP. When Tables 3 and 4 were compared, it was observed that there were significant increases (At what confidence level?) in the concentrations of various PAEs for most water samples that were kept outdoor than samples that were kept inside. Mean concentrations of DEHP in water samples in HPDE kept indoor and outdoor were 2.29 µg/L and 3.19 µg/L respectively while the mean concentrations in PET bottle water samples were 2.07 µg/L and 3.59 µg/L.

Table 4: Concentration of phthalates (µg/L) found in different brands of water samples at after storage for one month outdoor (31 – 33 ^{o}C)

	Water sample	DMP	DEP	DBP	BBP	DEHP
SPW	A	≤LOD	≤LOD	≤LOD	2.33±0.10	1.77±0.03
	B	4.50±0.07	≤LOD	2.15±0.14	1.39±0.02	1.83±0.12
	C	0.34±0.05	0.64±0.08	1.19±0.27	3.09±0.12	0.96±0.01
	D	≤LOD	≤LOD	0.76±0.12	≤LOD	4.19±1.63
	E	≤LOD	≤LOD	0.92±0.41	≤LOD	2.17±0.80
	F	≤LOD	≤LOD	≤LOD	≤LOD	3.94±0.08
	G	≤LOD	≤LOD	≤LOD	≤LOD	7.35±0.09
BPW	A	≤LOD	≤LOD	≤LOD	1.44±0.10	3.55±0.03
	B	≤LOD	≤LOD	≤LOD	0.78±0.02	0.36±0.10
	C	≤LOD	≤LOD	0.30±0.27	1.64±0.10	4.68±0.01
	D	1.25±0.02	2.84±0.14	2.80±0.90	1.71±0.07	7.76±1.01
	E	≤LOD	≤LOD	≤LOD	≤LOD	2.10±0.06
	F	≤LOD	≤LOD	≤LOD	≤LOD	2.21±0.08
	G	≤LOD	≤LOD	≤LOD	0.41±0.02	4.51±0.14

LOD: 0.04 µg/L - DMP, 0.01 µg/L -DEP, 0.007 µg/L - DBP, 0.009 µg/L – BBP and 0.093 µg/L - DEHP.SPW- Sachet Packaged Water, BPW- Bottled packed water.*Values: Mean ± SD (n = 3)

There were increased values of PAEs with increase in storage time and temperature as observed from Tables 2 to 4. Findings in the present result agreed with the observation of Keresztes *et al.* (2009) that dissolution rate of phthalates increases with temperature. Also, temperature and contact surface area influenced phthalate leaching as the higher contact surface between water and HPDE/PET packages translated to higher concentrations of PAEs as observed in the present study.

Phthalate esters are known to leach from HPDE/PET food packages into its content (Edjere *et al*., 2016). Some reported concentrations of migration of PAEs in drinking water samples from earlier studies are presented in Table 5. Their values agree with the ranges for concentrations of PAEs in water samples after purchase in this study but differed from the values obtained for stored values. This may be attributed to the difference in temperature under which the studies were conducted.

Table 5: Comparisons of PAEs Migration to drinking water samples.

Author/s	Samples	Concentration (µg/L)	Storage condition	Detection
Edjere *et al*., (2016)	Sachet water	0.04 to 0.095 for DMP, 0.16 to 12.44 for DEP, 0.56 to 3.38 for DBP, Nd to 0.03for BBP, 0.08 to 0.31 for DEHP.	After purchase	GC-MS
Sulentic *et al.*, (2019)	Bottled water	DBP–1.56 to 8.44 for DBP., 0.11 to 3.70 for DEHP	After purchase	GC-MS
Dada *et al*., (2018)	Bottled water	470.0 ± 0.01 to 635.0 ± 0.05 for DMP 122.0 ± 0.01 to 563.0 ± 0.01 for DEP, and 210.0 ± 0.002 to 125.0 ± 0.02 for DBP	After purchase	

	Sachet water	746.0 ± 0.01 to 857.0 ± 0.01 for DMP, 203.0 ± 0.01 to 283.0 ± 0.01 for DEP an 33.0 ± 0.01 to 237.0 ± 0.01 for DBP	After purchase	HPLC
Prapatpong *et al.,* (2010)	Bottled water	Nd – 0.38 ± 0.01 for DMP, Nd to 0.54 ± 0.03 for DEP, Nd to 0.71 ± 0.14 for DBP and 0.28 ± 0.01 to 0.50 ± 0.02	After purchase	GC-FID
Zaki*et al.,* 2017)	Bottled water	< 0.012 for DEP, < 0.043 to 0.171 for DBP and < 0.063 to 0.298 for DEHP	After purchase	GC-MS
		< 0.012 to 0.036 for DEP,0.07 to 0.195 for DBP and < 0.063 to 0.462 for DEHP	Indoor (25 ± 4ºC) for 1 month	
		< 0.012 to 0.042 for DEP, < 0.043 to 0.435 for DBP and 0.064 to 0.475for DEHP	Outdoor (36 ± 4ºC) for 1 month	
Keresztes*et al.,* (2009)	Bottled water	< 0.0066 to 0.8 for DBP, < 0.006 to 0.1 for BBP and < 0.016 to 1.7 for DEHP	22 ˚C – 60 ˚C for 90 days	GC-MS
This study	Bottled water	of ≤ 0.04 for DMP, ≤ 0.01 for DEP, ≤ 0.007 (LOD) to 0.471 ± 0.51for DBP, ≤ 0.009 (LOD) to 0.82 ± 0.04 for BBP and ≤ 0.093 (LOD) to 4.33 ± 0.03 for DEHP	After purchase	GC-FID
		≤ 0.04(LOD) for DMP, ≤ 0.001 (LOD) to 0.78 ± 0.01 for DEP, ≤ 0.007(LOD) to 0.95 ± 0.02 for DBP, ≤ 0.009 (LOD) to 2.97 ± 0.12 and 0.66 ± 0.03 to 5.92 ± 0.01 for DEHP	Indoor (23 – 25 ºC) for 30 days	
		≤ 0.04 (LOD) to 1.25 ± 0.02 for DMP, ≤ 0.01(LOD) to 2.84 ± 0.02 for DEP, ≤ 0.007 (LOD) to 2.28 ± 0.90 for DBP, ≤ 0.009 (LOD) to 1.71 ± 0.07 for BBP and 0.36 ± 0.10 to 7.76 ± 1.01 for DEHP.	Outdoor (31-33˚C) for 30 days	
	Sachet water	≤ 0.04 (LOD) to 1.58 ± 0.07 for DMP, ≤ 0.01 (LOD), for DEP ≤ 0.007 (LOD) to 0.84 ± 0.12 for DBP, ≤ 0.009 (LOD) to 1.90 ± 0.12 for BBP and ≤ 0.093 (LOD) to 2.46 ± 0.14 for DEHP	After purchase	
		≤ 0.04(LOD) to 3.86 ± 0.05for DMP, ≤ 0.007(LOD) to 0.85 ± 0.10 for DBP, ≤ 0.009 (LOD) to 2.78 ± 0.10 for BBP and 0.22 ± 0.34 to 4.35 ± 0.13for DEHP	Indoor (23 – 25 ºC) for 30 days	
		≤ 0.04(LOD) to 4.5 ± 0.07 for DMP, ≤ 0.01(LOD) to 0.64 ± 0.08 for DEP, ≤ 0.007 (LOD) to 2.15 ± 0.14 for DBP, ≤ 0.009(LOD) to 3.09 ± 0.12 for BBP and 0.96 ± 0.01to 7.35 ± 0.09for DEHP	Outdoor (31-33 ˚C) for 30 days	

Phthalate esters are considered as endocrine disruptors and studies have demonstrated their ability to negatively affect hormonal functions such as interfering with estrogens and thyroid hormones (Botelho *et al*., 2009 and Caporossi *et al*., 2020). Specifically, DEHP in addition to possessing the general property of PAEs, in vivo and in vitro research links DEHP or its metabolites to a range of adverse effects in the liver, reproductive tract, kidneys, lungs, and heart (Tickner *et al*., 2001). Except for DEHP, levels in drinking water for other phthalates are not specified. According to the USEPA, the maximum contamination level (MCL) for DEHP in drinking water is 6 µg/L while European Union (EU), World Health Organization (WHO) and China have set 8 µg/Las the MCL for DEHP in drinking water (Ref). Comparing the values obtained for DEHP in this study to the MCLs, the maximum value obtained was higher than 6 µg/L but was lower than 8 µg/L. Di (2-ethylhexyl) phthalate was also the most dominant phthalates detected in the drinking water samples.

Conclusions

This study investigated the migration of PAEs in packaged water, specifically drinking water in HPDE sachets and PET bottles in eight brands of water. Results showed that BBP and DEHP increased in the water samples at two storage conditions, namely: indoor (23 to 27 °C) and outdoor (31 to 33 °C) for 30 days. This study also showed that higher leaching was associated with PET bottles compared to HPDE sachets. This suggested that duration of storage and temperature affected the amount of PAEs leached. This is a major concern because phthalates have been linked to a variety of negative reproductive outcomes in both men and women, including type 2 diabetes and insulin resistance, overweight/obesity, allergy, and asthma (Wang *et al.*, 2021). The result also indicated that DEHP, a known endocrine disruptor, with anti-androgenic and possible human carcinogen effects exceeded the 6µg/L USEPA Maximum Contamination Level (MCL) for DEHP in drinking water, but lower than 8 µg/L which is the specified MCL by the European Union (EU), World Health Organization (WHO) and China. This is of concern because since leaching of PAEs occurred from the packaging materials to drinking water samples and increased from time of purchase to 30 days in both samples stored at indoor and outdoor temperatures, but was higher in samples stored under outdoor temperatures, packaged water should not be stored for extended time and effort should be made to store them at lower temperatures.

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