

Evaluation of Phthalates Contents and Their Health Effects in Consumed Sachet Water Brands in Delta State, Nigeria

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Abstract—This paper determines the presence and levels of phthalates in sachet and borehole water source in some parts of Delta State, Nigeria. Sachet and borehole water samples were collected from seven different water packaging facilities and level of phthalates determined using GC-MS instrumentation. Phthalates concentration in borehole samples varied from 0.00-0.01 (DMP), 0.06-0.20 (DEP), 0.10-0.98 (DBP), 0.21-0.36 (BEHP), 0.01-0.03 (DnOP) $\mu\text{g/L}$ and (BBP) was not detectable; while sachet water varied from 0.03-0.95 (DMP), 0.16-12.45 (DEP), 0.57-3.38 (DBP), 0.00-0.03 (BBP), 0.08-0.31 (BEHP) and 0-0.03 (DnOP) $\mu\text{g/L}$. Phthalates concentration in the sachet water was higher than that of the corresponding boreholes sources and also showed significant difference ($p < 0.05$) between the two. Sources of these phthalate esters were the interaction between water molecules and plastic storage facilities. Although concentration of all phthalate esters analyzed were lower than the threshold limit value (TLV), over time storage of water samples in this medium can lead to substantial increase with negative effects on individuals consuming them.

Keywords—Phthalate esters, borehole, sachet water, sample extraction, gas chromatography, GC-MS.

I. INTRODUCTION

PHthalates ESTERS are large group of compounds that share basic chemical similarities which are derived from 1, 2-benzenedicarboxylic acid [1]. However, the individual members of the group have unique physical and chemical properties. They are oily, colourless and odourless liquids, which rarely evaporate. Known plasticizers phthalates are used in the production of plastics, including polyvinyl chloride plastics; which are capable of leaching into the environment. Phthalates when used as plasticizers causes increase in flexibility and durability of plastics such as polyvinyl chloride (PVC). Plastics that contain phthalates are commonly used in applications that include building materials, clothing, cosmetics, perfumes, food packaging, toys, and vinyl products like flooring, shower curtains, and rain coats; and in medical applications that include blood transfusion bags and tubing, intravenous fluid bags and tubing, and other medical devices. Phthalates are also found in lubricating oils, solvents, and detergents.

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One percent of the phthalate ester content of plastic materials in direct contact with water or other liquids may be released to the aquatic environment. Some of these compounds are carcinogen and estrogenic [2], [3]. With respect to health effects, phthalates are often classified as hormonally active agents or endocrine disruptors due to their ability to affect the endocrine system in the body. Exposure to phthalates has been reported to result in increased incidence of developmental abnormalities such as cleft palate and skeletal malformations, and increased foetal death in experimental animal studies [4]. According to National Toxicology Program [5], seven of the most dangerous phthalate compounds are: butyl Benzyl phthalate (BBP), Di-n-Butyl phthalate (DBP), Di-(2-Ethylhexyl) Phthalate (DEHP) also known as Bis(2-ethylhexyl) Phthalate, Diisodecyl phthalate (DIDP), Diisononyl phthalate (DINP), Di-n-Hexyl-phthalate (DnHP) and Di-n-octyl phthalate (DnOP). Their selection is based on their extent of human exposure, use in children products and due to published evidence of reproductive or developmental toxicity. The United State Environmental Protection Agency [6] has set the maximum admissible concentration (MAC) or maximum contamination level (MCL) of DEHP at $6 \mu\text{g/L}^{-1}$ and threshold limit value (TLV) of 0.55, 0.45, 5.0 and 5.0 mg/L for DEP, DBP, DMP and DEHP respectively.

The ubiquity of phthalate esters has been widely reported in various environmental samples in developed and developing countries as reported by [7] in the water, fish, and other aquatic organisms of the Gulf of Mexico; [8] in Philadelphia drinking water; [9] in tap water from the Municipal Institute of Environmental Sciences, Shinike, Japan; [10] in Greater Manchester River; [11] in the Eastern Cape Province of South Africa and [12] in Venda freshwater systems, South Africa; while in Nigeria, [13] worked on some Nigeria river water; while [14] and [15] worked on the sewage oxidation pond at the Obafemi Awolowo University and Covenant University respectively. Adelagun et al. [16] and Oyo-Ita, et al. [17] carried out research on Ona River and Sediments of the Cross River System.

Water of adequate purity is of vital importance in the existence of life. The human body composes 65% of water and health experts stress that we should drink two litres of water a day [18]. Many of the world's population, lacks access to safe drinking water. With a population greater than six billion people on earth, more than one billion (one in six) lack accesses to safe drinking water [19]. The problem of paucity

of potable drinking water is endemic in developing countries like Nigeria.

Sachet water is any commercially treated water, manufactured, packaged and distributed for sale in usually sealed 500ml food grade containers and is intended for human consumption [20]. It has become an immensely popular form of packaged drinking water in the face of urban drinking water shortages in West Africa [21]. The production of sachet water started in the late 90's in Nigeria and achieved rapid growth in the mid-2000s [20]. It continues to fill gaps in consumer demand, particularly in areas with limited piped water services [22], [23].

The production of sachet water requires two important raw materials, water source (which is usually borehole or tap water) and the packaging materials. The ubiquity of sachet water is undeniable, yet little is known about its phthalate contents. Several studies have reported the bacteriologic and physiochemical quality of sachet water over the past decade [24].

Water is usually evaluated using the WHO, FEPA, NAFDAC, SON and other regulatory agencies guidelines. The problems associated with chemical constituents of drinking water arise primarily from their ability to cause adverse health effects after prolonged periods of exposure, of particular concern are contaminants that have cumulative toxic properties, such as heavy metals and substances that are carcinogenic. Many drinking water contaminants including various chemicals, physical, microbiological and radiological are known to be hazardous to health [19].

The present study focuses on the phthalate esters chemicals contents in popular sachet brands in Delta State, Nigeria as no known study has been done in this area.

II. MATERIALS AND METHODS

A. Location of the Research

Delta State lies approximately between Longitude 5°00' and 6°45' East and Latitude 5°00' and 6°30' North. It is generally low-lying without remarkable hill and lies within the humid tropical zone with defined dry season (November – March) and rainy season (April - October). The rainy season is brought about by the South-West Trade Wind blowing across the Atlantic Ocean, while the dry, dusty, and often cold North-East Trade Wind blowing across the Sahara Desert dominates the dry season with a short spell of harmattan [25]. The relative humidity of the area is high and increases from 70% in January to 80% in July. The average atmospheric temperature of the area is about 25.5°C in the rainy season and about 30°C in the dry season [26]. The State has huge deposits of crude oil and is one of the largest producers of petroleum products in Nigeria. The state is made up of 25 local government areas. It is situated in the region known as the South-South geopolitical zone with a population of 4,098,291 [27]. The state covers a landmass of about 18,050 km², of which more than 60% is land, while the rest are covered by rivers, creeks, and mangrove. The state has over 160 kilometre wide coastal belt

inter-lace with rivulets and streams, which form part of the Niger Delta.

B. Sample Collection and Storage

Samples were collected from Osubi, Ugbomro, Effurun and Ughelli Towns spread across Okpe, Uvwie and Ughelli Local Government Areas of the State. Sachet water samples were collected from seven sachet water sealing factories spread around three local government areas of Delta State in Nigeria. Detailed information on the stations and grid centres is presented in Table I. Borehole water used for the sachet water was also collected from each of these factories. The samples containers were pre-cleaned, kept in coded containers and stored in an ice chest. Exhaustive clean up of reagents and glassware was done to eliminate background phthalate that is not derived from the sample. The sample were refrigerated at 4°C and kept free from light from the time of collection until extraction.

C. Safety Measures

All procedures and associated reagents used during this research followed standard risk assessment protocols specified by Bachema Analytical Laboratories Switzerland where this work was carried out. The new method for analysis of Phthalate in water samples using GC/MS was validated according to Institute Bachema AG Quality Management Guidelines as certified by ISO 17025 (Institute Bachema QRL-Verzeichnis, version 04).

D. Reagents

Anhydrous Sodium Sulphate Oven heated at 400°C (Fluka), Cyclohexane distilled in an all glass (Scharlau), Acetone GC (Scharlau), 1,11-Dibromoundecan ISTD (Labor Dr. Ehrenstofer), Reagent Water (Nanopure/Water-Barnstead), ISTD-Solution: 2.5µl Dibromoundecan in 250ml Cyclohexane. 1ml of this solution contains Approx, 10ug ISTD. Phthalate Ester was Mix 0.2mg/ml in Methanol (Accu Standard M606), Phthalate and Adipate Esters Mix1, 100 ng/ul (Labor Dr. Ehrenstofer). All standards were stored at 4°C.

TABLE I
 SAMPLE LOCATION, CODES AND GRID

S/N	Sample Area	Local Government Area	Sampling Coordinates
1	Osubi	Okpe	N 05°35'29.70" E005°49'26.20"
2	Ugbomoro (Effurun)	Uvwie	N 05°34'06.11" E005°49'35.80"
3	Ugbomoro (Effurun)	Uvwie	N 05°33'24.20" E005°48'17.20"
4	Ugbomoro (Effurun)	Uvwie	N 05°34'14.90" E005°49'21.90"
5	Ughelli	Uvwie	N 05°30'03.60" E006°00'47.90"
6	Ughelli	Ughelli	N05°30'07.80" E006°00'46.20"
7	Ugbomoro (Effurun)	Uvwie	N 05°34'11.40" E005°49'21.90"

E. Extraction of Water Sample

A measured volume of Sample, 1L was weighed into a 1L calibrated Erlenmeyer flask. To this was added 1ml

cyclohexane internal Standard solution and then 9ml of cyclohexane. With the aid of a glass coated magnetic the Sample was then Liquid-Liquid intensively extracted for a minimum of one hour. Using a special glass-separating device the solvent Extract was isolated in a 10 ml vial. Sample volume is 1L in 10ml cyclohexane extract. This method was deliberately used to avoid Extract concentration so as to reduce contamination.

F. Blank Sample

A 1L aliquot of nanopure water is treated exactly as a sample including exposure to all glassware, equipment, solvents. This is done by the injection of the extracted blank at the beginning of all analytical series.

G. Instrumentation

The analytes in the extract were separated by means of capillary gas chromatography using temperature programming. The chromatographically separated phthalate esters were detected and measured with Mass Spectrometer. This process is made possible by large volume injection (LVI) technique used to introduce 10µl of the sample solvent extract at a rate of approx. 4.6ul/sec into the injector. The injector is kept at an initial temperature of 78°C and rises gradually at the rate of 5°C/sec to 300°C so as to enable complete volatilisation of solvent into the analytical column. Oven initial temperature was kept at 70°C and on injection rises to 300°C at a rate of 20°C/min. Injector's temperature is brought back quickly to normal by the use of a liquid Nitrogen cryo cooling unit. The new method for analysis of Phthalate in water samples using GC/MS was validated according to [28], [29] and Institute Bachema AG Quality Management Guidelines as certified by ISO 17025 [30], [31].

TABLE II
PHthalate ESTERS IN BOREHOLE WATER SAMPLE (µg/L)

S/N	Description	DMP	DEP	DBP	BBP	BEHP	DnOP	Total
1	Osubi	ND	0.06	0.16	ND	0.25	ND	0.47
2	Ugbomoro (Effurun)	0.01	0.20	0.84	ND	0.21	0.03	1.29
3	Ugbomoro (Effurun)	ND	0.10	0.98	ND	0.23	0.01	1.32
4	Ugbomoro (Effurun)	ND	0.16	0.33	ND	0.21	ND	0.70
5	Ughelli	ND	0.16	0.10	ND	0.36	ND	0.62
6	Ughelli	ND	0.20	0.85	ND	0.25	0.01	1.31
7	Ugbomoro (Effurun)	ND	0.17	0.41	ND	0.25	0.01	0.84
	Minimum	ND	0.06	0.10	ND	0.21	ND	0.47
	Maximum	0.01	0.20	0.98	ND	0.36	0.03	1.32
	Mean	0.001	0.15	0.53	ND	0.26	0.01	0.95
	s.d.	0.002	0.04	0.313	ND	0.031	0.007	0.32

ND: Not Detected

III. RESULT AND DISCUSSION

Tables II and III show various concentration of phthalate in borehole and sachet water samples and also the total phthalates present in each Station. DMP and BBP in the borehole water were below detection limit in all the samples except Station 2 for DMP, while DEP, DBP, BEHP and DnOP

ranges from 0.06-0.20µgL⁻¹, 0.10-0.98µgL⁻¹, 0.21-0.36µgL⁻¹ and ND-0.03µg L⁻¹ respectively (Table II). A similar trend was also observed in the corresponding sachet water. BBP was not detected in all the samples collected except Station 7, while the following range were recorded for the other phthalates: DMP (0.03-0.95µgL⁻¹), DEP (0.16-12.44µgL⁻¹), DBP(0.57-3.38µgL⁻¹), BEHP (0.08-0.31µgL⁻¹) and DnOP (ND-0.03 µgL⁻¹) respectively (Table III).

TABLE III
PHthalate ESTERS IN SACHET WATER SAMPLE (µg/L)

S/N	Description	DMP	DEP	DBP	BBP	BEHP	DnOP	Total
1	Osubi	0.48	8.31	3.38	ND	0.08	0.03	12.28
2	Ugbomoro (Effurun)	0.95	12.44	3.36	ND	0.22	0.02	16.99
3	Ugbomoro (Effurun)	0.03	0.55	1.28	ND	0.18	0.01	2.05
4	Ugbomoro (Effurun)	0.16	3.95	2.09	ND	0.15	0.01	6.36
5	Ughelli	0.04	0.16	0.57	ND	0.16	0.01	0.94
6	Ughelli	0.49	4.49	2.11	ND	0.27	ND	7.36
7	Ugbomoro (Effurun)	0.53	2.66	2.11	0.03	0.31	0.02	5.66
	Minimum	0.03	0.16	0.57	ND	0.08	ND	0.94
	Maximum	0.95	12.44	3.38	0.03	0.31	0.03	16.99
	Mean	0.41	4.65	2.13	0.00	0.20	0.02	7.38
	s.d.	0.26	3.27	0.71	0.01	0.06	0.01	4.15

ND: Not Detected

Concentration of DMP, DEP, BBP and DnOP obtained in sachet water was higher than that from their various ground water sources (borehole) with the exception of BEHP. This could be as a result of cumulative effects from water source, production pathway and storage time. Prokupkova et al [32] reported that Phthalate esters may migrate from the plastic bottle and the cap into the contents of bottle. It should be noted that virtually all the sachet factories use plastic overhead containers to store water pumped from the boreholes. The water may stay in this plastic container between one to ninety six hours before they are pumped and bagged into the plastic sachet containers. During the storage in the plastic overhead tanks, there is likely leakages and influx of phthalates from the containers into the water. This might have accounted for the higher concentration of phthalates in the sachet water compared to the raw borehole water.

Total concentration of phthalates in each of the borehole stations range from 0.47-1.32µgL⁻¹, while the concentration in the sachet water range from 0.94-16.99µgL⁻¹. Fig. 1 shows total phthalate concentration for borehole and sachet water samples with Station 3 having the highest concentrations for borehole (1.32µg/L) and Station 2 the highest for sachet (16.99µg/L), while Stations 1 and 5 has the lowest total phthalates concentrations for borehole (0.47µgL⁻¹) and sachet (0.94µgL⁻¹) water respectively. It has been argued that it is not appropriate to assess the risks from phthalates by evaluating each phthalate individually because individuals are exposed to many phthalates at the same time or during the same day. This approach significantly understates the risk and a more accurate estimate of risk would result if the exposures were added together and compared with the doses that produce

adverse effects [33], [34]. The implication is that adverse effects not seen with individual phthalates may be seen in the people exposed to multiple phthalate. This is reflected in the total phthalates obtained for each sample as they were all significantly higher than the concentrations of individual phthalates recorded for each sample as shown in Tables II and III respectively.

It was observed from the statistical data that the concentration levels of phthalates in sachet water were generally higher than that of the corresponding boreholes. The analysis of variance (ANOVA) between the two corresponding value also showed that they are significantly different ($p < 0.05$) from one another.

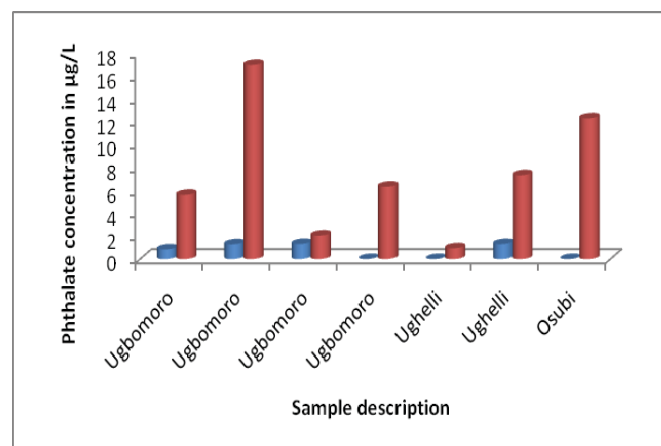


Fig. 1 Total Phthalate ester contents in borehole and sachet water sample

It was also observed that there is statistical difference in concentration of DMP and DBP for water samples collected from Ugbomoro (Table IV). This might be due to the channel for conveying the water sample from source to point of use. Leivadara et al [35] reported that sources of phthalates contamination might come from water treatment facilities, namely: pipes, storage tanks and filtering systems. Casajuana and Lacorte [36], in their findings, concluded that poor storage conditions (10 weeks outdoors at temperatures of up to 30°C) increased the concentrations of DBP, BBP and DEHP in bottled water. After exposure, the mean concentrations of DBP, BBP and DEHP were 0.046 µg/L, 0.010 µg/L and 0.134 µg/L respectively. As regards sunlight exposure experiments, Schmid et al. [37] detected DEHP (100 – 710 ng/L) at a level seven times higher than for the blank samples (110 ng/L). Treatment processes such as coagulation, filtration and chlorination would have led to alteration of hydrogen ion concentration. According to [38] concentrations of phthalate appeared to be influenced by the pH. The authors suggested that acidic pH stimulates diffusion of phthalates. Similarly, disparity in significant levels was also obtained for DMP, DEP and DBP concentration for borehole and sachet water samples in the seven regions studied as shown in Table V.

TABLE IV
MEAN CONCENTRATION (µG/L) OF PHTHALATE ESTERS FROM LOCATIONS IN EFFURUN METROPOLIS

Source	DMP	DEP	DBP
Borehole water	0.0014 ^a	0.1500 ^a	0.6657 ^a
Sachet water	0.3829 ^b	4.6514 ^b	2.1286 ^b
Standard	5000 ^c	550 ^c	5000 ^c

Values in the same column with different superscripts are significantly different ($p < 0.05$).

TABLE V
MEAN CONCENTRATION (µG/L) OF PHTHALATE ESTERS FROM LOCATIONS IN EFFURUN AND UGHELLI METROPOLIS

Source	DMP	DEP	DBP
Borehole water	0.0025 ^a	0.1575 ^a	2.211 ^a
Sachet water	0.4175 ^b	4.90 ^a	0.6400 ^b
Standard	5000 ^c	550 ^c	5000 ^c

Values in the same column with different superscripts are significantly different ($p < 0.05$).

A. Correlation Matrix

A significant positive correlation was found to exist between DEP and DMP (0.924), DBP and DEP (0.915); and DBP and DMP (0.880) as shown in Table VI. The strong correlation among these variables indicates their common origin especially from storage plastic tanks. Table VII shows values obtained for sachet water as DBP vs. DEP (0.921), DEP vs. DMP (0.874), and DBP vs. DMP (0.820). The significant positive correlation of these phthalate esters indicates that the variables may derive from similar sources as moving together [15]. On the other hand, significant negative correlations indicate the anthropogenic and geogenic sources of these variables. Phthalate esters with lower molecular weight are more positive correlated than the higher molecular weight phthalate esters. This is probably due to solvation of water molecules with lower carbon chain phthalate esters than the higher molecular weight phthalates esters.

TABLE VI
CORRELATION MATRIX FOR PHTHALATE IN BOREHOLE WATER

Parameter	DMP	DEP	DBP	BBP	BEHP	DnOP
DMP	1.000					
DEP	0.924	1.000				
DBP	0.880	0.915	1.000			
BBP	0.325	0.020	0.203	1.000		
BEHP	-0.072	-0.320	-0.420	0.358	1.000	
DnOP	0.397	0.444	0.577	0.240	-0.461	1.000

*. Correlation is significant at the 0.05 level
Correlation rating: >0.91= very strong; 0.91-0.81= strong; 0.81-0.31= moderate; <0.31=weak

TABLE VII
CORRELATION MATRIX FOR PHTHALATE IN SACHET WATER

Parameter	DMP	DEP	DBP	BBP	BEHP	DnOP
DMP	1.000					
DEP	0.874	1.000				
DBP	0.820	0.921	1.000			
BBP	0.196	-0.200	-0.008	1.000		
BEHP	0.359	-0.106	-0.100	0.649	1.000	
DnOP	0.414	0.517	0.626	0.258	-0.368	1.000

*. Correlation is significant at the 0.05 level
Correlation rating: >0.91= very strong; 0.91-0.81= strong; 0.81-0.31= moderate; <0.31=weak

IV. CONCLUSION

Result obtained from this research showed the presence of phthalate esters (DMP, DEP, DBB, BBP, BEHP and DnOP) in borehole and sachet water. Concentrations obtained was of the order DBP>BEHP>DEP>DnOP>DMP>BBP for borehole and DEP>DBP>DMP>BEHP>DnOP>BBP for sachet water. Concentrations of phthalates recorded for sachet water was significantly higher than the corresponding source boreholes. Although values obtained from this study are below set the maximum admissible concentration (MAC) and threshold limit value for the various phthalates investigated for drinking water [6], but their aggregate/total values in some of the investigated sachet waters were found to be higher than the US Environmental Protection Agency (USEPA) criterion of 3 µg/L for the protection of fish and aquatic life in rivers [39]. Therefore, this water-type should not be allowed to find their way into rivers and streams used for rearing these organisms. It was also observed that availability of Lower molecular ester phthalate shows possibility of increase in their concentration with storage time, since they can hydrolyze faster in solution. Presents of higher carbon chain esters phthalate can also provide large surface areas for adsorption of essential minerals in water and also act as sink for growth of anaerobic microorganism. Hence there is need for sachet water manufacturers to continuous monitor their finished products, while long storage of ground water in plastics tanks for household use should be avoided as there's possibility of esters phthalate leaching.

Although some countries like Canada and United States of America have developed some form of guidelines and criteria for phthalates in drinking water and for the protection of freshwater aquatic life [40], Nigeria at present does not have any regulatory standard for phthalates in its water systems. It is the view of the authors that a review of the country's drinking water policy is long overdue and there is a need to incorporate phthalate into not just the drinking water standard but also into the country's freshwater system as this is one of the emerging environmental pollutants.

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