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Consideration of phthalates distribution in underground water in some selected regions in Delta State, Southern Nigeria

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Abstract. The choice of phthalates as plasticizers have been on the increase especially in household products. They are ubiquitous environmental pollutants due to their physical attribute. This study was carried out to determine the occurrence and level of phthalates in the groundwater in some regions of Delta State. Groundwater samples were collected from fourteen sampling points and analyzed using standard procedures. The obtained results showed that the concentration (µg/l) of six phthalate ester compounds present in the water samples was of the order: < 0.05 - 0.05 BBP, < 0.05 - 3.71 BEHP, < 0.05 - 0.54 DBP, < 0.05 - 0.55 DEP, < 0.05 - 0.13 DMP, and < 0.05 - 0.48 DnOP. BEHP was observed to be the major compound of the phthalate acid esters present in most sampling stations, whilst others, especially BBP, were found to be in low concentration and does not pose any immediate threat to human health. The presence of BEHP in most samples from different locations suggests an inflow of the phthalate to underground water, hence it becomes imperative for continuous monitoring and a call to various governments and environmental regulatory agencies to establish standards for phthalate esters in order to monitor its presence in the environment.

Keywords: phthalates, underground water, Delta State.

1. Introduction

Phthalates are a group of aromatic chemicals containing a phenyl ring with two attached and extended acetate groups. They are typically colorless liquids, man-made substance used to make plastics more flexible, soft and resilient and as such there are widely used as additives in the production of paints, plastics and cosmetics. Since phthalates esters are not a part of the chain of chemicals (polymers) that makes up plastics, they can be released easily from these products. These plastics are found in products such as toothbrushes, automobile parts, tools, toys, and food packaging. Some are also used in cosmetics, insecticides, medical tubing, aspirin, blood storage bags and adhesives [1, 2].

Phthalates are simply released and migrate into foods, beverages and drinking water from the packaging or bottling materials or manufacturing processes. This process accelerates as plastic products age and break down. With respect to their endocrine-disrupting potential, phthalates such as benzyl butyl phthalate (BBP) and di-butyl phthalate (DBP) have been found to obtain estrogenic responses in vitro assays. Phthalates can migrate into the environment from plastics. In other words, the environmental effects of phthalates may occur during the technological process, manufacture, and use of plastic materials, or on their disposal after use [3-5]. The main route of phthalates entering the environment is the atmosphere, wherefrom they are washed out by precipitation. Phthalates partially dissolve in water in the form of residues and partially adsorbed to organic substances in the soil and sediment. Subsequently, they reach underground waters through continuous soil filtration, where a certain amount of phthalates undergoes slow-process disintegration, whereas the rest accumulates in the plants, fish, amphibians, birds, and eventually humans [3-5]. The presence of phthalates has been demonstrated in underground water.

Production of plastics has been on the increase, an estimated production of exceeding 25 million tons per year have been reported [3-5]. It is challenging to conceive any human activity free from the use of plastic materials. The proportion of plastics in solid waste increases by 1% a year and poses a considerable problem because of its volume and non-degradability [3-5]. Unrestrained disposal of plastic materials and packaging containers can pollute both the soil and underground water streams, whereas inappropriate incineration of plastics can trigger the formation of highly noxious compounds known as dioxins (dibenzodioxins and dibenzofurans) [7]. Unfortunately, many of these springs are out of function today because of contamination, primarily due to poor control of industrial wastewater release to the underground. In addition, the quality of underground waters has been found to deteriorate to some extent because of uncontrolled city waste disposal [8-10].

Previous research carried out by the authors [11] showed a correlation of phthalate ester in packaged water and the source (borehole). Undoubtedly, it may constitute a great harm to the populace in Delta State of

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Nigeria relying on underground water for drinking purpose. Hence, it is imperative to examine the level of phthalate esters within this source of water.

2. Experimental

2.1. Description of the study area

Delta states lie approximately between longitude 5'00 and 6' 45 East and Latitude 5'00 and 6'30 North. Delta State lies within the humid tropical zone with well-defined period of dry seasons (November – March) and rainy seasons (April - October). The rainy season caused by South-West Trade Wind blowing across the Atlantic Ocean, whilst the dry, dusty, and often referred to the North-East Trade Wind blows across the Sahara Desert dominates the dry season. The State is a conglomerate up of about 25 local government area. It is located in the south-south geopolitical zones with a land area of 18,050 km^2 of which more than 60 % consist of lands and the rest consist basically of rivers, creeks and mangroves [11].

2.2. Sample collection

Grab water samples were collected from fourteen sampling points as shown in Table 1. Samples were collected below the groundwater table 50 m depth. At each sampling point, water samples were collected using a clean 1 l glass bottle. Samples were then stored in an ice chest until arriving at the laboratory, where they were kept in the fridge.

Table 1. Sampling regions and Global Positioning System coordinate

S/ NO	Site code	Descriptions	Samples coordinates
1.	Sample 1	Sapele	N05˚88'27.4" E005˚70'41.6"
2.	Sample 2	Agbor	N06˚25'34.8" E006˚19'82.4"
3.	Sample 3	Umutu	N05˚92'46.1" E006˚23'27.7"
4.	Sample 4	Warri2	N05˚34'27.4" E005˚43'57.2"
5.	Sample 5	Effurun1	N05˚56'82.1" E00 5˚74'56.8"
6.	Sample 6	Ovwian	N05˚50'31.7" E005˚79'91.8"
7.	Sample 7	Asaba1	N06˚12'59.2" E006˚41'55.5"
8.	Sample 8	Asaba3	N06˚10'57.7" E006˚44'4.4"
9.	Sample 9	Asaba2	N6˚11'33.1" E006˚42'33.9"
10.	Sample 10	Effurun 2	N05˚34'27.4" E005˚49'14.0"
11.	Sample 11	Igun	N05˚44'4.5" E005˚58'2.2"
12.	Sample 12	Ughelli	N05˚26'43.116" E06˚13'22.26"
13.	Sample 13	Oleh	N05˚29'15.108" E06˚0'46.8"
14.	Sample 14	Agbor	N06˚26'13.5" E006˚16'73.8"

2.3. Chemicals and materials

1-Dibromoundecan (Sigma Aldrich) was used as internal standard for quantification of phthalates. Anhydrous sodium sulfate (Sigma Aldrich) as desiccant, cyclohexane for pesticide residue analysis (Carlo Erba Reagents) as extractant, water (Milli-Q) and acetone (Honeywell) were used as received, without further purification.

2.4. Sample handling, pre-treatment and extraction of water

Water samples were collected in amber glass containers and sealed with a glass stopper followed by a metal clip. Samples were refrigerated at 4 °C from the time of collection until extraction. To 0.5 l of sample were added 1 ml cyclohexane internal standard solution and then 9 ml cyclohexane. Liquid/liquid method of extraction [11] was done for an average of 1 h using a coated magnetic glass stirrer.

2.5. Quality control and GC/MS analysis of phthalate in water

Distilled water was used as a control sample during the experimental process. It was analyzed separately for all phthalates acid esters. To ascertain repeatability, a triplicate analysis was carried out, with error within the range of ±12-15%. Analytes were identified and quantified using a gas chromatograph coupled with a mass spectrometer. Large-volume injection (LVI) technique was used to introduce 10 µl of the sample solvent extract at an approximate rate of 4.6 µl/s into the injector. GC/MS was carried out according to procedure described by Institute Bachema Quality Management Guidelines as certified ISO 17025 [14-16]. The injector was kept at an initial temperature of 78 °C and rises to 300 °C at a heating rate of 5 °C/s. Oven initial temperature was kept at 70 °C with gradual increased to 300 °C at a rate of 20 °C/min. Liquid nitrogen cryocooling unit was used to cool the injector's temperature [12, 13].

3. Results and discussion

Table 2 shows the various concentrations of phthalates in borehole water samples and the total amount of phthalates present in each sampling point. The total concentration of phthalates ranges from < 0.05µg/l – 4.24 µg/l, with the highest total phthalates concentration recorded in Agbor 1 (sample 2) with a concentration of 4.24 µg/l followed by Effurun 2 (sample 5) and Ughelli with a concentration of 2.83 µg/l and 1.38 µg/l respectively, whilst the lowest total phthalates concentrations was recorded in Asaba1 and Asaba 3. The range of individual phthalates is of the order 0.2 – 1.7 µg/l. Generally, the pattern of the phthalate concentration shows BEHP > DEP > DBP > DnOP > DMP > BBP within this two sampling position. The concentration of BBP, BEHP, and DnOP obtained in sampling point 2 (Agbor 1) is higher than other sampling points except for DMP and DEP, which are below the detection limit which is 0.05 µg/l. It is noted that the concentration of BBP was not detected in all samples except in sample 2 (Agbor 1), thus it was below the detection limit of all samples which is at 0.05 µg/l. It was generally noted that BEHP was more prevalent and has the highest concentrations in most of the Station. It was followed by DEP and DBP. The least occurring phthalate was BBP, which was not detected in all the locations with the exception of sample 2. It was closely

followed by DnOP and DMP. Since the concentration of BEHP samples which is the most dominant phthalates in the groundwater, has the highest concentration of 3.71 µg/l at sample 2 of which, according to the standards for drinking water quality of USEPA, the maximum admissible concentration should be 3 µg/l. Therefore, the maximal values BEHP concentrations exceeded the MAC of USEPA, which indicates that the local government should pay more attention to the control of PAEs pollution in groundwater to prevent further pollution [17]. The concentration of DBP was present basically in only two samples which were sample 3 and sample 2 with a concentration of 0.54 µg/l and 0.48 µg/l respectively, whilst at other sampling points it was below the detection limit. Also, it was noted that DEP was not detected in all the sampling stations, with the exceptions of sampling point 4, 5 and 10 with concentrations of 0.1 µg/l, 0.55 µg/l and 0.09 µg/l respectively.

Table 2. Concentrations (µg/l) of phthalate esters in borehole water samples

	BBP	BEHP	DBP	DEP	DMP	DNOP	TOTAL
Sample 1	<0.05	0.89	<0.05	<0.05	<0.05	<0.05	0.89
Sample 2	0.05	3.71	<0.05	<0.05	<0.05	0.48	4.24
Sample 3	<0.05	0.89	<0.05	<0.05	0.05	<0.05	0.94
Sample 4	<0.05	0.99	0.48	0.1	0.13	<0.05	1.7
Sample 5	<0.05	1.77	0.54	0.55	<0.05	<0.05	2.86
Sample 6	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	0.2
Sample 7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sample 8	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sample 9	<0.05	0.25	<0.05	<0.05	<0.05	<0.05	0.25
Sample 10	<0.05	0.35	<0.05	0.09	<0.05	<0.05	0.44
Sample 11	<0.05	0.56	<0.05	<0.05	<0.05	<0.05	0.56
Sample 12	<0.05	1.38	<0.05	<0.05	<0.05	<0.05	1.38
Sample 13	<0.05	0.13	<0.05	<0.05	<0.05	0.13	0.26
Sample 14	<0.05	0.51	<0.05	<0.05	<0.05	<0.05	0.51

DMP was observed to be more in Station 4 (0.13 µg/l) and lesser in Station 3 (0.05 µg/l), these were the stations whereby it was above the detection limit, but others were less (< 0.05 µg/l). Hence, the possibility of DMP degradation is not ruled out since the water solubility of the alkyl phthalate ester generally varies inversely with the length of the alkyl side chain. Phthalates have a remarkable large variation in their solubility with DMP being moderately soluble [18]. This also explains why BBP (benzyl-butyl-phthalates) was detected only in Station 2 (< 0.05 µg/l).

BEHP is detected in virtually in all samples. Due to its suitable properties and the low cost, BEHP is widely used as a plasticizer in manufacturing of articles made of polyvinyl chloride, such as sewage pipes, and is a component of many household items, including tablecloths, floor tiles, shower curtains, garden hoses, rainwear, dolls, toys, shoes, medical tubing, furniture upholstery, and swimming pool line [19].

BEHP and DNOP are isomers with a higher molecular weight of 390.56 g/mol. Diisoctylphthlate (DNOP) is not detected in most samples, mainly because BEHP is found to have a fourfold solubility compared to DNOP [20]. High molecular weight esters persist more in the environment. This can be seen in Table 2 as most samples contain less of lower molecular weight phthalates. It may be possible that solubility of phthalate esters increases with increasing carbon chain.

In Fig. 1, the patterns of phthalate ester concentration for each of the stations are:

- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 1);
- BEHP > DnOP > DMP ≥ DEP ≥ DMP ≥ BBP (sample 2);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 3);
- BEHP > DBP > DMP > DEP > DnOP ≥ BBP (sample 4);
- BEHP > DEP > DBP ≥ DnOP ≥ DMP ≥ BBP (sample 5);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 6);
- BEHP ≥ DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 7);
- BEHP ≥ DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 8);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 9);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 10);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 11);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 12);
- BEHP ≥ DnOP > DBP ≥ DEP ≥ DnOP ≥ BBP (sample 13);
- BEHP > DMP ≥ DBP ≥ DEP ≥ DnOP ≥ BBP (sample 14).

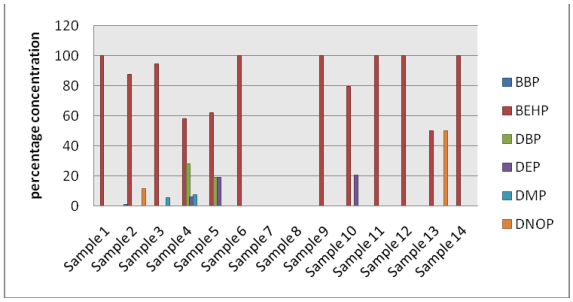

Figure 1. Variation of phthalate esters in sampling regions

In Fig. 2, the total phthalate acid ester concentration ranged between < 0.05 µg/l to 4.24 µg/l. It was noted that sample 7 and sample 8 have the lowest concentration of < 0.05 µg/l, while sample 2 and sample 5 have the highest total phthalate concentration of 4.24 and 2.86 µg/l respectively. The observed concentration of BEHP at this sampling point (sample 2) is 3.71 µg/l, which is the highest when compared to other phthalates, especially DMP, DBP and DEP, which are < 0.05 µg/l. Alarming concentration of BEHP (3.71 µg/l) may tend to pose threat. It is being considered a priority hazardous substance and also poses a serious risk of cancer in human, especially through dermal absorption (bathing) or ingestion (drinking). The concentration of DBP, BBP, DEP, and DMP in the groundwater was found to be at a level that does not pose an immediate threat, but when accumulated over some period of time may be highly dangerous. Geological setting of sampling in region 2 (Agbor) as described by Oyem et al. [21] is mainly compost of tertiary sedimentary sandstone with fine to coarse reddish sediments in texture giving it a porous nature. This might have provided leeway for easy passage of leachate into the groundwater in the underlying aquifer.

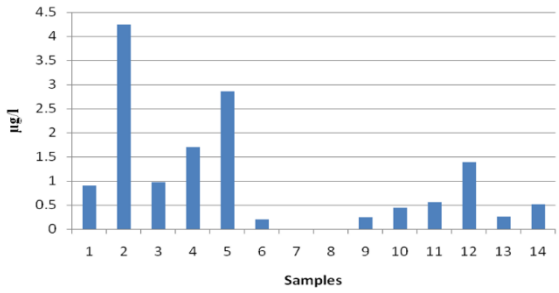

Figure 2. Total concentration of phthalate esters

As a result of this health threat, it is important that the Nigeria government should set up indigenous standards for phthalate acid ester in consumer products throughout the nation.

4. Conclusion

Groundwater is a major source of water for the urban regions of Delta State, in which it is used for drinking and some other domestic activities. This study was carried out to determine the occurrence and distribution of some phthalate groups in the groundwater of some selected region of Delta State. Six groups of phthalates were detected in the fourteen sampling stations with BEHP having the highest concentration in almost all regions. However, the amount of phthalates present in these regions is in low concentrations and thus it does not pose any immediate health threats to both humans and animals, especially when consumed.

Recommendation. Although the level of phthalates concentration observed in this study is very low to pose any threat to human health, the need for constant monitoring of the level of BEHP is essential, especially in Agbor study location due to the rising commercial activities within this suburb. It is also important that both the state and federal government of Nigeria should set up indigenous standards for phthalates to monitor and regulates its presence in the environment

Conflict of interest

Authors have declared that no conflict of interest exists.

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