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Quantitative Evaluation of Phthalate Esters in Three Tributaries of Asa River, Ilorin, Nigeria

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ABSTRACT: *This paper focuses on the determination of both the presence and concentration of phthalate esters in three tributaries of Asa River in Kwara State, Nigeria.Water samples were collected at different points from each of the three tributaries (Unity, Osere and Yidi streams) and a total number of 18 samples were collected and the concentration of the prevailing phthalates was determined using GC-MS. Seven different phthalates were found present in the samples and they are: DMP, BBP, DEHP, DNOP, DEP, DBP, and DNHP. The concentration of DMP in the 18 samples ranged from 0.114 - 0.525 µg/L, BBP (0.266-0.697 µg/L), DEHP (0.086- 0.198 µg/L), DNOP (0.062- 0.456 µg/L), DEP (0.162- 0.679 µg/L), DBP (0.168- 0.399 µg/L), and DNHP (0.010-0.064 µg/L). The total phthalate concentration in the three tributaries was lower than the USEPA limit of 3 µg/L for fishes and aquatic lives except for Unity stream where the total was 3.018 µg/L. This study was carried out during the rainy season and the result obtained here could be used as a reference for a further study during dry season to compare the impact of seasonal variation on the distribution and concentration of phthalate esters in the selected tributaries.*

KEYWORDS: Phthalate esters, Asa River, GC-MS, tributaries, extraction, stream

INTRODUCTION

One of the major rivers in Ilorin, Kwara State Nigeria with high community dependence is the Asa River (Lawal *et al*., 2023). It is surrounded by different industries whose effluents are usually released into the river. Apart from the industries, the river is also situated in close proximity to residential area where domestic effluents are also channeled directly and

indirectly into the river. In addition, the poor disposal system in the community has presented Asa River as a major recipient of different kinds of wastes especially plastic based which are non-biodegradable. Asa River is also being fed by some tributaries within the community and these tributaries are also characterized with indiscriminate disposal of plastic wastes, discharge of effluent from residents, industrial settlement, agricultural farms, block industries, mechanic workshops, hospitals and car wash. The different activities around these tributaries are indicators of possible contamination, the most prominent wastes observed in these areas are usually plastics and plastics have been reported to be rich sources of phthalate esters (Duan *et al*., 2018; Adelagun *et al*., 2021). Apart from plastics, some of the raw materials and chemicals used in the production process in some of the industries around are also known sources of phthalate esters.

Phthalate esters (PAEs) belong to a broad group of compounds which include dialkyl or alkyl aryl esters of 1,2-benzene, Dicarboxylic acid (phthalic acid). PAE types like Di-2-Ethylhexyl phthalate (DEHP), Dibutyl phthalate (DBP), Diethyl phthalate (DEP) and Dimethyl phthalate (DMP) are regularly used for different commercial purposes and have been tagged as pollutants with high priority in the area of health risk assessment. PAEs have wide applications in various fields mainly industrial, agricultural and domestic child cares products but the most important and crucial application is their use as nonreactive plasticizers for improving the flexibility and workability of polymeric materials (Guilivo et al., 2016). PAEs increase the plastic flexibility when added to plastic as the long polyvinyl molecules slide against one another.

Plastic (as one of the products utilized and accessible in our everyday lives) has been highlighted as one of the major factors that poses a global health threat to ecosystem and human health. Not mentioning the plastic polymer or product itself, the environment and man are at great health risks due to the release of various additives/chemicals used in manufacturing or processing the plastic (Carsten *et al.*,2020).

The tributaries of concern in this study are in close contact with human because they are used for different purposes like: fishing laundry, bathing, irrigation and other activities that are likely to put the dependent at risk. Phthalate esters have long been recognized as an organic pollutants present everywhere and of prime environmental concern, because literature shows they are identified as endocrine disruptors and are possibly responsible for a lot of carcinogenic, reproductive and hepatoxicity cases in man. Several research studies have reported prevalence, exposure pathways, toxicity, and impacts of PEs in lower animals and man (Baloyi *et al.,* 2021).

Quantifying PEs in the river is an important task in order to assess the potential impact of these compounds on the environment and human health. This study focused on the identification and quantification of phthalate esters in these tributaries because there has not been any study on the quantification of phthalate esters in the study area as at the time of this research. Also, in order to ascertain the level of phthalate contamination of these

streams, it is of utmost importance to carry out an investigation on the evaluation of phthalate.

MATERIALS AND METHODS

Study Area

This study was carried out in Ilorin, the capital of Kwara State, North-Central, Nigeria. It lies within Latitude 8° 24'N to 8° 34'N and Longitude 4° 28'E to 4° 39'E. The samples sites were Unity stream (Latitude 08^0 48.166N to N 08^0 47. 933^0 and Longitude E 004^0 56.075 to E 004^0 33. 56. 147^0), Yidi Stream (Latitude N 08^0 47.771 to N 08^0 47.615 and Longitude E 004^0 55.466 to E 004^0 55.428), and Osere Stream (Latitude N 08^0 45.905 to N 08^0 46.644 and Longitude E 004^0 53.388 to E 004^0 53.548) (Figure 1). These three are tributaries that flow into Asadam River. Activities around these streams include: commercial/business activities, domestic waste water channel to the stream, refuse dumps, irrigation of farmland and open defecation around Osere Stream (OS) while Yidi Stream (YDS) had industrial layout with pharmaceutical effluents discharge, cassava processing units discharge, mechanic workshops waste discharge, run offs from hotels, laundry outfits/car wash effluent, and Unity stream (UNS) is characterized with indiscriminate disposal of domestic wastes, plastic wastes, industrial effluents and car washing/laundry activities. Ilorin metropolis is mainly drained by River Asa, with many tributaries leading to a dendritic drainage pattern (Ajadi et al., 2016; Iroye, 2017).

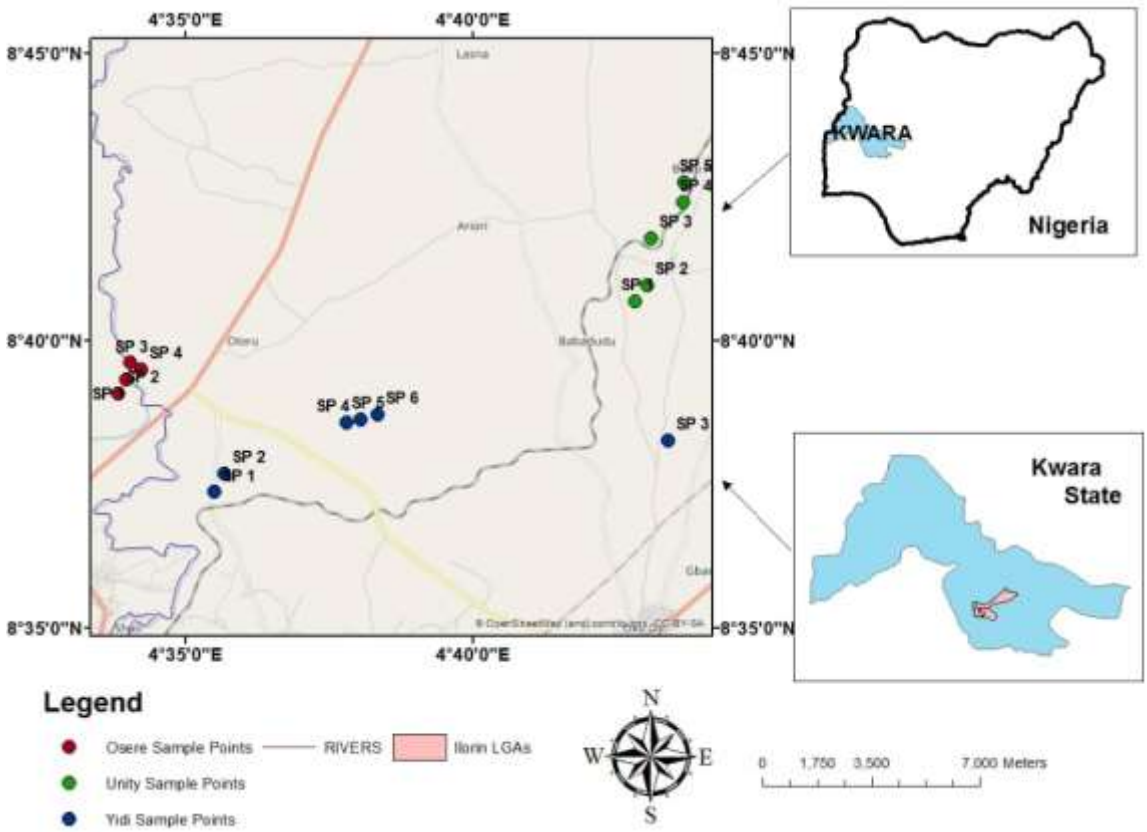

Figure 1. Map showing the sample collection points

Sample Collection

Water samples were collected using pretreated 500 ml amber glass bottles from the 18 different sample sites from the three streams. Prevention of both environmental and human interference was done by using aluminium foil to line the inside of the bottles' lids and the sample were transported under ice to the laboratory to prevent a raise in the temperature which can interfere with the concentration of the possible phthalates.

Extraction of water samples

The extraction of the water samples was carried out using liquid-liquid extraction following the guidelines on test procedure for the analysis of pollutants (USEPA, 1984). A 100 mL of each water sample and 10 mL of dichloromethane was agitated, extraction was done consecutively for three times; the extracts were combined and further placed in a rotary evaporator (BUCHI Rotavapor R-215, Switzerland) to obtain a concentrated extract of 2 ml each per sample.

Evaluation and Quantification of Phthalates in the Water Samples

The detection of the types of phthalates and their concentration in each sample was carried out using an Agilent gas chromatography mass spectrometry (GC-MS) (GC-6890-MS-5973 series Germany), with a ZB-5MS fused-silica capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness) and the methodology adopted was as described by Skoog et al.(1998); Edjere (2006); Institute Bachema (2004; 2006); Lawal *et al*., (2023)

RESULTS AND DISCUSSION

Evaluation of Phthalate Esters in Water Samples from the Three Locations

The eighteen (18) water samples obtained from the three locations i.e Unity, Yidi and Osere Streams, contain both the low and high molecular weight phthalates.

Table 1 contain the Global Positioning System (GPS) coordinates of the Unity stream (UNS) locations, and different concentrations of the phthalate esters obtained in the 8 locations sampled; BBP had the highest concentration with a range from 0.612 -0.697 µg/L, followed by DEP (0.612 µg/L- 0.679 µg/L) while DNHP had the least concentration in all the samples with a range from 0.055-0.064 µg/L. The other phthalates present were: DEHP (0.167-0.198 µg/L), DBP (0.368-0.399 µg/L), DMP (0.489-0.525 µg/L), and DNOP (0.434-0.456 µg/L).

Table 1. Quantification of All the Phthalate Esters in Water Sample Collected from Unity Stream (UNS).

Sampl ID	Sampling Point GPS Coordinate	di (2ethylhexyl) Phthalate (µg/L) (DEHP)	di-butyl-phthalate (µg/L) (DBP)	butyl-benzyl-phthalate (µg/L) (BBP)	di-methyl-phthalate (µg/L) (DMP)	di-ethyl-phthalate (µg/L) (DEP)	di-n-octyl phthalate (µg/L) (DnOP)	DiHexyl Phtalate (µg/L) (DnHP)
UNS 1	N 08^0 28.761 E 004^0 33.590	0.198	0.399	0.697	0.521	0.679	0.447	0.061
UNS 2	N 08^0 28. 778^0 E 004^0 33. 603^0	0.191	0.392	0.692	0.519	0.666	0.456	0.064
UNS 3	N 08^0 28. 827^0 E 004^0 33. 607^0	0.182	0.388	0.689	0.525	0.655	0.45	0.06
UNS 4	N 08^0 28. 865^0 E 004^0 33. 640^0	0.179	0.388	0.693	0.495	0.66	0.446	0.058
UNS 5	N 08^0 28. 886^0 E 004^0 33. 641^0	0.173	0.382	0.689	0.49	0.647	0.437	0.059
UNS 6	N 08^0 28. 889^0 E 004^0 33. 646^0	0.172	0.378	0.686	0.489	0.643	0.44	0.06

UNS 7	N 08^0 28. 890^0 E 004^0 33. 644^0	0.169	0.372	0.686	0.495	0.623	0.437	0.055
UNS 8	N 08^0 28. 892^0 E 004^0 33. 647^0	0.167	0.368	0.691	0.492	0.612	0.434	0.059
	Minimum	0.167	0.368	0.686	0.489	0.612	0.434	0.055
	Maximum	0.198	0.399	0.697	0.525	0.679	0.456	0.064
	Mean	0.179	0.383	0.690	0.503	0.648	0.443	0.059
	SD	0.011	0.010	0.004	0.015	0.022	0.008	0.003

Similarly, the concentration of the phthalate in Yidi stream from the six different locations is shown on Table 2. The ranges in the concentration of all the phthalates seen are as follows: 0.155-0.167 µg/L (DEHP); 0.356-0.365 µg/L (DBP); 0.561-0.571 µg/L (BBP); 0.361-0.388 µg/L (DMP); 0.409-0.422 (DEP); 0.268-0.301 (DNOP); and 0.020-0.042 µg/L (DNHP). The most abundant phthalate was BBP while the lowest was a high molecular weight phthalate, DNHP.

Table 2: Quantification of All the Phthalate Esters in Water Sample Collected from Yidi Stream (YDS)

SAMPLE ID	**Sampling Point GPS Coordinate**	**di (2ethylhexyl) Phthalate (µg/L) (DEHP)**	**di-butyl-phthalate (µg/L) (DBP)**	**butyl-benzyl-phthalate (µg/L) (BBP)**	**di-methyl-phthalate (µg/L) (DMP)**	**di-ethyl-phthalate (µg/L) (DEP)**	**di-n-octyl phthalate (µg/L) (DnOP)**	**DiHexyl Phtalate (µg/L) (DnHP)**
YDS 1	N 08^0 47.71 E 004^0 55.466	0.167	0.365	0.571	0.385	0.421	0.301	0.042
YDS 2	N 08^0 28.581 E 004^0 33.161	0.163	0.361	0.568	0.388	0.409	0.295	0.039
YDS 3	N 08^0 28.616 E 004^0 33.625	0.165	0.364	0.570	0.383	0.417	0.289	0.030
YDS 4	N 08^0 28.635 E 004^0 33.288	0.160	0.360	0.564	0.371	0.419	0.284	0.022
YDS 5	N 08^0 28.638 E 004^0 33.303	0.158	0.357	0.562	0.377	0.422	0.290	0.029
YDS 6	N 08^0 28.643 E 004^0 33.321	0.155	0.356	0.561	0.361	0.418	0.268	0.020
	Minimum	0.155	0.356	0.561	0.361	0.409	0.268	0.020
	Maximum	0.167	0.365	0.571	0.388	0.422	0.301	0.042
	Mean	0.161	0.359	0.566	0.378	0.418	0.288	0.030
	SD	0.005	0.004	0.004	0.010	0.005	0.011	0.009

Table 3 revealed the Global Positioning System (GPS) coordinates of the Osere Stream (OS) locations, and different concentrations of the phthalate esters obtained in the four location locations samples; DEHP (0.086-0.101); DBP (0.168-0.189);BBP (0.266-0.273); DMP (0.114-0.134); DEP (0.162-0.164); DNOP (0.062-0.102), and DNHP (0.010-0.015).

Table 3: Quantification of all the phthalate esters in the water samples collected from Osere Stream (OS).

Sample ID	Sampling Point GPS Coordinate	di (2ethylhexyl) Phthalate (µg/L) (DEHP)	di-butyl-phthalate (µg/L) (DBP)	butyl-benzyl-phthalate (µg/L) (BBP)	di-methyl-phthalate (µg/L) (DMP)	di-ethyl-phthalate (µg/L) (DEP)	di-n-octyl phthalate (µg/L) (DnOP)	DiHexyl Phtalate (µg/L) (DnHP)
OS1	N 08^0 45.91 E 004^0 53.389	0.101	0.189	0.273	0.134	0.164	0.102	0.015
OS2	N 08^0 46.08 E 004^0 53.454	0.098	0.176	0.269	0.122	0.160	0.094	0.013
OS3	N 08^0 46.20 E 004^0 53.487	0.088	0.168	0.270	0.114	0.162	0.088	0.011
OS4	N 08^0 46.64 E 004^0 53.548	0.086	0.172	0.266	0.120	0.161	0.062	0.010
	Minimum	0.086	0.168	0.266	0.114	0.162	0.062	0.010
	Maximum	0.101	0.189	0.273	0.134	0.164	0.102	0.015
	Mean	0.093	0.176	0.269	0.123	0.1618	0.087	0.012
	SD	0.007	0.009	0.003	0.008	0.002	0.017	0.002

Mean Concentration of Phthalate Esters present in the samples

The mean concentration of the phthalate in each stream is presented

The mean concentration of the different phthalates in each stream was compared and presented in Figure 3. It was observed that BBP was the most prominent in all the three samples with the mean concentration of 0.690 µg/L, 0.566µg/L and 0.269 µg/L for UNS, YDS and OS respectively. However, the phthalate ester with the lowest concentration of 0.059 µg/L (UNS), 0.030 µg/L (YDS), and 0.012 µg/L (OS) was DONP.

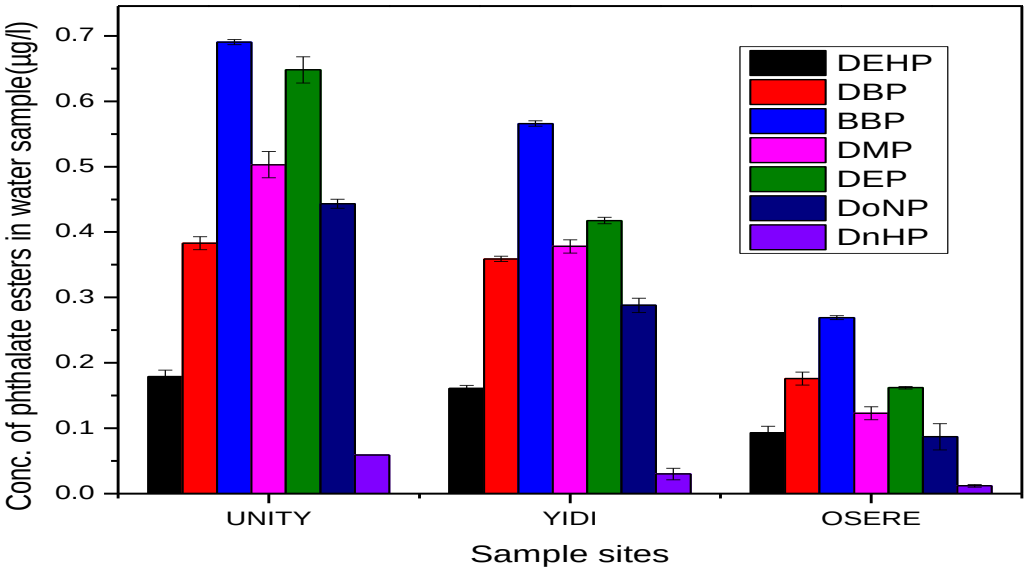

Figure 3: Comparison of mean concentration of phthalate esters in Unity, Yidi and Osere streams

DISCUSSION

The presence of seven phthalate esters were reported in this work : di (2ethylhexyl) Phthalate (DEHP), di-butyl-phthalate (DBP), butyl-benzyl-phthalate (BBP), di-methyl-phthalate (DMP) and di-ethyl-phthalate (DEP), di-n-octyl phthalate (DnOP) and DiHexyl Phtalate (DnHP). Unity stream samples (UNS) had the highest concentration of all the PAEs ranging from 0.064 to 0.697 µg/L followed by Yidistream samples (YDS) 0.042-0.571 µg/L and the least concentration of 0.014-0.273 µg/L Osere samples (OS). The concentration of each PAEs in the individual streams was lower than the recommended limit of 3 µg/L by the United States Environmental Protection Agency (USEPA) for the protection of aquatic lives. However, the total concentration of phthalate esters in UNS was 3.018 µg/L while YDS and OS were 2.256 and 0.978 µg/L respectively.

Unity samples had the highest concentration of all the phthalate esters evaluated and the total concentration was 0.018 µg/L higher than the set criterion by USEPA. Out of all the eight samples collected and evaluated for phthalate esters in unity stream, the percentage contribution of each PAE in the samples follows this order: DnHP (2.12%) < DEHP (6.56) < DBP (13.22%) < DnOP (15.11%) < DMP (17.40%) < DEP (22.5%) < BBP (23.10%). The percentage abundance of PAEs in UNS follows the same other for both YDS AND OS. Both BBP and DEP had the highest contribution to the total phthalate content of these three tributaries. The mean comparison carried out using Fisher's test on one way analysis of variance (ANOVA) showed that the hypothesis that there was no significant difference

in the population was accepted for DEHP and DnHP while it was rejected for DBP, BBP, DMP, DEP and DnOP; this implies that there was no significant difference in the mean value of these five phthalate esters.

The presence of phthalate esters in these three tributaries is as a result of activities around the sample sites which are basically anthropogenic. Osere samples were collected from the stream which flows through a residential area where commercial activities are in high gear, domestic wastewater are channeled into the flowing stream, refuse dumps are sited around the stream, open defecation is also done within the residents. All these are potential sources of phthalates and there is a possibility that the phthalate present in OS has its root from these sources. Similarly, Yidi stream is located within an industrial layout, a pharmaceutical industry discharges its effluents into the stream, a cassava processing unit and a mechanic workshop are also located around the stream.

In addition, run offs from hotels, laundry and car wash also washes debris and other plastic materials into the stream. Unity stream is situated in a place classified with commercial, residential and industrial activities and run offs from agricultural farms, indiscriminate disposal of waste from all this sources contributed to the elevated concentration of phthalate in the stream. The different activities carried out along these streams have been reported to contribute to the production and movement of phthalates in the environment. The lipophilic nature is responsible for the ease at which they find their way out of different plastic based products in the presence of heat and moves freely into different environment like water, soil, air, food and other living organism (Schierow and Lee, 2008;Oghenekohwiroro et al., 2015).

The overall effect of all the phthalate esters in this stream has a potential risk to the environment. The resultant effect to the aquatic lives is a concern that requires attention. Xueping *et al*. (2014) documented the risk caused to a 72 h old fish embryo when exposed to a cocktail of PAEs at 0.50 ppm, the interaction resulted in extreme toxicity and also induced toxicity in further development of the embryo. The PAE with the highest concentration in this study was 0.697µg/L from BBP; this phthalate has been documented for its toxicity to aquatic life with its potential as an endocrine disrupting compound (Willie and Jaap, 2006).

Five out of the seven phthalates present in the samples taken from the study area have been marked as priority pollutants (Dada and Ikeh, 2018) and their elevated concentration in this study showed that the three streams have potential risk to both the aquatic lives and human who depend directly or indirectly on the stream for several activities.

All the samples contained the same kind of phthalate all though in different concentrations, this could be as a result of the link between the three streams examined. Osere stream flows majorly through a residential area and joins YDS which also flows to UNS. There is a flow from one stream to another and they all eventually flow into Asa River. The results of the PAEs obtained in this study were compared to other work done both within and outside

Nigeria. Six out of the seven PAEs reported in this study except DnHP were also reported by Oghenekohwirono *et al*. (2015). The authors evaluated the presence of PAEs in Orogodo river in Delta state Nigeria. The average concentration ranged from 0.00 to 2.22 µg/L with both DBP and DEHP having the highest concentration of 2.22 and 0.883 µg/L respectively. The concentrations of DEP, BBP and DnOP in this study were higher than that of the authors while the concentrations of DBP, DEHP and DMP were higher than our report.

Additionally, Olutona and Dawodu (2014) also documented a report on quantification of phthalate esters in both water and sediments of Ori stream in Nigeria. Four phthalate esters were quantified with concentration ranging from 1.29± 1.3 µg/L for water and 152 ±140 µg/kg for sediments. These values were higher than the ones obtained in this study. A report was also made on the distribution of phthalate esters in both water and sediment of Hanjiang river in China. Six PAEs were estimated, DEHP and DBP were the most abundant phthalate with percentage abundance of 35.3-72.9% and 10.6-47.9%, other PAEs evaluated are DnOP, BBP, DMP and DEP (Dong *et al*., 2022).

The three streams evaluated in this study are tributaries of Asa River which is amajor river characterized by different activities which include fishing, irrigation for farming, recreation and other activities which makes it a river of great concern. The cumulative concentration of the phthalates (≤6.252 µg/L) from these tributaries is a great health concern in Asa River and these are just three out of many other tributaries within the community which flows into the river. This study was conducted during raining season and there could be a possibility of dilution of the streams as a result of constant heavy rainfall as at the time the samples were taken.

CONCLUSION

Asa River is a major source of water for different activities like fishing, irrigation for farming, washing, bathing, drinking and some recreational activities. This River is known to receive constant flow of water from several stream within the community and this flow includes the deposition of various waste materials into the river. Therefore, this study was carried out to evaluate the presence and concentration of phthalate esters in three selected streams which are tributaries to the river. Seven different phthalate esters were evaluated from 18 samples obtained from three tributaries (Unity, Osere and Yidi streams) and BBP had the highest concentration followed by DEP. Eventhough the individual concentration of each phthalates was lower than the USEPA limit of 3 µg/L set for fishes and aquatic organisms, the total concentration in one of the streams was higher than the set criterion. The total concentration of PAEs in the tributaries which flows into Asa River far exceeded the limit.

Recommendation

The level of phthalates present in some tributaries of Asa River is an indication of a high levelof phthalate contamination in the river,it is important to repeat the study during dry

season since the present study was carried out during the rainy season; this will enable adequate information on the effect of seasonal variation on the distribution and concentration of phlates in the sample site. In addition, a further investigation will also be needed to evaluate the presence and distribution on the Asa river in order to be able to evaluate the risk assessment of phthate esters in the highly dependent river.

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