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PHTHALATE ESTER PLASTICIZERS IN OROGODO RIVER DELTA STATE AND THEIR POTENTIAL HEALTH EFFECTS

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ABSTRACT: *This study was carried out to analyse the presence of different phthalates such as dimethyl phthalate (DMP), diethyl phthalates (DEP), dibutylphthalate (DBP), buttylbenzyl phthalate (BBP), di-n-octyl phthalate (DnOP), di-2-ethylhexylphthalate (DEHP) in Orogodo River. Samples were collected from eight points along the river channel, extracted using liquid-liquid method of extraction and was analysed using GC/MS. Levels of phthalates in water samples from the river ranged from 0.00µg/L to 2.22µg/L. The highest concentrations of phthalates were DBP and DEHP, which is consistent with their common use in plastic materials and other industrial chemicals. It was found that the individual phthalates concentration was low but total phthalate levels were high in most stations. Total phthalates for each of the location ranges from 1.34µg/L to 3.29µg/L at each station. Some of these were higher than the criterion of 3µg/L phthalates recommended by the United States Environmental Protection Agency (USEPA) for the protection of fish and other aquatic organisms. The high concentrations may be as a result of dumping of untreated effluent/solid waste and emissions arising from burning of refuse containing plastic materials along the stretch of the river. The results for phthalates in the water samples give cause for environmental and health concern for people living downstream of the river. These results can be used as reference levels for future monitoring programs for pollution studies of the river.*

KEYWORDS: Phthalate, Acid Esters, GC-MS, Surface water, Orogodo River

INTRODUCTION

In order to resolve issues that will lead to the threat on aquatic lives, continuous awareness of the potential impact of waste disposal into our rivers and streams need to be sustained. The quantum of waste is ever increasing due to increase in population, developmental activities, changes in life style, and socio-economic conditions. Plastics waste is a significant portion of the total municipal solid waste deposited in the water medium. Different waste products are being disposed into the aquatic environment from time to time. Some of which are variety of consumer products including medical devices, food wrap, building materials, paints, packaging, intravenous storage bags, automotive parts, electrical cords, children's toys, and childcare articles made of polyvinyl chloride (PVC). Most of these products contain synthetic chemicals known as phthalates (Peters, 2003a; Peters, 2003b).

Phthalates are class of widely used industrial compounds that are generally applied as plasticizers in industrial products such as polyvinyl acetate, polyvinyl chloride (especially soft PVC), adhesives and coatings (Haji *et al*., 2014). As plasticizers they add flexibility to the synthetic organic polymers. Report on Human Exposure to Environmental Chemicals (NCEH 2005) showed that these compounds are also found in personal care products, especially in hair spray, fingernail polish and perfumes. They are ubiquitous in environmental samples as they

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are release during manufacture, use, and disposal of industrial and consumer products. Their ubiquity has been widely reported in various environmental studies in the developed countries of Europe and America (Fatoki and Noma, 2001). According to Verschueren (1983); Hawley (1987); USEPA (1989); Babich (1998) and Schierow and Lee (2008), some of the commonly used phthalates in consumer products are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-(2-ethylhexyl) phthalate(DEHP), diisononyl phthalate (DINP), dibutyl phthalate (DBP), diisodecyl phthalate (DIDP), di-n-octyl phthalate(DnOP), and butylbenzyl phthalate (BBP or BzBP).

European Chemical Agency (ECHA), Agency for Toxic Substances and Disease Registry (ATSDR), and the U.S. Department of Health and Human Services have identified some phthalates as reproductive and developmental toxicants, though their toxicity varies somewhat depending on the specific phthalate structure. USEPA classifies DEHP and BBP as probable and possible human carcinogens. It should be noted that phthalates are not chemically bound to the PVC polymer. Phthalates are generally lipophilic, which influences their leaching and environmental partitioning characteristics (Schierow and Lee 2008; Babich, 1998). Thus, over time they leach out of products and diffuse into the air, water, food, house dust, soil, living organisms, and other media, particularly under conditions involving heat (Calafat and Hauser, 2005). Phthalates may pose risks for aquatic and terrestrial ecosystems particularly in the vicinity of phthalate processing industries. Some phthalates are bio accumulative and have been detected in aquatic organisms. Fatoki *et al.* (2010) studied phthalates in fresh water systems of Venda, South Africa and found that their levels were higher than the criterion of phthalates recommended by the United States Environmental Protection Agency for the protection of fish and other aquatic lives.BBP has been shown to be toxic to aquatic organisms and may cause long-term adverse effects in aquatic environments. Studies suggest BBP may have endocrine disrupting effects in fish (Willie and Jaap, 2006).

The potential health risk of exposure to phthalates is higher in the developing countries considering the fact that waters for domestic activities are sourced directly from streams with little or no treatment. A study carried out by Adewuyi (2012) to determine the levels of phthalate esters in a supposedly treated hospital effluents and in the waters of the receiving river using high performance liquid chromatography in Ibadan City, Nigeria and found that there is a possible negative impact on the receiving stream and possibility of deleterious effects of the phthalates on aquatic biota and people that depend on the receiving stream for fishing and recreational purposes. Ekpo *et al*. (2011) also detected phthalates, non-specific n-alkanes (mainly of even carbon numbered predominance), 4-hydroxybenzoicacid and biphenyl as well as minor amounts of polycyclic aromatic hydrocarbons in organic solvents believed to have been kept in plastic containers prior to dispensing into bottles by commercial chemical vendors in Nigeria. A report by Orok *et al*. (2014) on the levels, fate and distribution of phthalates and certain plastic additives in sediments of the Cross River System, Nigeria, detected the occurrence phthalates which they considered to originate primarily from direct discharge of untreated effluent/solid waste by the rubber processing/plastic industry and emissions arising from burning of refuse containing plastic materials, respectively.

Study Area

Orogodo River 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

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spell of harmattan (Oguntoyibo and Hayward, 1987). 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^oC in the rainy season and about 30^oC in the dry season (Gobo, 1998).

Orogodo River is located between latitudes 5^o 43'N and 5^o 30'N and longitudes 6^o 20'E and 6^o 12'E, and takes its source from Mbiri village at an elevation of 150m above sea level (Puyate *et al*, 2007). The river serves as a major source of water for drinking, bathing, fishing, washing, and recreation for the people of Agbor and Owa communities in Delta State, Nigeria. The Agbor and Owa communities, through which the Orogodo River traverses, are mainly peasant farmers whose products include food stuff such as yams, corn, vegetables, cassava, plantain and fruits. Agricultural activities in the area are mostly carried out along the bank of the Orogodo River, and agricultural wastes (domestic wastes, livestock manure, fertilizers, pesticides, etc) are discharged directly into the river or entrained in runoff into the river after rainfall. Although Agbor and Owa may not be described as industrial communities, there exist pockets of industries (paint and foam industries) as well as many educational institutions whose wastes also find their way into the river. Some physico-chemical characteristics of Orogodo River have been reported (Okokoyo and Rim-Rukeh, 2003; Rim-Rukeh, *et al.*, 2006).

It is the purpose of this study to determine and report some of the phthalates present in the River, assess their levels and evaluate their likely health implication of their occurrence on the people in the metropolis as there is no literature on the occurrence or distribution of phthalates in the River.

MATERIALS AND METHODS

Sample Collection

Grab water samples were collected from eight points upstream and downstream along the river channel within and outside Agbor metropolis in a glass bottle, preserved with dilute nitric acid and stored in an ice chest until arrival to the laboratory, where they were kept in fridge.

Chemicals and materials

Anhydrous sodium sulphate oven heated at 400°C; cyclohexane distillated in an all glass; acetone; 1,1-Dibromoundecan ISTD; reagent water; agilent gas chromatograph 6890N coupled with MS; Sample collection bottles; 1l Erlenmeyer flasks; glass coated metal magnetic mixer; Upward delivery glass separating funnel; 10ml vials with septum seals (Silicon/PTFE); Balance (3 decimal places); glass beakers; spatulas; forceps; aluminium foil; solvent reservoir bottle; calibrated syringe; ultrasonic bath; bunsen burner; drying oven; muffle furnace; desiccators; measuring cylinders; test tubes; pasteur pipettes; calibrated pipette.

Sample Handling and pre-treatment

Water samples were collected in amber glass containers. Conventional sampling practices were followed. No special sample preservations and storage steps were taken since phthalate are stable at pH 7.Samples were collected and sealed with a glass stopper followed by a metal clip. The samples were refrigerated at 4°C free from light from the time of collection until extraction.

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Extraction of Water Sample

A subsample of 1L was weighed into a calibrated Erlenmeyer flask of 1L. To this is added 1ml Cyclohexane internal Standard solution and then 9ml Cyclohexane. With the aid of a glass coated magnet the sample was then liquid / liquid intensively extracted for a minimum of an hour. Using an upward delivery glass separating funnel, the solvent Extract was then isolated in a 10 ml vial. Sample volume is 1L in 10ml Cyclohexane Extract.

Analysis of Phthalate in water using GC/MS

The new method for analysis of Phthalate in water samples using GC/MS was validated according to Skoog *et al.* (1998), Edjere (2006) and Institute Bachema AG Quality Management Guidelines as certified by ISO 17025 (Institute Bachema, 2004; 2006).

RESULTS AND DISCUSSION

The concentrations for DMP in different samples ranges between 0.15-0.80µg/L; DEP ranges from 0.15-0.32µg/L, while DBP range from 0.12-2.22µg/L. Almost all the samples were below detection limit for BBP, except for Station 1, that had a concentration of 0.04µg/L. Concentrations of DEHP in samples ranges from 0.45-0.88µg/L, while DnOP range from 0.02-0.08µg/L except Stations 3, 6 and 7 which were all below detection limit (Table 1).

Figure 1 and 2 shows the percentage and total contribution of phthalates to each of the sample areas. DBP concentrations were found to have the highest average percentage contribution (47%) in the River, followed by DEHP (25%) and DMP (15%). BBP has the least contribution (<1%), followed by DnOP and DEP respectively. The fact that DBP phthalate was the highest contributor to the contamination detected is because it is one of the most widely used in manufacturing processes and therefore it is the most commonly found phthalate in the manufactured products (Kimber and Dearman, 2010).

Table 1: Concentrations Phthalates in Orogodo River at different samples

S/N	Description	DMP	DEP	DBP	BBP	DEHP	DnOP	Total
		(µg/l)						
1	Warri/Abavo Rd	0.21	0.31	1.56	0.04	0.68	0.08	2.88
2	Alihame	0.55	0.32	0.96	ND	0.54	0.02	2.39
3	Slaughter	0.41	0.15	0.12	ND	0.66	ND	1.34
4	Car Wash	0.80	0.29	1.46	ND	0.45	0.02	3.02
5	OkohStr	0.15	0.22	2.22	ND	0.66	0.04	3.29
6	EdikeStr	0.28	0.23	0.20	ND	0.88	ND	1.59
7	Mr. Biggs	0.25	0.17	0.54	ND	0.60	ND	1.56
8	Iyekpen	0.23	0.19	1.70	ND	0.68	0.02	2.82
min		0.15	0.15	0.12	0.00	0.45	0.00	1.34
max		0.80	0.32	2.22	0.04	0.88	0.08	3.29
mean		0.36	0.24	1.10	0.01	0.64	0.01	2.36
s.d.		0.15	0.05	0.57	0.00	0.08	0.02	0.58

ND = Not detected

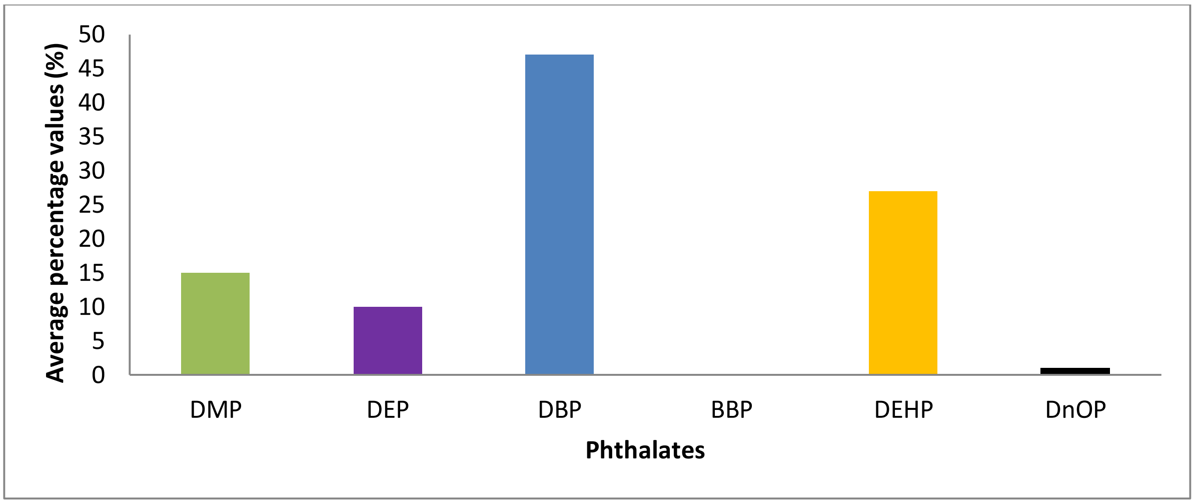

Figure1: Percentages contribution of each Phthalates in the sampled water

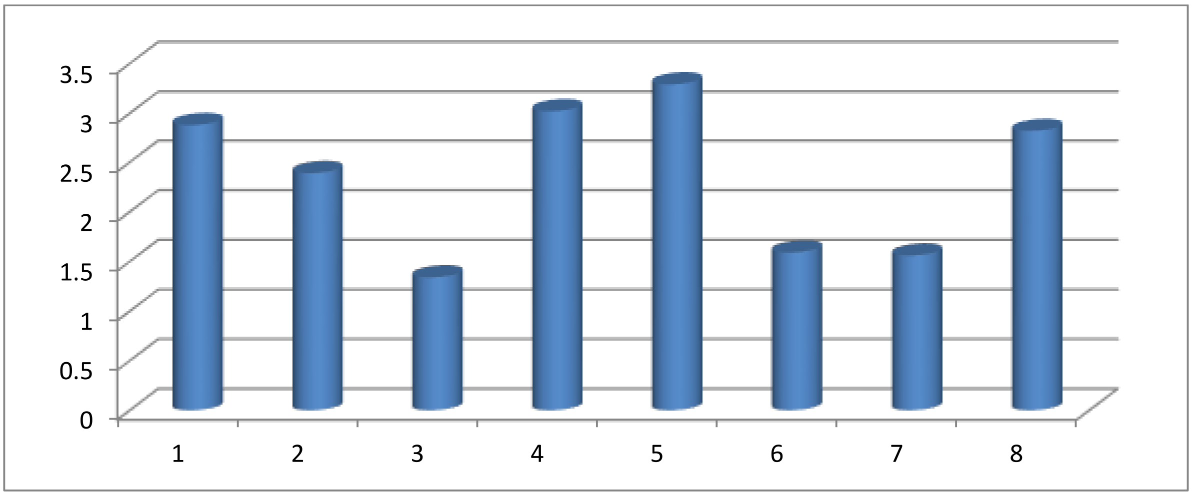

Figure 2: Total phthalate concentrations (µg/L) in each sampling location of Orogodo River

Stations 5 and 4 have the highest phthalate concentration with a total phthalate concentration of 3.29µg/L and 3.02µg/L. These concentrations are higher than the criterion of 3.0µg/L phthalates recommended by the United States Environmental Protection Agency (USEPA, 1989) for the protection of fish and other aquatic life (Fatoki *et al.*, 2010). These areas are characterised by high economic activities taking place continuously on the water front ranging from washing of cars, rugs, livestock sales, and a major market known as the Agbor Main Market (located about 400m uphill of the river). Other industrial and economic activities taking place at various locations within the Agbor Metropolis are laundry services, restaurants, household generated wastes, etc. Residues from burnt wastes, vehicle servicing shops and refuse from food processing such as cassava fermentation has contributed significantly to the high level of pollution experienced by the river. Stations 1 and 8 have total phthalates concentrations of 2.88µg/L and 2.82µg/L respectively. These locations also receive same waste stream but fairly distant from the metropolitan area of the city. The locations with the least

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concentration of phthalates were Stations 3 and 7 with total phthalates load of 1.34µg/L and 1.56µg/L respectively. Recent findings using a 72-h zebra fish embryo acute toxicity test, demonstrated that BBP, DBP and a mixture of BBP, DBP, DEHP, DIDP, DINP and DNOP with concentration of 0.50 ppm of each phthalate possessed high toxicity, and induced severe developmental toxicity in live embryos.(Xueping *et al*., 2014). This is of concern as most of the locations sampled exceeded this concentration.

The phthalates data from Orogodo River was subjected to the Duncan Multiple Range Test to compare the means of the different sampling points. The hypothesis was accepted for BBP, DMP, DnOP and DEP meaning that there was no significant difference among the means of these phthalates in the points sampled, but there was significant difference (P< 0.05) for DBP and DEHP in different sampling points.

Table 2: Duncan Multiple Range Test for DBP

Station	Replicates	Subsets for alpha = 0.05				
		A	B	C	D	E
3	3	0.12				
6	3	0.20				
7	3		0.54			
2	3			0.96		
4	3				1.46	
1	3				1.56	
8	3				1.70	
5	3					2.22
Significance		0.587	1.00	1.00	0.134	1.00

From Table 2, there are five subsets A, B, C, D and E which are significantly different from one another. It is clear that DBP concentration from samples in Station 4, 1 and 8 are not significantly different but different from Stations 3, 6, 7, 2 and 5. However concentration of DBP from stations 4, 1 and 8 implies that the economic activities in those areas are common.

Table 3: Duncan Multiple Range Test for DEHP

Stations	Replicates	Subsets for alpha = 0.05			
		A	B	C	D
4	3	0.4500			
2	3	0.5400	0.5400		
7	3		0.6000	0.6000	
5	3			0.6600	
3	3			0.6600	
8	3			0.6667	
1	3			0.6800	
6	3				0.8800
Significance		0.057	0.190	0.117	1.000

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Table 3 above indicates that there are four subsets A, B, C, and D. This implies that stations in a subset is analogous and differs significantly from the stations in others. Hence, it shows that Stations 5, 3, 8 and 1 have no significant difference just as Station 4 and 2. Station 2 is analogous to7 while 6 are entirely different from all others with a mean concentration value of 0.8800. This is an indication that the stations which have close mean values may be as a result of disposing the same type of consumer waste products containing phthalate plasticizers due to common economic activities in those areas.

CONCLUSION

Orogodo River is a major source of water for drinking, bathing, fishing, washing, and recreation for the host communities. Industrial and commercial activities are carried out along the stretch of the river and these involve direct dumping of untreated wastes into the river. This study was carried out to investigate the occurrence and distribution of some phthalates in the Orogodo Rivers in Agbor. Six phthalate groups were detected in all the locations sampled with DBP and DEHP being the highest. These phthalates are the most widely used in consumer products. Total concentrations of phthalates in some of the stations sampled exceeded USEPA regulatory limit of 3.0µg/L.

RECOMMENDATION

Due to the presence of phthalates in common household products, food wraps, cosmetics and toys, their disposal should be of utmost concern to all. With the level of phthalates detected in the River, the government should encourage and sponsor studies on how these chemicals affect people's health, work with manufacturers to help consumers understand the level of chemicals in these products, bring up policies that will control the impact of these chemicals on our rivers and ensure strict compliance to enacted environmental and health laws.

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