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LEVELS OF DI-ETHYLHEXYL PHTHALATE (DEHP) IN DOMESTIC DRINKING WATER DISTRIBUTION SYSTEM IN WARRI, NIGERIA

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ABSTRACT

Diethylhexylphthalate (DEHP) as phthalate plasticizers is commonly used to improve the quality of plastic products. It is physically bound to plastic products and as a result, can be released into the surrounding environment. A common material in our domestic water distribution system is polyvinyl chloride (PVC). Elevated levels of DEHP have been implicated in cancer cases. Levels of DEHP in water obtained from a domestic water distribution system have been experimentally determined. Within the study area, five boreholes which serve to provide water for drinking and domestic purposes were selected for the study. The choice of the five boreholes was guarded by the age of the household water distribution system. Gas chromatography (GC) coupled with a mass spectrometer (MS) was used to evaluate the levels of diethylhexyl phthalate (DEHP), in the water samples. The levels of DEHP in the water samples ranged from 1.77 to 4.71µg/l with the arithmetic mean value of 3.072µg/l which is below 6.0 µg/l limit for safe drinking water. Correlation analysis using Pearson's Product Moment showed a positive correlation between the levels the DEHP in water samples with the age of the domestic water distribution system. Ecological and health effects of this substance on humans through the consumption of this drinking water, even at this minute level needs further investigation because of the possibility of biomagnifications.

KEYWORDS: *Diethylhexylphthalate, Polyvinyl Chloride, Domestic Water Distribution System, Phthalates, Acid Esters, Plasticizers, Drinking Water*

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INTRODUCTION

Diethylhexylphthalate (DEHP) is the most commonly used chemical of a group of related chemicals called phthalates or phthalic acid esters for the manufacture of polyvinyl chloride (PVC) (Phthalates Information Centre Europe, 2005). This synthetic compound is added to PVC to enhance flexibility and durability of the product (Schettler, 2006). Studies have shown that soft PVC is made of 40% DEHP (Koch *et al.*, 2006). Diethylhexylphthalate as phthalate plasticizers is physically bound to plastic products and hence can be released into the surrounding environment (Latini, 2005). DEHP is ubiquitous in environmental samples as they are released during manufacture, use, and disposal of industrial and consumer products have been described as the most abundant man-made environmental pollutant (Latini, 2005).

Water distribution system infrastructure is generally the main asset of a water utility of any country. The American Water Works Association (AWWA, 1974) defines the water distribution system as "including all water utility components for the distribution of finished or potable water by means of gravity storage feed or pumps though distribution pumping networks to customers or other users, including distribution equalizing storage." These systems must also be able to provide water for non-potable uses like firefighting and agricultural purposes. Distribution system infrastructure is usually thought-out to consist of pipes, pumps, valves, storage tanks, reservoirs, meters, fittings, and other hydraulic equipment that link up treatment plants or well supplies to consumers' taps. The three requirements for a pipe include its capacity to deliver the quantity of water required, to resist all external and internal for reacting upon it, and to be durable and long-lasting (Clark and Tippen, 1990). The materials now used to achieve these goals are ductile iron, pre-stressed concrete, polyvinyl chloride (PVC), reinforced plastic, and steel.

Warri, the headquarter of Warri – South Local Government Area of Delta is a characteristically old industrial base and economically developed city with a population of over 1.1 million in South-South Nigeria. The central public water-works are non-functional and as a result, the common source of water for drinking and domestic purposes is groundwater obtained through the borehole. Materials used nowadays to achieve these goals today is polyvinyl chloride (PVC). To the best of our knowledge, the occurrence of DEHP in this source of water used for drinking and domestic purposes in this area have not previously been examined. DEHP levels in the drinking water in excess of the maximum contaminant level (MCL) (6.0µg/l) for many years have been implicated in liver and reproductive difficulties (Kummerer, 2010). Elevated levels of DEHP have also been reported to have an increased risk of getting cancer (USEPA, 2010). The objectives of this study were (i) to ascertain the amount of DEHP in the water source, (ii) to assess the possible adverse effects of DEHP on human health and (iii) to give a valuable record on the levels of DEHP in the drinking water in Warri city.

MATERIALS AND METHODS

Study Area

Warri is located between latitudes 5^0 30′ and $5^0$35′ N `and longitudes $5^0$29′ and $5^0$48′ E. Geopolitically, Warri is the headquarters of Warri-South Local Government Area of Delta State, Nigeria. It is within the oil-rich province of Nigeria, some 50 km away from the shores of the Atlantic Ocean. It occupies a low-lying area with a mean height of 6m above sea level. It is a flat land with the very gentle slope towards River Warri and its tributaries that empty their water into the Atlantic Ocean as shown by Warri satellite image (Figure 1). Warri town has two main entry points; one from Benin in Edo State and the other from Port Harcourt in Rivers State. Also, the numerous networks of roads from Effurun area to Warri- Sapele road through NPA/NNPC expressway make the town easily accessible for borehole sampling.

The climate of the area is the tropical equatorial type dominated by two seasons, a long wet season (April to October) and a short dry season (November to March), in response to the interplay between the southwest and the northeast trade winds that blow over Nigeria. Annual rainfall is usually in excess of 3000mm, as no month of the year is entirely devoid of rainfall. Temperature is above 28^0C and humidity is about 80% (Iloeje 1981). The vegetation is dominated by mangrove swamp forest, although further inland, it becomes rainforest. This natural vegetation setting has been extensively altered by human activities such as farming and lumbering and in many cases, has been replaced by grassland.

Figure 1: Satellite image of Warri (Source: Google Imagery, 2011)

Geologically, Warri town is underlain by a sequence of sedimentary formations with a thickness of about 8000metres, which include from bottom to top, the Akata Formation, the Agbada Formation, the Benin Formation and the Somebreiro Warri Deltaic Plain Sands (Short and Stauble, 1967).

The Benin Formation houses the most productive and hence most tapped aquifer in the Niger Delta region, especially in areas north of Warri where it is shallow. The thickness of the formation is variable but generally exceeds 2000m. The Somebreiro-Warri Deltaic Plain Sand is Quaternary to Recent in age and directly underlies the study area. It consists of fine to medium unconsolidated sands that are often feldspathic (with 30-40 % wt feldspars) and occasionally gravely (Allen *et al.*, 1974). The sequence is locally stratified with peat and lenses of soft and plastic clay that could be sandy and shelly. It generally does not exceed 120m in thickness and is predominantly unconfined.

Drinking Water Samples Collection

Within the study area, five boreholes which serve to provide water for drinking and domestic purposes were selected for the study. The choice of the five boreholes was guarded by the age of the household water distribution system. All sampling points were geo-referenced (Table 1).

Table 1: Geographical Coordinates of Borehole Water Samples

Sampling Codes	Physical Description of Water Borehole Sampling Points Location	Age of Domestic Water Distribution Systems	Sampling Coordinates	
			Northing	Easting
BH 1	Warri GRA	4 years	05^0 31’21.2’’N	005^0 45’ 59.3’’E
BH 2	Cemetry Road by OgedegbeJunction	20 years	05^0 30’58.4’’N	005^0 45’27.7’’E
BH 3	EnerehenJunction	13 years	05^0 31’4.9’’N	005^0 46’24.7’’E
BH 4	McDermott Road	16 years	05^0 30’30.0’’N	005^0 45’2.5’’E
BH 5	Warri main market	9 years	05^0 31’02.8’’N	005^0 45’44.8’’E

At each of the identified site, drinking water was collected in a labeled 2.5L plastic sample container that has been pre-treated by washing in 0.1M dilute HCl and rinsed with distilled water and sun-dried. At the collection point, containers were rinsed with relevant water sample twice. Placing labels on the containers identified samples. All samples were

transferred to the Federal University of Petroleum Resources, Department of Environmental Management and Toxicology Laboratory, Effurun Delta State. All study samples for the study were collected on 10/03/2017 within the hours of 900 hours and 11.00hours.

Analysis of Samples

At the Federal University of Petroleum Resources, Department of Environmental Management and Toxicology Laboratory,water samples were filtered under vacuum through glass fiber filters (0.7 μm pore sizes) and each sample spiked with surrogate standards prior to extraction. The liquid phase extraction method was used to extract the water samples (USEPA, Method 8061) with slight modifications. 1 L of water samples was placed in a separating funnel and extracted by means of mechanical shaking with 150 mL dichloromethane, and then, with filtration on sodium sulfate (about 20 g), rotary evaporator was used to concentrate the organic extracts. The solvent exchange was done by replacing dichloromethane with hexane. Finally, they were reduced to 0.5 mL under gentle nitrogen flow. The internal standard was added to the sample prior to instrumental analysis.

The extracted compound was determined by gas chromatography coupled to mass spectrometer analysis as described in other publications (Zhang *et al.*, 2003; Berset and Etter-Holzer, 2001). Extracted sample was injected into an Agilent 6890 Series GC equipped with a DB-35MS capillary column (Agilent; 30 m × 0.25 mm i.d.; 0.25 μm film thickness) and an Agilent 5973 MS detector, operating in the selective ion monitoring mode. 70°C was initially set as the column temperature for 1 min, then ramped at 10°C/min to 300°C and held constant for 10 min. The transfer line and the ion source temperature were maintained at 280 and 250°C, respectively. Helium was used as the carrier gas at a flow rate of 1 mL/min. The extracts (2.0 μL) were injected in splitless mode with an inlet temperature of 300°C. The methods of analysis were consistent with the standard methods of ATSDR (1995), ASTM (2015) and USEPA (2013).

RESULTS AND DISCUSSIONS

The DEHP levels in the borehole water samples from the sampling sites within Warri metropolis were determined and the results are presented in Table 2.

Table 2: Levels of Di (2-Ethylhexyl) (DEHP) in Borehole Water Samples

S/No	Sampling Locations	Levels of DEHP (µg/l)	Age of Domestic Water Distribution System	Regulatory Limits in Drinking Water (WHO, 2006)
1	Warri GRA	1.77	4 years	6.0µg/l
2	Cemetry Road by Ogedegbe Junction	4.71	20 years	
3	EnerehenJunction	2.94	13 years	
4	McDermott Road	3.08	16 years	
5	Warri main market	2.86	9 years	

DEHP levels in the Water Source: The concentrations of DEHP in the water samples as presented in Table 2 ranged from 1.77 to 4.71µg/l with the arithmetic mean value of 3.072µg/l. Results indicate the presence of DEHP in all water samples. DEHP is an important and popular additive in many industrial products including flexible PVC materials commonly used in the construction of domestic water distribution system (Schettler, 2006), is suggestive as the major source of DEHP contaminants in the water samples.

In addition, when the levels of DEHP was assessed in raw groundwater (water that has not passed through the domestic water distribution system) and compared with that collected from the domestic water distribution system results are as presented in Table 3 and illustrated in Figure 2. As shown in Figure 2, the measured concentrations of the analyzed DEHP in the raw groundwater samples did not vary strongly and lower than that obtained from the water distribution system.

Table 3: Levels of di (2-ethylhexyl) (DEHP) inthe Raw Groundwater Samples

S/No	Sampling Locations	Levels of DEHP Domestic Water Distribution Systems (µg/l)	Levels of DEHP (µg/l) in the Raw Groundwater Samples (µg/l)
1	Warri GRA	1.77	0.07
2	Cemetry Road by Ogedegbe Junction	4.71	0.05
3	EnerehenJunction	2.94	0.04
4	McDermott Road	3.08	0.06
5	Warri main market	2.86	0.05

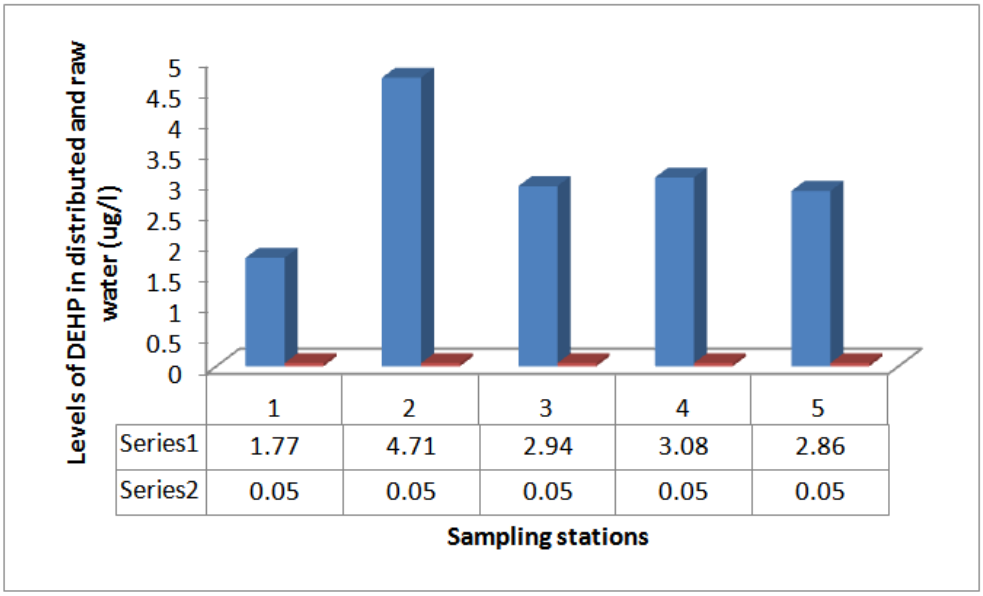

Figure 2: Comparison Levels of DEHP in Domestic Water Distribution System with that in Raw Groundwater Samples

The Distribution of DEHP: The distribution of DEHP in the drinking water samples from different sampling sites are shown in Figure 3. The highest levels of DEHP contamination were seen on the sampling site 2 (cemetery road by Ogedegbe junction), followed relatively by sites 4, 3 and 5, with site 1 being the lowest. In general, it should be noted that there might be a relation between the levels of DEHP in the water samples with the input of local sources, such as leaching of phthalate component of the PVC pipes into the drinking water that flows through it. Similar observation has also been reported for household drinking water distribution in Oregun, USA (US DHHS, 2003).

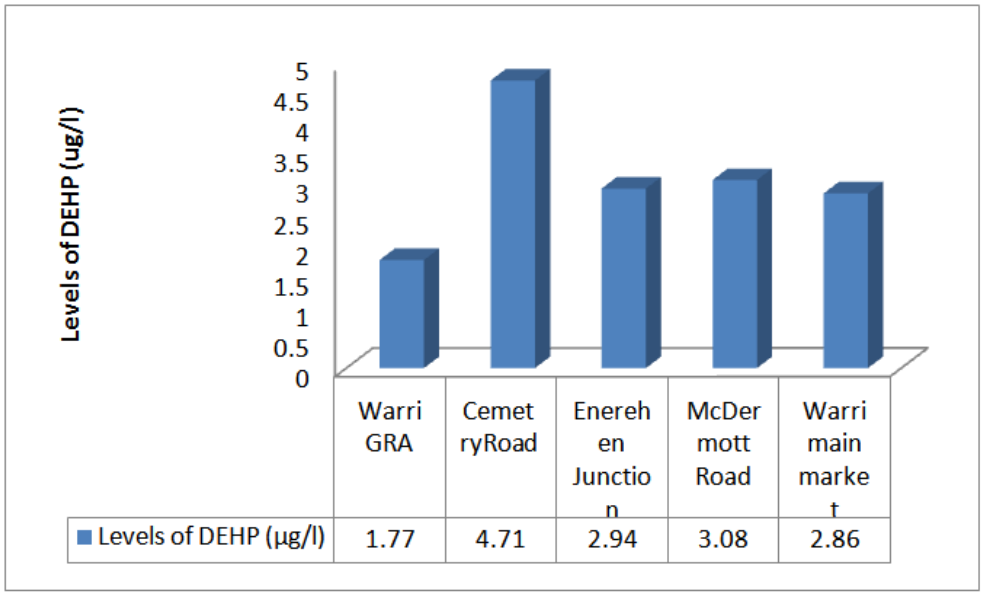

Figure 3: Spatial Distributions of DEHP in the 5 Sampling Sites

Using the Pearson's Product Moment correlation analysis, the variability of the levels the DEHP in water samples with the age of the domestic water distribution system shows a positive relationship as presented in Figure 4. A correlation coefficient(r) of 0.85 was obtained. This implies a strong positive correlation between the variables. In other words, the levels the DEHP in water samples increases with the age of the domestic water distribution system. When the correlation coefficient was squared (r^2) a value of 72.25 was obtained. This means that about 72.25 percent of the variation in the levels of DEHP in water samples can be explained with the age of the domestic water distribution system (Grayman *et al.*, 1988).

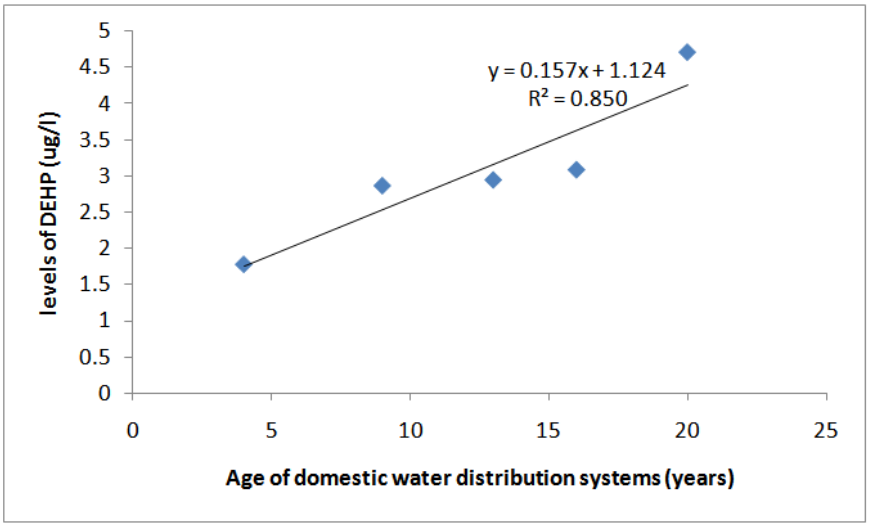

Figure 4: Correlation of Levels of DEHP with Age of Water Distribution Systems ***Comparison of the Levels of DEHP in this Study with Other Domestic Drinking Water Distribution Systems***

Results of comparison of DEHP concentrations obtained in this study and other published values for drinking water are shown in Table 4 and illustrated in Figure 5. The DEHP concentrations of the index study showed, to a large extent, higher concentration levels than those reported for drinking water in other studies.

Table 4: Average Levels of DEHP (µg/l) in Domestic Drinking Water Distribution System in Different Cities

Average Levels of DEHP (µg/l) in Domestic Drinking Water Distribution System in Different Cities			
Warri, Nigeria (This Study)	**Minnesota, USA (WHO, 1996)**	**Tokyo, Japan (Hirose et al., 2004)**	**Oregon, USA (US DHHS, 2003)**
3.072	0.006	1.50	1.0

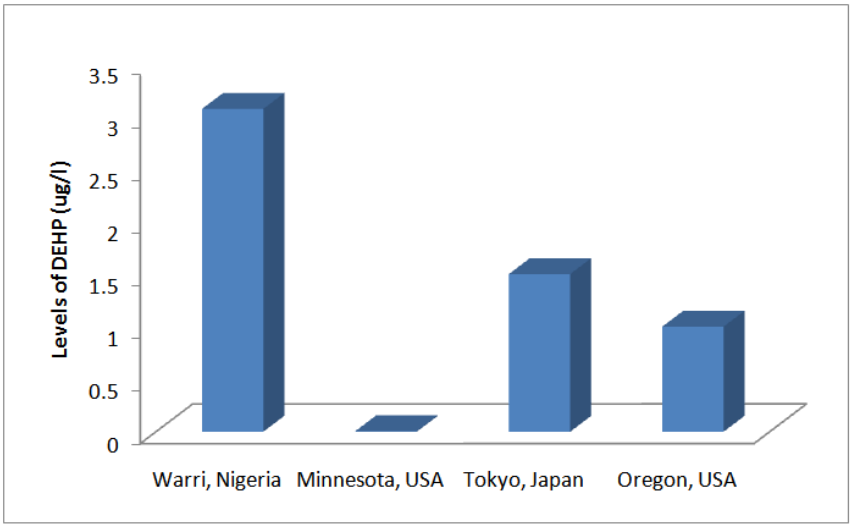

Figure 5: Average Levels of DEHP (µg/l) in Domestic Drinking Water Distribution System in Different Cities

Exposure Assessment of DEHP in Drinking Water: DEHP is considered to be endocrine disrupting chemical (EDC), whose effects may not be visible until long-term exposure (Gray *et al*., 1998). According to other studies, DEHP detected in the drinking water and frequently ingested in daily life, indicate that drinking water is a significant source of human exposure to DEHP contaminants (WHO, 1992; Wams, 1987).To assess the possible and adverse effects of DEHP, quality guidelines for surface water and drinking water standard were used (WHO, 1992). DEHP at levels obtained from this study was below (Figure 6) the reference value taken as safe by the USEPA for the surface water is 0.006 mg/L (NRC, 2006) and 0.008 mg/L for China (Li, *et al*., 2008).

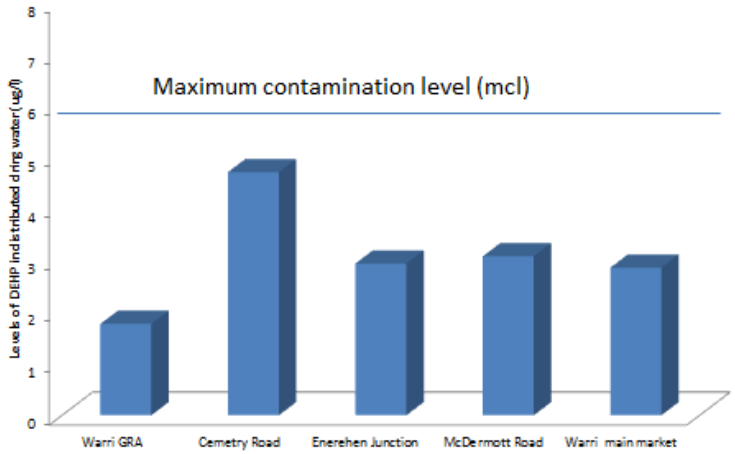

Figure 6: Exposure Assessment of DEHP in Drinking Water in this Study

Action for Safe DEHP Level in Drinking Water

Removing DEHP from drinking water is very important especially as its healthrelated issues is becoming a global concern. The following action may promote safe drinking water as it concern DEHP:

- Don't boil the water. There is no evidence that boiling removes DEHP.
- For operators of public drinking water systems and domestic water distribution systems: Avoid using piping or pump components that may contain diethyl phthalates to prevent contamination.
- Fixing granular activated carbon filtration to the domestic water distribution systems. DEHP can be reduced to below 6 ppb in drinking water using granular activated carbon filtration (Baustista-Toledo *et al.*, 2005).
- Regular monitoring of the levels of DEHP in Drinking Water Services for regulatory requirements. Untreated water should be tested at least every three years.

CONCLUSIONS

The amount and distribution of DEHP from various sampling sites water sources varied largely, this is suggestive of the spatial distribution of DEHPvaried according to the specific site. In addition, the variability levels of DEHP water samples may have been attributed the age of domestic water distribution system that has resulted from the leaching of the phthalate into the water.

In conclusion, the results reveal that no urgent treatment measures were required in respect to the DEHP levels, as its levels were below regulatory limits. However, the ecological and health effects from the consumption of these substances in drinking water, though at relatively low concentrations, further investigations in light of its possible biomagnifications still needs to be championed. Therefore, the long-term source control in the water and the addition of an advanced treatment process for drinking water supplies should be of focus in this area.

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