



Distribution of Phthalate Esters in Underground Water from Power Transmission Sites in Warri Metropolis, Delta State, Nigeria

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ABSTRACT: This study investigates the distribution of phthalate acid esters (PAEs) in groundwater from some power stations in Delta State. Groundwater samples were collected from eight power transmission and distribution stations. Concentrations ($\mu\text{g/L}$) of six phthalate acid esters compounds in the groundwater ranged from 0.000–2.547(DMP), 0.053–0.180(DEP), 0.100–0.443 (DBP), 0.400–0.660(DEHP) and 0.000–0.020 (DnOP), while BBP was not detected in all the locations. Lowest total PAEs concentration was recorded in Edjeba Station ($0.994 \pm 0.040 \mu\text{g/L}$) while the highest concentration was recorded in Mofo Station ($3.380 \pm 0.012 \mu\text{g/L}$). Analysis of variance showed significant difference in concentration of DMP ($p < 0.5$) from the eight transmission stations. DMP, DEP and DBP concentration in groundwater were found to be at level that does not pose immediate threat. Despite this, it would be advisable to continue to monitor the presence of these substances in water. DEHP content was high in most samples from the different stations and this is of serious concern, because it has been proven to be carcinogenic. It is advised that most of the old dilapidated transformers and other electrical equipment containing organic contaminant such polychlorobiphenyl (PCB) which is a major contributor of phthalate acids into water bodies be replaced with new ones and concrete bundwall built round the transformers to prevent unwholesome seepages into the environment. There should also be appropriate storage, decontamination and disposal of contaminated units prior to final disposal. Decommissioned transformers and equipment containing PCB should be stored on a concrete pad with curbs sufficient to contain the liquid contents. © JASEM

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Phthalate acid esters (PAEs) are industrially produced non-reactive plasticizers used in the production of plastics. They are formed when methanol, ethanol or other alcohols react with the carboxyl groups on the benzene ring of phthalic acids. They are diakyl or alkyl esters of 1, 2 benzene carboxylic acid (Adeniyi *et al.*, 2008). When added to plastics such as polyvinyl chloride, cellulosic and styrene, their softness and flexibility are improved. Many PAEs and their metabolites cause adverse effects on reproduction and development in humans and animals such as testicular and sexual differentiation effects (Ema *et al.*, 1998). Some of these phthalate acid esters are: dimethyl phthalate (DMP), dibutyl phthalate (DBP), di (2-ethylhexyl) phthalate (DEHP), butyl Benzyl phthalate (BBP), Diisodecyl phthalate (DIDP), Diisononyl phthalate (DINP), Di-n-Hexyl-phthalate (DnHP) and Di-n-octyl phthalate (DnOP). Other products that contain phthalates include polychlorinated dibenz-p-dioxins, polychlorinated dibenzofurans, Organochloropesticides, dichlorodiphenyl,

trichloroethylene, nonylphenols, steroid hormones and phthalates. A main route of exposure to phthalates is via water use as these chemicals find their way into the water system through effluent discharges, leaching from waste dumps and through several diffuse sources (WHO, 2003).

Urbanization, intensive agriculture, recreation, and the manufacturing industry are affecting water quality throughout the world. Waste generations by the industries and households have continued to increase. This has led to pollution of inland water bodies and coastal waters and subsequently increased water quality parameters such as heavy metals, nutrients and organic matter, soluble ions, oil and grease, and organic chemicals such as pesticides and poly-nuclear aromatic hydrocarbons (PAHs). Almost all major forms of electricity generation-fossil fuel based, nuclear, large hydro, newer renewable, as well as transmission have raised serious environmental concern (Hester and Harrison, 2006). Highly-refined, mineral insulating oils are used to cool transformers and provide electrical insulation between live

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components. They are typically found in the largest quantities at electrical substations and maintenance shops ((Ifterhar *et al.*, 2013). Sulfur hexafluoride (SF6) may also be used as a gas insulator for electrical switching equipment and in cables, tubular transmission lines, and transformers. SF6 may be used as an alternative to insulating oils. Polychlorinated Biphenyls (PCB) were widely used as a dielectric fluid to provide electrical insulation, although their use has been largely discontinued due to potential harmful effects on human health and the environment. Studies have detected these compounds in wastewater (Olujimi *et al.*, 2012), River water (Liu *et al.*, 2013), seawater and even in sediments (Bastos and Haglund, 2012). They have also been occasionally detected in drinking water (Dévier *et al.*, 2013; Blanchard *et al.*, 2013; Domínguez-Morueco *et al.* 2014; Irina *et al.*, 2015) and also bottled water (Levaidara *et al.*, 2007; Dumitrescu, 2012).

In Nigeria, high concentrations of DEHP and DBP (1000 times higher than run-off water samples) in leachates and sediment from a municipal waste deposit site were recorded in Owerri Town (Arukwe *et al.*, 2012). Others are that of Aina *et al.* (2015) on phthalate esters in Epe and Lagos Lagoons; Adeola and Taiwo (2013) on the sediments and waters of Rivers Ogun and Ibese in Southwestern Nigeria; while Maduka *et al.* (2009) reported some traces of phthalates in tap and rain water in Enugu.

Urgent attention is therefore necessary to mitigate water pollution problems in Nigeria through monitoring as well as enforcement of emission standards by industries. Assessment of water is not only for suitability for human consumption but also in relation to its agricultural, industrial, recreational, commercial uses and its ability to sustain aquatic life. Water quality monitoring is therefore a fundamental tool in the management of freshwater resources. To

underpin its importance, World Health Organization (WHO), United Nations Environment Programme (UNEP), United Nations Educational, Scientific and Cultural Organization(UNESCO) and World Meteorological Organization (WMO) launched in 1977, a water monitoring programme to collect detailed information on the quality of global ground and surface water. Since Phthalate acids esters in soil can be desorbed and infiltrate into groundwater by rainfall, groundwater may therefore be one of the important reservoirs for PAEs, while PAEs in surface water may directly permeate into groundwater through water flow. Hence this work is aimed at assessing the level of PAEs in groundwater from transmission and distribution power stations.

MATERIALS AND METHODS

Area of Study: Warri is the economic nerve center of Delta State. It is an oil producing community, second only to the city of Port-Harcourt. It is the most populated town in Delta State. Warri Metropolis comprises Warri, Uvwie and Okpe Local Government Areas with a population of about 800,000 (NBS, 2010). The metropolis have eight distribution substation at Okoloba, Army Barrack, Enerhen, Edjeba, Jeddo, NPA, Mofo, Warri Mains and a transmission station at Alegbo operating a 33,000 volts feeding the various distribution stations which operate at 11,000 volts (Figure 1). Virtually all the distribution substation was built over twenty years ago except Jeddo and Mofo which are less than twenty years old. Used transmission fluids were found spilled around the environment in some of the distribution stations, as there is no bund-wall to curtail their spread. This fluid easily percolates and seep into the underground or are washed into the nearby streams after heavy downpour of rain. There was a general poor housekeeping within most of the facilities visited except the new Mofo Station.

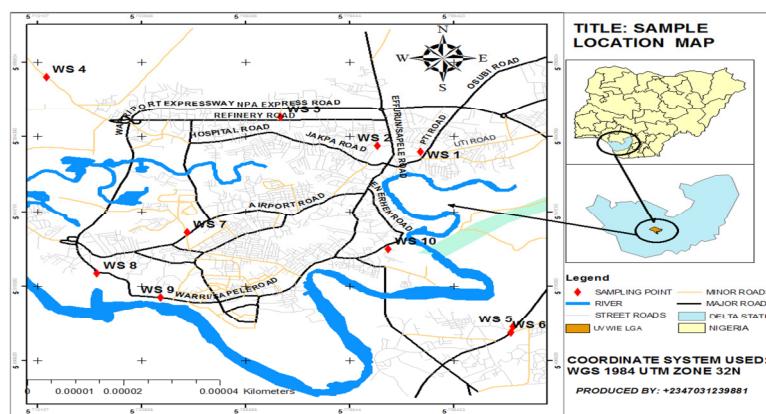


Fig1: Map of sampling location

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Sample Collection: Water samples were collected from eight transmission stations (Table 1) in a glass bottle, stored in an ice chest until arrival to the laboratory, where they were kept in fridge.

Table 1: Sample location, codes and grid coordinates

S/N	Site code	Description	Sampling co-ordinate
1	WS1	Alegbo	N 05°33'35.5" E005°47'29.7"
2	WS2	Okoloba	N 05°33'42.0" E005°46'57.5"
3	WS3	Army barrack	N 05°34'13.0" E005°45'45.2"
4	WS4	Jeddo	N 05°34'56.6" E005°42'50.5"
5	WS5	Mofo	N 05°30'24.3" E005°48'38.7"
6	WS6	Edjeba	N 05°32'07.4" E005°44'35.5"
7	WS7	Warri-Mains	N 05°30'56.8" E005°44'15.8"
8	WS8	Enerhen	N 05°31'49.2" E005°47'05.7"

Chemicals and materials: Anhydrous sodium sulphate oven heated at 400°C; cyclohexane distilled in an all glassware; acetone; 1,11-Dibromoundecane(ISTD); reagent water; Agilent gas chromatograph 6890N coupled with MS; Sample collection bottles; 11 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.

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.

Quality Control: Distilled water used during experimental process was analysed separately for all

phthalates acid esters and used as control. Triplicate analysis was carried out for each phthalates in the water sample.

Analysis of Phthalate in water using GC/MS: 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. 4.6µl/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 Skoog *et al.* (1998), Edjere (2006) and Institute Bachema AG Quality Management Guidelines as certified by ISO 17025 (Institute Bachema, 2004; 2006).

RESULT AND DISCUSSION

Total phthalate acid esters for each of the locations are shown in Table 2. Highest total phthalates concentration was recorded in Mofo Station ($3.38 \pm 0.0116 \mu\text{g/L}$) followed by Alegbo and Army Barracks Stations with a concentration of $2.623 \mu\text{g/L}$ and $2.15 \mu\text{g/L}$ respectively while the lowest total phthalates concentrations was recorded in Edjeba Station followed by Warri Main and Enerhen Stations with concentrations of $0.993 \mu\text{g/L}$, $1.143 \mu\text{g/L}$ and $1.213 \mu\text{g/L}$.

The pattern of phthalate acid concentration for each of the stations are:DEHP>DMP>DBP>DEP>DnOP>BBP(Edjeba), DEHP>DBP>DMP>DEP>DnOP>BBP (Okoloba), DMP>DEHP>DBP>DEP>DnOP>BBP (Army Barracks), DMP>DEHP>DBP>DEP>DnOP>BBP (Mofo), DMP>DEHP>DEP>DBP>DnOP>BBP (Jeddo), DEHP>DBP>DEP>DMP>DnOP>BBP (Warri Mains), DMP>DBP>DEHP>DEP>DnOP>BBP (Alegbo) and DEHP>DBP>DEP>DMP>DnOP>BBP (Enerhen) as shown in Figure 2. This shows that DEHP was generally more prevalent and has highest concentrations in most of the Station. It was followed by DMP and DBP. The least occurring phthalate was BBP, which was not detected in all the locations. It was closely followed by DnOP and DEP. Concentrationn of DEHP is pronounced in 50% of the sampling region, this is not surprising as DEHP is the most used phthalates. Jianlong *et al.*(2000) and Chang *et al.* (2004) pointed out that phthalates with shorter ester chains, like DMP, DEP, DBP, DPP and BBP can be readily biodegraded and mineralized, whereas phthalates with longer ester chains, such asDEHP, are less susceptible to biodegradation. This may account for the low concentrations of BBP and

DEP in the stations and high concentrations of DEHP. The biodegradability of the different phthalates is likely due to the steric effect of phthalates side ester chains, which hinders the hydrolytic enzymes from binding to the phthalates and thereby inhibits their hydrolysis (Xia *et al.*, 2004). Concentration of DEHP was lower than that reported by Wen-Long *et al.*, (2015) in source water with median value of 1.3 μ g/L entering the water treatment plant and 0.064 μ g/L after various treatment processes was carried out. Irina (2015) reported DEHP concentrations were below detection limits (<0.015 μ g/L) for all the samples analyzed inside drinking water treatment plant in Cluj, Romania.

DMP was observed to be more in Mofo Station (2.5467 μ g/L) and less in Warri Mains and Enerhen (0.000 μ g/L). Hence possibility of DMP degradation is not ruled out. Concentrations ranged from 0.0000-2.5467 μ g/L which is the highest phthalate acid ester concentration obtained. Water solubility of the alkyl phthalate ester generally varies inversely with the length of the alkyl side chain. Dimethyl phthalate (DMP) was the most hydrophilic and water soluble of the esters. The C₁₀, C₁₁, and C₁₃ esters are the most hydrophobic and least water soluble.

Table 2: Concentration (μ g/L) of phthalate esters from studied locations

S/N	Sites	DMP	DEP	BBP	DBP	DEHP	DnOP	Total
1	Edjeba	0.367 \pm 0.0058 ^a	0.0533 \pm 0.023 ^a	N.D	0.120 \pm 0.000 ^b	0.4533 \pm 0.0115 ^{bc}	N.D	0.9936 \pm 0.0403
2	Okoloba	0.260 \pm 0.0000 ^b	0.0933 \pm 0.05774 ^{ab}	N.D	0.400 \pm 0.000 ^c	0.6267 \pm 0.02309 ^e	N.D	1.3800 \pm 0.08033
3	Army barrack	1.267 \pm 0.0115 ^c	0.0533 \pm 0.0577 ^a	N.D	0.37 00 \pm 0.0173 ^d	0.4600 \pm 0.0000 ^c	0.0000	2.1503 \pm 0.0865
4	Mofo	2.5467 \pm 0.0000 ^d	0.1400 \pm 0.0000 ^{b,c}	N.D	0.2533 \pm 0.01155 ^c	0.440 \pm 0.0000 ^b	0.0000	3.38 \pm 0.01155
5	Jeddo	1.0200 \pm 0.0000 ^e	0.1133 \pm 0.0115 ^b	N.D	0.1000 \pm 0.000 ^a	0.4867 \pm 0.0462 ^d	N.D	1.72 \pm 0.0577
6	Warri mains	0.0000 \pm 0.0000 ^f	0.1233 \pm 0.0058 ^{b,c}	N.D	0.3600 \pm 0.0000 ^d	0.6400 \pm 0.00000 ^e	0.02 \pm 0.00	1.1433 \pm 0.0058
7	Alegbo	1.5800 \pm 0.0000 ^g	0.1800 \pm 0.000 ^c	N.D	0.4433 \pm 0.0058 ^f	0.4000 \pm 0.00000 ^a	0.02 \pm 0.00	2.6233 \pm 0.0058
8	Enerhen	0.00000 \pm 0.0000 ^f	0.1400 \pm 0.0000 ^{b,c}	N.D	0.4133 \pm 0.01155 ^c	0.6600 \pm 0.00000 ^f	N.D	1.2133 \pm 0.01155
Total		7.0407 \pm 0.0058	0.8965 \pm 0.1557	N.D	2.4599 \pm 0.1502	4.1667 \pm 0.0808	0.04 \pm 0.00	14.6038 \pm 0.3000
Min		0.000	0.0533	N.D	0.1000	0.4000	0.0000	0.9936
Max		2.5467	0.1800	N.D	0.4433	0.6600	0.02	3.38

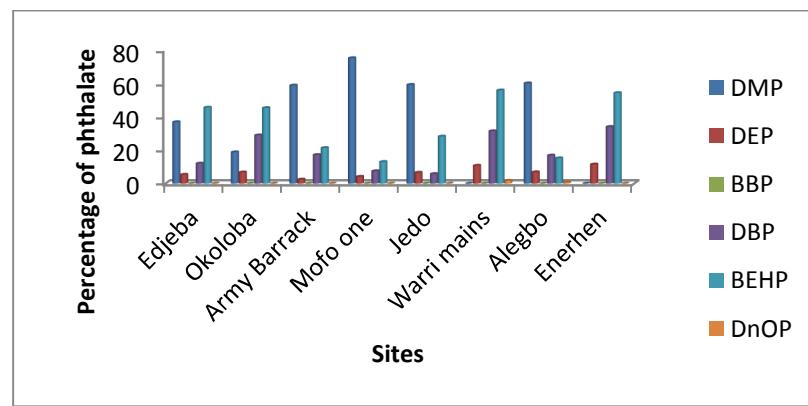


Fig 2: Percentages contribution of each Phthalates in the sampled water

The sorption of phthalate esters to soil, sediment, or suspended solids is partially governed by their relative hydrophobicity (Staples *et al.*, 1997). Although values obtained are less than the maximum contamination level (5.0mg/l). This is higher than that reported by Domínguez-Morueco *et al.*, (2014) for Phthalate levels in drinking water samples from the main supply areas for Madrid in contrast to river water samples in drinking water samples 0.0011 µg/L

DBP and DEP concentration tends to be less in most station ranging from 0.0533-0.1400µg/L for DBP and 0.120-0.4433µg/L for DEP. Highest concentration of these phthalate esters was obtained at Alegbo transmission station. Edjeba and Jeddo distribution station was the least contributor to DEP and DBP values. Result obtained was in agreement with that reported by Kanchanamayoonet *et al.*, (2012) where concentration of 0.11mg/l DEP was found in drinking water sample and DBP not detected. Hadjimohammadi *et al.*(2010) also reported that DEP

and DBP was not found in tap water sample in Babolsar, Mazandaran Province in the north of Iran. Although result showed that values of these pollutants are insignificant compared to allowable standard, bioaccumulation might pose health challenge if not checked.

In Figure 3, total phthalate acid ester concentration ranged between 0.9936µg/L ($\pm 0.0403\mu\text{g/L}$) to 3.38µg/L ($\pm 0.01155\mu\text{g/L}$). Edjeba and Warri Mains Station have lowest concentration while Mofo and Alegbo Stations have the highest concentration. Warri Mains distribution station was the first among all the station, which was built about 32 years ago. Microbial activities would have led to degradation of lower molecular weight phthalate. From Table 2, concentration of PAEs at Warri station is of the pattern DMB<DBP<DEP<DEHP with observed concentration of DEHP (0.6400 µg/L) at this station is on the high side compared to DMP (0.0000µg/L).

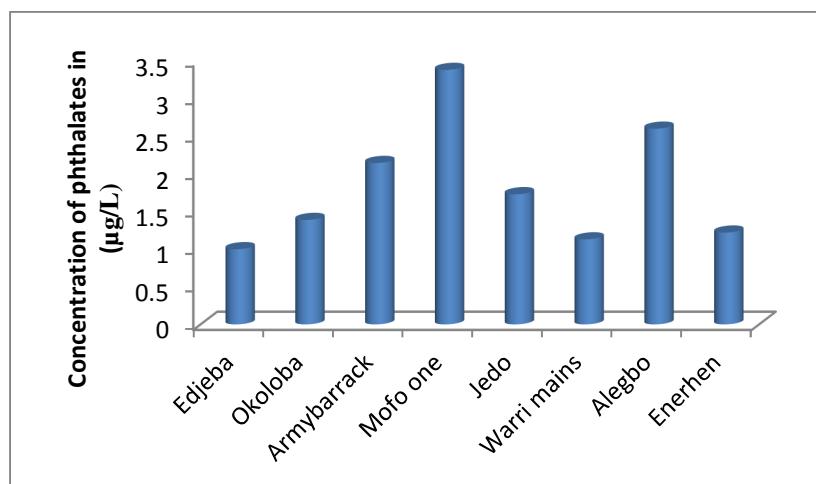


Fig 3: Total phthalate acid concentration from sampling region.

DMP, DEP and DBP concentration in the groundwater were found to be at level that does not pose immediate threat. DEHP content was high in most samples from the different stations and this is of serious concern, because the compound has been proven to be carcinogenic (WHO, 2003). DEHP also known as di-(2-ethylhexyl) phthalate is considered to be a priority hazardous substance in the latest proposed directive (Directive 2013/39/UE) from the European Parliament and the Council (2013) concerning priority substances in the field of water policy, so it is abnormal that it was found in samples. DEHP in water poses serious risks of cancer in humans, especially when using the water for dermal absorption (bathing) and drinking purposes.

It is in the opinion of the authors that existing transformers and other electrical equipment containing organic contaminant such polychlorobiphenyl (PCB) which is a major contributor of phthalate acids in the premises of power transmission and distribution should be appropriately stored in their warehouse with concrete bundwalls erected around them to prevent leakages into the open environment. Old and decommissioned units should be properly decontamination. Prior to final disposal, retired transformers and equipment containing PCB should be stored on a concrete pad with curbs sufficient to contain the liquid contents. Most important, Nigerian government should set up indigenous own standard for phthalate acid esters in consumed products.

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