

# Phthalate Levels in Wastewater Treatment Plants of Lake Victoria Basin

Onchiri R<sup>1</sup>, Mayaka A<sup>2</sup>, Majanga A<sup>3</sup>, Ongulu R<sup>4</sup>, Orata F<sup>4</sup>, Getenga Z.M<sup>5</sup>, Gichumbi J.M<sup>6</sup>, Ogora E.N<sup>6,\*</sup>

<sup>1</sup>Department of Civil Engineering, Technical University, Mombasa, Kenya, P.O BOX 000 – 80100, Mombasa
<sup>2</sup>Faculty of Engineering, Multi Media University, Nairobi, Kenya, P.O BOX 15653-00503, Nairobi, Kenya
<sup>3</sup>Department of Social Sciences, Masinde Muliro University, Kakamega, Kenya, P.O BOX 190 – 50100, Kakamega, Kenya
<sup>4</sup>Department Chemistry, Masinde Muliro University, Kakamega, Kenya, P.O BOX 190 – 50100, Kakamega, Kenya
<sup>5</sup>Department of Physical Sciences, Machakos University, Machakos, Kenya, P.O BOX 136 – 90100, Machakos, Kenya
<sup>6</sup>Department of Physical Sciences, Chuka University, Chuka, Kenya, P.O BOX 109 – 60400, Chuka, Kenya
\*Corresponding author: onyakwama@gmail.com

Received November 05, 2021; Revised December 08, 2021; Accepted December 16, 2021

**Abstract** Phthalates are examples of EDCs, which have been used as plasticizers for longtime worldwide. However, their occurrence in these environments causes adverse effects such as congenital anomalies, endocrine disruption and chronic toxicity. Wastewater is the source of these phthalates in the environment. The main aim of this study was to determine the levels of dimethyl phthalate (DMP), benzyl butyl phthalate (BBP) and bis (2-ethylhexyl) phthalate (BEHP) in wastewater sampled from wastewater treatment plants (WWTPs) of Nyalenda, Homabay and Kisii, in Kenya during wet and dry seasons. Thermos Scientific Dionex UltiMate<sup>TM</sup> 3000 HPLC system was used to analyze the residue levels at 0.004 and 0.005 mg/L limits of quantification during wet and dry seasons, respectively. Most sites sampled had detectable levels of DMP, BBP and BEHP. Higher concentrations were detected during wet season compared to dry season. At Nyalenda treatment plant, DMP was detected at 0.99  $\pm$  0.0005 mg/L and 0.79  $\pm$  0.0005 mg/L at the inlet sampling point during the wet and dry seasons, respectively. The concentrations detected were high at the inlet and lowest at the outlet sampling points. The residue levels obtained showed significant differences at 5% confidence limits with  $Z_{calculated}$  for DMP at Nyalenda, Homabay and Kisii WWTPs obtained as 0.2650, 0.2183 and 0.1983, respectively. These Z-score values ( $Z_{calculated}$ ) were less than the critical value ( $Z_{critical} = 1.96$ ). Similar observations were observed with BBP and BEHP.

**Keywords:** Dimethyl phthalate, Benzyl butyl phthalate. Bis (2-ethylhexyl) phthalate, Wastewater treatment plant. HPLC system, Limit of quantification

**Cite This Article:** Onchiri R, Mayaka A, Majanga A, Ongulu R, Orata F, Getenga Z.M, Gichumbi J.M, and Ogora E.N, "Phthalate Levels in Wastewater Treatment Plants of Lake Victoria Basin." *Applied Ecology and Environmental Sciences*, vol. 9, no. 12 (2021): 1011-1017. doi: 10.12691/aees-9-12-4.

#### 1. Introduction

Endocrine disrupters are chemicals disturb the functionality of the endocrine system. They interfere with natural hormone cycles in animals or humans, specifically affecting reproduction, development, metabolism and growth [1]. Most endocrine disrupting chemicals are man-made [2]. Many of these EDCs are mostly in well water, oceans, lakes, marines and food products [3]. They have negative health effects on male and female reproduction (natural estrogen and androgens), breast development, birth defects, thyroid, metabolism and obesity [4]. Examples of EDCs include persistent organic pollutants (POPs), pesticides, pharmaceuticals such as antibiotics, personal care products and phthalates. Phthalates are part of organic compounds that are being used in industry since 1930s, as plasticizers to make papers, ink, paper, cosmetics, ceramics and plastics [5]. In addition, they are used in different products as additives; insulators in electric disposals packaging, coverings and

insecticides [6]. In many years, there is a serious concern on these heterogenous contaminants capable of disrupting the endocrine system of human beings and other organisms [7]. Studies have shown that a significant portion of urban sewage effluent, surface waters and drinking portable waters contain phthalates [8,9,10]. In Kenya, reference [11] and [9] were able to report pharmaceutically active ingredients from Nairobi River. A challenge especially for developing countries is the cost associated with determining the levels and removal of non-conventional pollutants in waste waters.

#### 1.1. Occurrence of Phthalates in Water

Phthalates are found in wastewaters, sludge and surface waters due to their wide use [12]. They are among the most important industrial chemicals, with the most used being DMP, BEHP, BBP and DBP [13]. They are used as a coat of PVC resins and cellulose film coating [14]. They enter into the environment through losses during the manufacturing process [13]. Emissions of phthalates from

manufacturing processes are thought to be negligible due to manufacturing regulations [15] and high costs involved in production which makes it economically undesirable to have phthalate waste [16]. Phthalates are released from the municipal WWTPs majorly into different water bodies [17]. Therefore, the performance of WWTPs is a major concern to many as far as treating and removing of phthalates from wastewater is concerned [18]. This for instance is the case within Lake Victoria Basin, the largest fresh water lake in East Africa. All the effluents from selected WWTPs and many more are released directly into the lake or into its tributaries. Homabay WWTP releases its effluents directly to Lake Victoria. This leaves the aquatic organisms exposed to these phthalates, hence they put a health hazard impact to the entire food chain as a result of municipal wastewater [19]. These phthalates can also reach the ground through accidental spills and by agricultural effluents [20]. Therefore, the consequent uptake of these phthalates especially by vegetable and fruit crops indicates a significant potential exposure to human [21]. Many past researchers have reported that many processed foods contain phthalates, in particular packed products, which is as a result of coat that migrates to food products [22]. All these sources of phthalates are all treated in WWTPs whose effluents are discharged directly to Lake Victoria.

Phthalates are used in large quantities and have a higher environmental persistence and hence, they tend to bioaccumulate and get biomagnified in the environment up to the water systems and WWTPs [23]. Dimethyl phthalate is a widely used compound in our daily necessities [5]. It has been recorded in many parts of the environment. The WWTPs, which are the main source of phthalates are the major cause of these harmful chemicals used in industries and households [24]. This is because they are part of the sewage and surface runoff, therefore, the final amounts found are best indicators of their uses and emissions patterns in their originating areas as well as their occurrence in the receiving waters. Most phthalates cause harm to human and aquatic system even at low concentrations [25].

#### 1.2. Phthalates of Interest in This Study

The study focused on DMP, BBP, and BEHP whose chemical structures are shown in Table 1 below.

Mol. weight Sol. in water (mg/l) Name Structure DMP 194.2 4200  $\mathsf{CH}_3$ BBP 312.4 2.7 CH<sub>3</sub>  $CH_3$ **BEHP** 390.57 0.003 Ö  $CH_3$ CH<sub>3</sub>

Table 1. Physicochemical Properties of Phthalates

#### 2. Materials and Methods

#### 2.1. Study Area

The study site involved three urban centers which are within the Lake Victoria catchment region. These areas included the following; Kisumu, Homabay and Kisii counties which are located in the western part of Kenya. From Kisumu County, Kisumu WWTP (Nyalenda) located at 0<sup>0</sup>07' 09" S and 34<sup>0</sup>46'.32"E, with an elevation of 1124.4m above mean sea level was sampled. WWTPs

in Homabay county at Latitude:  $0^{\circ}$  30' 59.99" N and Longitude:  $34^{\circ}$  26' 59.99" E, and Kisii county at Latitude  $0^{\circ}$  39'30" S and Longitude  $34^{\circ}$  42'30" E were also sampled. Sampling was done in April, 2019 for the first sampling and August, 2019 for the second sampling. The two respective periods served as the rainy and dry seasons, respectively. The sampling points at wastewater treatment plants, were designated as  $S_1$ ,  $S_2$  and  $S_3$ .  $S_1$  was the sampling effluent point (inlet) while  $S_3$  was the sampling effluent (outlet) point. Sampling point  $S_2$  came between  $S_1$  and  $S_3$  sampling points.

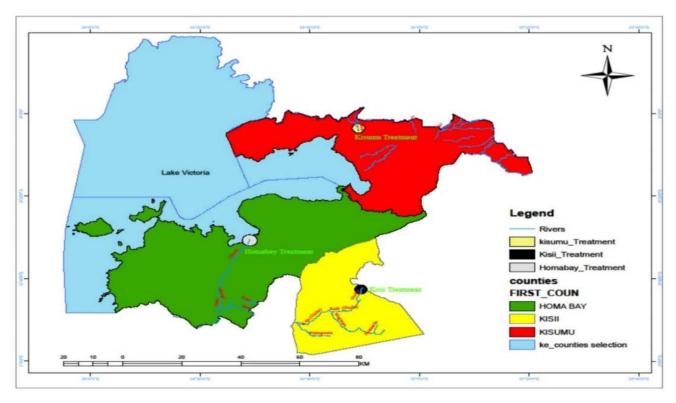


Figure 1. Map of sampling points, showing Kisumu, Homabay and Kisii wastewater treatment plants

#### 2.2. Chemicals, Reagents and Apparatus

Standards of purity (99.9%) of dimethyl phthalates (DMP), benzyl butyl phthalate (BBP) and bis (2-ethyl hexyl) phthalate (BEHP) were purchased from Sigma Chemical Co., Germany. Analytical grade methanol (HPLC grade), de-ionized water, 2 mm glass wool filter papers, 0.45 $\mu$ m glass micro filters, glass wool and C<sub>18</sub>-E<sup>TM</sup> Solid Phase Extraction (SPE) cartridges were purchased from Merck, Germany. Glassware was obtained from Kenya Bureau of Standards biochemistry laboratory, Nairobi.

## 2.3. Waste Water Sampling and Sample Preparation

Samples of waste water were collected in 1 litre brown amber bottles from Nyalenda, Homabay and Kisii WWTPS sampling points and their details were documented. During sampling, the temperature and pH of the sample was recorded at the sampling point. The collected water samples were stored in a cool box with ice to maintain low temperatures before they reached the laboratory. In the laboratory, the samples were transferred from the cool box to a refrigerator maintained at temperatures below 4°C before extraction was done. The water samples were collected in April, 2019 during the wet season and August, 2019 for the dry season.

# 2.4. Extraction of Phthalates Residues from Water Samples

An aliquot of 500 ml of each water sample was measured and filtered twice using a 2 mm glass wool filter to remove particulate matter. Using double distilled 25 ml

of dichloromethane, solid phase extraction cartridges were used to extract the samples from 500 ml waste water. The cartridges were treated with 5 ml methanol, then followed by 5 ml of distilled water as a process of preparing them prior to extraction. The samples were passed through the SPE at 5 ml per minute flow rate. Strict caution was observed to ensure that none of the cartridges dried during the sample extraction process. After the process was over, the cartridges were then dried via vacuum for a period of 10 minutes, just to remove the traces of any moisture contained. After the cartridges were dried, they were eluted with pure dichloromethane collected in 15 ml sample vial. The final extracts were then dried using anhydrous sodium sulfate, filtered using 0.45 µm nylon micro filters and then concentrated to 3 ml in readiness for cleanup.

#### 2.5. Optimization of SPE Cleanup Conditions

The solid phase cartridge was connected to 1-L separating funnel that was fitted with appropriate fittings. The cartridges were regularly prewashed using 5 ml by volume of methanol, 10 ml of distilled water at a flow rate of 2-3 ml/min and then 3 ml of n-hexane. The sample, 3 ml was loaded onto a column and was flowing at a rate of 1-2 ml/min under water aspirator vacuum. After the sample was applied, the SPEs were duly dried by blowing air for 3 minutes. The analytes obtained were then eluted with 70% hexane in methanol (2 x 3 ml) and then combined eluate, then dried with approximately 0.5 g of anhydrous sodium sulfate and concentrated to 1 ml in a micro Kuderna-Danish evaporator and a stream of nitrogen gas. The cleaned samples were reconstituted using HPLC methanol and hexane (volume ratio 1:1) in readiness for HPLC analysis.

#### 2.6. Preparation of Standard Solutions

Stock solutions of 1000 ppm of each phthalate standard were prepared. This was done by weighing 0.01 g of a phthalate standard and dissolved in a 10 ml conical flask containing methanol to the mark. The required concentrations of standard solutions were obtained by diluting the stock solution. Concentrations 0.5 ml, 1 ml, 1.5 ml, 2 ml and 3 ml obtained from the stock solution were pipetted into five different 100 ml volumetric flasks and then made to the mark with methanol, resulting in final concentrations of 5 mgL<sup>-1</sup>, 10 mgL<sup>-1</sup>, 15 mgL<sup>-1</sup>, 20 mgL<sup>-1</sup> and 30 mgL<sup>-1</sup>, respectively.

#### 2.7. Instrumental Calibration

Prior to analysis, the HPLC machine was calibrated with a minimum of 5 calibration level points of 5 mgL<sup>-1</sup>, 10 mgL<sup>-1</sup>, 15 mgL<sup>-1</sup>, 20 mgL<sup>-1</sup> and 30 mgL<sup>-1</sup> of the standards phthalates. A calibration curve for each of the standards was drawn and the coefficient of the regression curve was obtained before analysis of the processed samples commenced. The quantification limit was also determined.

#### 2.8. Sample Analysis

Thermos Scientific Dionex UltiMate<sup>TM</sup> 3000 HPLC system was used to analyze the water samples extracted. The HPLC conditions were: Mobile phase of 80:20 v/v (methanol: water) isocratic system; HPLC column; Reverse phase column (C18 column); Flow rate; 10  $\mu$ L; column temperature; 35°C. A calibration curve was generated by spiking a wide range of concentrations of DMP, BBP and BEHP, and the retention time and peak area of the standards and samples were used to quantify the particular phthalates of interest. An aliquot of 5  $\mu$ L of each sample was drawn by the use of syringe and injected into the HPLC machine. External standard area method was used to calculate the concentration of the respective phthalates in water samples.

#### 3. Results and Discussion

## **3.1. Environmental Parameters at the Sampling Points**

Table 2. Temperature and pH Values of the Wastewater Sampled During Wet and Dry Seasons

	Wet season		Dry season	
Sampling point	Temperature (Kelvins)	pН	Temperature (Kelvins)	pН
NS <sub>1</sub>	302.10	7.04	302.50	6.78
$NS_2$	301.10	10.00	302.10	7.38
$NS_3$	300.90	9.62	302.10	6.96
$HS_1$	294.80	8.33	298.60	6.64
$HS_2$	295.90	7.98	298.50	6.98
$HS_3$	292.40	8.51	298.50	8.00
$KS_1$	298.60	7.68	299.20	7.12
$KS_2$	298.20	7.54	298.90	7.00
KS <sub>3</sub>	298.20	8.22	298.80	6.89

**NS** = Nyalenda sewage, **HS** = Homabay sewage, **KS** = Kisii sewage, **12** & **3** for inlet, middle and outlet sampling points respectively.

From Table 2, most of the sites' influents are slightly on the basic side having the pH between 7.00 and 10.00. Although the temperature levels at the sampling sites seemed similar, they were higher in the dry season than wet season. Variation especially in pH values of wastewater also varied between the two seasons. There is lots of soluble (waste) materials travelling into the WWTP system [26]. The study by reference [16] also justifies that the accumulation of contaminants via polluted waters in Nyalenda wastewater treatment plant depends on environmental parameters, water temperature and pH inclusive. Environmental parameters in Table 2 were therefore necessary to study the levels of selected phthalates, as contaminants onto WHB as an adsorbent of removing them from WWTPs [27].

### **3.2.** Calibration Curves for DMP, BBP and BEHP

All the calibration curves for quantification of residual selected phthalates concentrations were obtained according to the batch method at room temperature. They showed a linear correlation coefficient,  $R^2 > 0.99$  at room temperature. The limit of quantification was 0.004 mg/L.

### 3.3. Levels of DMP, BBP and BEHP in Wastewater

Table 3. Levels of Phthalates in Wastewater (mgL  $\mbox{^{-1}}\mbox{)}$  During Wet Season

Sampling point	DMP	BBP	BEHP
$NS_1$	$0.99 \pm 0.0005$	$0.97 \pm 0.0005$	$0.95 \pm 0.001$
$NS_2$	$0.44 \pm 0.0007$	$0.38 \pm 0.0005$	$0.27 \pm 0.0005$
NS <sub>3</sub>	$0.16 \pm 0.0004$	$0.02 \pm 0.001$	0.09 ±0.0008
HS <sub>1</sub>	$0.89 \pm 0.0007$	$0.82 \pm 0.001$	$0.80 \pm 0.0006$
$HS_2$	$0.33 \pm 0.0005$	$0.23 \pm 0.001$	$0.27 \pm 0.0005$
HS <sub>3</sub>	$0.09 \pm 0.0007$	$0.01 \pm 0.0005$	<loq< td=""></loq<>
KS <sub>1</sub>	$0.83 \pm 0.0007$	$0.85 \pm 0.0005$	$0.80 \pm 0.0008$
$KS_2$	$0.36 \pm 0.0007$	$0.19 \pm 0.0006$	$0.24 \pm 0.0008$
$KS_3$	<loq< td=""><td><loq< td=""><td><loq< td=""></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""></loq<></td></loq<>	<loq< td=""></loq<>

Note: LOQ = 0.004 mgL-1. NS = Nyalenda sewage, HS = Homabay sewage, KS = Kisii sewage, 1 2 & 3 for inlet, middle and outlet sampling points. LOQ = limit of quantification, DMP = dimethyl phthalate, BBP = benzyl butyl phthalate, BEHP = bis (2-ethylhexyl) phthalate.

Table 4. Levels of Phthalates in Waste Water (mgL<sup>-1</sup>) During Dry Season

Sampling point	DMP	BBP	BEHP
NS <sub>1</sub>	$0.79 \pm 0.0005$	$0.81\pm0.0008$	$0.75 \pm 0.001$
$NS_2$	$0.26\pm0.0005$	$0.18\pm0.0006$	$0.09 \pm 0.0008$
NS <sub>3</sub>	$0.09\pm0.001$	$0.08\pm0.0008$	$0.009 \pm 0.0008$
HS <sub>1</sub>	$0.52\pm0.001$	$0.50\pm0.0008$	$0.61 \pm 0.0008$
$HS_2$	$0.10\pm0.0008$	$0.10\pm0.001$	$0.10 \pm 0.001$
HS <sub>3</sub>	<loq< td=""><td><loq< td=""><td><loq< td=""></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""></loq<></td></loq<>	<loq< td=""></loq<>
KS <sub>1</sub>	$0.47 \pm 0.0008$	$0.52 \pm 0.0005$	$0.54 \pm 0.0008$
$KS_2$	$0.11 \pm 0.0008$	$0.11\pm0.0008$	$0.07 \pm 0.0006$
KS <sub>3</sub>	<loq< td=""><td><loq< td=""><td><loq< td=""></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""></loq<></td></loq<>	<loq< td=""></loq<>

The results from Table 3 which represents concentrations of the selected phthalates in mg/L sampled during the wet season, showed that Nyalenda wastewater treatment plant accounted 83.84%, 97.94% and 90.53% removal efficiency of DMP, BBP and BEHP, respectively. Homabay wastewater treatment plant accounted 89.89%, and 98.78% removal

efficiency of DMP and BBP. The removal efficiency of BEHP was not recorded because their concentrations at the outlet were below the level of quantification. Similarly, the removal efficiency in Kisii WWTP was not determined because the levels of DMP, BBP and BEHP were found to be below their levels of quantification. The results from Table 4, which represents concentrations of the selected phthalates in mg/L sampled during the dry season, showed that Nyalenda wastewater treatment plant accounted 88.61%, 90.12% and 98.80% removal efficiency of DMP, BBP and BEHP from waste water. However, the removal efficiency for both Homabay and Kisii wastewater treatment plants could not be reported since the concentration levels for all the phthalates analyzed were below their quantification levels. It is evident that the percentage removal efficiency higher in the dry season, than in the wet season because actual levels found in the later were high.

From Table 3, Nyalenda treatment plant recorded highest levels of detected phthalates, followed by Homabay then Kisii treatment plant comes last. Nyalenda effluent recorded 0.99  $\pm$  0.0005 mg/L of DMP, 0.97  $\pm$ 0.0005 mg/L of BBP and  $0.95 \pm 0.001$  mg/L of BEHP. Homabay effluent recorded  $0.89 \pm 0.0007$  mg/L of DMP,  $0.82 \pm 0.001$  mg/L of BBP and  $0.80 \pm 0.0006$  mg/L of BEHP. Similarly, Kisii effluent recorded  $0.83 \pm 0.0007$ mg/L of DMP, 0.85  $\pm$  0.0005 mg/L of BBP and 0.80  $\pm$ 0.0008 mg/L of BEHP. According to reference [12], the high levels detected in Nyalenda sewage plant was due to lots of anthropogenic activities caused by huge population figures especially in Kisumu city, who use products suspected to contain phthalates. Products such as soft squeeze toys, food containers and teething rings contain phthalates [26].

High levels of concentrations of the phthalates were recorded at the inlet of all the sampling points sampled. For instance,  $0.99 \pm 0.0005$  mg/L,  $0.89 \pm 0.0007$  mg/L and  $0.83 \pm 0.0007$  mg/L of DMP was recorded at the sampling points of Nyalenda, Homabay and Kisii sewage plants, respectively. Levels of BBP at the inlet sampling points were recorded as  $0.97 \pm 0.0005$  mg/L in Nyalenda,  $0.82 \pm$ 0.001 mg/L in Homabay,  $0.85 \pm 0.0005 \text{ mg/L}$  in Kisii sewage plants. Similarly, BEHP was detected to be 0.95  $\pm$ 0.001 mg/L in Nyalenda,  $0.80 \pm 0.0006 \text{ mg/L}$  in Homabay and  $0.80 \pm 0.0008$  mg/L in Kisii sampling inlet points. These high levels could be attributed to the fact that phthalates are not chemically bonded to the plastics hence get into the environment by easy transfer from where they are contained [28]. Much of these phthalates are swept by surface run off [29]. Nyalenda recorded highest levels of phthalates compared to the rest of the sampled plants because of very many activities and high population in Kisumu city and its environments that contribute to the release of phthalates-related wastes to the environment [30].

From the results, it is evident that there are high concentrations of phthalates in the sewage before it is subjected to treatment in the lagoons and notably lower at the outlets. Reference [12] explains out that the WWTPs have high capacity of removal of these phthalates. Treatment processes that take place after the preliminary treatment at the inlet and before the outlet point, reduces their levels drastically as indicated from the results obtained in this research. However, higher levels were

recorded at Nyalenda sewage plant compared to the other sampled plants for all phthalates. This might have been caused by the fact that during the sampling process, it was noted that two of the three parallel lagoons had been closed for desludging, lining and component improvements as also reported by reference [12]. Retention times and depth of the lagoons for all sampled plants might have not been appropriate in reference to oxygen supply. These operating conditions on the bed support the growth of larger organisms such as protozoa and macro-invertebrates, often termed as "grazing organisms" to control the growth of biological film and reduce surplus sludge [31].

Low levels of dimethyl phthalate were detected at the outlet sampling points of Nyalenda and Homabay sewage plants and recorded as  $0.16 \pm 0.0004$  mg/L and 0.09±0.0007 mg/L, respectively. It was however, below the level of quantification at the sampling outlet point of Kisii sewage plant. Benzyl butyl phthalate was detected also in the outlet sampling points of Nyalenda and Homabay sewage plants as 0.02  $\pm$  0.001 mg/L and 0.01  $\pm$  0.0005 mg/L, respectively. Benzyl butyl phthalate was below the level of quantification at the sampling outlet point in Kisii sewage plant. However, BEHP was only detected at the outlet sampling point of Nyalenda sewage plant with a concentration level of 0.09 ± 0.0008 mg/L. It was below the level of quantification in the sampling outlet points of both Homabay and Kisii sewage plants. The very low concentrations detected at the outlets shows the decomposition of these phthalates in the treatment systems of the lagoons especially at the points of aerobic and anaerobic treatment processes [12]. However, the results indicate sufficient levels of all the phthalates for this work were recorded at the outlet sampling points, especially for Nyalenda sewage plant. This can be connected to the low performance of the lagoons which is caused by poor maintenance, overloading of sewage than its expected performance limits and inefficiency of certain components, according to the design report for the proposed rehabilitation of Kisumu sewage [32]. In addition, high concentrations of these phthalates and probably with other chemicals present may have not been exhausted during the treatment process by these lagoons [33]. This is so since the existing facilities might be inadequate and may not serve the high population of the city that has increased dramatically over the last two decades with the result that, even when the WWTP is operating at maximum, the existing infrastructure are overloaded [34].

Table 4 shows that the concentrations detected were much less that those recorded during the wet season (Table 3). All the sampled points, from the inlet to outlet points, recorded less concentrations of phthalates. This shows that in the absence of surface run off, most of the phthalates released to the environment tend to just remain at the point of release by being adsorbed to the sediments [35]. Most of them do not get the way to the stream or treatment plant. Therefore, this makes their concentrations during the entire dry period generally low. From the levels detected, similar trends were observed like in the case in Table 3.

All the sampled inlet points from all treatment plants recorded the highest concentrations of the phthalates. Concentrations of 0.79  $\pm$  0.0005 mg/L, 0.81  $\pm$  0.0008 mg/L and 0.75  $\pm$  0.001 mg/L, were recorded for DMP, BBP and

BEHP, respectively in Nyalenda WWTP inlet. The concentrations kept on reducing along the treatment stages since most of the phthalates could be adsorbed by sediments [12]. The concentration of DMP in Nyalenda sampling points were detected at  $0.79 \pm 0.0005$  mg/L,  $0.26 \pm 0.0005$  mg/L and  $0.09 \pm 0.001$  mg/L at the inlet, midpoint and outlet sampling points respectively. In Homabay, sewage plant, BBP was recorded at levels of  $0.50 \pm 0.0008$  mg/L,  $0.10 \pm 0.001$  mg/L and <LOQ at the inlet, midpoint and outlet sampling points respectively. Similarly, in Kisii sewage plant, BEHP was only detected at the inlet and midpoint sampling points with concentrations of  $0.54 \pm 0.0005$  mg/L and  $0.07 \pm 0.0006$  mg/L. It was below the level of quantification at the outlet sampling point. All the phthalates in this study were below the level of quantification at the outlet sampling points of Homabay and Kisii treatment plants. This was in connection with the low levels that were recorded at the preliminary points. In general, DMP recorded the highest concentrations in most of the sampled points, which shows that it is the most widely used phthalate among the three selected in this study in the areas sampled [36].

#### 4. Conclusion

- Most of the sites sampled had detectable levels of DMP, BBP and BEHP in wastewater.
- High concentrations were detected during wet seasons compared to dry seasons in all sampled sites.
- At Nyalenda treatment plant, DMP was detected at 0.99 ± 0.0005 mg/L and 0.79 ± 0.0005 mg/L at the inlet sampling point during the wet and dry seasons, respectively. Similarly, BEHP was found at 0.80 ± 0.0008 mg/L and 0.54 ± 0.0005 mg/L at the inlet sampling point for Kisii treatment plant during wet and dry seasons, respectively.
- Nyalenda wastewater treatment plant recorded highest concentrations of the phthalates in all sampled sites compared to the other two WWTPs in this study. Benzyl butyl phthalate was detected at 0.08 ± 0.0008 mg/L from the Nyalenda outlet sampling point during the dry season. However, it was below the level of quantification at both Homabay and Kisii outlet sampling points in the same season. Similar trend was noted during the wet season.
- The concentrations of DMP, BBP and BEHP recorded highest at the inlet sampling points from all WWTPs. This was consistent in both wet and dry seasons.
- The concentrations reduced consistently up to the outlet sampling points. Dimethyl phthalate was 0.89 ± 0.0007 mg/L, 0.33 ± 0.0005 mg/L and 0.09 ± 0.0007 mg/L at the inlet, mid and outlet sampling points, respectively for Homabay wastewater treatment plant sampled during the wet season. Similarly, benzyl butyl phthalate was 0.52 ± 0.0005 mg/L, 0.11 ± 0.0008 mg/L and below the level of quantification at the inlet, mid and outlet sampling points respectively, for Kisii waste water treatment plant sampled during the dry season. Almost all the phthalates in this study were below

the level of quantification in the outlet sampling points of Homabay and Kisii waste water treatment plants in both wet and dry seasons. This was an exception of dimethyl phthalate and benzy butyl phthalate with was detected at  $0.09 \pm 0.0007$  mg/L and  $0.01 \pm 0.0005$  mg/L at the Homabay sampling point sampled during the wet season.

#### 5. Suggestions for Further Research

This study only focused on Nyalenda (Kisumu), Homabay and Kisii WWTPs. This represents only three counties within Lake Victoria catchment area. Therefore, future research must take into consideration other WWTPs in the counties from western Kenya especially Kakamega, Busia, Migori, Bungoma and Eldoret.

#### **Statement of Competing Interest**

The authors declare no competing interest.

#### Acknowledgements

We gratefully acknowledge the financial support from the National Research Fund (NRF-Kenya).

#### References

- Jackson, J., & Sutton, R., "Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, CA". Science of the Total Environment, 405(1-3), 153-160, 2008.
- [2] Iñigo-Nuñez, S., Herreros, M., Encinas, T., & Gonzalez-Bulnes, A., "Estimated daily intake of pesticides and xenoestrogenic exposure by fruit consumption in the female population from a Mediterranean country (Spain)". Food Control, 21(4), 471-477, 2010.
- [3] Annamalai, J., & Namasivayam, V., "Endocrine disrupting Chemicals in the Atmosphere: Their effects on humans and wildlife". Environment International, 76, 78-97, 2015.
- [4] Diamanti-Kandarakis, E., Bourguignon, J., Giudice, L., Hauser, R., Prins, G., Soto, A., Zoeller, R. & Gore, A., "Endocrine-disrupting chemicals: an endocrine society scientific statement". *Endocrine Reviews*, 30(4), 293-342, 2009.
- [5] Pan, Z., Huang, B., & Zhang, C., "Preparation of a sludge-based adsorbent and adsorption of dimethyl phthalate from aqueous solution". *Desalination and Water Treatment*, 57(42), 20016-20026, 2016.
- [6] Dargnat, C., Teil, M., Chevreuil, M., & Blanchard, M., "Phthalate Removal throughout Wastewater Treatment Plant". Science of the Total Environment, 407(4), 1235-1244, 2009.
- [7] Casajuana, N., & Lacorte, S., "Presence and Release of Phthalic Esters and other Endocrine Disrupting Compounds in Drinking Water". *Chromatographia*, 57(9-10), 649-655, 2003.
- [8] Furlong, E.T., Burkhardt, M.R., Gates, P. M., Werner, S.L. & Battaglin, W.A., "Routine determination of sulfonylurea, imidazoline, and sulfonamide herbicides at nanogram-per-liter concentrations by solid-phase extraction and liquid chromatography/mass spectrometry". Science of the Total Environment, 248, 35-146, 2000.
- [9] Ngumba, E., Gachanja, A. & Tuhkanen, T., "Occurrence of selected antibiotics and antiretroviral drugs in Nairobi River Basin, Kenya". Science of the Total Environment, 539, 206-213, 2016.
- [10] Sotelo, J.L., Ovejero, G., Rodríguez, A., Álvarez, S, Galán, J. & García, J., "Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon". *Chemical Engineering Journal*, 240, 443-453, 2014.

- [11] K'oreje, K.O., Demeestere, K., De Wispelaere, P., Vergeynst, L., Dewulf, J. & Van Langenhove, H., "From multi-residue screening to target analysis of pharmaceuticals in water: Development of a new approach based on magnetic sector. Mass spectrometry and application in the Nairobi River basin, Kenya". Science of the Total Environment, 437, 153-164, 2012.
- [12] Salaudeen, T., Okoh, O., Agunbiade, F., & Okoh, A., "Fate and impact of phthalates in activated sludge treated municipal wastewater on the water bodies in the Eastern Cape, South Africa". *Chemosphere*, 203, 336-344, 2018.
- [13] Clara, M., Windhofer, G., Hartl, W., Braun, K., Simon, M., Gans, O., Scheffknecht, C., & Chovanec, A., "Occurrence of Phthalates in Surface Runoff, Untreated and Treated Wastewater and Fate During Wastewater Treatment". *Chemosphere*, 78(9), 1078-1084, 2010.
- [14] Chen, J., Liu, Z., An, B., Lu, Y., & Xu, Q., "Determination of Paraquat and Diquat in Drinking Water and Environmental Water by High Performance Liquid Chromatography Coupled with On-Line Clean-Up and Solid Phase Extraction". Chinese Journal of Chromatography, 30(10), 1068-1073, 2013.
- [15] Kümmerer, K., "The presence of pharmaceuticals in the environment due to human use; present knowledge and future challenges". *Journal of Environmental Management*, 90, 354– 2366, 2009.
- [16] Orata, F., & Birgen, F., "Fish tissue bio-concentration and interspecies uptake of heavy metals from waste water lagoons". *Journal of Pollution Effects and Control*, 04(02), 157 (1-6), 2016.
- [17] Li, H., Helm, P., & Metcalfe, C., "Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine-disrupting substances using the passive polar organic chemical integrative sampler". Environmental Toxicology and Chemistry, 29(4), 751-762, 2010.
- [18] Chatterjee, S., & Karlovsky, P., "Removal of endocrine disrupter butyl benzyl phthalate from the environment". Applied Microbiology and Biotechnology, 87(1), 61-73, 2010.
- [19] Zolfaghari, M., Drogui, P., Seyhi, B., Brar, S., Buelna, G., & Dubé, R., "Occurrence, fate and effects of Di (2-ethylhexyl) phthalate in wastewater treatment plants": A review. *Environmental Pollution*, 194, 281-293, 2014.
- [20] Tapia-Orozco, N., Ibarra-Cabrera, R., Tecante, A., Gimeno, M., Parra, R., & Garcia-Arrazola, R., "Removal strategies for endocrine disrupting chemicals using cellulose-based materials as adsorbents": A review. *Journal of Environmental Chemical Engineering*, 4(3), 3122-3142, 2016.
- [21] Lu, J., Wu, J., Stoffella, P., & Wilson, P., "Uptake and distribution of bisphenol A and nonylphenol in vegetable crops irrigated with reclaimed water". *Journal of Hazardous Materials*, 283, 865-870, 2015.
- [22] Lorber, M., Schecter, A., Paepke, O., Shropshire, W., Christensen, K., & Birnbaum, L., "Exposure assessment of adult intake of bisphenol A (BPA) with emphasis on canned food dietary exposures". *Environment International*, 77, 55-62, 2015.
- [23] Nageeb, R.M., "Adsorption technique for the removal of organic pollutants from water and wastewater". Organic Pollutants -Monitoring, Risk And Treatment. Aswan University, Aswan, Egypt, 48, 167-194, 2013.

- [24] Fauser, P., Vikelsøe, J., Sørensen, P., and Carlsen, L., "Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant--fate modelling based on measured concentrations in wastewater and sludge". Water Research, 37(6), 1288-1295, 2003.
- [25] Balest, L., Mascolo, G., Di Iaconi, C., & Lopez, A., "Removal of Endocrine disrupter Compounds from Municipal Wastewater by an Innovative Biological Technology". Water Science and Technology, 58(4), 953-956, 2008.
- [26] Tran, B., Teil, M., Blanchard, M., Alliot, F., & Chevreuil, M., "BPA and phthalate fate in a sewage network and an elementary river of France. Influence of hydroclimatic conditions". *Chemosphere*, 119, 43-51, 2015.
- [27] Xu, Q., Hunag, Z., Wang, X., & Cui, L., "Pennisetum sinese Roxb and Pennisetum purpureum Schum, as vertical-flow constructed wetland vegetation for removal of N and P from domestic sewage". *Ecological Engineering*, 83, 120-124, 2015.
- [28] Hadjmohammadi, M., Fatemi, M., & Taneh, T., "Coacervated extraction of phthalates from water and their determination by high performance liquid chromatography". *Journal of the Iranian Chemical Society*, 8(1), 100-106, 2011.
- [29] Esfandian, H., Yousefi, E., & Sharifzadeh B. M., "Removal of dimethyl phthalate from aqueous solution by synthetic modified nano zeolite using Cu<sub>2</sub>O nanoparticles". *International Journal of Engineering*, 29(9), 1198-1207, 2016.
- [30] Musungu, C.P., Ogoche, I.J., Lalah, J., Ongeri, D., Chepkui, R., & Kiema, F., "The extent of nutrient removal by wastewater treatment plants along the Nyalenda WWTP and the River Kisat (Kenya)". Ecohydrology and Hydrobiology, 13(4), 236-240, 2013.
- [31] Olujimi, O., Fatoki, O., Odendaal, J., & Daso, A., "Chemical monitoring and temporal variation in levels of endocrine disrupting chemicals (priority phenols and phthalate esters) from selected wastewater treatment plant and freshwater systems in Republic of South Africa". *Microchemical Journal*, 101, 11-23, 2012.
- [32] Bahadir, A., "UNESCO/DAAD/Exceed conference "Water in Africa", Kisumu, Kenya October 1-3, 2012". Ecohydrology and Hydrobiology, 13(4), 234-235, 2013.
- [33] Shen, Y., Li, H., Zhu, W., Ho, S., Yuan, W., Chen, J., & Xie, Y., "Microalgal-biochar immobilized complex: A novel efficient bio sorbent for cadmium removal from aqueous solution". *Bioresource Technology*, 244, 1031-1038, 2017.
- [34] Selvarajan, R., Sibanda, T., Venkatachalam, S., Kamika, I., & Nel, W., "Industrial wastewaters harbor a unique diversity of bacterial communities revealed by high-throughput amplicon analysis". *Annals of Microbiology*, 68(7), 445-458, 2018.
- [35] Manohar, S., Otieno, A, A., & Kitur, EL., "Planktonic diatoms species composition and water characteristics Along selected sites of river Kisat, Kisumu County, Kenya". *Journal of Environmental* and Analytical Toxicology, 07(04), 1-7, 2017.
- [36] Yousefi, E., Esfandian, H., & Sharifzadeh, M., "Removal of dimethyl phthalate from aqueous solution by synthetic modified nano zeolite using Cu<sub>2</sub>O nanoparticles". *International Journal of Engineering*, 29(9), 1198-1207, 2016.



© The Author(s) 2021. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).