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Endocrine disrupting chemicals in wastewater treatment plants in Kenya, East Africa: Concentrations, removal efficiency, mass loading rates and ecological impacts

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ABSTRACT

This study investigated the levels, mass loadings, removal efficiency, and associated ecotoxicological risks of selected endocrine disrupting chemicals (EDCs), namely, dibutylphthalate (DBP), diethylhexylphthalate (DEHP), dimethylphthalate (DMP), linuron (LNR) and progesterone (PGT) in wastewater, sludge, and untreated dry biosolid (UDBS) samples from twelve wastewater treatment plants (WWTPs) in nine major towns in Kenya. Analysis was done using high-performance liquid chromatography coupled with triple quadrupole mass spectrometry (LC-MS/MS). All the wastewater influents had quantifiable levels of EDCs with DBP being the most abundant (37.49%) with a range of 4.33 ± 0.63 to 19.68 ± 1.24 μg L^{-1}. DEHP was the most abundant in sludge and accounted for 48.2% ranging between 278.67 and 9243.49 ng g^{-1} dry weight (dw). In the UDBS samples, DEHP was also the most abundant (40%) of the total EDCs detected with levels ranging from 78.77 to 3938.54 ng g^{-1} dw. The average removal efficiency per pollutant was as follows: DMP (98.7%) > DEHP (91.7%) > PGT (83.4%) > DBP (77.9%) > LNR (72.2%) which can be attributed to sorption onto the biosolid, biological degradation, photolysis, and phytoremediation. The pH was negatively correlated to the EDC concentrations while total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and electrical conductivity (EC) were positively correlated. The mass loadings were as high as 373.33 g day^{-1} of DBP in the treatment plants located in densely populated cities. DEHP and PGT had their Risk Quotients (RQs) > 1, posing a high risk to biota. DMP, DBP, and LNR posed medium risks as their RQ values were between 0.1 and 1. EDCs are therefore loaded to environmental compartments through either the effluent that loads these pollutants into the receiving aquatic ecosystem or through the UDBS, which are used as fertilizers in agricultural farmlands causing potential toxicological risks to aquatic and terrestrial life.

1. Introduction

Endocrine disrupting chemicals (EDCs) are natural or exogenous chemicals that can interfere with the normal functioning of the natural blood-borne hormones in the body (Zoeller et al., 2012). They disrupt the production, biosynthesis, secretion, metabolism, transport, or

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peripheral action of endogenous hormones resulting in a deviation from normal homeostatic control or reproduction and, consequently, causing adverse health effects to the organism (Diamanti-Kandarakis et al., 2009). These adverse health effects include congenital anomalies, tumors, reproductive health issues, cardiovascular and respiratory diseases, neurological and behavioral disorders, thyroid problems, Alzheimer's, cancer, and obesity (Kasonga et al., 2021). EDCs include selected pesticides, plastics, plasticizers, hormones, pharmaceutical agents, and industrial chemicals and their byproducts such as polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), dioxins, per- and poly-fluoroalkyl substances (PFASs), (Diamanti-Kandarakis et al., 2009; Mohapatra et al., 2020; Olujimi et al., 2012; Ssebugere et al., 2020). These chemicals are originally designed for a specific beneficial action but negatively affect the body's normal functions when absorbed into the body (Schug et al., 2011).

In the environment, EDCs and other emerging contaminants are chemically stable to biodegradation, can form complexes, hazardous derivatives, and byproducts (Kumar et al., 2022), and therefore cannot be effectively removed to molecular levels by conventional wastewater treatment methods that involve physicochemical treatments such as coagulation, flocculation and settling processes (Kasonga et al., 2021; Mukherjee et al., 2021; Ng et al., 2021; Orata, 2018). Moreover, advanced methods like oxidation processes, nanofiltration, reverse osmosis, and membranes are costly, especially for developing countries (Mukherjee et al., 2021). As a result, these compounds may escape from the conventional wastewater treatment plants (WWTPs) *via* effluents (Ojoghoro et al., 2021) into the aquatic environment and subsequently to the drinking water (Orata, 2018) potentially posing detrimental effects on aquatic life, wildlife, and human beings. Furthermore, the application of untreated dry biosolid (UDBS) from WWTPs in farmlands as fertilizer (Grassi et al., 2013), seepage from septic tanks, and landfilling regions, (Ng et al., 2021), and indiscriminate disposal of a wide range of consumer products (Lee and Ji, 2022; Rachoń, 2015) are other sources of EDCs.

Despite the hazardous effects of EDCs, they are poorly inventoried and regulated and insufficient information exists regarding their occurrence, fate, and impact on the environment in Africa (Gavrilescu et al., 2015; K'oreje et al., 2020). While several studies in other parts of the world have reported EDCs in consumer products and in different environmental matrices (Basile et al., 2011; Bergman et al., 2013), there is a paucity of literature on the contamination levels of EDCs in East Africa. A few studies have focused on legacy contaminants such as PFASs (Chirikona et al., 2022) and dioxins (Omwoma et al., 2015). Those who have investigated the occurrence of emerging pollutants like pharmaceuticals and personal care products (K'oreje et al., 2020; Ngigi et al., 2020) did not investigate the point sources of the contaminants in the environment. To date, only one study, Onchiri et al. (2021), has reported on the presence of phthalates in three WWTPs in Kenya.

The present study involves target screening and seeks to determine the abundance and frequency of representative EDCs such as dibutylphthalate (DBP), diethylhexylphthalate (DEHP), and dimethylphthalate (DMP) which are industrial chemicals (phthalates); linuron (LNR) a herbicide, and progesterone (PGT), a hormone. The structures of these selected compounds and their physicochemical properties are presented in the online supplementary material (Table S1). DBP, DMP, and DEHP are phthalic acid esters (PAEs) used as plasticizers in polymeric materials to ease production and improve flexibility and toughness (Nantaba et al., 2021). LNR is used as a herbicide to promote productivity in the agricultural sector. PGT is a steroid hormone commonly used in the regulation of the menstrual cycle, preparing the uterus for implantation of the blastocyst, assisted reproduction, and sustenance of pregnancy through hormonal balancing, and hormonal therapy for menopausal women (Cui et al., 2021; Manickum and John, 2014; Ojoghoro et al., 2021). These natural hormones are excreted into the environment by both human beings and animals through sewage discharge and animal waste disposal (Manickum and John, 2014).

The research objectives of this study were: (1) to determine concentration levels of the selected EDCs (DBP, DEHP, DMP, LNR, PGT) in wastewater, sludge and the UDBS samples from WWTPs in major towns of Kenya; (2) to evaluate the mass loadings of the EDCs to the environment through the effluents; (3) to assess the removal efficiency of WWTPs, and (4) to evaluate potential health risks to aquatic life in the receiving aquatic ecosystem.

2. Materials and methods

2.1. Chemicals, standards, and reagents

Reference standards for DBP and DMP were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) while DEHP, LNR, and PGT were bought from Sigma-Aldrich. All the standards were above 99% purity. Analytical grade and high-performance liquid chromatography (HPLC) grade solvents for extraction and analysis were purchased from Fluka Chemicals, Germany. Solid phase extraction (SPE) cartridges and nylon microfilters were procured from Merck Chemicals. Analytical grade anhydrous sodium sulfate was supplied by Sigma-Aldrich. All the glassware was thoroughly cleaned by first soaking them for 2 h in warm tap water mixed with a phosphate-free detergent and then rinsed with hot water and de-ionized water followed by acetone. The glassware was then dried in an oven for 3 h at 105 °C before use.

2.2. Description of the study area

The study was carried out in the WWTPs of Nairobi and the major towns in the larger western region of Kenya, namely, Kisumu, Kakamega, Bungoma, Busia, Kisii, Kericho, Eldoret and Nakuru (Fig. 1).

These were purposely selected because the WWTPs in these towns (except Nairobi and Nakuru) release their effluents directly into streams and rivers that eventually drain into Lake Victoria, the biggest freshwater lake in Africa. These major towns in western Kenya have moderately dense human settlements, various agricultural and industrial activities, and open mountainous dumpsites with no drainage or leachate collection systems and are probable sources of EDCs to the lake through effluent release and rainwater runoff. The high-intensity agricultural activities were also a major factor in collecting samples from Kericho, Kisii, Nakuru, and Eldoret. Nairobi was included because it is highly urbanized, heavily industrialized, and densely populated with informal settlements that harbor open dumpsites for waste management for example the Dandora dumpsite.

The WWTPs in the sampling areas were either using conventional treatment systems (trickling filters) or wastewater stabilization ponds (WSPs) (aerated lagoons). Due to the high cost of maintenance and complexity of conventional WWTPs, most towns have constructed WSPs in addition to the conventional WWTPs. Examples of such towns are Nairobi, Nakuru, Eldoret, and Kisumu. The conventional WWTPs were in Kisat (Kisumu), Kericho, Eldoret, and Kariobangi (Nairobi). The lagoons were in Nyalenda (Kisumu), Kisii, Ruai (Nairobi), Bungoma (Busia), Shirere, and Masinde Muliro University of Science and Technology (MMUST) (both in Kakamega). Table 1 indicates the characteristics of the sampled WWTPs.

2.3. Determination of water quality parameters

Using a Hydrolab Quanta Multi-Probe Meter, water quality parameters such as pH, total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and electrical conductivity (EC) were measured *in situ* at the influent locations in the WWTPs. BOD_5 was estimated by measuring the O_2 content in a representative sample, repeating the process after a 5-day incubation period, and calculating the difference.

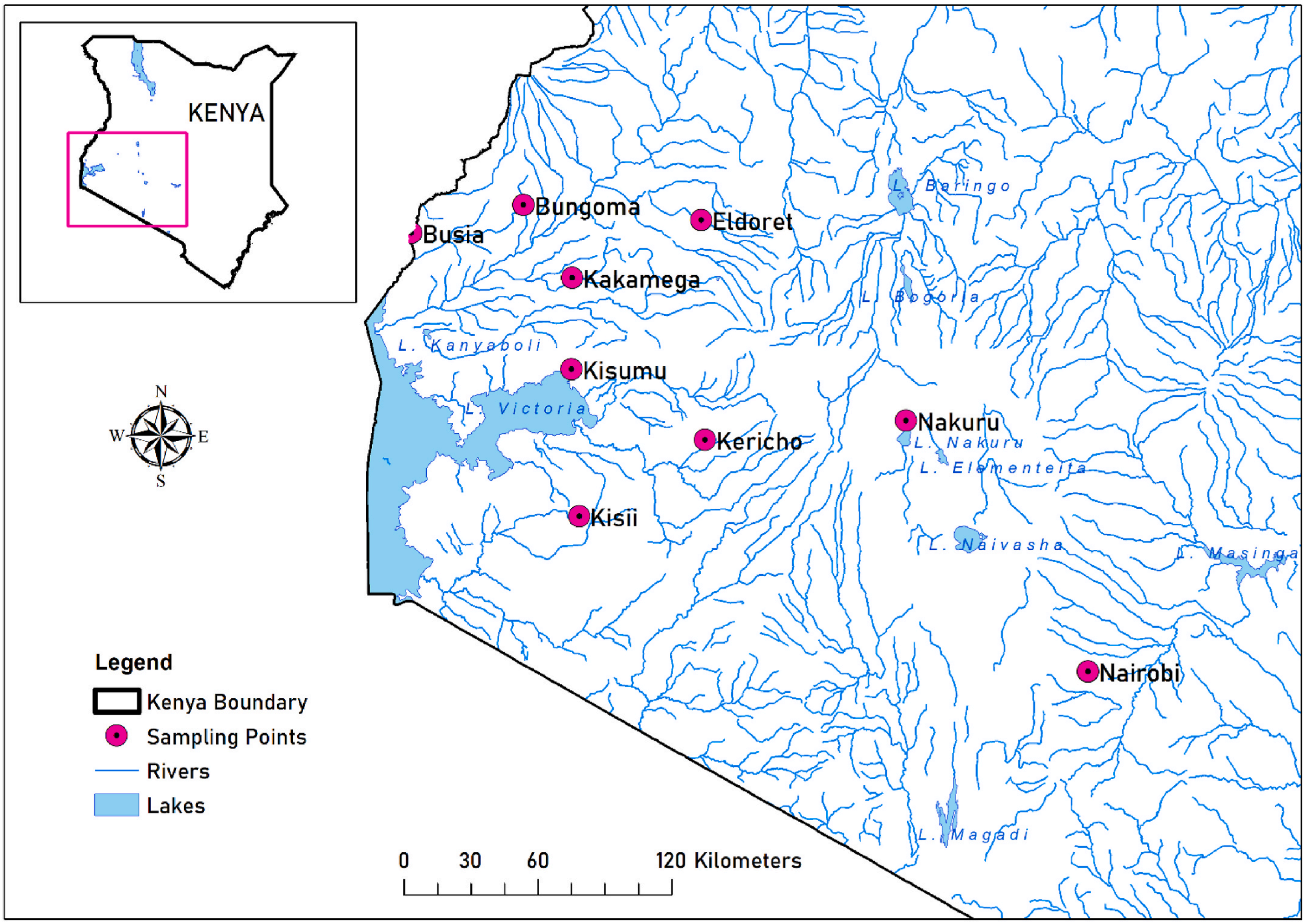

Fig. 1. Sampling sites.

Table 1
Characteristics of the WWTPs.

WWTPs' location	City population	Type of wastewater treated	Treatment type	Capacity (C_{wwtp}) (M^3 day^{-1})
Bungoma	298,696	Domestic	Wastewater stabilization ponds	9200
Busia	113,753	Domestic	Wastewater stabilization ponds	2150
Kisii	112,417	Domestic and Agricultural run offs	Wastewater stabilization ponds	4000
Kisat	397,957	Domestic and industrial	Conventional treatment system	8000
Kisumu-Nyalenda	397,957	Domestic and industrial	Wastewater stabilization ponds	18,000
Kakamega-Shirere	252,611	Domestic	Waste stabilization ponds	2000
MMUST	21,000	Domestic	Wastewater stabilization ponds	425
Eldoret-Kipkenyo	165,450	Domestic and Agricultural run offs	Conventional treatment system	8000
Nakuru Old town	409,908	Domestic and industrial	Conventional treatment system	6600
Nairobi Kariobangi	4,397,073	Domestic and industrial	Conventional treatment system	23,000
Nairobi-Ruai	4,397,073	Domestic and industrial	Wastewater stabilization ponds	80,000
Kericho	228,318	Domestic and Agricultural run offs	Conventional treatment system	990

Source of data: Adopted from Chirikona et al. (2015); Kimosop et al. (2016); Kenya Population Census (2019).

2.4. Sampling

One liter (1 L) water samples (N = 60) were collected in triplicate into pre-cleaned amber glass bottles which were then tightly covered and preserved in an icebox to limit microbial activities. From the conventional treatment systems, water samples were picked from the influents, primary ponds, secondary ponds, tertiary ponds, and the treated effluent. From the WSPs, the sampling locations were identified as influent, anaerobic ponds, facultative ponds, maturation ponds, and effluent release. In the laboratory, the water samples were spiked with 10 mL formaldehyde (86% v/v) and stored in a refrigerator below 4 °C to avoid microbial degradation before extraction. Extraction was carried out within 48 h of sample collection.

Sludge samples were collected from the anaerobic ponds (for the lagoons) and primary ponds (for the conventional treatment plants) just below the influent flow of the 12 WWTPs. Approximately 2 kg of the wet weight of the sludge samples were wrapped in aluminum foil then placed in a cooler box with ice and transported to the laboratory. In the laboratory, the samples were air-dried under a shade for two weeks. The UDBS (1 kg dry weight) were collected from the drier beds of the WWTPs. They were wrapped in aluminum foil and transported to the laboratory.

2.5. Extraction and clean-up of wastewater samples

Wastewater samples were extracted following the method described by Olaniyan and Okoh (2020) with slight modifications which are given in **Text S1**.

2.6. Extraction and clean-up of sludge and UDBS samples

Sludge and the UDBS samples were extracted and cleaned using the method reported by George et al. (2019) with modifications that are given in **Text S2**.

2.7. Instrumental analysis

High-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) analysis was done using an Agilent 1200 Infinity system hyphenated with a tandem MS detector (Agilent MS quadruple 6420). The optimized HPLC-MS/MS parameters are presented in the supplementary information (**Text S3**).

2.8. Removal efficiency of selected EDCs in the sampled WWTPs

Removal efficiency was calculated from the concentrations in the effluent and influent using equation (1). The percentages of EDCs abstracted during treatment by conventional/aerated lagoon method gave the efficiency of the treatment method.

$$\%\ \text{Removal Efficiency} = \frac{\left(C_{\text{influent}} - C_{\text{effluent}}\right)\ x\ 100}{C_{\text{influent}}} \qquad \text{(Equation 1)}$$

Where C_{influent} is the concentration of EDCs in the raw sewage and C_{effluent} is the concentration of EDCs in the treated sewage (Kairigo et al., 2020).

2.9. Mass loading of EDCs into the environment

The daily discharge load from WWTPs was estimated based on the assumption that the concentrations of EDCs in the effluent wastewater recorded were constant throughout the day and that the WWTPs were performing to their full capacity (Kimosop et al., 2016). This was done using equation (2):

$$Dd = C_W \times C_{WWTP} \times 1000 \times 10^{-3}\left(\text{mg day}^{-1}\right) \qquad \text{(Equation 2)}$$

Where.

Dd = Daily discharge of EDCs (mg day^{-1}).
C_W = Concentration of individual EDC in the effluents (μg L^{-1}).
C_{WWTP} = Capacity of WWTP (M^3 day^{-1}) (Table 1),
1000 = Conversion factor from cubic meters to liters.
10^{-3} = Conversion from microgram to milligram.

2.10. Potential health risks to the receiving aquatic ecosystem

To assess the toxic risks posed by the chemicals, Risk Quotients (RQ) were calculated (equation (3)) for three different trophic levels (fish, crustaceans *(Daphnia)*, and algae) following the European Commission's Technical Guidance Document on risk assessment (European Commission, 2003).

$$RQ = \frac{MEC}{PNEC} \qquad \text{(Equation 3)}$$

Where MEC is the maximum measured environment concentration and PNEC is the Predicted No Effect Concentration. A PNEC is regarded as a concentration below which an unacceptable effect will most likely not occur. It is calculated (equation (4)) by dividing the lowest short-term concentration causing 50% death (LC50) or effect (EC50) or lowest observed effect concentration (LOEC) or long-term no observed effect concentration (NOEC) value for the most sensitive indicator species by an appropriate assessment factor (AF). The AF reflects the degree of uncertainty in extrapolation from laboratory toxicity test data for a limited number of species to the natural environment. AF applied for long-term tests is lower and is preferred as the uncertainty of the extrapolation from laboratory data to the natural environment is minimal (European Commission, 2003).

For detected EDCs where NOEC values for species representing only one trophic level (*Daphnia* or fish) were available, AF 100 was used for PNEC calculations. AFs 50 and 10 were used when NOEC values were available for species representing two trophic levels (fish, and/or *Daphnia*, and/or algae) and three trophic levels (usually fish, *Daphnia*, and algae), respectively. Additionally, an AF of 1000 was used for acute toxicity data (European Commission, 2003).

$$PNEC = \frac{NOEC(\text{or } L(E)C50)}{AF} \qquad \text{(Equation 4)}$$

For every EDC, RQ was calculated based on the worst-case scenario, by considering the maximum concentration detected among all the sites, as well as the lowest NOECs or E(L)C50. The RQ for chronic cases was also calculated for every EDC per site. An RQ value > 1 indicated a suspected high ecotoxicological risk, and $0.1 < RQ < 1$ and $RQ < 0.1$ represented possible medium and low risks, respectively (Huang et al., 2018; Keisuke & Jun 2020). Data **(Table S2)** were obtained from the Norman network and ECOTOX database.

2.11. Quality control and assurance

External standards calibration was used for quantification. Calibration curves (6–8 points) were obtained by preparing individual standards at different concentrations (5–150 μg L^{-1}) using blank solvents. The linearity of the calibration was evaluated based on the coefficients of determination (R^2) of the calibration curves. In all cases, R^2 was $\geq$0.992. The precision of the HPLC–MS/MS method for each EDC analyte investigated was determined by analyzing all the samples in triplicates. Since phthalates are ubiquitous in nature, maximum care had to be taken to avoid the risk of contamination. These procedures included minimal sample manipulation, careful choice of equipment, and proper cleaning and baking of glassware at high temperatures before use.

Procedural blanks (1 L of ultrapure Milli Q water) were analyzed to monitor for background contamination. Signals were observed with the phthalates' procedural blanks and the data were therefore blank corrected by calculating the mean of all procedural blanks and subtracting from the sample values for every analyte. Analytes whose concentrations after blank correction were lower than three times the standard deviation of the blank values were considered as not detectable (n.d.). Analytes in the samples that were not detected before blank correction were also taken as non-detectable.

Recovery tests were also conducted. Water, sludge, and UDBS samples were spiked with 50 μL of a standard solution (20 μg L^{-1}) of each target analyte and the samples were analyzed using the same procedure as the samples. The recovery ranges were between 74 and 109% which are within the acceptable values of 60–120% and therefore, the data were not corrected for recoveries.

The determination of limits of detection (LOD) and limits of quantification (LOQ) are explained in **Text S4** and the values are tabulated in Table S3. PAEs showed high LODs in all the matrices ranging from 6.33 to 8.38 ng g^{-1} (sludge/UDBS) to 0.004 μg L^{-1} (wastewater) and LOQs ranging from 21.09 to 27.94 ng g^{-1} (sludge/UDBS). LNR had the least LOD (3.86 ng g^{-1} (sludge/UDBS); 0.003 μg L^{-1} (wastewater)) and the LOQ was 12.87 ng g^{-1} (sludge/UDBS); 0.01 μg L^{-1} (wastewater).

2.12. Statistical data analysis

Descriptive statistics reporting means, standard deviations, and ranges were calculated for only positive quantifiable samples. For further statistical analysis, half the LOD was assigned to the n. d. Normality of the data was assessed using Shapiro-Wilk's test and visual inspections of their histograms and box plots. The data for the sludge samples were normally distributed. Therefore, parametric tests (one sample and paired sample t-tests) were applied to check for statistical differences among levels of EDCs in each location. One-way ANOVA was used to evaluate the differences in levels among sites and the different matrices. For the data that were not normally distributed, (levels of EDCs in water and the UDBS samples) non-parametric tests were applied. These included the Kruskal-Wallis tests and the Friedman tests which were used to compare the levels of EDCs among themselves, between sites, and among the different matrices. All differences were deemed significant if $p < 0.05$. Spearman's rank-order correlation coefficients (r_s) were calculated to evaluate bivariate associations between WWTPs' water quality parameters and the pollutant levels, as well as those amongst the different pollutants. All statistical analyses were conducted using Excel, SPSS version 20 (IBM, Chicago IL, USA), and OriginPro, version 9 (OriginLab Corporation, Northampton, MA, USA).

3. Results and discussion

3.1. Water quality parameters

Table S4 reports water quality metrics (pH, TDS, COD, BOD5, and EC) measured *in situ* at influent locations of the WWTPs. There was not much variation in the pH with the values ranging from 6.67 (Ruai) to 6.99 (Kericho). These values are comparable to those obtained by K'oreje et al. (2018) which were between 6.5 and 7.1. Lower pH values are reported in WWTPs serving larger populations (Ruai) implying that an increase in contamination increases acidity. TDS was lowest in a smaller WWTP (749.4 mg L^{-1}-Busia) and highest in a larger WWTP (765.7 mg L^{-1}- Kariobangi). BOD_5 followed the same trend with 51.8 mg L^{-1} in MMUST and 59.5 mg L^{-1} in Ruai. TDS and BOD_5 are comparable to those reported by Shikuku et al. (2017). The lowest value of COD was in Busia (154.5 mg L^{-1}) while the highest was in Ruai (172.0 mg L^{-1}). The variance in EC was minimal (1500 1554 μS/cm). The elevated values of TDS, COD, BOD_5, and EC could be due to the impact of increased waste brought about by a rapidly increasing population coupled with various commercial and industrial activities. This will consequently lead to the discharge of enormous amounts of waste to WWTPs.

3.2. Levels of EDCs in wastewater samples

The levels of the selected EDCs are represented in Table 2. In the influents, DBP was the most abundant PAE congener (37.49%) as well as EDC detected in the 12 WWTPs. The values varied from 4.33 ± 0.63 μg L^{-1} in Bungoma to 19.68 ± 1.24 μg L^{-1} in Ruai. DEHP was the second most abundant EDC (26.2%) with levels ranging from 2.86 ± 0.24 μg L^{-1} in Nakuru to 14.33 ± 1.50 μg L^{-1} in Kariobangi. Levels of DMP in the influents were between 1.13 ± 0.29 μg L^{-1} in Shirere and 15.88 ± 1.41 μg L^{-1} in Nakuru, contributing 19.56%. PGT (15.73%) ranged from 0.88 ± 0.15 μg L^{-1} in Nakuru to 14.69 ± 1.11 μg L^{-1} in Ruai. LNR was between 0.05 ± 0.01 μg L^{-1} in Nyalenda and 2.48 ± 0.55 μg L^{-1} in Eldoret (i.e., 1.02% of the ∑12WWTPs). The total means ± standard deviations (SD) of the EDCs in all the influents are given in Table S5.

There were significant spatial variations ($p < 0.05$; Friedman) in the levels of EDCs detected in the influent wastewater samples at different sites. For example, high levels of EDCs were detected in Ruai (Sum of five EDCs per site (∑5EDCs) = 48.01 μg L^{-1}) while lower levels were detected at Kisat (∑5EDCs = 15.86 μg L^{-1}). Therefore, EDCs loading to the WWTPs were dependent on the location (industrial activities, population density and agricultural activities), the wastewater treatment system, and connectivity to the sewer line. Elevated levels of PAEs were found in Kariobangi and Ruai influents which are both located in

Table 2
Levels of EDCs (ug L^{-1}) in the wastewater samples.

	Location	DBP	DEHP	DMP	LNR	PGT
Nakuru	Influent	8.32 ± 0.99	2.86 ± 0.24	15.88 ± 1.41	0.08 ± 0.02	0.88 ± 0.15
	Primary ponds	6.78 ± 0.78	1.77 ± 0.10	1.02 ± 0.09	0.04 ± 0.01	0.78 ± 0.17
	Secondary ponds	5.01 ± 0.40	1.02 ± 0.04	1.06 ± 0.09	0.03 ± 0.01	0.59 ± 0.17
	Tertiary ponds	2.13 ± 0.28	0.19 ± 0.08	0.18 ± 0.05	0.02 ± 0.01	0.46 ± 0.15
	Effluent	1.61 ± 0.30	<LOQ	0.02 ± 0.01	0.02 ± 0.01	0.25 ± 0.16
Eldoret	Influent	10.54 ± 0.82	6.87 ± 1.05	7.51 ± 0.68	2.48 ± 0.55	20.26 ± 1.49
	Primary ponds	7.15 ± 0.89	6.10 ± 0.99	5.24 ± 0.42	0.08 ± 0.01	11.45 ± 1.02
	Secondary ponds	7.12 ± 0.82	5.81 ± 0.57	1.87 ± 0.17	0.07 ± 0.01	3.11 ± 0.36
	Tertiary ponds	3.77 ± 0.5	2.18 ± 0.34	1.57 ± 0.22	0.02 ± 0.01	1.81 ± 0.13
	Effluent	2.46 ± 0.53	1.84 ± 0.22	0.24 ± 0.08	0.02 ± 0.01	1.27 ± 0.16
Bungoma	Influent	4.63 ± 0.63	6.99 ± 0.98	8.41 ± 0.95	0.05 ± 0.01	0.99 ± 0.06
	Anaerobic ponds	4.43 ± 0.48	6.37 ± 0.82	2.78 ± 0.38	0.04 ± 0.01	0.55 ± 0.10
	Facultative ponds	4.10 ± 0.48	2.42 ± 0.09	2.64 ± 0.41	0.03 ± 0.01	0.38 ± 0.14
	Maturation ponds	3.37 ± 0.56	<LOQ	0.06 ± 0.01	0.03 ± 0.01	0.32 ± 0.08
	Effluent	2.60 ± 0.43	<LOQ	0.12 ± 0.02	0.02 ± 0.01	0.26 ± 0.06
Busia	Influent	5.47 ± 0.45	6.74 ± 1.08	3.72 ± 0.73	0.07 ± 0.01	2.18 ± 0.28
	Anaerobic ponds	3.70 ± 0.58	2.66 ± 0.73	3.10 ± 0.59	0.06 ± 0.01	1.81 ± 0.11
	Facultative ponds	3.46 ± 0.33	2.10 ± 0.41	1.78 ± 0.36	0.04 ± 0.01	1.73 ± 0.26
	Maturation ponds	2.09 ± 0.22	1.95 ± 0.30	<LOQ	0.03 ± 0.01	0.35 ± 0.03
	Effluent	1.89 ± 0.18	1.58 ± 0.41	0.03 ± 0.01	0.03 ± 0.01	0.37 ± 0.04
Kisii	Influent	13.63 ± 1.23	4.56 ± 0.58	1.40 ± 0.26	0.05 ± 0.01	0.89 ± 0.13
	Anaerobic ponds	1.87 ± 0.27	4.11 ± 0.48	0.18 ± 0.02	0.04 ± 0.01	0.79 ± 0.12
	Facultative ponds	1.13 ± 0.18	2.40 ± 0.29	0.03 ± 0.01	0.04 ± 0.01	0.51 ± 0.11
	Maturation ponds	<LOQ	1.02 ± 0.23	0.02 ± 0.01	0.03 ± 0.01	0.23 ± 0.10

(continued on next page)

Table 2 (*continued*)

	Location	DBP	DEHP	DMP	LNR	PGT
	Effluent	<LOQ	0.83 ± 0.17	0.02 ± 0.01	0.02 ± 0.01	0.10 ± 0.04
MMUST	Influent	5.84 ± 0.91	7.99 ± 0.98	2.03 ± 0.35	0.06 ± 0.01	1.31 ± 0.28
	Anaerobic ponds	7.32 ± 0.61	3.51 ± 0.70	0.32 ± 0.10	0.05 ± 0.01	0.78 ± 0.11
	Facultative ponds	6.12 ± 0.60	1.72 ± 0.65	0.04 ± 0.01	0.03 ± 0.01	0.59 ± 0.16
	Maturation ponds	4.55 ± 0.51	1.29 ± 0.39	0.02 ± 0.01	0.03 ± 0.01	0.44 ± 0.03
	Effluent	4.80 ± 0.46	<LOQ	0.02 ± 0.01	0.03 ± 0.01	0.40 ± 0.02
Ruai	Influent	19.68 ± 1.24	9.21 ± 0.89	4.36 ± 1.16	0.08 ± 0.01	14.69 ± 1.11
	Anaerobic ponds	17.31 ± 1.01	9.05 ± 0.81	4.80 ± 1.11	0.07 ± 0.01	1.30 ± 0.15
	Facultative ponds	13.66 ± 0.79	2.87 ± 0.31	4.63 ± 0.98	0.07 ± 0.01	1.08 ± 0.06
	Maturation ponds	10.45 ± 0.94	2.74 ± 0.27	2.26 ± 0.66	0.06 ± 0.01	1.01 ± 0.04
	Effluent	4.67 ± 0.61	1.98 ± 0.07	0.12 ± 0.08	0.05 ± 0.01	0.86 ± 0.10
Shirere	Influent	7.85 ± 1.04	5.60 ± 0.76	1.13 ± 0.29	0.13 ± 0.05	2.10 ± 0.21
	Anaerobic ponds	7.48 ± 0.92	3.69 ± 0.50	0.76 ± 0.19	0.08 ± 0.01	1.39 ± 0.33
	Facultative ponds	4.58 ± 0.56	1.05 ± 0.29	0.08 ± 0.01	0.06 ± 0.01	0.19 ± 0.05
	Maturation ponds	<LOQ	<LOQ	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01
	Effluent	<LOQ	<LOQ	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
Kisat	Influent	5.64 ± 0.94	4.17 ± 0.78	5.00 ± 0.99	0.10 ± 0.03	0.94 ± 0.08
	Primary ponds	3.45 ± 0.53	4.21 ± 0.73	0.07 ± 0.01	0.02 ± 0.01	0.315 ± 0.08
	Secondary ponds	0.86 ± 0.08	3.80 ± 0.52	0.04 ± 0.01	0.03 ± 0.01	0.05 ± 0.01
	Tertiary ponds	0.75 ± 0.06	0.79 ± 0.14	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
	Effluent	<LOQ	<LOQ	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
Nyalenda	Influent	11.17 ± 0.99	6.63 ± 1.02	1.67 ± 0.47	0.05 ± 0.01	2.65 ± 0.39
	Anaerobic ponds	3.77 ± 0.27	3.65 ± 0.41	1.33 ± 0.41	0.03 ± 0.01	0.49 ± 0.09
	Facultative ponds	6.52 ± 0.61	2.13 ± 0.21	0.26 ± 0.03	0.03 ± 0.01	0.41 ± 0.07
	Maturation ponds	3.65 ± 0.54	<LOQ	0.12 ± 0.08	0.03 ± 0.01	0.24 ± 0.08
	Effluent	3.63 ± 0.55	<LOQ	0.06 ± 0.01	0.02 ± 0.01	0.13 ± 0.05
Kericho	Influent	10.05 ± 1.01	8.86 ± 1.06	5.07 ± 0.92	0.07 ± 0.02	2.18 ± 0.26
	Primary ponds	5.70 ± 0.87	6.77 ± 0.80	1.271 ± 0.40	0.07 ± 0.02	1.67 ± 0.35
	Secondary ponds	4.22 ± 0.72	3.87 ± 0.58	0.07 ± 0.01	0.06 ± 0.02	1.11 ± 0.16
	Tertiary ponds	4.09 ± 0.44	0.83 ± 0.06	0.02 ± 0.01	0.03 ± 0.01	0.69 ± 0.18
	Effluent	<LOQ	0.62 ± 0.09	0.01 ± 0.01	0.02 ± 0.01	0.05 ± 0.01
Kariobangi	Influent	18.48 ± 1.11	14.33 ± 1.50	7.09 ± 0.70	0.08 ± 0.02	1.82 ± 0.17
	Primary ponds	11.13 ± 1.02	1.33 ± 0.33	4.80 ± 0.51	0.04 ± 0.01	1.09 ± 0.18
	Secondary ponds	9.36 ± 0.84	1.13 ± 0.12	4.61 ± 0.35	0.04 ± 0.01	1.94 ± 0.12
	Tertiary ponds	7.14 ± 0.46	1.39 ± 0.15	3.08 ± 0.17	0.02 ± 0.01	0.75 ± 0.09
	Effluent	3.43 ± 0.33	0.69 ± 0.08	0.07 ± 0.01	0.02 ± 0.01	0.60 ± 0.14

DBP = dibutylphthalate, DEHP = diethylhexylphthalate, DMP = dimethylphthalate, LNR = linuron and PGT = progesterone. Results are reported as mean concentrations ± standard deviation, n = 3, <LOQ - Below the limit of quantification.

Nairobi, a city with dense human habitation, and a wide array of commercial, industrial, and manufacturing activities. There is also a paucity of stringent measures of waste disposal, a case in point being that of Dandora open dumpsite. Kisat is in Kisumu, a city with lower levels of EDCs regardless of a medium population. This could be attributable to improved garbage management by the county, which has recently invested resources in eliminating open dumpsites. The other locations (Busia, Kisii and Kericho) registering less concentration have lower populations and lesser industrial, commercial, and manufacturing activities. Another aspect is that some houses utilize septic tanks and pit latrines, resulting in diminished sewerage connectivity.

As shown in Table 2 and Fig. 2, the levels of EDCs in the influent water samples were significantly higher than those in the effluents ($p < 0.05$; Kruskal-Walis). Generally, the levels kept reducing at the different ponds as the wastewater moved towards the effluent within each WWTP. The higher concentrations in the influents than the effluents are because they are entry points to the WWTPs. Furthermore, the target EDCs have high log K_{OW} (Table S1) implying that they are more likely to adsorb onto the sludge (Kumar et al., 2020a,b) consequently giving less detection in the effluents.

The effluents are a concern since they are point sources of pollutants to receiving waters that act as habitats for aquatic organisms and may find their way into drinking water sources. In the effluents, EDCs were dominated by DBP (65.9%), followed by DEHP (20.3%), PGT (11.2%), DMP (1.8%), and LNR (0.73%). The ranges of DBP, DEHP, PGT, DMP, and LNR (in μg L^{-1}) were: < LOQ to 4.80 ± 0.46, < LOQ to 1.98 ± 0.07, 0.01 ± 0.01 to 1.27 ± 0.16, 0.01 ± 0.01 to 0.24 ± 0.08, and 0.02 ± 0.01 to 0.05 ± 0.01, respectively. The means ± SD of the EDCs in the effluents are presented in Table S5. As noted, some maturation ponds and effluents had less concentration than the LOQ. This can be ascribed to EDCs' adsorption to the sludge that is eventually dried to obtain UDBS

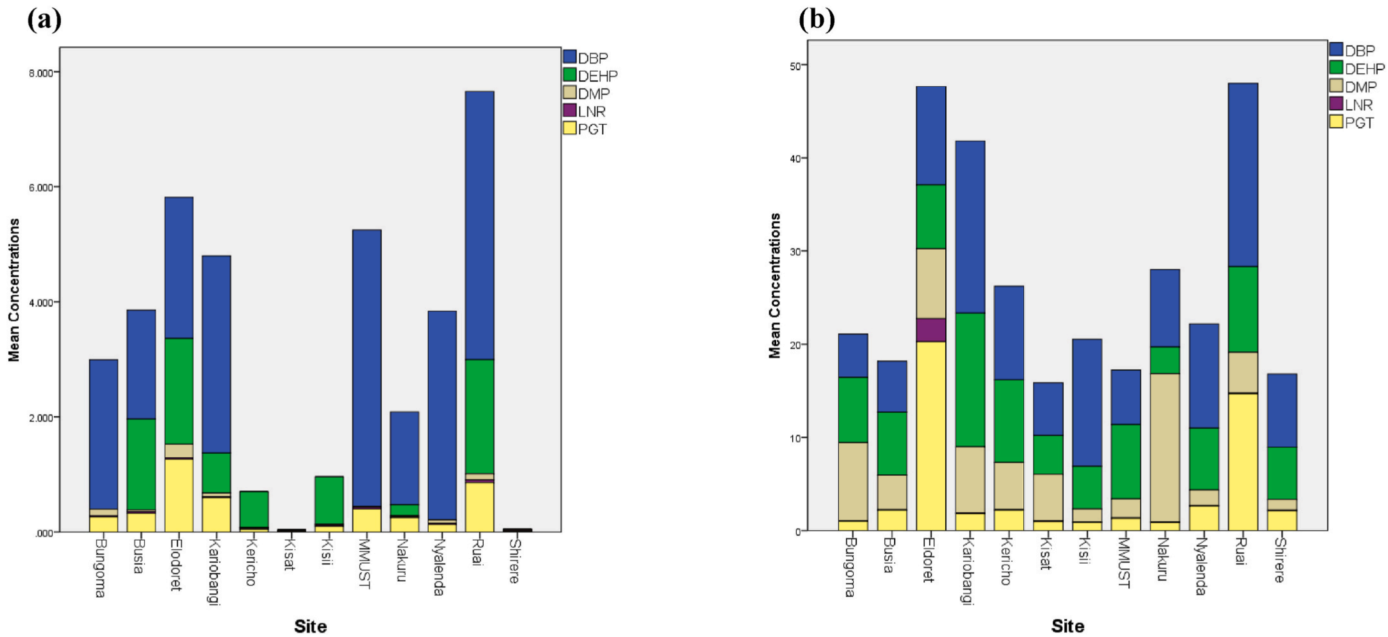

Fig. 2. Levels of EDCs at the (a) influents and (b) effluents in μg L^{-1}.

which is used as fertilizer. The absorption is due to the hydrophobicity of the EDCs due to their high log K_{OW} (Mohapatra et al., 2020). The levels of EDCs in the effluent samples displayed no significant differences ($p > 0.05$; Kruskal-Walis) suggesting that the WWTPs have comparable efficiency, regardless of the concentration, in reducing the EDCs in wastewater.

For both influents and effluents, PAEs had higher concentrations than PGT and LNR. This is attributed to the PAEs' widespread use in industry and within households, as additives in plastics and pipes. PAEs are also not chemically bonded to plastics (Cong et al., 2022) and are leached out of plastic packaging and containers into the environment (Metcalfe et al., 2022). Plastic manufacturing is a major investment in Kenya (estimated at USD 50 million (Nyagah, 2013); However, inadequate plastic waste disposal may expose environmental compartments to EDCs.

It is noteworthy that PGT was detected at higher levels than LNR. As of October 2021, Volza Grow Global (2021) indicated that Kenya had a yearly import of 211 shipments of PGT either from South Africa, Germany, or India. On the contrary, LNR levels were high in agricultural areas (Eldoret and Kericho). This is attributed to extensive farming activities (wheat, maize, and tea) in the locations where LNR is used in the control of weeds. Rain runoffs from farmlands, atmospheric deposition during aerial sprays, and wastewater effluents are significant sources of LNR to WWTPs.

The levels of EDCs in wastewater in this study were higher than those reported in our pilot study (Onchiri et al., 2021) which recorded influent mean levels of DMP in Kisumu, Homabay, and Kisii to be 0.099 and 0.079 μg L^{-1} during the wet and dry seasons, respectively. The low values in the pilot study can be attributed to fewer sampling areas and less populous towns which consequently gave a reduced mean. In our study, DBP and DEHP ranges were higher than those reported by Nantaba et al. (2021) (DBP: 0.35–16 μg L^{-1}; DEHP: 0.210–23 μg L^{-1}) along the shores of Lake Victoria, Uganda. The difference is attributed to varied sampling sites whereby our study focused on WWTPs that are known to be point sources of pollutants, unlike shores. In South Africa, Salaudeen et al. (2018) reported higher DBP influent ranges (2.7 and 2488 μg L^{-1}) and effluent (4.90–8.88 μg L^{-1}) than our study in three WWTPs in Eastern Cape. Kenya banned plastic bag packaging in February 2017, and this could explain the lower ranges in addition to being less populous and industrialized. The same can be said of Nigeria since Adeogun et al. (2015) reported much higher concentrations of DBP and DEHP concentrations in water at the Lagos lagoon at 130 ± 4 and 180 ± 10 μg L^{-1}, respectively. Weizel et al. (2018) detected much lower values of PGT in the range of 0.0003–0.0013 μg L^{-1} in the municipal waters of Germany. Šauer et al. (2018) recorded progestogenic activities in all effluents ranging from 0.00006 to 0.00047 μg L^{-1} indicating the presence of PGT in the municipal waters of the Czech Republic and Slovakia. Appa et al. (2018) found the range of PGT to be 0.017–0.20 μg L^{-1} in treated and non-treated sewage water in Central India. Khazri et al. (2022) reported the presence of LNR in the Bizerte wastewater, Tunisia at a mean concentration of 3.94 μg L^{-1}. EDCs are said to be ubiquitous in aqueous matrices as summarized in Table S6.

3.3. Levels of EDCs in sludge samples

All the sludge samples collected had quantifiable levels of the EDCs and the spatial distribution is represented in Fig. 3 and further illustrated in Fig. S1(a).

DEHP was the most abundant and accounted for 48.2% of the sum of the pollutants detected in sludge. It ranged from 278.67 ng g^{-1} dw in Kisii to 9243.49 ng g^{-1} dw in Kariobangi. This was followed by DBP, (22.7%) with ranges from 97.13 ng g^{-1} dw in Kisii to 2999.99 ng g^{-1} dw in Kariobangi. DMP contributed 15.02% with ranges between 452.50 ng g^{-1} dw in Kericho and 1858.45 ng g^{-1} dw in Kariobangi. PGT represented 13.11% with ranges between 257.41 ng g^{-1} dw in Kisii and 1165.53 ng g^{-1} dw in Ruai. LNR was the least recorded representing 0.99% with ranges of 18.47 ng g^{-1} dw in MMUST to 132.68 ng g^{-1} dw in Eldoret. The means ± SD of the EDCs in the sludge are given in Table S7.

The high concentrations of the PAEs in sludge samples as compared to PGT and LNR, reflect increased plastic use (toys, water pipes, smart screens, packaging films, etc.). Furthermore, it was noted that DEHP concentrations were higher than DMP and DBP. This can be explained by the fact that DMP and DBP are classified as low-molecular-weight PAEs used in the production of packaging bags, finishing materials, personal care products, and insecticides. Plastic packaging bags were outlawed in Kenya, which could explain the reduced DBP and DMP concentrations. Conversely, DEHP is a high-molecular-weight PAE used for the manufacturing of vinyl-based products, toys, construction, polyethylene terephthalate bottles, food packages, medical devices (bags and tubing used for blood transfusion, kidney dialysis or dosing antibiotics

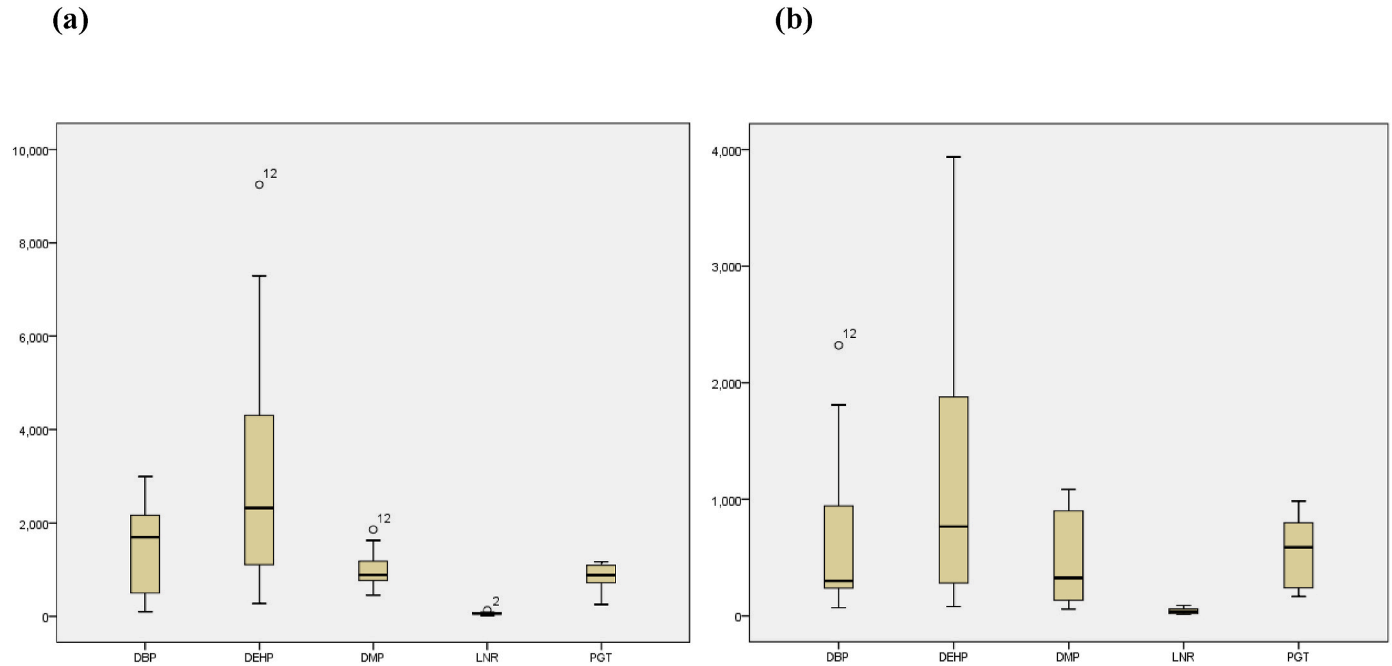

Fig. 3. Box plots for EDCs in (a) sludge (b) UDBS (The dots represent sites with high concentrations of EDCs).

intravenously (Cong et al., 2022; Zhu et al., 2019). All these products of DEHP are still in use in Kenya. Additionally, from Table S1, it is noted that DEHP has a lower water solubility and a higher log K_{OW} than other PAEs implying that it partitions more to the sludge and is more resistant to biodegradation.

Kariobangi and Ruai recorded higher concentrations of most EDCs except LNR than the rest of the sampled WWTPs. This can be attributed to the two WWTPs receiving domestic and industrial wastewater from the populous city of Nairobi, which is industrialized, highly urbanized, and densely populated. It is also often contaminated by runoff and stormwater drainages, open landfills, agricultural practices, and pesticide use. The highest concentration of LNR was observed in Eldoret, an agricultural area with large-scale pesticide-intensive wheat and maize farming.

The $\sum$5EDCs in sludge in the sampled WWTPs decreased in the following order (in μg g^{-1} dry weight (dw)): Kariobangi (15.27) > Ruai (13.09) > Nyalenda (8.46) > Nakuru (8.24) > Eldoret (7.52) > Kisat (6.19) > Bungoma (5.89) > Kericho (4.31) > Shirere (3.41) > Busia (2.82) > MMUST (2.56) > Kisii (1.48). The order depicts the effect of urbanization, population density, and industrialization of the city where the WWTP is located. For instance, Kariobangi and Ruai recorded higher concentrations in the $\sum$5EDCs reflecting the fact that the two WWTPs are in a populous city (Nairobi). Conversely, the less urbanized regions like Shirere (Kakamega), Busia, and Kisii had low levels of EDCs, which reflects their low populations and less industrialization. It can also be associated with poor sewerage connectivity in some towns.

The levels of EDCs in sludge in the present study were compared to those reported elsewhere (Table S6). In China, Zhu et al. (2019) reported an abundance of DEHP congener in sludge samples which is consistent with the current study. In their study, PAEs were detected in the same order (DEHP > DBP > DMP). However, the mean concentration of DEHP (14,700 ng g^{-1}) was higher than that observed in our study while DBP and DMP were detected at lower levels (means of 957 and 195 ng g^{-1}, respectively). Dong et al. (2020) also confirmed the ubiquity of DEHP in their study that found out that 99% of the PAEs in the sludge of some WWPTs in Taiwan were DEHP with ranges from 1569 ng g^{-1} to 35,670 ng g^{-1} dw. Other related environmental matrices like sediments have also been reported to contain EDCs. For example, Adeogun et al. (2015) reported much higher concentrations in sediments sampled from Epe lagoon, Nigeria (DBP and DEHP were 0.18 ± 0.01 mg g^{-1} and 0.28 ± 0.02 mg g^{-1}, respectively). Additionally, Cong et al. (2022) also noted that DEHP had slightly higher concentrations with a mean of 4594 ng g^{-1} dw in sediments from the Eastern Indian Ocean. The reduced concentrations in Kenya could be attributed to the ban on plastic bag use effected in February 2017.

3.4. Levels of EDCs in the UDBS samples

All the UDBS samples collected from the different locations had quantifiable levels of the EDCs (Fig. 3 and Fig. S1(b)). DEHP was the most abundant (40%) of the total EDCs detected with levels ranging from 78.77 ng g^{-1} dw in Kisii to 3938.54 ng g^{-1} dw in Kariobangi. This was followed by DBP (22.76%) with levels between 69.43 ng g^{-1} dw in Kisii and 2320.50 ng g^{-1} dw in Kariobangi. PGT represented 19.31% with its levels ranging from 166.97 ng g^{-1} dw in Shirere to 984.57 ng g^{-1} dw in Ruai. DMP represented 16.46% with its levels varying from 57.84 ng g^{-1} dw in Kericho to 1084.87 ng g^{-1} dw in Kariobangi. LNR had the lowest levels (1.46%) with levels ranging from 13.46 ng g^{-1} dw in Kisat to 88.79 ng g^{-1} dw in Eldoret. The means ± SD of the EDCs in the UDBS samples are given in Table S8. The data displayed significant differences ($p < 0.05$; Kruskal-Wallis) between the EDCs in the different study sites. The high levels of the PAEs, especially in the more urbanized Nairobi city are consistent with their use and less stringent measures in plastic disposal. DEHP was much higher than DMP and DBP due to its use in a wide array of plastic consumer products. PGT, from medical facilities, was higher in the UDBS samples than DMP implying less biodegradation capacity and stronger sorption capacity in the WWTPs. LNR had elevated concentrations in areas with high intensity agricultural activities such as Eldoret.

There was a decrease in the total sum of EDCs ($\sum$5EDCs) in the UDBS samples in the following order (μg g^{-1} dw): Kariobangi (8.25) > Ruai (5.22) > Kisat (4.18) > Nyalenda (3.31) > Eldoret (2.92) > Nakuru (2.20) > MMUST (2.13) > Bungoma (1.83) > Kericho (1.54) > Busia (1.33) > Kisii (0.94) > Shirere (0.73). Nationwide research related to EDCs in UDBS may help to determine the quality of the UDBS in land application consequently supplementing the data concerning human exposure to EDCs.

In this study, the concentration of EDCs in UDBS from the drier beds of WWTPs have been reported for the first time. Closely related studies have reported PAEs in soil and street dust. For example, Škrbić et al. (2016) analyzed soils and dust from Novi Sad, Serbia. The study reported concentrations of PAEs as 0.2–4820 ng g^{-1} dw, with DEHP being the most dominant (70–96%). The presence of these EDCs in UDBS is of great concern since they are used as fertilizers causing potential toxicological risks to terrestrial life. As a result, relevant government agencies must develop and enforce regulations for both the disposal of EDCs and the use of UDBS from WWTPs as fertilizer.

3.5. Association between the EDC concentrations in wastewater, sludge, and UDBS

There was a positive correlation (paired samples *t*-test) between the concentrations in the influents and sludge (Table S9). However, the levels of EDCs in some influent wastewaters were significantly lower ($p < 0.05$; ANOVA) than those observed in sludge with DEHP being ubiquitous in sludge. This could be attributed to the accumulation of pollutants over time in the receiving ponds, atmospheric deposition and surface runoffs, and storm waters from neighboring farmlands and polluted sites (Kumar et al., 2020a,b). The UDBS samples, however, had considerably lower concentrations relative to those in the sludge. The UDBS from the drier beds also had higher concentrations than the effluents. This suggests that EDCs partition more to the sludge than to the water. This is also confirmed through the Spearman's rank order correlation coefficient where positive correlations were noted between the EDCs' concentration levels and the TDS, COD, BOD_5 and EC (Table S10). This can be attributed to their lower water solubility and high log K_{OW} hence stronger sorption and lower degradation capacity (Cong et al., 2022; Mukherjee et al., 2021). Therefore, sludge acts as a sink to the EDCs, which is then subsequently used as fertilizer in the form of UDBS posing a risk in agricultural farmlands.

To highlight one notable exception, DEHP was more prevalent in the sludge and UDBS, but DBP was abundant in the influent wastewater. This is consistent with their physicochemical parameters (Table S1). A general rule used to frequently predict the sorption capacity of micropollutants on solids is: log $K_{OW} < 2.5$ indicates low sorption potential, $2.5 < \log K_{OW} < 4$ indicates medium sorption potential and log $K_{OW} > 4$ indicates high sorption potential (Orata, 2018). This demonstrates why DEHP (log K_{OW}: 7.6) had greater concentrations in sludge and UDBS while DBP (log K_{OW}: 4.5) had greater concentrations in wastewater samples.

3.6. Relationship between EDC concentrations and water quality parameters

Spearman's rank order correlation was used to show the association between the water quality parameters and the concentration of the EDCs at the influents (Table S10). The pH was negatively correlated with all the EDCs detected at the influent points (r_s values ranged from −0.032 to −0.529). This implies that increased contamination increases acidity thus lowering the pH. This may be attributed to increased solubility, an observation made in other pollutants like heavy metals (Kumar et al., 2020a,b). Therefore, contaminants increase the acidity of wastewater making them undesirable. Conversely, for TDS, BOD_5, COD and EC, there were positive correlations (r_s values 0.014–0.678) implying that the greater the water quality parameter the higher the concentration of the EDCs. The correlations, however, were not significant ($p > 0.05$; $p > 0.01$*) in most of the compounds except for DBP which was strongly significant ($p < 0.05$) for TDS, BOD_5, COD, and EC. Pollution is thus often associated with the worst water quality metrics.

Among the EDCs, there were mainly positive correlations between the PAEs and negative correlations to PGT and LNR. PGT and LNR were however positively correlated. This implied that the sources of PAEs were the same as those of PGT and LNR.

3.7. Removal efficiencies of selected EDCs in the sampled WWTPs

The removal efficiencies for each analyte were calculated as illustrated in section 2.8. The percentages are shown in Table 3 and the ranges were between 17.8% and 100%. The average removal per pollutant was as follows: DMP (98.7%) > DEHP (91.7%) > PGT (83.4%) > DBP (77.9%) > LNR (72.2%). DMP had greater abstraction percentages while WWTPs were less efficient in removing LNR. Some WWTPs were old (constructed in the 1960'with little to no servicing done periodically. DEHP removal efficiency is slightly lower than that reported by Marttinen et al. (2003) (94%). Up to 95% removal of DMP and DBP have been attributed to biotransformation and adsorption to sludge (Zhu et al., 2019).

Sorption, biological degradation, photolysis, and phytoremediation may be factors affecting removal efficiencies, as these mechanisms can be effective in elimination (Chen et al., 2012). Sorption guarantees that contaminants are transferred to the sludge and then to the UDBS as a result of the EDCs partitioning onto the biosolid. Plastics can also undergo biodegradation and photodegradation (Zeenat et al., 2021) which explains the increased DMP sequestration ranges. Some EDCs (LNR) showed relative stability over the whole treatment process, possibly due to their chemical structure and physiochemical properties making them persistent with weak adsorbility. The removal efficiencies of EDCs are primarily dependent on the physicochemical properties (mostly log K_{OW}) of the EDCs which will consequently affect their sorption mechanisms. It may also be influenced by environmental factors such as light, temperature, humidity, and precipitation which tend to impact their degradation mechanism (Nath et al., 2022). The percentages are important to regulators as they serve to inform them of the efficiencies of WWTPs. It also serves to inform them on how pollutants are transferred from wastewater to UDBS which are used as fertilizer.

3.8. Mass loading of EDCs into the environment

The daily discharges (Dds) of the EDCs are shown in Table 4 and were calculated only for analytes above the LOQ.

The Dd loads from the twelve WWTPs varied depending on the pollutant and the geographical difference. The Dd in densely populated areas like Nairobi, represented by Kariobangi and Ruai were considerably high. DBP recorded the highest in Ruai (373.33 g day^{-1}). This implies that large quantities of EDCs are being released into receiving waters eventually finding their way into surface waters, potable water, and drinking water. The potential dangers to human beings and biota are undeniable. The synergistic effects of the combination of varied EDCs are unknown. More studies should be carried out to investigate the concentrations of other EDCs in different environmental compartments and their mass loadings into the environment. Some attempts have been made on pharmaceuticals' mass loadings (K'oreje et al., 2018; Kimosop et al., 2016) but more work is needed particularly in East Africa.

Table 3
Percent (%) removal efficiency of EDCs.

Site	DBP	DEHP	DMP	LNR	PGT
Nakuru	58.9	93.3	99.9	65.1	71.5
Elodoret	76.7	89.9	98.5	98.2	97.1
Bungoma	43.9	100.0	99.2	61.8	73.8
Busia	65.4	100.0	99.3	63.7	85.0
Kisii	100	81.9	98.9	61.2	89.0
MMUST	72.4	100.0	99.2	69.5	69.4
Ruai	76.3	78.5	97.6	71.0	94.2
Shirere	100	100	98.6	83.3	99.4
Kisat	100	100	99.9	81.2	98.7
Nyalenda	67.5	76.1	96.7	57.8	95.1
Kericho	100	93.0	99.8	76.0	97.7
Kariobangi	74.0	87.2	96.7	78.1	30.2

Table 4
Daily discharge of EDCs to the environment through the effluents (mg day^{-1}).

Location	DBP	DEHP	DMP	LNR	PGT
Nakuru	22606.86	1256.53	104.16	175.73	1658.27
Eldoret	19641.42	5551.67	925.98	366.22	4760.49
Bungoma	23881.23	–	608.99	181.07	2388.37
Busia	4068.96	–	59.48	55.69	701.73
Kisii	–	3298.56	62.64	84.34	389.71
MMUST	685.00	–	6.71	7.26	170.59
Ruai	373327.79	158716.08	8408.88	1878.19	68680.73
Shirere	–	–	31.56	42.93	23.80
Kisat	–	–	44.76	153.83	95.20
Nyalenda	65270.40	28465.54	995.24	406.25	2357.16
Kericho	–	615.53	10.09	17.37	49.49
Kariobangi	110468.11	42220.71	5439.57	420.75	29149.67

(- represents those areas whose effluents were below the LOQ).

3.9. Potential ecotoxicological risks to the receiving aquatic ecosystem

Three trophic levels were chosen to assess the ecotoxicological risks for the selected EDCs in effluents released to surface water. Table 5 shows the calculated RQs for the selected EDCs based on the worst-case scenario obtained by considering the maximum concentration detected among all the sites and the lowest NOECs or E(L)C50. DEHP (chronic) and PGT (acute and chronic) had their RQs >1 posing a high risk to biota. DMP, DBP and LNR posed medium risks as their RQ values were between 0.1 and 1.

The RQs for chronic cases were also calculated for every EDC per site (Fig. 4**)**.

DBP displayed medium risks in Ruai and Kariobangi and low to no observed risks in the rest of the sites. DEHP posed high risks in Eldoret, Kisii, Ruai, Nyalenda, Kericho, and Kariobangi while recording medium risks in Nakuru and low risks in the rest of the sites. DMP posed low to no observed risks in all the sites. LNR displayed medium risks in all the sites while PGT posed high risks in Nakuru, Eldoret, Bungoma, Busia, MMUST, Ruai, and Kariobangi. It is worth noting that sites that recorded high concentrations of EDCs due to denser populations and industrial activities also indicated high risks. More risk assessments should be carried out on more pollutants and sites to fully understand their health impacts on aquatic organisms. Sadly, there is limited data on adverse effects e.g., behavioral effects, endocrine disruption, and neurotoxicity due to minimal testing strategies. Very few studies have reported hormonal changes on only one trophic level (fish) and for a few EDCs. Ecotoxicological risks to the terrestrial ecosystem, so far, can be attributed to trophic transfer and more studies should be carried out on how EDCs affect the terrestrial ecosystem.

3.10. Study strengths, limitations, and recommendations

To the best of our knowledge, this is the first study in Sub-Saharan Africa that has evaluated EDCs in UDBS manure samples taken from WWTPs and utilized as fertilizer in agricultural areas. We are also reporting PGT and LNR in wastewater and sludge for the first time in East Africa. Related research has focused on lakes and rivers, ignoring the largest source of EDCs, which are WWTPs. Nonetheless, there were some study limitations encountered; firstly, due to financial constraints at the beginning of the study, we did not use isotope-labeled standards or internal standardization to validate our analytical method. However, we conducted several quality assurance and quality control strategies (such as triplicate analyses, recovery tests, spiked blanks, LODs, and LOQs) to ensure the robustness, accuracy, and reliability of our analyses. Our QA/QC results showed that our method was sufficiently robust and accurate. Secondly, not all WWTPs in Kenya were sampled therefore reducing the sample size (N = 60). Prospective studies may wish to explore these pollutants in all WWTPs in Kenya to provide conclusive results. Furthermore, the transformational study of EDCs to analyze their metabolites is also a recommended area in future studies. Finally, seasonal variations which will enable the calculation of dissipation kinetics should also be carried out in future studies.

4. Conclusions

This study investigated the levels of selected endocrine disrupting chemicals (EDCs): dibutylphthalate (DBP), diethylhexylphthalate (DEHP), dimethylphthalate (DMP), linuron (LNR) and progesterone (PGT) in wastewater, sludge and in untreated dry biosolid (UDBS) samples from twelve wastewater treatment plants (WWTPs) in nine major towns in Kenya. The EDCs were detected in all the influent wastewater, sludge, and UDBS samples from all the WWTPs, with DEHP and DBP having higher concentrations than other EDCs. There was higher partitioning of the EDCs to the sludge and the UDBS than to the water samples. Notably, DEHP had higher mean concentrations in the sludge and in UDBS (3181.16 and 1153.10 ng g^{-1} respectively; $p < 0.05$) in all the sites sampled than the rest of the EDCs. The influent wastewater samples indicated significant variations ($p < 0.05$) with DBP (mean of 10.11 μg L^{-1}) being higher in the influent wastewater samples as compared to the rest of the EDCs. LNR had the lowest concentration in the wastewater samples, sludge, and UDBS. The occurrence of some EDCs in the discharged effluents indicates that the WWTPs are not as efficient as desired in completely abstracting organic micropollutants. The daily discharges and high-Risk quotients to the receiving water portrayed a potential risk to the environment that policymakers need to put in structures to regulate the uses and disposal of EDCs.

Credit author statement

Emily Ngeno: Conceptualization, Methodology, Formal analysis, Investigation; Methodology, Writing - Original Draft and Funding acquisition. **Roselyn Ongulu**: Supervision, Conceptualization, Writing – Review, Editing and Funding acquisition. **Francis Orata**: Conceptualization, Supervision, Writing - Review and Editing. **Henry Matovu**: Writing - Review and Editing. **Victor Shikuku**: Writing - Review and Editing. **Richard Onchiri**: Writing - Review and Editing and Funding acquisition. **Abel Mayaka**: Writing – Review, Editing and Funding acquisition. **Eunice Majanga**: Writing – Review, Editing and Funding Acquisition. **Zachary Getenga**: Writing – Review, Editing and Funding Acquisition. **Joel Gichumbi**: Writing – Review, Editing and Funding Acquisition. **Patrick Ssebugere**: Conceptualization, Writing - Review and Editing, Supervision and Funding acquisition.

Table 5
Calculated RQs for the selected EDCs.

EDC	Maximum recorded effluent concentration (μg/L)	Effect value used (mg/L)	No. of trophic levels	Acute or Chronic	AF	PNEC converted to μg/L	RQ
DEHP	1.984	0.32 (EC50)	3	Chronic	1000	0.32	6.2
DBP	4.803	0.4 (lowest NOEC)	3	Chronic	10	40	0.12
DMP	0.237	180 (EC50)	3	Chronic	1000	180	0.0013
PGT	0.859	0.069 (lowest NOEC)	2	Acute	1000	0.069	12.45
		0.0085 (lowest NOEC)	2	Chronic	50	0.17	5.05
LNR	0.046	0.1 (lowest NOEC)	2	Acute	1000	0.1	0.46
		0.001 (Lowest NOEC)	3	Chronic	10	0.1	0.46

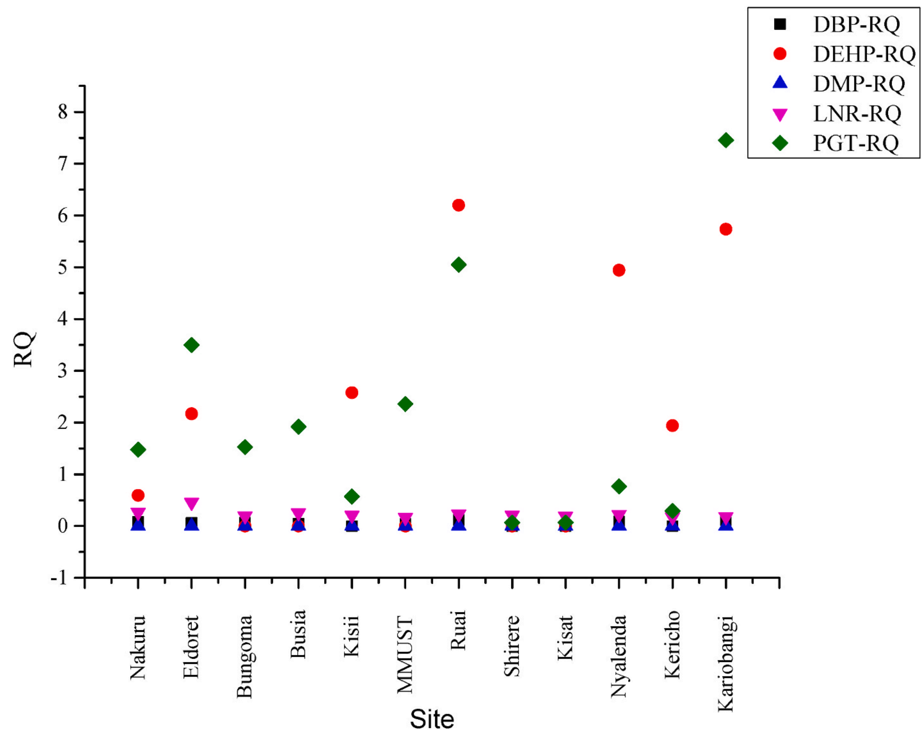

Fig. 4. RQs for chronic cases calculated for every EDC per site.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2023.117076.

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