Phthalates and Heavy Metals in Sewer and Outlet Stream in a part of Lagos Southwest Nigeria

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Research Article

Keywords: Human activity, metals, phthalates, pollution, wastewater

Posted Date: September 28th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2070565/v1

Abstract

Contaminants and pollutants impact on the availability of clean water for the human population is huge as clean water is increasingly scarce for human consumption on earth most especially in major cities of the world; As water is used they are heavily contaminated and hence there is the need to examine the persistent pollutants most especially phthalates and heavy metals in wastewater and outlet stream. This research examined the level of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), and heavy metals viz; Pb, Cr, Cd, As and Hg in the sewer and outlet stream in a part of Lagos, Nigeria. DMP ranged from 0.0070 ± 0.036 to 0.0278 ± 0.324, DEP ranged from 0.0367 ± 0.204 to 0.0526 ± 0.496, and DBP ranged from 0.0406 ± 0.241 to 0.1472 ± 1.667 µg/mL, lead ranged from 0.117 ± 0.024 to 0.157 ± 0.048, chromium ranged from nd (not detected) to 0.319 ± 0.245, cadmium ranged from 0.004 ± 0.002 to 0.063 ± 0.021, arsenic ranged from 0.002 ± 0.001 to 0.021 ± 0.006, and mercury ranged from nd to 0.007 ± 0.001 µg/mL. The concentration of lead in this study was higher than the WHO recommended value of 0.1 mg/L in surface water. This research established that phthalates and heavy metals were released into the wastewater from the immediate environment. We suggest that the sewer treatment of the wastewater be reviewed and improved to eliminate the contaminants in the wastewater.

Introduction

Human activities have been a major determinant of pollutants and contaminants in the environment as well as the natural resources in the immediate environment and this could lead to scarcity of the clean resources. Water is a major resource that has been put to use since the existence of man. This impact sometimes leads to pollution and at some other times the disruption of the immediate environment. The materials found in wastewater include heavy metals, anilines, polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers, bisphenols and phthalate esters (Sanchez − Avila, *et al.*, 2009; Zhu et al., 2019). The main sources of these pollutants in wastewater includes domestic, municipal, industrial, hospital, agricultural, and livestock as well as inadequate disposal of waste in the environment (Perez-Alvarez et al., 2018). A recent study has found phthalate esters in surface water, groundwater and drinking water, linked to phthalate ester-laden wastewater (Gani and Kazmi, 2016). At times the polluted water could be processed and recycled but the processing methods are usually not, perfectly efficient to purify wastewater to portable water. Phthalate esters and trace heavy metals have been found in treated water. Phthalate esters and heavy metals get into hospital wastewater through usage in pharmaceutical products, medical devices as well as wash down from polymer materials, blood bags, infusion tubes, breathing masks, catheters, hand gloves, and through waste generated from these materials, a recent study has found fourteen phthalate esters in polyvinyl chloride medical devices (Gimeno et al., 2014; Perez-Alvarez et al., 2018). Phthalate esters are not covalently bound to these materials, thus, they leach into the immediate environment, and hence, they have been found in air, water, and soil (Zhang et al., 2020).

Phthalate esters and heavy metals have been implicated as endocrine disruptors in humans, the effect of which could last a lifetime; the mechanism of phthalate effect on the endocrine system has been

suggested to affect the neurodevelopment such as reduced dopaminergic activity in the brain, obstruction of calcium signaling activity, lipid metabolism and thyroid hormone level (Day et al., 2021). Dimethyl phthalate (DMP), diethyl phthalate (DEP), and Dibutyl phthalate (DBP) have been implicated to the delay onset of puberty in boys, but accelerate puberty in girls, while also increasing childhood obesity, allergic symptoms, asthma, hypertension, poor attention performance and DNA damage in children (Du et al., 2018). However, a more recent study suggested that DEP and DBP exposure in mothers' early pregnancy could impair the offspring, most especially the girl child social responsive behavior, and increase the chances of autism in female birth (Day et al., 2021). Lead has been strongly linked with fatigue, irritability, myalgia, coma, organs such as kidney, liver, and brain damage, seizures, encephalopathy, nervous system dysfunction, and cancer development, besides, cadmium has been strongly associated with itai-itai disease, in addition to bone disease, anosmia, and yellow discoloration of teeth and loss of olfactory abilities (Onipede and Rahman 2017). Furthermore, zinc accumulation in the human body has been positively associated with electrolyte imbalance, nausea, anaemia, and lethargy (Onipede et al., 2015).

The wastewaters and the receiving channels eventually discharge into the rivers and then the ocean, but some of these water bodies are eventually purified to potable water. However, the methods of purification do not eliminate the phthalate esters as well as the heavy metals. And these could lead to persistent exposure in the purified potable water-consuming population. There is no scientific information and paucity of data on the level of phthalate esters and heavy metals and outlet stream around the Hospital A in Lagos, Nigeria. To the best of our knowledge, this is the first study to examine the level of phthalates and heavy metals in wastewater most especially around the Hospital A in Lagos, Nigeria. Hence this study examines the level of phthalate esters (DMP, DEP and DBP), and heavy metals (Pb, Cr, Cd, As, and Hg) in Hospital A in Lagos, Nigeria sewage drains and outlet stream with the view to determining the impact of the wastewater on the immediate aquatic environment. In addition, the seasonal variation of the phthalate esters and heavy metals in the wastewater and the immediate aquatic environment was examined.

Materials And Method

Standards and reagents

Dimethyl phthalate (DMP), diethyl phthalate (DEP), and dibutyl phthalate (DBP) standards were purchased from Merck (Germany). HPLC grade acetonitrile, dichloromethane, ethyl acetate, n-hexane, 60 – 300 mesh size silica gel, analytical grade nitric acid, sodium chloride, sodium sulphate, and sodium carbonate were also purchased from Merck (Germany).

Cleaning of glass wares

All glasswares were cleaned by soaking in dilute nitric acid for 24 hours; this was followed by soaking in acetonitrile and then rinsed in n-hexane. They were heated in the oven at 240^{o}C for 6 hours. They were

rinsed with HPLC grade acetonitrile before use in the analytical procedure.

Sampling

Two sets of forty (40) wastewater samples were collected into 100 mL amber bottles in the dry and rainy seasons, in the wastewater channels, and outlet stream at the Hospital A in Lagos. Each sample of wastewater for phthalate esters determination obtained was acidified with 2mL of 1 M orthophosphoric acid to prevent enzymatic hydrolysis of phthalate esters in the wastewater and was thereafter transported to the laboratory within 2 hours of collection and stored in the freezer at − 20^{o}C until the time of the analysis. Each sample for heavy metals determination was acidified with 2 mL of 1 M nitric acid and was transported to the laboratory within 2 hours of collection and was stored in the freezer at – 20^{o}C until the time of the analysis.

Phthalate esters extraction

The extraction was done using the procedure of Ogunfowokan *et al.*, (2006) with a slight modification: 20 mL of the wastewater was put in the boiling tube and 4 g of NaCl was added to it. It was then extracted 3 x 5 mL of dichloromethane: hexane (12.5: 87.5) in an ultrasonic bath. The extracts were pooled. The pooled extract was washed with 3 x 5 mL of 0.1M of sodium carbonateto remove free fatty acid interference. The extract was then concentrated to 2mL before cleanup.

Cleanup

The cleanup was done using the procedure of Ogunfowokan et al., (2006) with slight modification, briefly, 2 mL of the extract was made into slurry on 2 g of 60 – 300 mesh size activated silica gel and was allowed to air dry. Five grammes of the silica gel was loaded into the column and thereafter 2 g of anhydrous sodium sulphate was loaded into the column as a drying agent and the slurry of the extract was then loaded into the column. The column was conditioned with 5 mL n-hexane and subsequently eluted with 40 mL of 30 % ethyl acetate in hexane. The eluate was evaporated to dryness and reconstituted into 1 mL of acetonitrile for injection into the HPLC.

Recovery Studies

The recovery study was done by spiking replicate samples with internal standards of DMP, DEP, and DBP to make the concentration of 5 µg/mL in each of the replicate samples. Each was then extracted and cleanup like other samples.

AAS analysis

The heavy metals analysis of lead, chromium, cadmium, arsenic, and mercury was done with AAS Thermo Scientific ICE 3000 series at wavelengths of detection; 217.0, 357.9, 228.8, 193.7, and 253.7 nm respectively.

HPLC analysis

The phthalate esters analysis was done on Agilent Technologies 1200 HPLC, the column was Zorbax XDP RP C8 150 x 4.6 mm, 5 µm, with UV detector. The mobile phase was acetonitrile: water (80:20 v/v). The temperature of operation was ambient while the injection volume was 10 µL; the flow rate was 0.5 mL/minute. The wavelength of detection was 226 nm and the mode of quantification was peak area. Microsoft excel 2016 was used to prepare the calibration curve of the standards of peak area against concentration. The individual concentration of the sample was extrapolated from the calibration curve.

Linearity and sensitivity

A seven (7) points calibration curve of the range 1 – 50 µg/mL of the phthalate ester internal standard was used to evaluate the linearity of the HPLC. The concentration of each of the phthalate esters in each of the samples was extrapolated from the calibration curve. The regression coefficient was 0.9967 for DMP, 0.9927 for DEP, and 0.9974 for DBP in this study.

Limit of detection and limit of quantification

The limit of detection was three (3) times the standard deviation of series of analytes determinations close to the blank value, it represents the noise to signal ratio in the sample, while the limit of quantification was nine (9) times the standard deviation of series of analyte determinations close to the blank value. It is a representation of the lowest quantifiable concentration with acceptable accuracy and precision in the real sample. The limits of detection for the HPLC-UV for DMP, DEP, and DBP were 0.0015, 0.00028, and 0.0003 µg/mL respectively, while the limit of quantification for DMP, DEP, and DBP were 0.0045, 00084, and 0.00088 µg/mL respectively, as shown in table 1.

Results

Percentage recovery

The percentage recoveries of DMP, DEP, and DBP in this study were 94.86%, 95.22%, and 72.81% respectively as shown in table 1. This is suggestive that the method used in extraction and determination of the samples in this study was maximally efficient and excellently good for the samples examined and analytes determined in this study.

Frequency of detection of phthalates in the wastewater

The frequency of detection of each of the phthalate esters was determined, that is the number of samples in which each phthalate ester examined was found, divided by the total number of samples. And the frequency of detection was found to be 100% for all the phthalate esters in all wastewater examined in this study. This could be suggestive that there was phthalate esters contamination of the wastewater as well as the outlet stream in the area examined in this study.

Table 1: Phthalate esters concentrations in sewer and outlet stream (n= 40)

Sample Description	DMP (µg/mL)	DEP (µg/mL)	DBP (µg/mL)
LOD	0.0015	0.00028	0.0003
LOQ	0.0045	0.00084	0.00088
Sewer (Rainy season)	0.0278 ±0.324	0.0526 ±0.496	0.1472 ±1.667
Outlet stream (Rainy season)	0.0070 ±0.036	0.0469 ±0.294	0.0483 ±0.290
Sewer (Dry season)	0.0079 ±0.038	0.0367 ±0.204	0.0644 ±0.589
Outlet stream (Dry season)	0.0248 ±0.050	0.0462 ±0.087	0.0406 ±0.241
Percentage Recovery	94.86%	95.22%	72.81%

Keys: DMP; Dimethyl phthalate, DEP; Diethyl phthalate DBP: Dibutyl phthalate, LOD; Limit of detection, LOQ; Limit of quantification.

Discussion

DMP levels in sewer and outlet stream

The DMP levels in our study area showed independent variability in both space and time from one sample point to the other as shown in table 1. The level of DMP in the rainy season was 0.0278 ± 0.324 µg/mL (mean± standard deviation, at 95% confidence interval), this is far higher than that obtained in a study in a China study, in which the DMP level found in the water was 0.05 ± 0.11 µg/L (median± interquartile range) (Liu *et al.*, 2014). Also, this study obtained a 100 percent detection ratio as compared to 88.9% obtained in the China study, which seems to suggest a higher level of leaching of the phthalate esters to the sewer in our study than that in China study. The DMP levels in the sewer in the dry season in our study was 0.0079 ± 0.038 µg/mL, this is far higher than that obtained in the Guangzhou China study which had a mean concentration of 0.018 µg/L, and however, the Guangzhou study recorded 100% detection frequency just like this study (Zeng *et al.*, 2008). The level of DMP in the sewer in the dry season was lower by a factor of three, as compared to the rainy season. This could be basically because the rainy season encourages the wash down of plasticizers from the immediate environment into the nearest sewer which might not be possible during the dry season.

Also, the DMP level in the outlet stream in the rainy season was 0.0070 ±0.036 µg/mL, this had the lowest value for all the phthalate esters and all the samples examined in this study. Nonetheless, this is far higher than that obtained in a Taihu, China study, which had a mean DMP concentration of 0.05 µg/L in the wet season (Luo *et al.*, 2021). Besides, the detection frequency in the China study was 94%, which is lower than that in this study which was 100%. The DMP level in the outlet stream in the dry season was

0.0248 ±0.050 µg/mL, this is far higher than that obtained in the Taihu, China study, in which a mean DMP concentration in the dry season was 0.06 µg/L (Luo *et al*., 2021). The detection frequency in the China study was 95%, which is lower than that obtained in this study which was 100%. The level of DMP in the wastewater in the dry season in this study was higher by a factor of three more than in the rainy season. This could be because the dry season is hotter and encourages the leaching of the phthalates esters from the polymer materials in the immediate wet environment.

DEP levels in sewer and outlet stream

The mean DEP in the sewer in the rainy season in our study was 0.0526 ±0.496 µg/mL, this was the highest recorded for all seasons and sample points for DEP in the wastewater examined in this study. The level of DEP in the rainy season in our study is far higher than that obtained in a Saudi Arabia study in which the mean DEP obtained in Wadi Hanifah wastewater was 0.304 ± 0.155 µg/L (mean ± std. dev.) (Al-Saleh *et al*., 2016). This suggests a higher level of DEP leaching in our study wastewater as compared with that in the Saudi Arabia study. The level of DEP in the sewer in the dry season in this study was 0.0367 ±0.204 µg/mL, this is far higher than that obtained in a China study lake which was 0.165 µg/L (Li *et al*., 2020). The China lake also had a 100% detection frequency for DEP just like in this study. The DEP level in the dry season in this study was lower by a factor of 1.4 than that in the rainy season, which suggests higher wash-down in the rainy season.

DEP in the outlet stream in the rainy season in this study was 0.0469 ±0.294 µg/mL, this is far higher than that obtained in the rainy season in Taihu lake water in China which had a mean DEP concentration of 0.06 µg/L (Luo *et al*., 2021). The Taihu lake water had a detection frequency of 71% for DEP in their samples examined, which is far less than that obtained in this study which had a detection frequency of 100%. The DEP in the outlet stream in the dry season in this study was 0.0462 ± 0.087 µg/mL, this is far higher than that obtained in the dry season in Taihu lake in China study which had a mean of 0.09 µg/L (Luo *et al*., 2021). The China study had a detection frequency of 84% for DEP in the samples examined, whereas, the detection frequency for this study was 100%, which suggests a higher level of leaching in this study. There was no significant difference between the mean DEP in the wet and dry seasons, which suggests persistence in contamination in both seasons examined.

DBP in sewer and outlet stream

The mean DBP in the sewer in the rainy season in this study was 0.1472 ±1.667 µg/mL, this was the highest value obtained in this study for all the phthalate esters and all the sample points examined in this study. The level of DBP obtained in this study is far higher than that obtained in a China study which had DBP a concentration of 0.19 ± 0.63 µg/L (median ± interquartile range) (Liu *et al*., 2014). The frequency of detection for DBP in the China study was 98%, which is slightly lower than that in this study which was 100%. DBP in the sewer in the dry season in this study was 0.0644 ±0.589 µg/mL; this is far higher than that obtained in a China study, which had a DBP median concentration of 6.420 µg/L (Li *et al*., 2020). The China study had a frequency of detection of 100% similar to that in this study. DBP in the sewer in the

rainy season in this study was higher by a factor of 2.3 than that in the dry season, which suggests that the rain encouraged wash-down in our study.

DBP in outlet streams in the rainy season in this study was 0.0483 ± 0.290 µg/mL, this is far higher than that obtained in a China study, which had a rainy season mean of 1.31 µg/L (Luo *et al*., 2021). The China study had a similar detection frequency as this study which was 100% for DBP. The mean DBP in outlet stream in the dry season in this study was 0.0406 ±0.241 µg/mL, this is far higher than that obtained in a China study which had a mean DBP of 2.03 µg/L for Guangzhou lake water (Zeng *et al*., 2008). The China study had an exact frequency of detection in DBP with that in this study which was 100%. There is no significant difference between DBP level in the rainy season and the dry season even though the rainy season was higher, which may suggest wash-down in the rainy season.

Heavy metals in the sewer and outlet stream

The mean concentrations, limits of detection, and limits of quantifications of heavy metals in wastewater in both rainy and dry seasons examined in this study are as shown in table 2. The limits of detection were 0.0015, 0.0015, 0.0005, 0.0005 and 0.0005 µg/mL for Pb, Cr, Cd, As, and Hg respectively. And the limits of quantification were 0.0045, 0.0045, 0.0015, 0.0015, and 0.0015 µg/mL for Pb, Cr, Cd, As and Hg respectively.

Table 2; Concentration of heavy metals in sewer and outlet stream (n = 40)

Sample description	Heavy metals concentration (µg/mL)				
	Pb	Cr	Cd	As	Hg
Sewer (Rainy s.)	0.139±0.081	nd	0.005±0.003	0.002±0.001	0.007±0.001
Outlet stream (Rainy s.)	0.137±0.106	0.319±0.245	0.004±0.002	0.003±0.001	0.004±0.03
Sewer (Dry s.)	0.117±0.024	0.076±0.029	0.063±0.021	0.021±0.006	0.003±0.001
Outlet stream (Dry s.)	0.157 ±0.048	0.317±0.079	0.062±0.014	0.021±0.005	nd
Limit of detection	0.0015	0.0015	0.0005	0.0005	0.0005
Limit of quantification	0.0045	0.0045	0.0015	0.0015	0.0015

Keys; values are mean± standard deviation, Rainy s.; Rainy season, Dry s.; Dry season, nd; not detected

Lead in sewer and outlet stream

The mean concentration of lead in the sewer in the rainy season in this study was 0.139 ± 0.081 µg/mL (mean ± standard deviation, at 95% confidence interval), as shown in table 2, this is higher than that obtained in hospital effluent in a Mexico study which had a mean lead concentration of 0.123 ± 0.001 mg/L (Perez-Alvarez *et al*., 2018). This suggests that lead leaches into wastewater from hospitals in most

parts of the world. The mean concentration of lead in the sewer in the dry season in this study was 0.117 ± 0.024 µg/mL, this indicates that there was no significant difference between the level of lead in the wastewater in the rainy and dry seasons. It possibly suggests that lead is a persistent waste from the hospital environment in both rainy and dry seasons. The level of lead in obtained in the dry season in this study was higher than that obtained in the Ethiopia study in which the mean lead concentration in sample site 1 was 0.031 ± 0.008 mg/L (Mekuria *et al*., 2021), which suggests that lead leaches into the wastewater more in our study than that in the Ethiopia study.

The outlet stream in the rainy season had a mean lead concentration of 0.137±0.106 µg/mL, this is lower than that obtained in a Pakistan study, which had a mean lead concentration in seawater of 16.03±0.13 mg/mL (Chan *et al*., 2021). The seawater is a receiver of much more sources of a pollutant than, the outlet stream considered in this study. Again there was no significant difference between the level of lead in the sewer and the outlet stream in the rainy season in this study. This could suggest that the waste from the hospital wastewater could be the main source of lead in the outlet stream. The outlet stream in the dry season had a mean lead concentration of 0.157 ±0.048 µg/mL, this is lower than that obtained in the Dhaka Bangladesh study which had a mean lead concentration in textile wastewater of 0.22 ± 0.02 mg/L (Islam *et al*., 2016), the Dhaka study examined textile industrial wastewater which could necessitate the high value observed as against hospital wastewater in this study. There was no significant difference between the lead concentration in the outlet stream in the rainy season and the dry season in this study. The concentration of lead in the sewer and outlet stream examined in this study was in all cases higher than the WHO recommended value in wastewater which was 0.1 mg/L. This suggests there is a need to review the purification process in the sewer examined in this study.

Chromium in sewer and outlet stream

The mean chromium concentration in the sewer in the rainy season in this study was nd, this was the lowest level obtained in this study in all the heavy metals in the wastewater in this study. This is lower than that obtained in a Mexico study which had a mean chromium concentration of 0.051 ± 0.001 mg/L in hospital effluent (Perez-Alvarez *et al*., 2018). The chromium level obtained in the sewer in the dry season was 0.076 ± 0.029 µg/mL, this is lower than that obtained in a study in Dhaka Bangladesh, in which the chromium level was found in textile industrial wastewater was 4.9 ± 0.92 mg/L (Islam *et al*., 2016). This could be expected in textile industrial wastewater since pieces of machinery are involved in most of the textile processes. It could however be observed that the chromium level in the rainy season in this study was higher than that in the dry season.

Chromium in the outlet stream in the rainy season in this study was 0.319±0.245 µg/mL, this is lower than that obtained in a study in Pakistan in which the chromium level in seawater was 40.06±0.21 mg/mL (Chan *et al*., 2021). The seawater considered in the Pakistan study had much pollutants as a result of the influence of the river Lyari. The chromium in the outlet stream in the dry season in this study was 0.317±0.079 µg/mL, this is higher than that obtained in a recent study in Saudi Arabia in which the chromium found in site 1 of the gulf was 0.34 ± 0.006 µg/L (Mahboob *et al*., 2022), the level obtained in

the Saudi Arabia seawater was relatively lower, even though there was the influence of industries in their study area. There was no significant difference between the level of chromium in rainy and dry seasons in this study. All the wastewater examined in this study had chromium concentration below the WHO recommended level which was 2 mg/L in wastewater (Islam *et al*., 2016).

Cadmium in sewer and outlet stream

The cadmium concentration in the sewer in the rainy season in our study was 0.005 ± 0.003 µg/mL, this is lower than that obtained in a Mexico study in which the effluent received from the hospital had 0.039 ±0.001 mg/L (Perez-Alvarez *et al*., 2018). The effluent in our study was treated before the discharge into the receiving stream whereas the effluent in the Mexico study was not treated before being discharged into the receiving stream, this could have necessitated the relatively high level obtained in the Mexican study. The cadmium concentration in the dry season in sewer obtained in this study was 0.063±0.021 µg/mL, this is higher than that obtained in an Ethiopian study in which the concentration of cadmium in Akaki river water was 0.017 ± 0.007 mg/L (Mekuria *et al*., 2021). The level of cadmium in this study was far higher than all the range of cadmium in the Ethiopian study as the range in the ten samples analyzed was < 0.014 ± 0.0007 to 0.02 ± 0.001mg/L. This suggests that the wastewater in this study is a higher source of contamination to the immediate environment than that examined in the Ethiopian study.

The cadmium concentration in the outlet stream in the rainy season in our study was 0.004 ± 0.002 µg/mL, this is lower than that obtained in the Bangladesh study in which the mean concentration obtained in textile wastewater was 0.08 ± 0.07 mg/L (Islam *et al*., 2016). The equipment and machine used in the textile industry in Bangladesh could have accounted for the high value obtained in the study. However, the level obtained in this study was lower than the WHO recommended value in inland surface water which was 0.1 mg/L (Islam *et al*., 2016). The cadmium concentration in the outlet stream in the dry season in this study was 0.062 ± 0.014 µg/mL, this was far higher than that obtained in sample 4 water obtained from the Gulf of Saudi Arabia which had a concentration of 0.003 ± 0.000 µg/L (Mahboob *et al*., 2022). This could suggest that the wastewater outlet stream examined in this study was a higher source of contamination to the immediate environment than that in the Saudi Arabian study.

Arsenic in sewer and outlet stream

The arsenic concentration obtained in the sewer in the rainy season in this study was 0.002 ± 0.001 µg/mL, this is lower than that obtained in a Mexican study in which the level of arsenic was obtained in the hospital effluent was 0.014 ± 0.001 mg/L (Perez-Alvarez *et al*., 2018). The effluent in this study was treated before the discharge into the receiving sewer but the effluent in the Mexico study was not treated before discharge into the receiving stream. However, the level of arsenic obtained in this study is lower than the WHO recommended limit in wastewater which was 0.2 mg/L (Islam *et al*., 2016). The level of arsenic in the sewer in the dry season in this study was 0.021 ± 0.006 µg/mL, this is similar to that obtained in the Saudi Arabian study in which the arsenic concentration in water from the gulf of Saudi Arabia in sample site 1 was 21.07 ± 1.19 µg/L (Mahboob *et al*., 2022). This suggests that the wastewater from this study had a similar level of contamination to the gulf water of Saudi Arabia that was said to be

polluted from a large industrial effluent. The arsenic concentration in the sewer in this study showed ten (10) folds increase in the dry season as compared to the rainy season.

The arsenic concentration in the outlet stream in the rainy season in this study was 0.003 ± 0.001 µg/mL, this is lower than that obtained in a Mexico study in which the concentration of arsenic in wastewater used as drinking water for cow was 0.01 ± 0.004 mg/L (Numa Pompilio *et al*., 2021), this is expected as the wastewater in the Mexican study was said to be polluted by textile, refreshment and chemical industries in addition to volcanic sources. The concentration of arsenic in the outlet stream water in the dry season in this study was 0.021±0.005 µg/mL, this is lower than that obtained in a study in Dhaka in Bangladesh in which the mean arsenic concentration obtained in textile wastewater was 4.5 ± 0.75 mg/L (Islam *et al*., 2016). This suggests that the industrial waste had impacted a high level of arsenic in the Dhaka wastewater analysed in the Bangladesh study. There was about a seven (7) folds increase in the concentration of arsenic in the dry season as compared with the rainy season in this study.

Mercury in sewer and outlet stream

The concentration of mercury obtained in the sewer wastewater in the rainy season in this study was 0.007 ± 0.001 µg/mL, this is three (3) folds lower than that obtained in Mexico study in which the mercury concentration in hospital effluent was 0.021 ± 0.001 mg/L, (Perez-Alvarez *et al*., 2018). This could suggest that the treatment of the effluent in this study had taken care of the mercury concentration in the wastewater as compared to that in the Mexico study. The concentration of mercury obtained in the sewer in the wastewater in the dry season in this study was 0.003±0.001 µg/mL, this is higher than that obtained in a Paris study in France in which the median mercury concentration obtained in wastewater in the dry season was 0.12 µg/L and the range was 0.07 – 0.29 µg/L (Gasperi *et al*., 2008). This could suggest that the Paris wastewater treatment system had better efficiency than that examined in this study. There was a reduction in concentration to less than one-half of mercury concentration in the dry season in this study as compared to the rainy season.

The mean concentration of mercury in the outlet stream obtained in this study in the rainy season was 0.004 ± 0.03 µg/mL, this is far higher than that obtained in an Italian study in which the mercury obtained in the study was 144.7 ng/L in the chlor-alkali channel (Covelli *et al*., 2009). This suggests that the outlet stream in this study is a more potent source of mercury contamination as compared to that examined in the Italy study. The mean concentration of mercury in the outlet stream in the dry season in this study was nd, this is far lower than that obtained in Arabian Gulf in which the mercury concentration was 0.84 ± 0.15 µg/L (Mahboob *et al*., 2022). The treatment in the sewer in this study area could have eliminated mercury in the dry season which necessitates the low level obtained in this study as compared to that in the Arabian Gulf. There was no significant difference between the mercury concentrations in the outlet streams obtained in the rainy season and dry season in this study.

Conclusion

This study observed an absolute frequency of detection (100%) for all the phthalate esters (DMP, DEP, and DBP) in all the samples in all seasons, which suggests that comprehensive activity in the hospital and homes in the area studied resulted in phthalate esters leaching extensively into the sewer wastewater and the outlet stream. The phthalate esters concentrations in the wastewater were very high in both sewer and outlet stream which suggests the possible contamination in the food chain along the stream channel. The heavy metals (Pb, Cr, Cd, As, and Hg) examined almost showed a similar trend in the frequency of detection except for chromium and mercury which were not detected in the sewer in the rainy season and outlet streams in the dry season respectively. There was a considerable impact on lead levels in the wastewater as the lead concentrations in all the wastewaters examined in this study were higher than the WHO recommended limit in surface water. This high level of heavy metals observed in the wastewater could be a source of contamination to the population in the immediate environment who could depend on this stream for various purposes. This research established leaching of phthalate esters as well as heavy metals contamination in the sewer wastewater and the outlet streams examined in this study. The observed level of phthalate esters and heavy metals in the sewer and outlet stream provides ample evidence of the need to review the sewage treatment methods in the sewer examined in this study.

Declarations

Acknowledgement

The authors gratefully acknowledge the Head of the Department of Chemical and Food Sciences, College of Natural and Applied Sciences, Bells University of Technology, Ota, Ogun State Nigeria, for the conducive environment provided for this research.

Conflict of Interest

The authors declare that no funding has been received and therefore no conflict of interest

Funding

The authors declare that this research was not funded by any organization

Authors Contribution statement

1. Olumayowa Joshua ONIPEDE, (Corresponding author): Supervised the field and laboratory work of this study and prepared the manuscript.
2. Dr. Chijioke Emmanuel CHIGBUNDU, (Co-Author): Co-Supervised the field and laboratory work of this study and made contribution to the preparation of the manuscript.
3. Mr. Olayinka Omoniyi ONIFADE, (Co-Author): Carried out the field and laboratory work of this study and made contribution to the preparation of the manuscript.
4. Prof. G.O. ADEWUYI, (Co-Author): Provided mentorship on the field and laboratory work of this study as well as in the preparation of the manuscript.

Data Availability Statement

The data generated from this study have been included in this published article.

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