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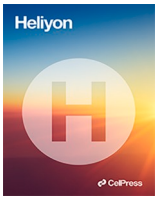

Research article

Phthalate esters in water and sediment of Asunle stream of Obafemi Awolowo University, Ile-Ife, Nigeria: Distribution and human health risks

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ABSTRACT

This study determined the concentrations and seasonal variations of phthalate esters (PAEs) in water and sediment samples of the receiving stream within the vicinity of the Obafemi Awolowo University, Ile-Ife dumpsite. The objective of this study was to evaluate the pollution status of the study area by determining the levels of PAEs in water and sediment samples. This assessment aimed to understand the presence and extent of phthalate ester pollution in the study area. Water and sediment samples were collected from six selected stations along the receiving stream for analysis that included one upstream and five downstream points for four months during both wet season and dry season. The liquid-liquid extraction (LLE) method was employed to extract PAEs from the water samples collected, while microwave extraction method was optimized for their extraction in sediment samples. Quantification of the PAEs was conducted using Gas Chromatography coupled with a quadrupole Mass Spectrometer (GC-MS) in this study. The mean concentration of phthalates varied in the water and sediment samples. In the water samples, the phthalate concentrations ranged from 1.88 ± 0.16 μg/L for diethyl phthalate to 15.74 ± 0.33 μg/L for di(2-ethylhexyl phthalate) (DEHP). Also, butylbenzyl phthalate and DEHP will pose potential carcinogenic risks when used for bathing and drinking purposes, due to their relatively higher carcinogenic risk values. In the sediment samples, the concentrations ranged from 0.09 ± 0.02 mg/kg for dimethyl phthalate to 14.27 ± 1.76 mg/kg for di(2-ethylhexyl phthalate). The seasonal variation analysis of PAE congeners revealed that higher levels were observed during the dry season in the collected samples. The study concluded that the stream was heavily contaminated with di(-2-ethylhexyl)phthalate at levels that gave cause for human health and environmental concerns.

1. Introduction

Globally, the contamination of drinking water with several chemicals including emerging contaminants, heavy metals etc. is becoming a public health concern [1]. This is particularly brought about by an upsurge in anthropogenic activities tied to the increasing global population. Consequently, this results in the indiscriminate disposal of wastes into the environment [2,3]. More

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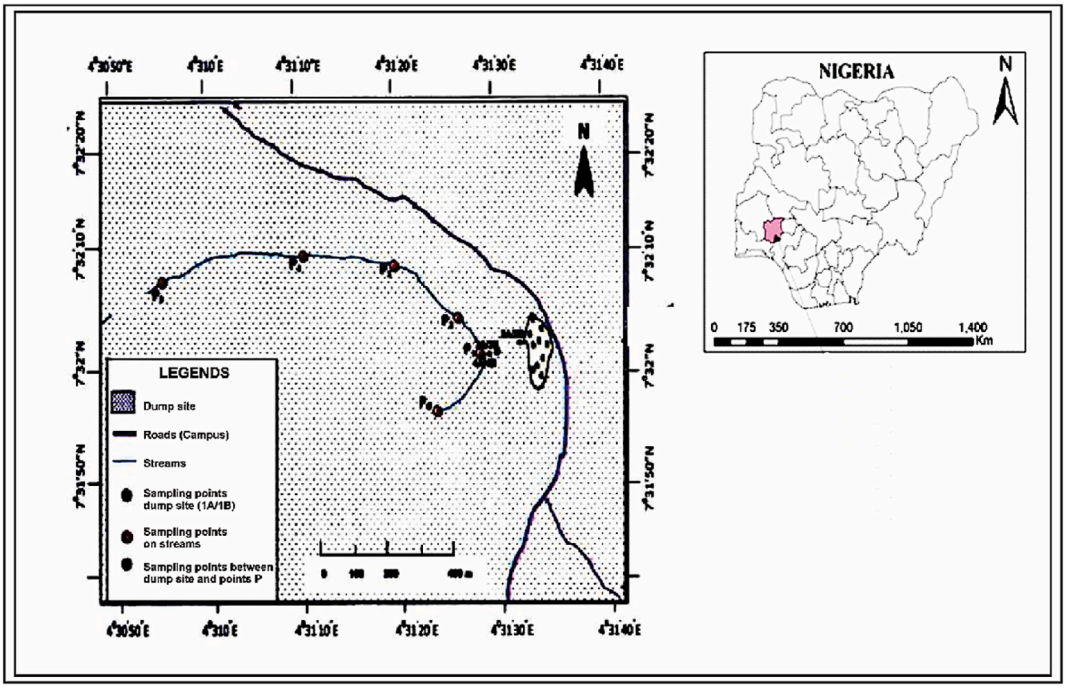

Fig. 1. Map of the study area.

recently, the presence of emerging contaminants has been identified as a predominant problem in the environment, commonly found in water [4,5].

The extensive use of phthalic acid esters (PAEs) as plasticizers and additives is well recognized in various industries and has led to its occurrence in plastic products, rubber, pesticides, furnishings, medical devices, toys, paints, nutritional supplements, pharmaceuticals, and cosmetics products [6–9]. Their particular introduction into these products is aimed at increasing the flexibility, durability, longevity and transparency of plastics and polymers such as Polyvinylchloride (PVC), polyethylene terephthalate, cellulosic and polyvinyl acetate [10]. PAEs have been classified as priority pollutants by the U.S. Environmental Protection Agency (EPA 2009). They are either high (7–13 carbon atoms) or low molecular weight (3–6 carbon atoms) compounds and are not chemically bounded to substances. Hence, they can easily be injested, absorbed to the skin, inhaled and also released into food processing and packaging materials [11,12].

The disposal of these products into the environment as from sources like solid and liquid waste from industrial and municipal wastes, usage of sewage sludge and evaporation of PAE containing products brings about release of PAEs into the environment [11–13]. This is because of the poor covalent bonding between these plasticizers and the vinyl polymer matrix of the polymers [8].

Studies have reported the presence of PAEs and their metabolites in human blood, urine, and breast milk [9]. Exposure to PAEs has been associated with detrimental effects on various human systems, including the liver, respiratory system, kidney, and endocrine system [10]. These effects can be significant and have been reported as being potentially harmful. Other known effects of PAEs include increased abdominal obesity and insulin resistance, reproductive problems, and asthma [13].

The indiscriminate dumping of refuse and its inadequate management in Nigeria has emerged as a significant environmental concern. Some of these waste materials sometimes dumped near rivers and streams have resulted in gross contamination of both surface and ground water along with associated sediments [14,15]. The current study site has been designated as the primary dumpsite for the disposal of waste from the Obafemi Awolowo University, located in Ile-Ife, Nigeria for over four decades. Adjacent to the dumpsite is the Asunle stream, which serves as a vital water source for rural communities located downstream. Unfortunately, the proximity of the stream to the dumpsite exposes these communities to the chemicals present in the waste, posing potential health risks and consequences. To date, no scientific study has been conducted to assess the presence and concentrations of PAEs in the aquatic ecosystems of the Asunle stream. This knowledge gap highlights the need for further research to investigate the potential contamination and impact of PAEs on the stream's ecosystem. Therefore, this study determine the levels of phthalate ester plasticizers, including dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), and di (2-ethylhexyl)phthalate (DEHP), in both water and sediment samples collected from the receiving stream of Obafemi Awolowo University, Ile-Ife. It also investigate the seasonal variations in their concentrations and evaluate the associated health risks.

2. Materials and methods

2.1. Description of the study area

Asunle stream is a perennial river that originates from a location known as point P_0 (Fig. 1) The Asunle stream is situated within the coordinates of latitude 7°32′104″N and longitude 4°30′780″E. Its location is approximately 0.1 km uphill from the Obafemi Awolowo University, lle-Ife refuse dumpsite. The Asunle stream runs for a distance of over 10 km, passing through various human communities including Abagbooro, Agbogbo and Amuta. There are constant and vigorous human activities around the stream; Along the course of the river, farmers rely on water from the Asunle stream for various agricultural activities. This includes using the water for palm oil processing, irrigation of vegetables, as well as mixing and diluting pesticides for spraying on crops such as cocoa and others downstream, the water from the Asunle stream is utilized for household purposes by the local residents [16]. The farmlands surrounding the Asunle stream are primarily used for cultivating a variety of crops. Cash crops such as cocoa, cola nut, and palm trees are commonly planted, while food crops including cassava, maize, yam, cocoyam, plantain, banana, pineapple, oranges, pepper and various vegetables are also cultivated in the area. The major dumpsite of Obafemi Awolowo University, which has been operational since 1971, is located within the latitudes 07°31′994″N-07°32058″N and longitudes 00431470″E−00431490″E. Situated at an elevation of 318 m above sea level, this dumpsite contributes to continuous runoff into the Asunle stream. The dumpsite at Obafemi Awolowo University serves as the ultimate disposal site for a significant quantity of plastic product wastes, as well as other forms of waste generated within the university community. It acts as the final destination for the disposal of various waste materials accumulated on the university premises. The amount of this waste has increased over time because of increase in population of the University community over the years and the refuse are subjected to open air incineration at regular interval.

2.2. Reagents, standards and equipment

Sodium chloride, hydrochloric acid was purchased from Aldrich-Sigma, South Africa through their Nigerian based vendors. Ethyl acetate, acetonitrile, acetone, dichloromethane, sodium tetraoxosulphate, hexane, phthalate standard stock solutions (1000 mg/L), butyl benzoate (internal standard), silica gel (Kieselgel, 60–200 and 230–400 mesh) and others were bought from Aldrich-Sigma, Merck, Fisher and WVR Scientific Chemicals, USA. In this study, all solvents used were of high-performance liquid chromatography (HPLC) grade, ensuring their high purity and suitability for analytical purposes. Additionally, other chemicals employed in the study were of analytical grade, meeting the required standards for accurate and reliable analysis. A working phthalate ester standard mix containing 2000 mg/mL (of each phthalate of interest) standard solution made from USEPA PAEs mix (4S8231) procured from Supelco Analytical (Philadelphia, PA, USA) was appropriately processed and made ready for use by transferring 500 μL from a stock solution into a 5 mL Teflon capped graded amber glass vial and filled to volume with dichloromethane. The working standard solutions were prepared on a monthly basis and subsequently stored at a temperature of 4 °C for preservation and stability. On the day of analysis, calibration standard solutions were freshly prepared using the working standard. The concentrations of the calibration standards were set at 1.0, 1.5, 3.0, 6.0, 12.0, 24.0, and 50.0 mg/L. The preparation involved diluting the working standard in dichloromethane. Microwave Biotage initiator classic (MAE) and Gas Chromatography–Mass Spectrophotometry (GC-MS) – Hewlett-Packard 6890 with Hewlett-Packard 5973 Mass Selective Detector available at University of Idaho, USA, was used for this study.

2.3. Sample collection and pre-treatment

To conduct this study, a total of six water and sediment sampling stations were established and strategically located within the study area as depicted on the corresponding map (Fig. 1). These stations were chosen to ensure representative sampling across different sections of the area under investigation. The first section (the stream source and control site) was taken as the control point (P_0), while the remaining five points (P_1) (closest site to the dumpsite), were sampled between June 2014 and September 2014, during the wet season, monitoring points (P_2, P_3, P_4, and P_5) were established at approximately 100-m intervals along the river downstream. Similarly, from November 2014 to February 2015, during the dry season, these same monitoring points were utilized for data collection purposes. Water samples were collected using 2.5 L Winchester bottle with screw caps. The water collected from the specific location was utilized to rinse the bottles on three occasions prior to conducting the sampling process. To preserve the samples and prevent any changes in the organic compounds caused by microbial activities, approximately 5 mL of concentrated hydrochloric acid (HCl) was added immediately to acidify the samples. Following acidification, all water samples were stored in a refrigerator at a temperature of 4 °C until they were ready for analysis. Bottom sediment samples were collected from the identical water points using a clean handheld trowel. Aluminum foil, which had been pre-cleaned with acetone, was used to wrap the collected sediment samples, ensuring their preservation and preventing contamination during transportation and storage. Upon collection, the samples were air dried within a period of five days. Subsequently, the dried samples were ground and passed through a 500-μm stainless steel sieve that had been pre-cleaned with acetone. The sieved samples were then stored in airtight aluminum foil to maintain their integrity and kept at a temperature of 4 °C in a refrigerator until the time of analysis. This storage method helped preserve the samples and minimize potential degradation prior to analysis [17].

To mitigate potential contamination from phthalates, precautions were taken during the sampling process. No plastic apparatus was utilized to avoid introducing additional phthalate sources. Instead, amber bottles made of glassware were employed for sample collection. Prior to use, all glassware underwent a thorough cleaning procedure. Sequentially, the glassware was washed with a 10 % soap solution (Laboline, Fischer Scientific) and tap water. Subsequently, it was rinsed with a 50 % hydrochloric acid solution to further

ensure cleanliness and eliminate any residual contaminants. These measures were implemented to maintain the integrity of the samples and prevent potential interference from external sources of phthalates. The washed glassware were soaked in dilute H_2SO_4, dried in an oven 105 °C for 4 h, and then thoroughly rinsed with HPLC grade acetone prior to use.

To assess the potential background contribution from laboratory media, glassware, solvents, and instruments, blank samples were analyzed. These blank samples, devoid of any target analytes, were subjected to the same sample preparation and analytical procedures as the actual samples. By analyzing these blanks, any potential contamination or interference originating from the laboratory environment or the analytical process itself could be identified and accounted for, ensuring accurate assessment of the target analytes in the samples. Blanks were prepared using ultrapure Milli-Q water, which is known for its high purity. The blanks were subjected to the same processing steps and procedures as the actual samples. The method's accuracy was evaluated by analyzing seven replicate samples of ultrapure Milli-Q water blanks. These blanks were spiked with PAEs standards at a concentration level of 2.5 mg/L. The accuracy was assessed by calculating the recovery percentage, which represents the extent to which the spiked PAEs were successfully recovered from the blanks. Furthermore, the precision of the analysis was assessed by calculating the relative standard deviation (RSD) of the seven replicates for the spiked concentrations mentioned above. The RSD provides an indication of the variability within the replicates and is used to evaluate the precision of the analytical method.

To determine the limit of detection (LOD) and limit of quantitation (LOQ), a practical approach was employed. This approach involved measuring increasingly diluted concentrations of the analytes in an empirical manner. The LOD represents the lowest concentration at which the analyte can be reliably detected, while the LOQ represents the lowest concentration at which the analyte can be accurately quantified with acceptable precision [18].

2.4. Extraction of phthalates from sample matrices

2.4.1. Water sample

Each water sample, totaling 500 mL (x3), underwent a salting process in a1 L separatory funnel with the addition of 20 g of sodium chloride (NaCl). Following salting, the sample was subjected to exhaustive liquid-liquid extraction using 10 mL (x6) of dichloromethane (DCM). The DCM extracts were combined, and to eliminate interference from free fatty acids (FFA), an additional extraction step was performed using three portions of 10 mL of 0.1 M sodium carbonate (Na_2CO_3). After the alkali washing step, the DCM extract was subjected to drying using anhydrous sodium sulfate (Na_2SO_4) and then evaporated to dryness at room temperature. The resulting dried extract was reconstituted in 2 mL of DCM, preparing it for subsequent chromatography clean-up on a column, followed by GC-MS determination [19].

2.4.2. Microwave-Assisted Extraction (MAE) of phthalate esters from sediment samples

United State Environmental Protection Agency (USEPA) method 2546 (USEPA 2007) as explained by Liang et al. [20] was adopted. The parameters that were optimized includes temperature (60, 80, 100, 120, 149, 160 °C), time (5, 10, 15, 20, 30 min), solvent and solvent mixture (DCM; Acetonitrile; ethyl acetate; Acetone (2:1, 1:1): DCM), volume of solvent and sample ratio (5mL/2.5g, 10 mL/5.0 g). The reference soil sample, both spiked and unspiked, was subjected to a series of preparation steps. Firstly, the soil sample was air dried and then sieved using a sieve with a pore size of 0.50 μm. For the spiked sample, 5 g of the sieved soil was taken and spiked with 2 mL of a mixture containing 2.5 mg/L of each of the phthalate standards. Additionally, 12.5 mg/L of the internal standard (benzyl benzoate) was also added to the spiked sample. The specified volume of soil sample was placed in the MAE (Microwave-Assisted Extraction) extraction vessel, and then the extraction solvent was added to the vessel. The extraction vessel was tightly sealed to ensure a gas-tight environment, and then it was vigorously shaken for several seconds to facilitate the extraction process, subsequently, the sealed extraction vessel was placed inside the microwave sample preparation system for further processing. Before the actual extraction process, the sample in the extraction vessel was pre-stirred for a duration of 10 s. This step was conducted to ensure thorough mixing and distribution of the sample within the extraction solvent. Once the extraction process was completed, the vessel was taken out of the microwave and left to cool down to room temperature. The extracted solution was transferred from the extraction vessel to a centrifuge bottle. The centrifuge botle containing the extract was then placed in a centrifuge and spun at a speed of 3000 rpm(revolutions per minute). The remaining residue in the centrifuge bottle was subjected to three washes. Each wash involved adding 5 mL of the extraction solvent to the residue,and this process was repeated three times. The collected portions of the solvent were combined, and the resulting mixture was subjected to evaporation using a gentle stream of nitrogen until it reached a near-dry state. The remaining residue was reconstituted by dissolving it in 2 mL of dichloromethane (DCM). This step was performed to prepare the residue for chromatography clean-up. Qualitative identification and qualitative estimation of the analytes of interest was done using GC-MS.

2.5. Column chromatographic clean-up for the extracts

The extract from water and sediment (reconstituted in 2 mL of DCM) was introduced onto silica gel chromatographic column (250 mm × 10 mm i.d.) to remove interference molecules. A column was prepared by first placing a small piece of glass wool at the base, followed by 2 g of sand. On top of the sand, a slurry of 5 g of silica gel in 20 mL of n-hexane was added. This packing arrangement helped to create an effective chromatography column for the clean-up process. The sand and silica gel served as adsorbents, which would selectively retain impurities while allowing the target compounds to pass through. Above the silica gel, a layer of anhydrous sodium sulfate measuring 2 cm in height was added. This addition of sodium sulfate helped to further remove any residual moisture present in the sample. Once the column was properly packed, it was washed with 10 mL of ethyl acetate, and the extract containing the

Table 1
Used to generate exposure dose estimates.

Specific parameters	Units
Body weight (kg)	70
Life time (yrs)	70 yrs
Exposure period (yrs)	30 yrs
Drinking water	350 days/yr; 2 L/day, 2 days/week, 100 % fraction contaminated
Dermal absorption	350 days/yr; 2300 cm^2 skin surface, 12 min/day

Source: Fatoki et al. (2010)

target compounds was carefully loaded onto the column, After loading the extract onto the column, it was eluted sequentially with 20 mL of n-hexane. This step aimed to selectively remove hydrocarbons that might be present in the sample. The phthalate compounds were specifically eluted from the column using 20 mL of ethyl acetate. The eluate containing ethyl acetate was subjected to gentle stream of nitrogen to facilitate evaporation and drying of the solvent. The dried residue obtained from the previous step was reconstituted by dissolving it in 2 mL of a solution containing 12.5 mg/L of benzyl benzoate, which served as the internal standard. This mixture was prepared in n-hexane. The reconstituted sample was then transferred to a glass vial in preparation for analysis using GC-MS(Gas Chromatography-Mass Spectrometry).

2.6. Instrumental analysis

The analysis of phthalates in water samples using GC-MS was validated following the quality management guidelines of Institute Bachema AG, which are certified by ISO 17025. (Institute Bachema, 2004; 2006). The instrumental analysis was performed using GC-MS equipment located at the Mass Spec Core Lab., Renfrew Hall, Room 30, University of Idaho, USA. Phthalate calibration standards were prepared in methylene chloride across a range of 0–50 mg/L; the calibration standards contained five phthalates. The identification of analyteswas conducted by comparing their retention times with those of reference standards. Quantification was performed by measuring the peak area of the targeted compounds using the internal standard technique. The amount of each compound was calculated by determining the ratio of the peak response of phthalate standards to the peak response of the internal standard, utilizing a multipoint calibration curve.

2.7. Human health risk assessment of phthalates in the stream water

The primary focus of this study was on the resident communities in the area who rely on water from the sources of Asunle stream for drinking and bathing. The Health Risk Assessment Programme (Risk*Assistant™, 1995) was utilized in calculating the potential exposure concentrations (Table 1). The exposures that were taken into consideration in the assessment encompassed the following factors.

(a) Exposure via Drinking of Untreated Water

In a quantitative health risk assessment,the numerical estimates of human exposure to toxic effects are quantified using an exposure index (EI), The exposure index (EI) for exposure via drinking is calculated as the amount of the substance taken into the body on a daily basis during the exposure period and it is mathematically expressed in equation (1) below:

$$EI = \frac{(C_{medium} \times IR \times ED \times EF)}{BW} \times AT\left(\frac{\frac{\mu g}{kg}}{bw/day}\right) \quad [1]$$

where: EI (μg/kg bw/day) is the contaminant exposure to adult through ingestion of drinking.

water; C_{medium}(μg/L) is the concentration of phthalate in the contaminated water; IR is the daily water intake in liters; ED (exposure duration) is designated as lifetime in years; EF is the exposure frequency which is the number of days (365) exposure in years; BW is the body weight and AT (averaging time) is exposure duration x 365 days/year [21].

Equation (2) was used to determine the hazard quotient (HQ) based on the calculated average daily dose (ADD) to assess the potential non-carcinogenic risk (USEPA, 1989) as;

$$HQ = \frac{ADD}{RfD} \quad [2]$$

where RfD represents individual phthalate reference dose as given in USEPA(2013). The RfD for DEP, DBP, BBP and DEHP were 0.8, 0.1, 0.2 and 0.02 mg/kg/day, respectively.

The carcinogenic risk (CR) of DEHP and BBP was calculated using equation (3) below:

$$CR = SF \times ADD \quad [3]$$

Table 2
Quality Assurance/quality parameters for phthalates extraction and analysis.

Percentage RSD	7.2	5.3	4.9	5.6	7.6
Percentage Recovery for water simple (n = 3)	78	106	96	101	111
LOQ mg/L n = 7	0.1	0.01	0.01	0.01	0.1
LOD mg/L n = 7	0.01	0.001	0.001	0.001	0.01
Retention time	6.05	7.02	9.60	12.20	13.16
Quantifier ion (*m/z*)	163	149	149	149	149
Qualifier ions (*m/z*)	163, 77, 194, 72	149, 177, 76, 105	149, 223, 205, 56	149, 91, 65, 206	149, 167, 279, 91
Linearity	0.998	0.998	0.998	0.998	0.996
Chemical formula	$C_{10}H_{10}O_4$	$C_{12}H_{14}O_4$	$C_{16}H_{22}O_4$	$C_{19}H_{20}O_4$	$C_{24}H_{38}O_4$
Pthalates	DMP	DEP	DBP	BBP	DEHP

Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butylbenzyl phthalate (BBP), and Di(2-ethylhexyl)phthalate (DEHP).

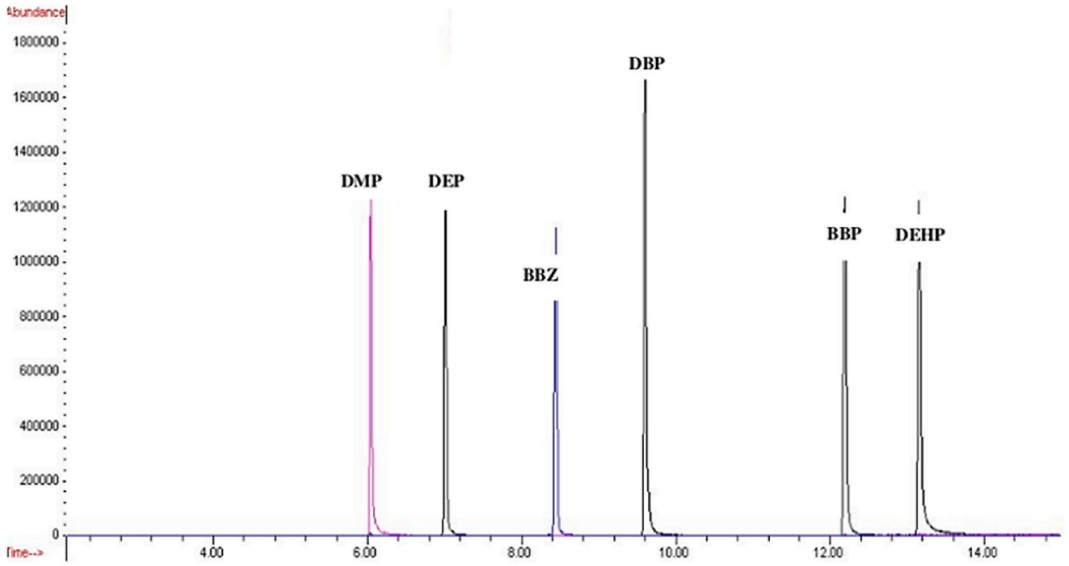

Fig. 2. Gc spectrum of phthalates standard and internal standard.

Where SF is the slope factor $(mg/kg/day)^{-1}$ (DEHP = 0.014; BBP = 0.019; USEPA 2013). If $R < 10^{-6}$,we have low carcinogenic risk; and $R > 10^{-6}$ implies high carcinogenic risk.

(b) Exposure via Bathing with Untreated Water (Dermal Contact)

Dermal absorption of contaminants in water can occur during activities such as bathing or swimming, and its significance as a route of exposure depends on the specific characteristics of the substances involved. The Dermal Risk Assessment (USEPA 1989) provides dermal permeability coefficients for phthalates, with values of 0.001, 0.004, 0.024 and 0.025 assigned to DMP, DEP, DBP and DEHP, respectively. These coefficients are used to assess the potential dermal exposure and absorption of these phthalates. When the permeability coefficient for a chemical is known, the dermal absorption of the chemical from water can be estimated using equation (4):

$$EI = \frac{(C_{medium} \times P \times SA \times ET \times CF)}{BW}\left(\frac{\frac{mg}{kg}}{bw/day}\right) \quad [4]$$

where: EI (mg/kg bw/day) is the contaminant exposure to adult through bathing with the stream water; C_{medium} (mg/L) is the concentration of phthalate in the contaminated water; P is the Permeability Coefficient in cm/hr; SA exposure surface area in cm^2; ET is the exposure time in hours/day; CF is the conversion factor (1 L/1000 cm^2) and BW is body weight in kg [21,22].

2.8. Ecological risk assessment

The calculation of risk quotient (RQ) was used in assessing the ecological risks posed to the three sensitive aquatic species (EC

Table 3
Levels (μ g/L) of PAEs in Water of Asunle Stream.

Year	MONTH	DMP	DEP	DBP	BBP	DEHP	$\sum_s$PAEs
2014	JUNE	BDL	$0.58 \pm 0.39^{b,a}$	2.47 ± 0.25^{a}	1.92 ± 0.34^{a}	$9.54 \pm 1.02^{a,b}$	14.51 ± 2
	JULY	BDL	0.61 ± 0.34^{a}	3.51 ± 0.26^{a}	4.69 ± 0.22^{a}	$9.13 \pm 0.26^{a,b}$	17.94 ± 1.08
	AUGUST	BDL	0.30 ± 0.17^{a}	0.58 ± 0.26^{a}	BDL	45.02 ± 0.39^{b}	45.90 ± 0.82
	SEPTEMBER	BDL	BDL	1.48 ± 0.11^{a}	0.94 ± 0.11^{a}	1.39 ± 0.14^{a}	3.81 ± 0.36
	NOVEMBER	BDL	0.05 ± 0.02^{a}	0.87 ± 0.10^{a}	0.58 ± 0.06^{a}	0.91 ± 0.14^{a}	2.41 ± 0.32
	DECEMBER	BDL	0.06 ± 0.03^{a}	1.05 ± 0.20^{a}	BDL	$10.92 \pm 0.12^{a,b}$	12.03 ± 0.35
2015	JANUARY	BDL	0.07 ± 0.03^{a}	BDL	BDL	1.86 ± 0.20^{a}	1.93 ± 0.23
	FEBRUARY	14.12 ± 0.22^{b}	11.52 ± 0.16^{a}	14.93 ± 0.22^{b}	1.66 ± 0.11^{b}	$47.21 \pm 0.41^{a,b}$	89.44 ± 1.12
	Mean	14.12 ± 0.22	1.88 ± 0.16	3.55 ± 0.20	1.95 ± 0.16	15.74 ± 0.33	

❖BDL = below detection limit, Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butylbenzyl phthalate (BBP) and Di(2-ethylhexyl)phthalate (DEHP).

2003). The risk quotient was calculated using equation (5) [23]:

$$RQ = \frac{MEC}{PNEC} \quad [5]$$

Where MEC = Measured environmental concentration and PNEC = predicted no-observed-effects concentration. The PNEC value shows the concentration of a sample whereby an unfavourable effect may not occur. Values of required parameters are detailed elsewhere [24].

2.9. Quality control and quality assurance

The reliability of the analytical procedures used in this study was assessed by testing the sensitivity of the calibration curves. Linear curves with high correlation coefficients (R^2) ranging from 0.996 to 0.998 were obtained for the five analyzed PAEs using linear least squares analysis. The recovery, precision (%RSD), LOD and LOQ are given in Table 2. The extraction method for water showed recoveries of 78–111 % for the phthalates and the %RSD was between 4.9 and 7.6. The limit of detection (LOD, n = 7) and the limit of quantitation (LOQ, n = 7) for congeners are in the order of 0.001–0.01 mg/L and 0.001–0.1 mg/L, respectively. The highest percentage recoveries for microwave extraction of the five phthalates was recorded when 2.5 g of the reference soil was extracted with 5 mL of acetonitrile at a temperature of 120 °C, a pressure of 8 barr and within a time frame of 20 min. The recovery is in the range of 71.00–113.24 % and the relative standard deviation (RSD) ranged from 2.53 to 7.00 %. The PAE congeners eluted based on their molecular size where compounds with low molecular weight were eluted first followed by heavier molecules. The order of elution of these compounds was DMP < DEP < DBP < BBP < DEHP and the retention time are 6.05, 7.02, 9.60, 12.20 and 13.15, respectively (Table 2). For the internal standard, BBZ, the retenton time was 8.40. The quantification of the PAEs using MS was based on the detection of the phthaic anhydride ion signal at *m/z* 149, except for DMP which had a base peak at *m/z* 163 (Table 2). The chromatogram of phthalate congeners standard at concentration of mg/L is shown in Fig. 2.

2.10. Data analysis

Graphical analysis was performed using Microsoft Excel 2019 and statistical analysis was conducted using the Statistical Package for Social Scientists (SPSS) version 20. The principal component analysis was the chosen statistical method to identify the sources of PAE chemical compounds in Asunle river. Mean value and standard deviations were calculated to summarize the data.

3. Results and discussion

3.1. Seasonal variation of PAE concentration in water and sediments of Asunle Stream

The levels of PAEs in the water samples are provided in Table 3. The $\sum_5$PAEs concentraions ranged from 1.93 ± 0.23 μg/L in January to 8.94 ± 1.12 μg/L in February. Wet season in the study area is between June and September while dry season is between November and February. The levels of DMP was below detection limit (BDL) during the wet season while it ranged from BDL - 14.12 ± 0.22 μ g/L during the dry season. DEP levels ranged from BDL - 0.61 ± 0.34 μ g/L during wet season and 0.05 ± 0.02–11.52 ± 0.16 μ g/L during dry season. The concenrations of DBP ranged from 0.58 ± 0.26–3.51 ± 0.06 μ g/L during wet season while it ranged from BDL – 14.93 ± 0.22 μ g/L during dry season. BBP levels during wet season ranged BDL - 4.69 ± 0.22 μ g/L while it ranged from BDL - 1,66 ± 0.11 μ g/L during dry season. DEHP levels ranged from 1.39 ± 0.14–45.02 ± 0.39 μ g/L during wet season while it ranged from 0.91 ± 0.40–47.21 ± 0.41 μ g/L during dry season. Against the popular idea that leaching of contaminants during rainfal1 from nearby refuse dumpsites into the receiving stream was the principal source of PAEs in stream water, PAEs concentrations of the studied water samples were relatively higher during the dry season. The presence of PAEs in the water samples may be attributed to the deposition of

Table 4
Levels (mg/kg) of PAEs in sediments of Asunle stream.

Year	MONTH	DMP	DEP	DBP	BBP	DEHP	∑$_s$PAEs
2014	JUNE	0.19 ± 0.04^{a}	0.16 ± 0.05^{b}	1.31 ± 0.11^{a}	0.66 ± 0.08^{a}	4.94 ± 0.38^{a}	7.26 ± 0.66
	JULY	BDL	0.19 ± 0.20^{a,b}	0.78 ± 0.15^{a}	1.01 ± 0.31^{a}	14.28 ± 0.25^{a,b}	16.25 ± 0.91
	AUGUST	BDL	BDL	0.17 ± 0.07^{a}	0.10 ± 0.05^{a}	1.64 ± 0.17^{a}	1.91 ± 0.29
	SEPTEMBER	BDL	0.21 ± 0.21^{a,b}	0.18 ± 0.12^{a}	0.18 ± 0.11^{a}	8.46 ± 0.70^{a}	9.03 ± 1.14
	NOVEMBER	BDL	BDL	0.29 ± 0.04^{a}	0.97 ± 0.19^{a}	13.62 ± 0.42^{a,b}	14.88 ± 0.65
	DECEMBER	0.07 ± 0.01^{a}	BDL	7.34 ± 1.04^{b}	17.35 ± 1.77^{b}	26.99 ± 4.59^{b}	51.75 ± 7.41
2015	JANUARY	BDL	0.10 ± 0.04^{a,b}	1.64 ± 0.38^{a}	6.47 ± 1.38^{a}	2.93 ± 0.45^{a}	11.14 ± 2.25
	FEBRUARY	0.01 ± 0.03^{a}	0.08 ± 0.22^{a,b}	0.24 ± 0.08^{a}	0.22 ± 0.18^{a}	1.40 ± 0.31^{a}	1.95 ± 0.82
	Mean	0.09 ± 0.02	0.15 ± 0.14	1.49 ± 0.24	3.37 ± 0.50	9.28 ± 0.90	

❖BDL = below detection limit, Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butylbenzyl phthalate (BBP) and Di(2-ethylhexyl)phthalate (DEHP).

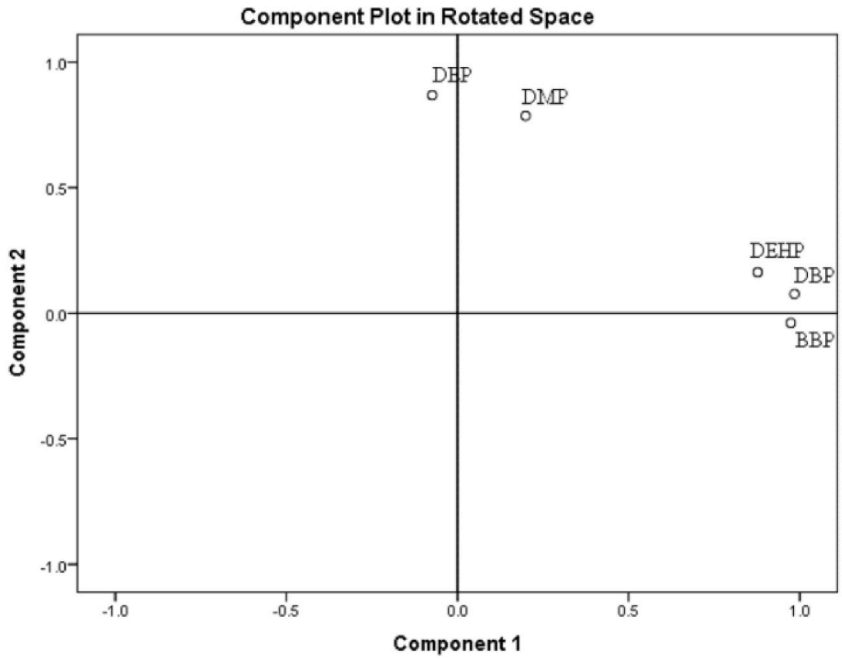

Fig. 3. Component plot of PAEs in water and sediments of Asunle stream.

these compounds from the atmosphere, which could result from the frequent open incineration of solid wastes at the dumpsite [24,25]. Of all the analyzed PAEs, DEHP was detected in the samples during the entire months of study with significantly higher levels during the dry season due to decreased water level which resulted in increased concentration of constituents and contaminants in the water. DEHP is a popular additive in the production of many domestic and industrial products, suggesting that it is the main contributor to the levels of phthalates contamination in the water [23,25]. PAEs levels in the studied stream water were lower than the previous finding of Olutona and Dawodu [25,26] but higher than those ported by He et al. [27], Selvaraj et al. [28], Edjere et al. [29] and Weizhen et al. [30]. The levels of PAEs in the stream sediments are presented in Table 4. The ZsPAEs levels ranged from 1.91 ± 0.29 mg/kg in August to 51.75 ± 7.41 mg/kg in December. During the wet season, the levels of DMP in the water samples varied from below the detection limit (BDL) to 0.19 ± 0.04 mg/kg, while in the dry season, the range was from BDL to 0.07 ± 0.01 mg/kg. DEP levels in the water samples ranged from BDL to 0.21 ± 0.21 mg/kg during the wet season, and from BDL to 0.10 ± 0.04 mg/kg during the dry season in the wet season, the concentration of DBP in the water samples ranged from 0.17 ± 0.07 mg/kg, while in the dry season, it ranged from 0.24 ± 0.08 to 7.34 ± 1.04 mg/kg. BBP concentration ranged from 0.10 ± 0.05–1.01 ± 0.31 mg/kg during wet season while it ranged from 0.22 ± 0.18–17.35 ± 1.77 mg/kg during dry season. The levels of DEHP ranged from 1.64 ± 0.17–14.28 ± 0.25 mg/kg during wet season and from 1.40 ± 0.31–26.99 ± 4.59 mg/kg during dry season. As observed in the water samples, DEHP also had the highest concentration in the sediment samples. There are existing evidences that high loads of PAEs are preferentially associated with sediments rather than water [31] due to the high octanol water partition coefficient and high hydrophobic nature of PAEs [32]. However, the levels of PAEs except for BBP in the studied stream sediments were relatively lower than the PAEs levels of its water. This could be due to sediment resuspension that easily occurs under the influence of wind action, thus leading to the redistribution of PAEs into water, bringing about an upsurge in its PAEs concentrations in the process [33]. The concentrations of PAEs in the sediments of the

Table 5
Health risk assessment of PAEs in water.

PAEs	$EI_{drinking}$	RfD	$HQ_{drinking}$	SF	$CR_{drinking}$	$EI_{bathing}$	$HQ_{bathing}$	$CR_{bathing}$
DMP	4.03E-01	10	4.03E-02	NA	NA	2.78E-04	2.78E-05	NA
DEP	5.37E-02	0.8	6.71E-02	NA	NA	3.71E-05	4.63E-05	NA
DBP	1.01E-01	0.1	1.01E+00	NA	NA	7E-05	7E-04	NA
BBP	5.57E-02	0.2	2.78E-01	0.019	5.29E-03	3.84E-05	1.92E-04	3.65E-06
DEHP	4.49E-01	0.02	2.24E+01	0.014	3.14E-01	3.10E-04	1.55E-02	2.17E-04

❖EI = exposure index, RfD = oral reference dose, HQ = hazard quotient, SF = slope factor, CR = carcinogenic risk, Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butylbenzyl phthalate (BBP) and Di(2-ethylhexyl)phthalate (DEHP).

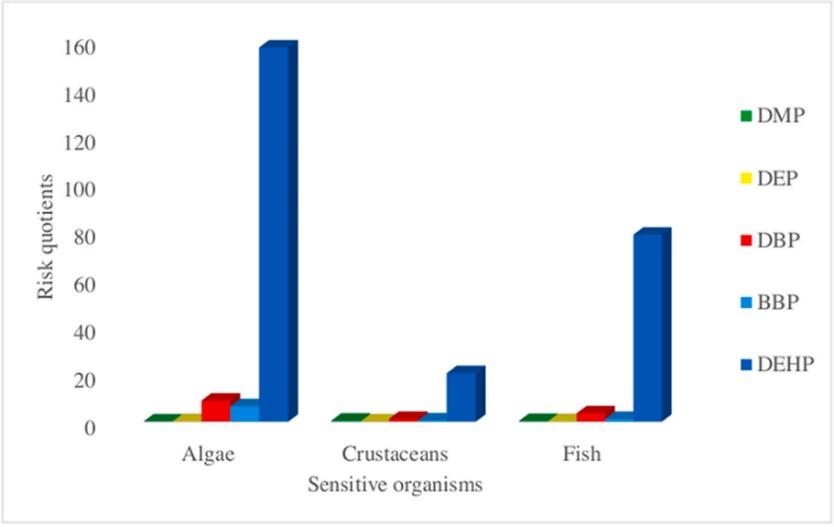

Fig. 4. Ecological risk assessment for PAEs in water of Asunle stream.

investigated stream were found to be elevated compared to the findings of Lee et al. [34] and Li et al. [35].

3.2. Source apportionment of PAEs in water and sediments

Principal component analysis (PCA), a data reduction method utilized to generate interpretable components, was employed to identify the potential sources of PAEs in both water and sediment samples. The number of retained components (via varimax rotation) were determined using eigen values greater than 1. As revealed in the component plot in Fig. 3, two principal components (PC) were retained for the water and sediments of the studied stream. Strong factor loadings, accounting for 55.711 % of data variance, were observed between DBP, BBP and DEHP in PC1 while PC2 had factor loadings of 0.868 and 0.786 for DEP and DMP, respectively. DEHP which represents the major contributor of PAEs contamination in the stream, finds major use in clothing and polyvinyl chloride plastic. Therefore, the main sources of PCl is attributed to plastic pollution. The use of DEP in the production of personal care products, lacquers and cosmetics is also known [36]. Therefore, the main source of PC2 is attributed to the use of personal care products. Summarily, PAEs in water and sediments of Asunle stream probably originated from personal care and plastic products.

3.3. Human health and ecological risk assessment of PAEs in water and sediments

Table 5 presents the calculated non-carcinogenic and carcinogenic health risks associated with the studied phthalates in water samples. Among the prioritized phthalates, DMP, DEP, and DBP are categorized as non-human carcinogens, while BBP and DEHP are classified as human carcinogens [37]. Drinking and bathing are the primary routes of exposure to contaminants present in water. Upon drinking the water, the exposure index (EI) of all the PAEs except DEHP (4.49E-01) were below the reference dose. This indicates that the major concern of non-carcinogenic risks to local residents consuming the water is associated with DEHP. Exposure to the stream water via bathing will not pose any non-carcinogenic risks as EI values are below reference dose. Upon exposure via drinking and bathing, BBP and DEHP will pose potential carcinogenic risks due to their relatively higher CR values than 1E-06, the tolerable limit set by USEPA (2022). While human health risk assessment is an effective estimation of the risks associated with different exposure pathways, many phthalates are endocrine disruptors that possess the ability to induce sever toxicity even at low levels [38].

The ecological risk assessment of PAEs to sensitive organisms at the three trophic levels (algae, crustaceans and fish) in water is shown in Fig. 4. The aquatic toxicity of the investigated PAEs were estimated by calculation of the risk quotients. The risks posed by

Table 6
Screening benchmark (SCB) for phthalates in river and coastal sediment (USEPA 2006).

Phthalate	River sediment MEC (mg/kg)	River sediment SCB (mg/kg)	Estuarine sediment MEC (mg/kg)	Coastal sediment SCB (mg/kg)
DEP	0.185	0.603	0.0013	0.2
DBP	0.664	6.47	0.0085	1.16
BBP	0.0078	10.9	0.0014	16.8
DEHP	1.4	0.18	0.276	0.182

❖Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butylbenzyl phthalate (BBP) and Di(2-ethylhexyl)phthalate (DEHP).

DMP and DEP to the aquatic environment based on algae, crustaceans and fish is negligible or very low. This is in consonance with previous findings [16,33]. The risks posed by DMP and BBP is moderate. DEHP constitutes very high risk to the aquatic environment. This is consistent with the reports of previous findings [16,23,25]. Increased levels of DEHP have been reported to bring about an alteration in immune-related genes as well as inducing oxidative stress in fish [39]. Potential risks associated with phthalates are likely to be expected from aquatic organisms in Asunle stream.

The risk assessment of phthalates in sediments involved the comparison of their average concentrations with the screening benchmark (SCB) values provided in Table 6. All the investigated PAEs had their quantifiable levels lower than SCB freshwater guideline value except for DEHP. The average DEHP level in the studied sediments is over 80 times the SCB guideline value. This assessment is a clear demonstration that the ecologically sensitive species in water are vulnerable to potential risks emanating from DEHP.

4. Conclusion

This present study examined the levels and distribution of PAEs in the water body of the stream receiving the waste from the Obafemi Awolowo University (OAU) dumpsite. The analysis of water and sediment samples from the Asunle stream revealed that the concentrations of PAEs were significantly higher in the water compared to the sediment. Re-suspension of sediments during wind action may have been responsible for this observation. Principal component analysis identified plastic and personal care products pollution as the primary sources of PAEs in the environmental matrix. The health risk assessment indicated that DEHP (diethylhexyl phthalate) was the most significant contributor to potential risks in both water and sediments. Ecological risk assessment indicated that the aquatic wildlife may be expected to exhibit probable risks due to the levels of DEHP. Considering the fact that the water and farm land facilities within the vicinity of the stream are utilized regularly for human uses, appropriate safety and regulatory measures should be adopted to reduce health hazards to humans and the general biota.

CRediT authorship contribution statement

J.O. Fagbemi: Writing – review & editing, Supervision. **J.A.O. Oyekunle:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **A.O. Ogunfowokan:** Writing – review & editing, Supervision, Conceptualization. **I.F. Cheng:** Writing – review & editing, Supervision, Methodology. **L. Deobaki:** Writing – review & editing, Supervision, Methodology.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: J.O. Fagbemi reports travel grant from TETFUND Nigeria and equipment, supplies and consumable were provided by University of Idaho. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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