



Phthalate Esters in Water and Surface Sediments of Anambra River in Dry Season: Distribution and Human Health Risks Assessment

Okeke Abuchi Princewill^{a*}, Ogbuagu Josephat Okechukwu^a,
Arinze Rosemary Uche^a and Ogbuagu Adaora Stellamaris^a

^a Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University Awka, Anambra State, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: <https://doi.org/10.56557/jogee/2024/v20i48886>

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://prh.ikpress.org/review-history/12440>

Original Research Article

Received: 28/07/2024
Accepted: 02/10/2024
Published: 08/10/2024

ABSTRACT

This study investigated phthalate ester (PAE) contamination in water and sediment samples due to their persistence and potential health risks as endocrine disruptors. Sediment analysis revealed pH ranged from 5.35 to 6.72, with total organic carbon (TOC) levels varying between 0.74% and 2.56%. Water pH values were within WHO guidelines (5.5–8.5), and turbidity levels ranged from 0.60 to 1.40 NTU. Phthalate concentrations in sediment revealed Monobutyl phthalate (MBP), Diethyl phthalate (DEP), Dipentyl phthalate (DPP), Butyl benzyl phthalate (BBP), Dibutyl phthalate (DBP), and Di(2-ethylhexyl) phthalate (DEHP). Sample SA exhibited the highest levels of MBP

*Corresponding author: E-mail: abuchiokeke4@gmail.com;

Cite as: Princewill, Okeke Abuchi, Ogbuagu Josephat Okechukwu, Arinze Rosemary Uche, and Ogbuagu Adaora Stellamaris. 2024. "Phthalate Esters in Water and Surface Sediments of Anambra River in Dry Season: Distribution and Human Health Risks Assessment". *Journal of Global Ecology and Environment* 20 (4):52-65. <https://doi.org/10.56557/jogee/2024/v20i48886>.

(0.40 mg/kg) and DEP (0.93 mg/kg). In water samples, MBP peaked at 0.01 mg/kg, while DEP reached 0.03 mg/kg, with DBP (0.07 mg/kg) and DEHP (0.08 mg/kg) also detected. Phthalate contamination in water remained below harmful thresholds. A health risk assessment calculated Chronic Daily Intake (CDI) and Hazard Quotients (HQ) for both children and adults. CDI results indicated higher risks for children, with DBP (2.20×10^{-6} mg/kg/day) and DEHP (2.46×10^{-6} mg/kg/day) showing the greatest concern. The HQ for children was highest for DBP (0.22), though still below the risk threshold. Adults exhibited lower CDI and HQ values, with minimal non-carcinogenic risk. These findings highlight the need for continued monitoring of phthalate pollution, especially given children's heightened vulnerability.

Keywords: Phthalate esters; anambra river; distribution; health risk assessment.

1. INTRODUCTION

Anambra River is a tributary of the majestic River Niger. Due to massive urbanization and economic activities, the level of pollution within the water bodies is a major concern to the ecosystem. Due to discharge of waste and common pollutants such as personal care product, industrial and farming effluents, persistent organic pollutants (POPs) finds its way thereby causing both short and long term effect on human and the environment. According to research, common POPs such as heavy metals, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, phthalates esters, bisphenol A etc. are possible contaminant that can be detected in the river estuary [1,2,3]. Synthetic chemical compounds known as phthalate esters (PAEs) are popular endocrine disruptor that antagonize the actions of hormones in the body system and are well known for their high level of toxicity. Esters of phthalate are commonly used as plasticizers (an additive added to plastic) to help in the manufacturing process by giving the material toughness, flexibility, and softness. In addition, a variety of consumer and industrial goods, such as pharmaceutical coatings, gels, dispersants, lubricants, binders, medical equipment, waxes, detergents, textile fabrics, and kid's toys, are enhanced in quality by PAEs. According to [1,4,5], PAEs are easily absorbed by the environment and are present in soil, water, sediments, the atmosphere, and the biota, which includes humans everywhere. PAEs can contaminate aquatic environments in a number of ways, such as surface runoff and wastewater discharge. Furthermore, PAEs pose a significant risk to aquatic environments due to their ability to bioaccumulate and develop resistance in aquatic organisms. According to [6], by inhibiting the activity of acetyl cholinesterase, several PAEs, such as diethyl phthalate (DEP) and DBP, can cause neurotoxicity in aquatic life. According to other research, the majority of PAEs have

endocrine-disrupting effects. As a result, there is fear that eating aquatic life could expose humans to PAEs in addition to drinking contaminated surface water. In respect to sediments which serves as a sink for PAEs, continuous breakdown of plastics particles containing phthalates bioaccumulate and increases its toxicity coefficient with time. [7] evaluated the seasonal occurrence of selected phthalate esters congeners in sediment, water, and biota in two freshwater bodies (River Owena and River Ogbese) in Nigeria, and to calculate their ecological risks they pose to aquatic organisms. Dibutyl-phthalate (DBP), di-2-ethylhexyl phthalate (DEHP), and dimethyl-phthalate had an all-year presence in various environmental matrices. DBP has a significant capacity to bioaccumulate in fish tissues and was the most common phthalate congener in all environmental matrices. According to the computed estimated risk quotient, both freshwater bodies' fish, invertebrate, and algal populations were very vulnerable to DBP and DEHP. [8] investigated the PAE concentrations and ecotoxicological risk evaluations in eight Pearl River, Xijiang River, river network, and nature reserve reservoir estuaries. Between 2012 and 2014, sediment and water samples were gathered, and 14 distinct PAEs were extracted utilizing solid phase and ultrasonic techniques. The analytical average recovery of PAEs was $75.4\% \pm 4.9\%$ and $121.5\% \pm 8.9\%$, respectively. PAEs were detected in all samples, with detection rates ranging from 66.7 to 100%. The concentrations of $\Sigma 14$ PAEs in water and sediments showed an increasing trend year after year. This research aims to ascertain the ecological and health risk assessment effect of phthalates in water and sediment through ingestion and dermal route in Anambra river by determining the physicochemical properties of the water and sediment, the concentration of phthalates in the water and sediment using Gas Chromatography Mass Spectroscopy (GCMS). Also, it will

investigate the potential carcinogenic and non-carcinogenic risks arising from such exposure.

2. MATERIALS AND METHODS

2.1 Materials Used

The materials used in this research are water and sediments samples.

2.2 Equipment Used

Surface water grab, 5 mm sieve, beakers, filter paper, volumetric flask, separatory funnel, trawls, and neuston nets (for collecting water samples) HANNA pH 209, U.S.A.; Agilent model 6890N GC-5973 MSD gas chromatography mass spectrometry; ADS-102 electrical conductivity meter are some of the tools utilized in this investigation.

2.3 Chemical Reagents Used

The reagents used in this research includes: hydrogen peroxide, NaCl solution, potassium hydroxide, pH 4.0 buffer solutions, concentrated nitric acid (HNO₃), ferrous ammonium sulphate, ethanol, dichloromethane, acetone, and ultrapure water, dimethyl phthalate (DMP), diethyl phthalate (DEP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP) in isooctane at 1 g/L each, and surrogate standards, which included diisophenyl phthalate, di-n-phenyl phthalate, di-n-benzyl phthalate, and an internal standard (benzyl benzoate) in acetone at 0.5 mg/L each, HPLC grade n-hexane, neutral silica gel (100–200 mesh) was deactivated by adding 5% distilled water.

2.4 Study Area

This study was conducted at Anambra River, which is within the jurisdiction of Anambra East Local Government. Approximately 100 kilometers north of Nsukka, in the Nigerian state of Kogi, lies the source of it in the Ankpa highlands. The river is located east of the Niger between latitudes 6°10' and 7° 40'. It travels south, traversing the border between the states of Kogi and Enugu. After that, it passed through Ogorugu and Otuocha, from which it flows down to Onitsha, where it meets the Niger. The length of the main river channel is approximately 207.40 km. *Echinoclae* spp., *Salviniana mnellula*, *Ludiwigia decurrens*, *Imperita cylindrica*, *Andropogon* spp., *Jussiaea* spp., *Pennisetum* spp., and *Cynodon* spp. are among the species that cover the riverbank. There are two seasons:

rainy season (April – September/October) and dry season (October/November - March). The mean annual rainfall is between 150 cm and 200 cm. The harmattan affects the basin from December to January or February, but its impact is not very noticeable. The water temperature and Secchi disc reading in the river ranges from 24°C to 31°C and 5 cm to 85 cm, respectively. The occupations of people living within the area are mostly farming and fishing.

2.5 Experimental Design

2.5.1 Preparation of sampling equipment, glass wares and reagents

Every piece of sample equipment is made of glass. Amber glass bottles were heated in a muffler oven for at least an hour at 400°C following two complete cleanings with acetone, hexane, and dichloromethane of High Performance Liquid Chromatography (HPLC) grade and a thorough detergent wash. After baking, the bottles were rinsed three times with acetone, methanol, hexane, and dichloromethane, and then cleaned with new aluminum foil. Before being used, aluminum foils were additionally cleaned with acetone and hexane and roasted in a hot oven for ten hours at 45°C. Buckets, flat trays, and stainless steel spoons were cleaned and covered in aluminum foil prior to sampling. The glass water samplers and sediment grab samplers were cleaned using lab-grade detergent and then washed three times with HPLC grade of acetone, C-H, O-Hexane as well as dichloromethane, respectively.

2.5.2 Pre-sample collection

All sample equipment, containers, and tools were cleaned with ultrapure water before sampling. Throughout the sampling process, nitrile gloves and a cotton coat were always used.

2.5.3 Collection of sediments and water samples

Ten surface waters were gathered at the exact spot where the silt was gathered. This was done before the sediments were collected to stop pollution from becoming over-concentrated and exploding from the sediments. Following the protocol described by [9,10,11], sediments were scooped up to a mass of around 50 g at a depth of 5 cm using a stainless-steel shovel. Seven sediment samples were preserved and sealed in tin foil pouches before being subjected to further analysis.

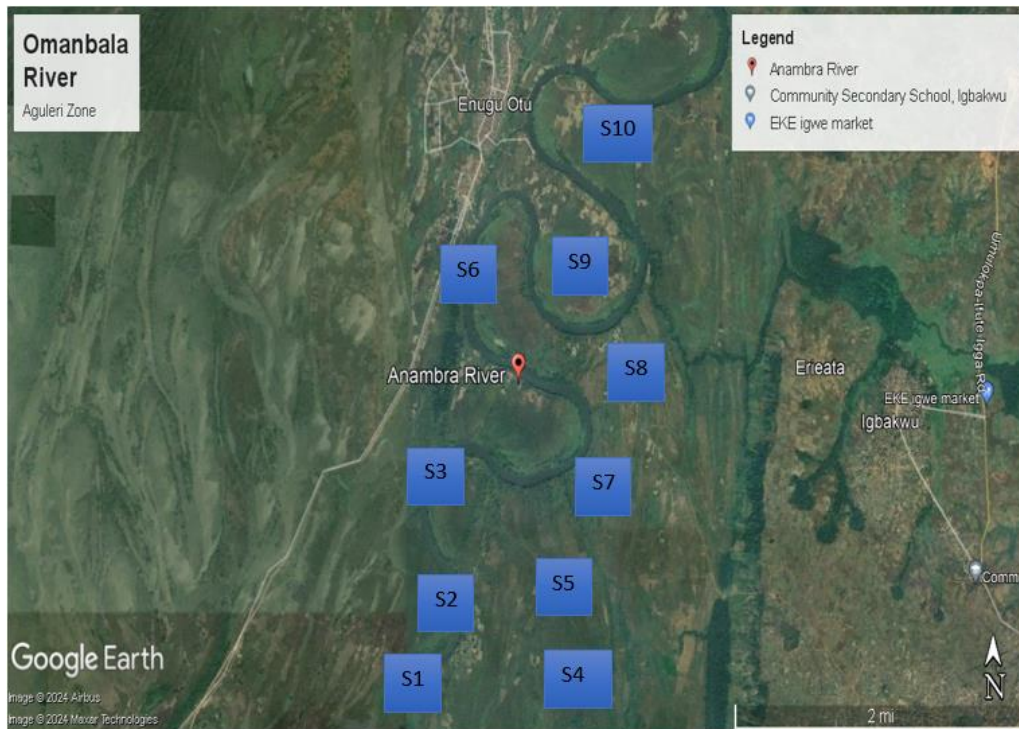


Fig. 1. Google Earth map of Anambra river



Fig. 2. Survey of sampling location

Table 1. Code for sample collection

Sampling location	Water code	Sediment code
1	W _A	S _A
2	W _B	S _B
3	W _C	S _C
4	W _D	S _D
5	W _E	S _E
6	W _F	S _F
7	W _G	S _G
8	W _H	S _H
9	W _I	S _I
10	W _J	S _J

2.6 Physicochemical Analysis in Water Samples

2.6.1 Determination of pH

The samples were measured for pH using a portable pH meter (HANNA pH 209) that was calibrated and stored in a 4 M KCl solution, in accordance with the procedure described by [12]. To determine the pH of each sample, the probe was dipped into 50 milliliters of the sample in the beaker, the result was read and recorded, and the probe was then rinsed in deionized water. Every sample underwent this procedure twice, and the outcomes were noted.

2.6.2 Determination of dissolved solid [12]

Twenty beakers were totaled, cleaned, oven dried, and cooled in the desiccators. A volume of 50 milliliters of each sample was filtered into each beaker and heated with a heating mantle until it was completely dry. After that, the beakers were cooled in the desiccators and their final weights were noted.

2.6.3 Determination of suspended solid [12]

Each of the filter papers was weighed in an electrical analytical weighing balance, oven dried, and allowed to cool in the desiccators after a 50 ml amount of each water sample was filtered into a different beaker. After the cooling process was finished, the weight of each filter paper was measured.

2.7 Physicochemical Analysis in Sediment Samples

2.7.1 pH [12]

A soil to distilled water ratio of 1:1 was used to determine the pH of the soil sample. Ten grams of soil, ten milliliters of distilled water, and a vigorous shake were added to a beaker, which was then allowed to stand for thirty minutes. A microprocessor pH 213 meter that had been calibrated before being immersed in the supernatant of the soil solution was used to measure the sample's pH. The pH values of 4 and 7 in a buffer solution were used to calibrate the pH meter. Three measurements of the sample's pH were made.

2.7.2 Determination of electrical conductivity

With an electrical conductivity meter (model ADS-102), the analysis was carried out in

accordance with the guidelines given by [12]. Three sections of the water sample were used to rinse the conductivity cell, and the temperature of the sample was adjusted to $20 \pm 0.1^\circ\text{C}$. After that, the conductivity meter was turned on, the electrode-containing conductivity cell was immersed in a large enough volume of the sample, and the sample values were recorded.

2.8 Determination of Phthalates

2.8.1 Digestion of Water Sample for Phthalates Analysis [13]

The 250 mL water sample was pre-concentrated using solid-phase extraction (SPE) after being filtered through a $0.45 \mu\text{m}$ Millipore membrane. The SPE cartridge containing florisil was activated with 1, 2, 3, and 5 milliliters of hexane, acetone, methanol, and clean water, respectively. After loading the water samples, the SPE cartridge was let to air dry for three minutes. One milliliter per minute of eluent was filtered using the dehydrated cartridge. The eluate was partially dried through evaporation by using a slow flow of nitrogen gas. The residue was once more dissolved in 2 ml of n-hexane, an extraction solvent, and an isotope surrogate standard prior to the GC-MS analysis.

2.8.2 Digestion of sediment samples for phthalates analysis

The sediment sample pretreatment was carried out utilizing a method from [14,15]. All of the sediment samples were homogenized and crushed with a mortar and pestle. This was passed through a 60-mesh stainless steel sieve and then placed in brown glass vials at -20°C to extract. Glass centrifuge tubes containing 10 grams of weighted riverine sediment samples were filled with 10 milliliters of acetone/hexane (1:1 v/v) and left overnight. The sediment samples were then extracted using an ultrasonic technique for 30 minutes. After doing the process twice, each extract was filtered into a flask with a spherical bottom. Following a solvent switch with n-hexane and dichloromethane, the filtrates were cleaned using solid phase extraction procedures (SPE) and concentrated to 1-2 mL using a rotary evaporator. The SPE cartridge containing florisil was activated in stages using 15 mL of C-H, O-Hexane, 15 mL of acetone/C-H, O-Hexane (1:1, v/v), and the eluents were disposed of appropriately. After transferring the PAEs extract to the extraction cartridge, 10 mL of acetone/n-hexane (1:4, v/v) was added to elute it. The

resultant eluent was then collected and placed into sample containers. Before being injected into brown vial bottles for GC-MS analysis, the PAE-containing part was concentrated to 2 mL, adjusted to a constant volume of 1 mL, and filtered through a 0.25 µm membrane filter.

2.8.3 Instrumental analysis of phthalates by GC-MS

Every sample was analyzed using a GC/MS gas chromatograph/mass spectrometer, functional electron influence, and an HP-5 MS in selective ion monitoring mode (30 mm × 0.25 mm × 0.25 mm). Chromatographic separation was achieved via a fused-silica capillary column. The carrier gas was pure helium gas (99.9999%), with a constant flow rate of 1 milliliter per minute. The temperature program of the oven was set at 30°C for one minute, 70°C for one minute, and 90°C for four minutes. Each 2.0 µl extract volume was injected into the GC-MS device in splitless, non-pulse mode at a temperature of 100°C using the injector temperature.

2.9 Pollution Assessment

2.9.1 Ecological risk assessment of phthalates [16]

The ecological risk posed by PAEs in water, sediment was assessed using the risk quotient (RQ) method, following the European Technical Guidance Document (TGD) on chemical pollutant risk assessment. The RQ was calculated by dividing the measured environmental concentration (MEC) of individual PAEs by the predicted no-effect concentration (PNEC). MEC was determined from PAE concentrations in water and sediment samples, while PNEC was derived from no-observed-effect concentrations

(NOEC) or median effective concentrations (EC50), adjusted by an assessment factor (AF). The ecological risk was categorized based on RQ values: insignificant (RQ < 0.1), low (0.1 ≤ RQ < 1), moderate (1 ≤ RQ < 10), and high (RQ ≥ 10). The RQs of PAEs were estimated by using the formula:

$$RQ = \frac{MEC}{PNEC}$$

2.9.2 Health risk assessment of phthalates [17]

To evaluate human health risks, the study focused on children and adults, considering two main exposure routes: ingestion of contaminated water and dermal absorption during personal hygiene activities. The assessment methodology drew from [17,18] and US EPA guidelines [19], with adjustments for this study. Average daily exposure levels, termed average daily dose (ADD), were calculated using the equation:

$$CDI = \frac{C_{mean} \times IR \times ED \times Fc}{BW \times AT}$$

where, C_{mean} is the concentration of PAEs in the polluted tap water samples collected from four waterworks in the study area; IR represents the average daily consumption rate; ED is referred to the exposure period (in years); Fc simply means the fraction contaminated; BW simply means the average body weight; AT represents the average lifetime of exposure (mg/kg/day).

Carcinogenic risk assessment as a result of lifetime exposure was evaluated by using the following formula:

$$HQ = \frac{CDI}{RfD}$$

Table 2. Exposure parameters used for risk assessment

Parameter		Value
Reference dose (RfD)	DBP	0.2 mg/kg/day
	DEHP	0.02 mg/kg/dy
	DEP	0.02 mg/kg/day
	DPP, BB	0.1 mg/kg/day
	MBP	0.115 mg/kg/day
Concentration of PAEs(C)	Mean value of PAEs	from result
Intake rates (IR)	Adults/Children	1.5
Exposure frequency (EF)	Adults	365 years
Exposure duration (ED)	Children	6 years
Body weight (BW)	Adults	60 kg
	Adolscent	30 kg
	Children	15kg

Parameter		Value
Average time (AT)	Non-cancer risk	365 x ED
	Cancer risk	365x 70
Slope factor (SF)	PAEs	0.014 mg/kg/day

Source: [10]

Table 3. Exposure parameters used to generate exposure estimate of PAEs

Exposure parameter	Unit
Drinking water	365 events/year, 2L/event (adult), 1L/event (children); 100% portion of contaminated tap water
Dermal absorption	365 events/year; 12 min/event, 6 min/event; 5700 cm ² skin surface (adult), 2800 cm ² skin surface (children); Skin adherence factor = 0.7 mg/cm ² /day; ABS is dermal absorption factor = 0.1 for all PAEs congeners

Source: [17]

3. RESULTS AND DISCUSSION

Table 4. Physicochemical analysis of sediment

Sample code	pH	EC(μS/cm)	TOC (%)
S _A	5.35±0.002	110±0.1	1.64±0.021
S _B	5.90±0.001	90±0.20	1.17±0.03
S _C	5.70±0.011	85±0.14	2.56±0.02
S _D	6.10±0.001	130±0.10	0.74±0.015
S _E	5.85±0.002	120±0.14	0.96±0.021
S _F	6.30±0.10	130±0.03	1.54±0.10
S _G	6.50±0.001	120±0.04	2.20±0.006
S _H	6.30±0.002	105±0.11	1.67±0.00
S _I	6.72±0.022	140±0.00	1.67±0.00
S _J	6.40±0.02	138±0.13	2.20±0.10

Results presented as mean ± standard deviation of three replicates.

The physicochemical properties of sediment samples are the concentrations of pH, electrical conductivity, and total organic carbon of samples S_A to S_J and are given in Table 4. By analyzing the sediment pH of each station and day, it was obtained from 5.35 to 6.72 making the sediments moderately acidic and near to neutrality. The least acidic sample is S_I with pH 6.72 together with S_I while the most acidic sample is S_A with pH 5.35 showing that most of the sediments are slightly acidic. As stated by [20] pH values between 5.0 and 6.8 were found for agricultural area sediments due to the decomposition of organic matter and leaching. Other earlier researchers including [8] have also observed that pH of sediments in aquatic systems varies between 5.0 and 7.5 depending on land use and pollution. The EC is the measure of salinity or ionic content of sediments; It varies between 85 μS/cm of sample S_C and 140 μS/cm of sample S_I. According to the EC values, 140 μS/cm for S_I, 130 μS/cm for S_D, and 130 μS/cm for S_F have high degrees of ionic content that might have

been impacted by neighbouring anthropogenic influences, such as urban runoff that contains dissolved salts. The EC values of S_C and S_B (85 μS/cm and 90 μS/cm respectively) reveal lesser exposure to such inputs. These results are similar to those of [21], who also identified comparable EC values (80-145 μ S/cm) in sediments of river impacted by urban areas. Impacts of EC by urban runoff and agricultural inputs have also been reported in the various sediment observation of rivers nearby industrial regions [20].

The TOC which represents the organic carbon content of the sediments vary between 0.74% in S_D and 2.56% in S_C. This is apparent since the TOC values are higher; S_C = 2.56%, S_J = 2.20% and this could have resulted due to biomass generation, living organisms and organic wastes like vegetation litter, or sewage effluent discharges. These values are similar to those we obtained when comparing with TOC percentages ranging from 1.5 to 3.0% revealed by [2] in

estuarine deposited sediments with high human impact. Conversely, the lower TOC values of SD (0.74%) and SE (0.96%) implies less organic matter, which may be as a result of lesser turnover of organic materials applied or lower rate of biological activity. Both, [22] have also observed similar TOC values in less polluted riverine systems where natural organic matter contributions are limited. In summary, this study's results are consistent with the findings from other studies. The near-neutral pH of the sediment indicate that the chemistry of the sediments by organic matter together with apparent contributions from natural processes supplemented by anthropogenic pollutants. This encompasses drainage from other adjacent regions, farming, and deposition of organic matter that are understood to alter sediment quality in many water bodies [17,22,23].

The physicochemical analysis of water samples presented in Table 6 reveals variations in pH, turbidity, conductivity, total dissolved solids (TDS), alkalinity, and chloride concentrations across samples W_A to W_J . The pH values range from 5.90 to 6.82, indicating that the water samples are generally slightly acidic to neutral. The sample with the lowest pH is W_A (5.90), while W_C exhibits the highest pH (6.82), which is closer to neutral. These pH values are consistent with the World Health Organization (WHO) guidelines, which suggest a permissible range of 5.5 to 8.5 for drinking water [24]. Studies, such as those by [10], have similarly reported pH levels in surface waters ranging from 5.5 to 7.5, influenced by natural organic inputs and anthropogenic activities. Turbidity levels in the samples range from 0.60 NTU in W_E to 1.40 NTU in W_I , with W_A and W_C both measuring 1.25 NTU. These values suggest low to moderate turbidity, which can indicate the presence of suspended particles or organic matter. High turbidity can impair water quality and is often associated with runoff or sediment disturbance. The turbidity levels recorded here are lower than those found in polluted river systems, where values can exceed 5 NTU [10]. Maintaining turbidity within the range observed is crucial for protecting aquatic ecosystems and ensuring safe drinking water. Electrical conductivity (EC) varies among samples, ranging from 85 $\mu\text{S}/\text{cm}$ (W_C) to 140 $\mu\text{S}/\text{cm}$ (W_I). The highest conductivity values indicate a higher concentration of ions in the water, potentially due to the presence of dissolved salts or pollutants. Sample W_I , with an EC of 140 $\mu\text{S}/\text{cm}$, may reflect increased salinity or urban runoff. These findings align with

previous research by [2], which found that EC levels in urban waters can vary significantly due to anthropogenic influences, often falling between 100 and 200 $\mu\text{S}/\text{cm}$. The total dissolved solids (TDS) levels range from 38 mg/l in W_G to 123 mg/l in W_I , indicating varying degrees of dissolved material in the water. Higher TDS levels can impact water quality and aquatic life, particularly when influenced by pollutants. TDS values here are within acceptable limits, as the WHO guideline for TDS is 500 mg/l [24]. Studies by [12] reported similar TDS levels in freshwater bodies, highlighting the influence of nearby land use and activities. Alkalinity, a measure of water's ability to neutralize acids, ranges from 7.5 mg/l in W_G to 42.5 mg/l in W_A . These values indicate a moderate buffering capacity, which is important for maintaining stable pH levels in aquatic ecosystems. The alkalinity levels observed are consistent with findings by [13], who noted that alkalinity in freshwater sources typically ranges from 10 to 50 mg/l, influenced by carbonate and bicarbonate concentrations. Chloride concentrations range from 14.05 mg/l in W_B to 88.05 mg/l in W_J . Elevated chloride levels can indicate pollution, especially from road salts or agricultural runoff. The chloride levels in this study are generally within acceptable limits; however, they approach the WHO guideline maximum of 250 mg/l [24]. Similar studies have reported chloride concentrations in freshwater sources that reflect varying degrees of pollution, often between 10 and 100 mg/l, depending on proximity to urban areas [3]. In summary, the physicochemical properties of the water samples suggest a range of influences from both natural and anthropogenic sources. The slight acidity, low to moderate turbidity, and variable ionic concentrations indicate the need for continued monitoring to ensure water quality, especially in the context of human activities and environmental changes. The findings align with previous studies, emphasizing the importance of understanding local hydrology and pollution sources to maintain water safety and ecosystem health.

The analysis of phthalate concentrations in sediment samples (S_A to S_J) reveals the presence of various phthalates, including Monobutyl phthalate (MBP), Diethyl phthalate (DEP), Dipentyl phthalate (DPP), Butyl benzyl phthalate (BBP), Dibutyl phthalate (DBP), and Di (2-ethylhexyl) phthalate (DEHP). The results indicate significant variability in phthalate concentrations across the samples. The highest concentration of MBP is found in sample S_A at

Table 5. Physicochemical analysis of water

Sample code	pH	Turbidity NTU	Conductivity (µS/cm)	TDS mg/l	Alkalinity	Chloride mg/l
W _A	5.90±0.01	1.25±0.01	110±0.001	76±0.014	42.5±0.03	77.29±0.01
W _B	6.30±0.001	0.90±0.001	90±0.012	53±0.001	15±0.002	14.05±0.02
W _C	6.82±0.02	1.25±0.00	85±0.011	48±0.01	15±0.012	28.10±0.11
W _D	6.45±0.001	0.80±0.15	130±0.001	82±0.00	22.5±0.4	35.31
W _E	6.70±0.1	0.60±0.24	120±0.005	59±0.032	17.5±0.052	35.31
W _F	6.60±0.11	0.70±0.003	130±0.001	72±0.1	15±0.002	42.37
W _G	6.50±0.12	1.20±0.002	120±0.00	38±0.011	7.5±0.014	63.55
W _H	6.30±0.002	1.0±0.001	105±0.00	80±0.002	17.5±0.2	63.55
W _I	6.72±0.01	1.40±0.023	140±0.001	123±0.003	25±0.032	73.25
W _J	6.40±0.21	1.0±0.0	138±0.004	107±0.140	10±0.00	88.05
WHO (2017)	5.5 - 8.5	5	500	500	100	250

Table 6. Concentration of phthalates in sediments

Sample code	Phthalates (mg/kg)					
	MBP	DEP	DPP	BBP	DBP	DEHP
S _A	0.40	0.93	0.32	0.00	0.92	0.28
S _B	0.01	0.05	0.04	0.01	0.00	0.04
S _C	0.02	0.12	0.01	0.00	0.31	0.11
S _D	0.00	0.00	0.00	0.00	0.002	0.001
S _E	0.00	0.00	0.00	0.00	0.01	0.00
S _F	0.001	0.002	0.001	0	0.001	0.003
S _G	0.011	0.052	0.03	0.01	0.00	0.04
S _H	0.02	0.32	0.03	0.001	0.04	0.15
S _I	0.01	0.03	0.001	0.00	0.33	0.13
S _J	0.002	0.002	0.02	0.002	0.003	0.043

MBP: Monobutyl phthalate
 DPP: Dipentyl phthalate
 DBP: Dibutyl phthalate

DEP: Diethyl phthalate
 BBP: Butyl benzyl phthalate
 DEHP: Di (2ethylhexyl) phthalate

0.40 mg/kg, while other samples, such as S_B and S_C, show much lower levels (0.01 mg/kg and 0.02 mg/kg, respectively). The prevalence of MBP in S_A may indicate localized contamination, possibly from nearby industrial or urban activities, which is consistent with findings by [16], who noted that MBP is often associated with plasticizers and may be released into the environment through various pathways, including wastewater discharge. DEP concentrations are also highest in S_A at 0.93 mg/kg, with S_B and S_C exhibiting lower levels (0.05 mg/kg and 0.12 mg/kg, respectively). These findings suggest that DEP, commonly used in consumer products, may similarly contribute to sediment pollution, as observed in studies [25], where DEP concentrations in sediments were linked to urban runoff and industrial emissions. DPP and BBP concentrations are notably low across most samples, with only S_A and S_H showing measurable levels (0.32 mg/kg and 0.03 mg/kg, respectively). This low prevalence may reflect

either lower usage rates of these compounds in the surrounding area or efficient degradation processes in the sediment. The findings align with research by [26], which reported low concentrations of DPP in sediments near industrial zones, suggesting limited accumulation. DBP concentrations are generally low, with S_A again showing the highest concentration at 0.92 mg/kg. Other samples display either negligible or zero levels, indicating potential degradation or reduced input of this compound. Research has demonstrated that DBP can rapidly degrade in sediment environments under certain conditions [19]. DEHP, a commonly studied phthalate due to its widespread use and potential health impacts, shows a maximum concentration of 0.28 mg/kg in sample S_A and lower levels in other samples, particularly in S_D and S_E, which report negligible concentrations. The presence of DEHP in sediment is often linked to plastic waste and industrial effluent, and its concentration levels in

this study are comparable to those reported by [27], who found DEHP concentrations ranging from 0.1 to 0.5 mg/kg in contaminated sediments. The sediment samples show a distinct distribution of phthalate compounds, with SA exhibiting the highest concentrations of several phthalates, indicating possible localized contamination. The overall low levels of phthalates in other samples suggest varying degrees of pollution across the study area, potentially influenced by urban and industrial activities. These findings are in line with previous studies, highlighting the importance of monitoring phthalate pollution in sediment environments due to their environmental persistence and potential ecological risks.

The analysis of phthalate concentrations in water samples (WA to WJ) indicates the presence of various phthalates, including Monobutyl phthalate (MBP), Diethyl phthalate (DEP), Dipentyl phthalate (DPP), Butyl benzyl phthalate (BBP), Dibutyl phthalate (DBP), and Di (2-ethylhexyl) phthalate (DEHP). The results show that phthalate concentrations in water are generally low, with detectable levels of several compounds across different samples. MBP is detected in multiple samples, with the highest concentration in WA at 0.01 mg/kg. Other samples, such as WH (0.011 mg/kg) and WG (0.009 mg/kg), show lower but measurable levels. These concentrations suggest minimal contamination, likely from plastic products or industrial sources, as noted in previous studies. [15,16] found similar low levels of MBP in surface water near urban areas, which are often impacted by runoff. DEP is also present in several samples, with the highest concentration recorded in WA (0.03 mg/kg). Lower concentrations are observed in WC (0.023 mg/kg) and WH (0.03 mg/kg). The occurrence of DEP in these samples is consistent with findings by Khan et al. (2020), who reported DEP levels in water bodies influenced by domestic waste and

agricultural runoff, highlighting its ubiquity in contaminated environments. DPP shows minimal presence in water, with the highest level of 0.02 mg/kg in WA and undetectable levels in several other samples. This aligns with the findings of [27], where DPP concentrations in water were found to be generally low, often reflecting limited usage or rapid degradation in aquatic environments. BBP is absent in all samples except for low concentrations in WJ (0.01 mg/kg). The negligible levels of BBP suggest that it may not be a significant contaminant in this water source. This is in line with previous research indicating that BBP is often less frequently detected in aquatic systems compared to other phthalates [21,26]. DBP shows a detectable concentration of 0.07 mg/kg in WA and lower levels in WH (0.02 mg/kg) and WC (0.08 mg/kg). The presence of DBP reflects potential contamination from plasticizers, as highlighted by studies that report DBP in water systems near industrial and urban areas [26]. DEHP, a compound of significant concern due to its toxicity and prevalence, is detected at concentrations up to 0.08 mg/kg in WA, with lower concentrations in other samples. The presence of DEHP in water is a notable finding, as it is often associated with plastic pollution and industrial discharge. Similar levels of DEHP have been reported in studies by [25], where concentrations ranged between 0.01 mg/kg and 0.1 mg/kg in polluted water sources. Overall, the concentrations of phthalates in the water samples are generally low, indicating that while there is some contamination, it may not be widespread or severe. The findings highlight the need for ongoing monitoring of phthalate levels in water, especially given their potential ecological and health risks. The results are consistent with previous studies that have documented the presence of phthalates in aquatic environments, emphasizing the importance of controlling pollution sources to safeguard water quality.

Table 7. Concentration of phthalates in water

Sample code	Phthalates (mg/l)					
	MBP	DEP	DPP	BBP	DBP	DEHP
WA	0.01	0.03	0.02	0.00	0.07	0.08
WB	0.00	0.02	0.01	0.00	0.00	0.01
WC	0.008	0.02	0.00	0.00	0.08	0.06
WD	0.00	0.00	0.00	0.00	0.00	0.00
WE	0.00	0.00	0.00	0.00	0.00	0.00
WF	0.001	0.00	0.00	0.00	0.00	0.00
WG	0.01	0.01	0.01	0.00	0.00	0.03
WH	0.01	0.03	0.01	0.00	0.02	0.03

Sample code	Phthalates (mg/l)					
	MBP	DEP	DPP	BBP	DBP	DEHP
W _i	0.01	0.01	0.00	0.00	0.07	0.03
W _j	0.00	0.001	0.01	0.01	0.00	0.03

MBP: Monobutyl phthalate
 DPP: Dipentyl phthalate
 DBP: Dibutyl phthalate
 DEP: Diethyl phthalate
 BBP: Butyl benzyl phthalate
 DEHP: Di (2ethylhexyl) phthalate

3.1 Risk Assessment of Phthalate Esters

Table 8. Health risk of phthalate esters in water media in dry season in adult

PAEs	Mean (mg/L)	RfD	CDI	HQ
MBP	0.004	0.1	5.88E-08	0.0006
DEP	0.013	0.8	1.70E-07	0.0002
DPP	0.006	0.1	7.67E-08	0.0015
BBP	0.001	0.2	1.34E-08	7.0E-05
DBP	0.024	0.01	3.23E-07	0.032
DEHP	0.027	0.02	3.61E-07	0.018
Total			1.67E-07	0.009

Table 9. Health risk of phthalate esters in water media in dry season in children

PAEs	Mean (mg/L)	RfD	CDI	HQ
MBP	0.004	0.1	4.01E-07	0.0004
DEP	0.013	0.8	1.16E-06	0.0014
DPP	0.006	0.1	5.23E-07	0.0104
BB	0.001	0.2	9.17E-08	0.0005
DBP	0.024	0.01	2.20E-06	0.22
DEHP	0.027	0.02	2.46E-06	0.123
Total			1.14E-06	0.059

For the six phthalates (MBP, DEP, DPP, BBP, DBP and DEHP), the Chronic Daily Intake (CDI) was determined with the aid of the mean concentrations from the environment. CDIs are estimates of the rate of uptake of a specific contaminant during a long duration (a lifetime), based on weight and dose rate given per day. In children, CDI for DBP reached 2.20E-06 mg/kg/day; for DEHP, it was 2.46E-06 mg/kg/day, and it was significantly higher comparing to other compounds. The CDI is higher in children than in adults because children are more likely to be contaminated relative to their body weight. The CDIs of MBP, DEP, DPP, and BBP were comparatively lower, this suggesting that these substances poses less risk through environmental contact. In adults, the mean CDI values were lower relative to children have a bigger body size, hence, they consumed comparatively smaller intakes per body weight units. DBP and DEHP were once more found be the most dominant contaminants in this study with the CDIs estimated to be 3.23E-07 mg/kg/day and 3.61E-07 mg/kg/day respectively. CDI values obtained from children are higher

than those obtained from adults because children are more vulnerable to any environmental impact. Comparing the impacts of genotoxins exposure at different age- group is crucial in any health risk assessment. The Hazard Quotient (HQ) is another measure of carcinogenic risk that is very significant. A value below 1 implies that exposure is unlikely to result in adverse health effects, while a value above 1 indicates a potential risk. For children, the HQ for DBP (0.22) is notable. Although it is below the threshold of 1, it is relatively high compared to the other phthalates, suggesting that children are at a higher risk of non-carcinogenic effects from DBP exposure. DEHP (0.123) is also a significant concern, but it remains under the risk threshold. The HQ for MBP, DEP, and BBP is quite low, indicating minimal risk from these compounds. For adults, all HQ values are significantly lower than 1, with DBP (0.032) being the highest among the six phthalates. This suggests that adults face minimal risk of non-carcinogenic health effects from these compounds. In general, children are more vulnerable than adults, with DBP posing the most substantial risk in both groups.

3.2 Comparison to Other Studies

The following research has found out that out of all the phthalates, DBP (Dibutyl phthalate) and DEHP (Di(2-ethylhexyl) phthalate) are the most dangerous since they are widely used and resistant to biodegradation. A study by [19] on phthalate exposure in Chinese children revealed similar concentrations of DBP and DEHP as the current study and, an HQ value of 0.95 for DBP was comparable with the current study. This is consistent with the current study where the risk of DBP figured highest in children. A research by [25] on phthalates in indoor dust from different parts of China also found DBP and DEHP as a cause of high health concern with children's HQ values slightly above 1 as obtained in this study. Research has shown that MBP and DEP have lower toxicity compared with DBP and DEHP. [26] reported Mean Hazard Quotient (HQ) for MBP and DEP below 1 when analyzing the concentrations of phthalates in household dust and human urine. This implies that, there are very few effects of these two compounds on the health of human beings in various populations. In the case of DPP (Di-n-propyl phthalate) and BBP (Butyl benzyl phthalate) exposure and risk levels presented in scientific works such as [27] are relatively low. In the present study, the HQ values for DPP and BBP have been below 0.05 in both the children and the adults [11,18,15].

4. CONCLUSION

Approximately all the phthalates evaluated in this study exhibit insignificant health risks ($HQ < 1$) to children and adults; however, DBP and DEHP are characterized as potentially dangerous for children. With a HQ of 0.22 for DBP in children, it is close to the level of concern and may cause adverse health impact with long term exposure. Such observations have been observed in other research, especially to kids because of their small stature and immature body systems. MBP, DEP, DPP and BBP on the other hand represent very low hazard to kids and grown ups their total HQ is insulated under both thresholds proposed for kids and adults (0.009 and 0.059 accordingly). On the basis of the current study, it is clear that efforts should be made to minimize the DBP and DEHP exposure and for this purpose, the areas that are potentially vulnerable to children should be targeted because children are most probably to be exposed to DBP and DEHP therein including homes, schools, and playgrounds.

DISCLAIMER

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Selvaraj KK, Sundaramoorthy G, Ravichandran PK, Girijan GK, Sampath S, Ramaswamy BR. Phthalate esters in water and sediments of the Kaveri River, India: environmental levels and ecotoxicological evaluations. *Environmental Geochemistry and Health*. 2014;37(1):83–96. Available: <https://doi.org/10.1007/s10653-014-9632-5>.
2. Ogbuagu JO, Obi EN, Okeke AP, Ukpai UE. Pollution status and health risk assessment of polycyclic aromatic hydrocarbons in surface water, sediment and fish from Ezu-River, Anaku, Anambra State, Nigeria. *Asian Journal of Applied Chemistry Research*. 2021;10(1):26-39.
3. Ogbuagu JO, Ukpai UE, Okeke AP, Nweke EN. Occurrence and fate of Polychlorinated Biphenyls in water and sediments: A case study of Bodo River in Ogoni, River State Nigeria. *Asian Journal of Applied Chemistry Research*. 2021; 10(3-4): 12-20.
4. Zhang ZM, Zhang HH, Zou YW, Yang GP. Distribution and ecotoxicological state of phthalate esters in the sea-surface microlayer, seawater and sediment of the Bohai Sea and the Yellow Sea. *Environmental Pollution*; 2018. Available: <https://doi.org/10.1016/j.envpol.2018.04.056>.
5. Adeniyi AA, Okedeyi OO, Yusuf KA. Flame ionization gas chromatographic determination of phthalate esters in water, surface sediments and fish species in the Ogun river catchments, Ketu, Lagos, Nigeria. *Environmental Monitoring and Assessment*. 2011;172(1–4):561–569. Available: <https://doi.org/10.1007/s10661-010-1354-2>.
6. Net S, Delmont A, Sempéré R, Paluselli A, Ouddane B. Reliable quantification of

- phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. *Science of the Total Environment*. 2015;515–516:162–180. Available:<https://doi.org/10.1016/j.scitotenv.2015.02.013>.
7. Wormuth M, Scheringer M, Vollenweider M, Hungerbühler K. What are the sources of exposure to eight frequently used phthalic acid esters in Europeans? *Risk Analysis*. 2006;26(3):803–824. Available:<https://doi.org/10.1111/j.1539-6924.2006.00770.x>.
 8. Wang J, Bo L, Li L, Wang D, Chen G, Christie P, Teng Y. Occurrence of phthalate esters in river sediments in areas with different land use patterns. *Science of the Total Environment*. 2014a;500–501:113–119. Available:<https://doi.org/10.1016/j.scitotenv.2014.08.092>.
 9. Cheng L, Zhao Y, Li L, Chen B, Zhang Y. Exposure assessment of phthalates in non-occupational populations in China. *Science of the Total Environment*. 2013;427–428:60–69. Available:<https://doi.org/10.1016/j.scitotenv.2012.03.090>.
 10. USEPA (U.S. Environmental Protection Agency). Edition of the tap water standards and health advisories. Washington, DC: U.S. EPA; 2012. Available:<http://water.epa.gov/action/advisories/drinking/upload/dwstandards2012.pdf> (Last accessed October 2017).
 11. Ogbuagu JO, Okeke AP, Ukpai UE, Obi EN. Ecological and Health Risk Assessment of Polychlorinated Biphenyls in Water and Sediments in Bodo Riverine Area, River State, Nigeria. *J Mat Sci Eng Technol*. 2023;1(3): 1-7. DOI: doi.org/10.61440/JMSET.2023.v1.13
 12. APHA. Standard methods for the examination of water and sediments for physicochemical parameters, 23rd Edition, Washington, DC. 2017;148- 176.
 13. Deng H, Wei R, Luo WY, Hu LL, Li BW, Shi HH. Phthalates pollution in water and sediment in a textile industrial area. *Environ. Pollut*. 2020;258:113658. Available:<https://doi.org/10.1016/j.envpol.2019.113658>.
 14. Wang J, Bo L, Li L, Wang D, Chen G, Christie P, Teng Y. Occurrence of phthalate esters in river sediments in areas with different land use patterns. *Science of the Total Environment*. 2014a;500–501:113–119. Available:<https://doi.org/10.1016/j.scitotenv.2014.08.092>.
 15. Ogbuagu JO, Nweke EN, Okeke AP, Ukpai UE. Concentration and risk assessment of selected polycyclic aromatic hydrocarbons in water and sediment samples from Ezuriver, Anaku, Anambra State. *Iconic Research and Engineering Journals*. 2021;5 (4): 77-84.
 16. Li R, Liang J, Gong Z, Zhang N, Duan H. Occurrence, spatial distribution, historical trend and ecological risk of phthalate esters in the Jiulong River, Southeast China. *Science of the Total Environment*. 2017a ;580:388–397. Available:<https://doi.org/10.1016/j.scitotenv.2016.11.190>.
 17. European commission. Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC, Commission Directive 98/8/EC, Commission Regulation (EC) No 1488/94, Commission Directive 93/67/EEC. EUR 20418 EN/2; 2003.
 18. Princewill AO. Risk Assessment of heavy metal contamination in apples sold within Awka metropolis in Anambra state Nigeria. *Journal of Applied Chemical Science International*. 2022;13(2):46-51. Available:https://ikprress.org/index.php/JA_CSI/article/view/7516.
 19. Guo Y, Wang L, Kannan K, Fan S. Phthalates and parabens in personal care products from China: Concentrations and human exposure. *Environmental Science & Technology*. 2012;46(5): 2493-2500. Available:<https://doi.org/10.1021/es2035049>
 20. Olujimi OO, Aroyeun OA, Akinhanmi TF, Arowolo TA. Occurrence, removal and health risk assessment of phthalate esters in the process streams of two different wastewater treatment plants in Lagos and Ogun States, Nigeria. *Environmental Monitoring and Assessment*. 2017;189(7). Available:<https://doi.org/10.1007/s10661-017-6028-x>.
 21. Fatoki OS, Bornman M, Ravandhalala L, Chimuka L, Genthe B, Adeniyi A. Phthalate ester plasticizers in freshwater systems of Venda, South Africa and potential health effects. *Water SA*. 2010b ;36(1)117–126. Available:<https://doi.org/10.4314/wsa.v36i1.50916>.

22. Liu X., Shi J, Bo T, Zhang H, Wu W, Chen Q. Occurrence of phthalic acid esters in source waters: A nationwide survey in China during the period of 2009 and 2012. *Environmental Pollution*. 2014;184:262–270. Available: <https://doi.org/10.1016/j.envpol.2013.08.035>.
23. Keresztes S, Tatar E, Czegény Z, Zaray G, Mihucz VG. Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water. *Sci. Total Environ*. 2013;458:451–458.
24. World Health Organisation, (WHO). *Guidelines for Drinking Water Quality, 4th Edition; Incorporating the first addendum*, A publication of World Health Organisation, Geneva Switzerland. 2017;1-631.
25. Tranfo G, Paci E, Pignini D, Bauleo L, Minoia C. Human biomonitoring of phthalate exposure in Italian workers: Implications for occupational exposure limits. *International Journal of Environmental Research and Public Health*. 2018;15(8):1738. Available: <https://doi.org/10.3390/ijerph15081738>
26. Xie Z, Wang Y, Zhang Y, Sun Z, Luo Q, Chen Z. Phthalate exposure and human semen quality: Results from an infertility clinic in China. *Environmental Science & Technology*. 2016;50(12): 6933-6940. Available: <https://doi.org/10.1021/acs.est.6b00572>
27. Zhang X, Zeng Q, Liu X, Huang Y, Wu W, Tang Q. Exposure to phthalates and phthalate alternatives among Chinese children: Assessment of health risks based on urinary biomarkers. *Journal of Exposure Science & Environmental Epidemiology*. 2020;30(4):751-759. Available: <https://doi.org/10.1038/s41370-020-00232-7>.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of the publisher and/or the editor(s). This publisher and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

© Copyright (2024): Author(s). The licensee is the journal publisher. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<https://prh.ikpress.org/review-history/12440>