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Occurrence and human exposure assessment of parabens in water sources in Osun State, Nigeria

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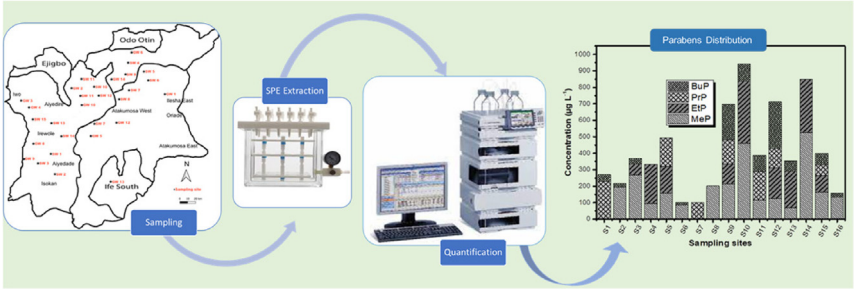
HIGHLIGHTS

- MeP, EtP, PrP and BuP were detected at high levels in surface and groundwater.
- MeP was the most dominant of the parabens and has the highest concentration.
- Strong correlation exists between MeP and EtP.
- No significant difference between concentrations of parabens in urban and rural sampling sites

GRAPHICAL ABSTRACT



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ABSTRACT

Parabens are chemicals extensively used in pharmaceuticals, cosmetics, personal hygiene and food products as preservatives. They are classified as emerging contaminants with endocrine-disrupting capability. In this study, the concentrations of Methylparaben (MeP), Ethylparaben (EtP), Propylparaben (PrP) and Butylparaben (BuP) were obtained from groundwater, surface-water and packaged water samples collected from urban and rural areas of Osun State, Nigeria using HPLC-UV equipment. Data obtained were subjected to descriptive (Mean ± SD), inferential (Kruskal-Wallis test) and multivariate analyses. MeP had the highest average concentration of 163 and 68 μg L^{-1} in surface water and groundwater respectively while concentrations of MeP, EtP, PrP and BuP were higher than previously reported in other countries. Methylparaben had the highest detection frequencies (88.0 and 50.0%) followed by BuP (69.0 and 50.0%) in surface water and groundwater respectively. No significant difference was observed for concentrations of parabens in groundwater samples in urban and rural sampling sites, suggesting that people living around these sites are equally exposed to any health implications from the use of paraben-polluted potable water. Principal Component Analysis (PCA) data suggest that the pairs MeP & EtP, PrP & BuP (in surface water samples) and MeP, EtP, & PrP (in groundwater samples) are from similar pollution sources. Ecological risk assessment using Algae, Fish, and Daphnia suggests Daphnia as the most sensitive organism while BuP and PrP show the highest health risk. Human exposure assessment showed that higher overall median estimated daily intake (EDI) values for groundwater were observed in infants (1.71 μg kg^{-1} bw day^{-1}, ΣPBs) compared to toddlers (1.03 μg kg^{-1} bw day^{-1}, ΣPBs),

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children (0.64 μg kg^{-1} bw day^{-1}, ΣPBs), teenagers (0.51 μg kg^{-1} bw day^{-1}, ΣPBs) and adults (0.62 μg kg^{-1} bw day^{-1}, ΣPBs). Although these values are below limits set in a few countries, potential bioaccumulation could lead to severe health consequences.

1. Introduction

Pharmaceutical and personal care products (PPCPs) are classified as contaminants of emerging concerns in water. They are present in water bodies through treated or untreated sewer discharges from households and hospitals, runoff, industrial waste effluents, agricultural and recreational activities (Awfa et al., 2018; Kasprzyk-Hordern et al., 2008; Mohan et al., 2020). Parabens are a group of chemicals extensively used in pharmaceutical and personal care products; they belong to a group of alkyl esters of p-hydroxybenzoic acid and are used as preservatives predominantly against yeast and moulds in foods, beverages, cosmetics and pharmaceuticals because they have antibacterial and antifungal activity that can disrupt the plasma membrane and intracellular proteins of micro-organisms, resulting in a modification in the enzyme action of these cells (Crovetto et al., 2017; Kung et al., 2018). Man is also exposed to parabens through inhalation, ingestion, or dermal absorption (García-Espiñeira et al., 2018). Parabens are present in several environmental and human samples such as; wastewater, surface water, drinking water, soil, sludge, urine, serum and seminal plasma, breast tissues, placenta (Becerra-Herrera et al., 2019; Błędzka et al., 2014; Bolujoko et al., 2021; Ferreira et al., 2011; Frederiksen et al., 2011; Jiménez-Díaz et al., 2011; Karthikraj et al., 2017; Radwan et al., 2020; Shanmugam et al., 2010). There are serious concerns over the effect of parabens on human and animal health. The United States Environmental Protection Agency classified parabens as endocrine-disrupting contaminants (EDCs) (Błędzka et al., 2014). Parabens can affect the proper functioning of the endocrine system in human body which could be harmful (Dhillon et al., 2015; Vo et al., 2011). Exposure to parabens has also been linked to childhood overweight development by altered Pro-opiomelanocortin-mediated neuronal appetite regulation (Leppert et al., 2020). Also, parabens are said to enable multiple cancer hallmarks in the human breast (Darbre and Harvey, 2014), malfunction of the central nervous system and immune system (Kim et al., 2011; Miodovnik et al., 2011), homeostasis of lipids (Raza et al., 2018), hinder the proper functioning of the thyroid particularly in pregnant women (Aker et al., 2016) and telomere shortening (inability for cells to replicate) that leads to ageing, cancer and possibly death (Finot et al., 2017).

The presence of parabens in waters has been studied across various countries: in Brazil (MeP: 0.11–0.98 μg L^{-1}, EtP: 0.38–9.70 μg L^{-1}, PrP: 0.70–7.90 μg L^{-1}, BuP: 1.90–11.0 μg L^{-1}) (Derisso et al., 2020), Chile (MeP: 0.63–4.34 μg L^{-1}, PrP: 2.46–14.91 μg L^{-1}, BuP: 0.44–0.90 μg L^{-1}) (Becerra-Herrera et al., 2019), China (MeP: 0.02–5.96 μg L^{-1}, EtP: 0.002–0.11 μg L^{-1}, PrP: 0.001–0.32 μg L^{-1}, BuP: n.d.–0.003 μg L^{-1}) (Lu et al., 2017), Australia (MeP: 4.62–13.78 μg L^{-1}, EtP: 2.75–305.55 μg L^{-1}, PrP: 2.42–8.29 μg L^{-1}, BuP: 3.86–8.47 μg L^{-1}) (Evans et al., 2016), Japan (MeP: n.d.–0.53 μg L^{-1}, EtP: n.d.–0.07 μg L^{-1}, PrP: n.d.–0.18 μg L^{-1}) (Kimura et al., 2014), Spain (MeP: 0.009–0.03 μg L^{-1}, EtP: 0.009–0.02 μg L^{-1}, PrP: 0.03–0.05 μg L^{-1}) (Cacho et al., 2016), USA (MeP: 0.002–0.02 μg L^{-1}, PrP: n.d.–0.012 μg L^{-1}, BuP: n.d.–0.002 μg L^{-1}) (Renz et al., 2013), Egypt (MeP: 1.74 μg L^{-1}, PrP: 0.59 μg L^{-1}, BuP: 6.38 μg L^{-1}) (Radwan et al., 2020) and India (MeP: 0.004–0.27 μg L^{-1}, EtP: 0.002–0.06 μg L^{-1}, PrP: 0.003–0.58 μg L^{-1}, BuP: 0.0007–0.01 μg L^{-1}) (Karthikraj et al., 2017). China and Japan have set the maximum allowable concentration of 0.4% and 1% respectively for the use of parabens in cosmetics (Shen et al., 2007) while in Europe, it is set at 0.4% for single parabens and 0.8% for mixed parabens (Błędzka et al., 2014). Several sample preparation methods have been used in the extraction of parabens from aqueous matrices, some of which are: solid phase microextraction (Ariffin et al., 2019; Farahmandi et al., 2021), stir bar sorptive extraction (Han et al., 2021; Ramírez et al., 2012), liquid phase microextraction (Chen et al., 2019; Fernández et al., 2021; Mafra et al., 2019).

Owing to limited data on the presence of parabens in different matrices in many developing countries, particularly in Africa, limits for their use are yet to be established (Bolujoko et al., 2021). There is a limited report on the occurrence of parabens in various water matrices in Africa. The only available report was the study carried out to monitor these contaminants in Egypt (Radwan et al., 2020). To the best of our knowledge, this study is the first report from Nigeria on the occurrence of parabens in surface water, groundwater and drinking water sources. The study is aimed at i) determining the occurrence and concentration of certain parabens: methylparaben, ethylparaben, propylparaben and butylparaben in surface water, groundwater and packaged drinking water systems in Osun State, Nigeria ii) evaluating the risk and exposure of humans to these contaminants using the measured environmental concentration. The choice of these water sources (surface water, groundwater and packaged drinking water) is premised on the fact that over 80% of the population in Osun State in Nigeria rely on these sources of water as their means of potable water especially groundwater and packaged drinking water.

2. Materials and methods

2.1. Standards and reagents

Analytical standards of methyl 4-hydroxybenzoate (99.7%), ethyl 4-hydroxybenzoate (99%), propyl 4-hydroxybenzoate (≥99.0) and butyl 4-hydroxybenzoate (≥99.0) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile and methanol of HPLC grade and Oasis HLB SPE cartridges (500 mg, 12 mL) were purchased from Sigma-Aldrich (St. Louis, MO, USA). ultrapure water was obtained with Milli-Q Direct 8/16 System. The standard stock solutions of each analyte (200 mg L^{-1}) were prepared singly in methanol and stored at 4 °C. Working solutions (10 mg L^{-1}) of mixed parabens were prepared by dilution of stock solution with ultrapure water fresh before use. Table S1 shows the chemical structures of parabens used in this study.

2.2. Description of study area

Osun State lies in the tropical rainforest climatic region, in the South-West of Nigeria. It lies between Lat. 06° 30′ N and Long. 04° 30′ E. and covers an area of approximately 14,875 sq. km. It receives an annual solar radiation of 210–240 W m^{-2} day^{-1}. Osun State records the annual average maximum temperature of 34 °C. Its highest monthly average temperature occurs in February (36.1 °C) while it also records the minimum (night time) temperature of 18.5 °C–21.5 °C. Osun state receives a cumulative annual rainfall of 1300–1500 mm and the least amount of rainfall occurs in August (0–50 mm of rain) (NIMET, 2020). The Osun river (used as sampling area for surface water) spans through commercial farming and fishing settlements, formal and informal settlements. It empties into Asejire Dam on the border between Oyo and Osun States in Nigeria. The river catchment has several domestic, commercial activities, sewers, and industrial activities that are potential primary sources of the parabens of interest in this present study. In some of the sampling sites, there are vivid evidences of freelance grazing of animals, confined animal grazing points, poor sanitation, inadequate wastewater treatment services, and industrial pollution, which can result in high levels of contamination of the river water. The coordinates of the sampling points for the present study are presented in Table S2.

2.3. Sample collection

Water samples were collected from urban and rural areas of the Osun State, Nigeria. Surface water, groundwater and packaged water (bottled and sachet) samples were collected between November 2020 and February 2021 within Osun state, Nigeria. Surface water samples were collected at six different sites while groundwater samples were collected at fourteen different sites, comprising seven rural and seven urban sites. Surface water samples were collected in Osun river at Asejire (SW1–SW3), Okini (SW4–SW6), Osogbo (SW7–SW9), Ede (SW10–SW11), Iwo (SW13–SW15) and Osun-Jela (SW16). Groundwater samples collected at urban sites were at: Ilesa (GW1), Ede (GW2), Iwo (GW3), Gbongan (GW5), Ikire (GW8), Ile-Ife (GW13) and Osogbo (GW14), while rural sites were collected at: Olupona (GW4), Okini (GW6), Ode-Omu (GW7), Asejire (GW9), Elewure (GW10), Akoda (GW11) and Edunabon (GW12). Sampling sites and their coordinates are shown in Table S2 while the map showing the sampling sites are shown in Fig. 1. Surface and groundwater samples were collected at each sampling site. Groundwater samples ($n = 3$) were collected and composited. Similarly, for surface water, grab samples (n = 3) were collected from different points on Osun river in Osun State, Nigeria. Samples were collected in 500 mL amber bottles which were pre-washed in the laboratory and rinsed on-site with sample water before usage. Packaged waters were also purchased from shopping points at different sampling sites as shown in Fig. 1. These samples were all transported to the laboratory and stored at 4 °C in the laboratory refrigerator until extraction. A total of 68 water samples were collected comprising of surface water, groundwater and packaged water.

2.4. Sample extraction

The water samples were filtered and 200 mL of each sample was spiked with a known concentration of the mixed analytes (methyl-, ethyl-, propyl- and butylparaben) and adjusted to pH 6.0 with 0.1 M HCl and 0.1 M NaOH. A blank sample containing no analyte was prepared with ultrapure water and adjusted to pH 6.0 with 0.1 M HCl and 0.1 M NaOH. The Solid Phase Extraction (SPE) cartridges (Oasis HLB, 500 mg, 12 mL) were conditioned with 3 mL of HPLC grade methanol followed by equilibration with 3 mL of ultrapure water. 200 mL of samples adjusted to pH 6.0 was passed through the cartridges at a flow rate of between 5 and 8 mL/min. Washing was done by passing 3 mL of ultrapure water through the cartridges. The cartridges were dried in the vacuum oven for 5 min and elution was done with 3 mL of HPLC grade methanol, followed by 3 mL of HPLC grade acetonitrile. The eluate was evaporated to dryness in the vacuum oven and reconstituted with 0.5 mL of HPLC grade methanol.

2.5. Instrumental analysis

All analyses were carried out on LC-UV system comprised of Agilent Series 1100 LC system (Agilent Technologies, Germany). Separation of analytes was done on LC C_{18} column (5 μm particle size, 250 × 4.6 mm i.d) and all injections were done automatically by an autosampler. The chromatographic conditions were as follows: mobile phase, isocratic elution of water/methanol (30/70, v/v); flow rate, 0.7 mL/min; injection volume, 40 μL; column temperature, 20 °C and detector wavelength, 254 nm.

Fig. 1. Map of Osun State, Nigeria showing study area.

2.6. Quality assurance and quality control

Procedural blanks were carried out for each extraction batch (8) to monitor for possible contamination from the solvents and materials used in the extraction processes. The concentrations of analytes found in two procedural blanks were subtracted from the measured concentration in the samples. Methanol blank and midpoint calibration standard was injected after each batch analysis to check for drift in instrumental response and also for carry-over of target analytes from prior injections. Quantification of analytes was carried out using external standards, a calibration curve was constructed by analysing aqueous solutions containing the analytes ranging from concentration of 10 to 1000 μg L^{-1}.

The limit of detection was calculated as three times the signal to noise ratio using the standard deviation of the seven-point calibration intercepts divided by the slope. The limit of quantification (LOQ) was calculated as ten times the ratio. The LOD was between 8 and 16 μg L^{-1} and coefficients of determination (r^2) of calibration curves were >0.999. The coefficients of determination, LOD and LOQ are presented in Table 1. The recovery of target analytes was between 73.7% and 96.8% while the relative standard deviation (RSD) was less than ≤20.0%. The data are also presented in Table 1.

2.7. Risk assessment

Several studies have shown that parabens are toxic to aquatic organisms (Nagar et al., 2020; Terasaki et al., 2015; Yamamoto et al., 2011). To assess the risk to organisms, the risk quotient (RQ) was computed for algae, daphnia and fish. The risk quotient was calculated based on the parabens concentration recorded for this study in surface and groundwater using the formula:

$$RQ = MEC/PNEC$$

where MEC is the measured environmental concentration in surface and groundwater and PNEC is the predicted no-effect concentration. The PNEC was calculated for both acute and chronic tests using the EC_{50}/LC_{50} and NOEC respectively, divided by an assessment factor (AF) (Yamamoto et al., 2011).

$$PNEC_{acute} = (EC_{50}/LC_{50} \text{ of three acute toxicity tests})/AF_{acute}$$

$$PNEC_{chronic} = (NOEC \text{ in chronic tests})/AF_{chronic}$$

where EC_{50}/LC_{50} is the median effect/lethal concentration and NOEC is the no observed effect concentration. The EC_{50}/LC_{50} and NOEC values were obtained from literature. An assessment factor of 100 was used for the acute tests while an assessment factor of 10 was used for chronic tests for algae and daphnia only (Yamamoto et al., 2011). The risk quotient is classified as: High risk (RQ ≥ 1); medium risk (1 < RQ ≤ 0.1); and low risk (RQ < 0.1) (Kairigo et al., 2020).

2.8. Statistical analysis

Statistical analyses were done using the Statistical Package for The Social Sciences (SPSS Statistics23; IBM Corporation, Cornell, NY, USA) and Origin (Origin lab 9.1). Kruskal-Wallis test was conducted to compare the concentrations of parabens between urban and rural sampling sites. Correlation among the concentration of parabens was evaluated with non-parametric Spearman correlation. Statistical significance was set at *p*-value less than 0.05. Multivariate statistical analysis was carried out using the Principal Component Analysis (PCA) software, which was used to extract factors for establishing associations among the parabens (Loska and Wiechuła, 2003). Principal component analysis is one of the most commonly used multivariate statistical methods of analysis in environmental studies (Adesanya et al., 2020; Ogunlaja et al., 2019). It is extensively used to detect the relationship between different environmental variables and/or total variability of a data set (Awolusi et al., 2018). It has been used as tool in contamination or pollution source identification (Ogunlaja et al., 2019).

3. Results and discussions

3.1. Occurrence of parabens in surface and groundwater

In the course of the analysis of packaged water samples (bottled and in sachets), none of the target analytes (Methylparaben-MeP, Ethylparaben-EtP, Propylparaben-PrP and Butylparaben-BuP) was detected. These parabens may be present in these water samples at concentration levels below the range of 8 and 16 μg L^{-1} which is the limit of detection (LOD) of the HPLC equipment used for the analysis of these parabens (Table 1). However, they were detected in surface and groundwater samples. In surface water, MeP had the highest detection frequency of 88.0% with BuP accounting for the second-highest detection frequency of 69.0%. EtP (63.0%) and PrP (63.0%) were the least detected in surface water. MeP (50.0%) and BuP (50.0%) were the most detected in groundwater, while PrP (43.0%) and EtP (36.0%) were found less frequent. The concentrations of parabens are summarized in Table 2.

In surface water samples, MeP and EtP had the highest average concentration; 163 μg L^{-1} (ranging from n.d. to 527 μg L^{-1}) and 113 μg L^{-1} (ranging from n. d. to 377 μg L^{-1}) respectively. The average concentration of 62 μg L^{-1} (BuP) and 64 μg L^{-1} (PrP) was about two to three times lower than that of MeP and EtP. MeP (25 μg L^{-1}), EtP (22 μg L^{-1}), PrP (17 μg L^{-1}) and BuP (24 μg L^{-1}) had comparable average concentrations

Table 1
Linear range, regression coefficient, limit of detection (LOD), limit of quantification (LOQ), recovery and relative standard deviation (RSD) for analysis of parabens in water samples.

Analyte	Linear range (μg L^{-1})	r^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	Spiked conc. (μg L^{-1})	Intra-day		Inter-day	
						Recovery (%) ± SD	RSD (%) $n = 6$	Recovery (%) ± SD	RSD (%) $n = 18$
MeP	10–1000	0.9998	16	53	200	73.7 ± 1.02	1.14	82.6 ± 9.52	9.46
					400	91.6 ± 1.35	0.81	96.8 ± 16.8	9.59
					600	89.4 ± 2.05	0.85	85.3 ± 12.5	5.46
EtP	10–500	0.9998	9	29	200	82.0 ± 1.82	2.16	78.8 ± 10.7	13.2
					400	87.6 ± 1.04	0.69	91.4 ± 16.2	10.3
					600	88.1 ± 1.50	0.68	84.1 ± 9.68	4.63
PrP	25–500	0.9999	8	26	200	91.9 ± 1.35	1.62	87.4 ± 11.0	13.9
					400	92.2 ± 1.64	1.08	93.8 ± 13.4	8.69
					600	90.7 ± 2.13	0.98	86.7 ± 12.0	5.76
BuP	10–1000	0.9999	10	34	200	92.6 ± 0.71	0.97	89.9 ± 14.3	20.0
					400	93.4 ± 1.54	1.13	95.1 ± 13.4	9.69
					600	92.3 ± 3.32	1.65	88.0 ± 15.1	7.88

Table 2
Summary of concentrations of parabens in various water samples (μg L^{-1}).

	Analytes	MeP	EtP	PrP	BuP
Groundwater	Mean	68	56	43	55
	Minimum	n.d.	n.d.	n.d.	n.d.
	Maximum	212	210	217	293
	Median	12	n.d.	n.d.	4
	Frequency (%)	50	36	43	50
Surface water	Mean	163	113	64	62
	Minimum	n.d.	n.d.	n.d.	n.d.
	Maximum	527	377	229	283
	Median	127	83	10	33
	Frequency (%)	88	63	63	69
Packaged water	Mean	n.d.	n.d.	n.d.	n.d.
	Minimum	n.d.	n.d.	n.d.	n.d.
	Maximum	n.d.	n.d.	n.d.	n.d.
	Median	n.d.	n.d.	n.d.	n.d.
	Frequency (%)	–	–	–	–

n.d. - not detected.

in groundwater. MeP had the highest concentrations of 527 μg L^{-1} among all the parabens in this study in surface water at **SW14** as shown in Fig. 2A. The highest concentration of MeP was about one to two times higher than the highest concentrations of EtP (377 μg L^{-1}) at **SW10**, PrP (229 μg L^{-1}) at **SW1** and BuP (283 μg L^{-1}) at **SW12**. The highest concentration of MeP in groundwater was 212 μg L^{-1} at **GW13**, EtP (210 μg L^{-1}) at **GW8**, PrP (217 μg L^{-1}) at **GW13**, BuP (293 μg L^{-1}) at **GW13** as shown in Fig. 2B.

The concentration of parabens found in this study is considerably higher than those reported in surface water in other countries: Brazil (MeP: nd–27.5 μg L^{-1}, EtP: <0.8–30.5 μg L^{-1}, PrP: <0.5–52.1 μg L^{-1}, BuP: <0.8–19.9 μg L^{-1}) (Galinaro et al., 2015), Chile (MeP: 0.63–4.34 μg L^{-1}, PrP: 2.46–14.91 μg L^{-1}, BuP: 0.44–0.90 μg L^{-1}) (Becerra-Herrera et al., 2019), Australia (MeP: 4.62–13.78 μg L^{-1}, EtP: 2.75–305.55 μg L^{-1}, PrP: 2.42–8.29 μg L^{-1}, BuP: 3.86–8.47 μg L^{-1}) (Evans et al., 2016). Also, the concentrations of parabens in groundwater reported in this study are higher than those from other studies in other countries as shown in Table 3. For example, studies from Egypt showed MeP: 1.74 μg L^{-1}, PrP: 0.59 μg L^{-1}, BuP: 6.38 μg L^{-1} (Radwan et al., 2020); Spain: MeP: 0.018 μg L^{-1}, PrP: 0.017 μg L^{-1} (Esteban et al., 2014); and Colombia: MeP: 0.08 μg L^{-1}, EtP: n.d., BuP: 0.007 μg L^{-1} (Aristizabal-Ciro et al., 2017).

However, the highest concentration of MeP (527 μg L^{-1}) in this study found in surface water (Table 2) is about three folds higher than MeP in Brazilian water (170.87 μg L^{-1}) (Pompei et al., 2019) and about two folds higher than in River Ely, United Kingdom (305 μg L^{-1}) (Kasprzyk-Hordern et al., 2009). MeP is used for the formulation of cosmetics and the indiscriminate discharge of wastewater containing cosmetics into these surface water bodies may have contributed to this high value. For example, the Osun river (where samples SW1–SW3 were collected) flows through residential areas with several activities like laundry, bathing, etc. taking place in and around the river causing an increase in the concentration of these parabens in the water body. Besides, it has been found that MeP is ubiquitous since EtP, PrP and BuP can biodegrade to MeP (Lu et al., 2018). Also, the highest EtP concentration (377 μg L^{-1}) found in this study is comparable with EtP concentration in an Australian stormwater (305.55 μg L^{-1}) (Evans et al., 2016). PrP highest concentration (229 μg L^{-1}) in this study is about four times higher than PrP concentration in Mogi Guaçu River, Brazil (52.10 μg L^{-1}) (Galinaro et al., 2015). The raw data for the concentration of these parabens from the different sampling sites is shown in Table S3.

The trend of concentration of MeP > EtP > PrP > BuP in surface water is in good agreement with literature (González-Mariño et al., 2011; Jonkers et al., 2009; Kasprzyk-Hordern et al., 2009). The trend follows the magnitude of hydrophobicity, with MeP being the least hydrophobic (it has lowest LogP value among all parabens) and hence more soluble in water.

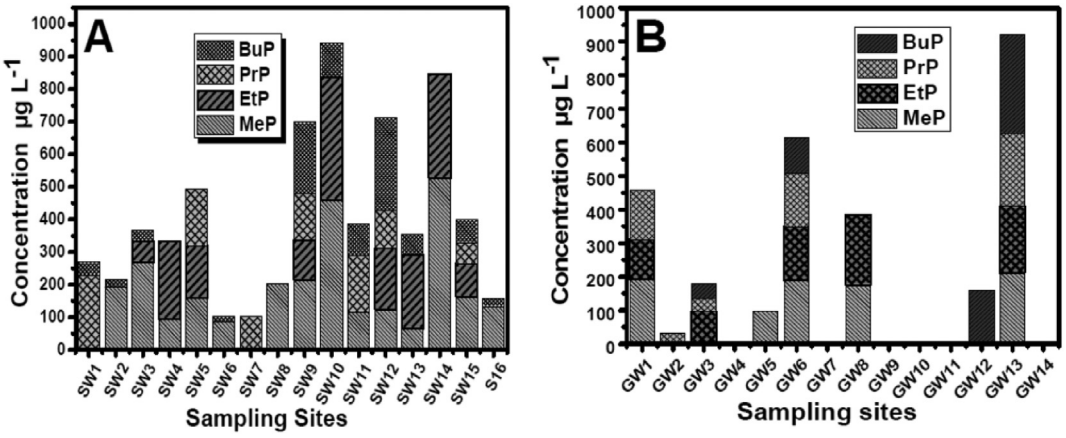

Fig. 2. Concentrations of parabens in (A) surface water and (B) groundwater samples.

Table 3
Comparison of concentrations of paraben with previous studies (μg L^{-1}).

Country	Sample matrix	MeP	EtP	PrP	BuP	References
Brazil	River	n.d.–27.50	<0.8–30.50	<0.5–52.10	<0.8–19.90	(Galinaro et al., 2015)
Egypt	Groundwater	1.78	–	0.59	6.38	(Radwan et al., 2020)
Australia	Storm water	4.62–13.78	2.75–305.55	2.42–8.29	3.86–8.47	(Evans et al., 2016)
Brazil	River	170.87	–	–	–	(Pompei et al., 2019)
Chile	River	0.63–4.34	–	2.46–14.91	0.44–0.90	(Becerra-Herrera et al., 2019)
UK	River	<0.3–305	<0.5–15	<0.2–22	<0.3–16	(Kasprzyk-Hordern et al., 2009)
Colombia	Groundwater	0.08	n.d.	–	0.007	(Aristizabal-Ciro et al., 2017)
Spain	Groundwater	0.018	–	0.017	–	(Esteban et al., 2014)
Nigeria	Groundwater	n.d.–212	n.d.–210	n.d.–217	n.d.–293	This study
Nigeria	River	n.d.–527	n.d.–377	n.d.–229	n.d.–283	This study

However, the relatively high concentration of parabens in groundwater can also be associated with percolation of these chemicals (parabens) into water aquifers from septic systems, uncontrolled hazardous waste release, landfills and rain run-off (Serra-Roig et al., 2016).

In view of the fact that most persons among the population living in the sample sites depend on groundwater as their means of potable water, comparison was made between concentrations of parabens in groundwater in urban and rural settings. It was observed that concentrations of parabens were higher in urban areas than in rural areas. The highest concentration of MeP, EtP, PrP and BuP in urban and rural settings respectively are: MeP (211 and 189 μg L^{-1}), EtP (210 and 160 μg L^{-1}), PrP (217 and 160 μg L^{-1}), and BuP (293 and 214 μg L^{-1}). However, statistical analysis showed there was no significant difference between these concentrations (Kruskal-Wallis test, at $p < 0.05$). The insignificant difference between sampling sites (urban and rural) shows that the level of contamination is similar. Consequently, the indigenous people (rural) are equally exposed to the detrimental effects of the elevated concentration of the studied parabens as well as the urban people in Osun State in Nigeria. The insignificant difference could be due to indiscriminate discharge of untreated sewage into the environment in both settings. Although it has been reported that paraben levels in surface water in the United States of America and in Europe are higher relative to other regions in the world (Wei et al., 2021), this current study from Nigeria suggests otherwise. Results obtained in this study are higher (in most cases) than those reported by Wei et al. (2021).

3.2. Multivariate statistics: principal component analysis

Principal components analysis (PCA) is a distance-based ordination method, it is mainly used to show patterns in multivariate data. In PCA, the relative positions of data points are shown and associations between dependent variables can be determined (Syms, 2008). In this study, PCA was used to determine the association between the target analytes (MeP, EtP, PrP and BuP).

The results of the PCA using varimax normalized rotation for the concentrations of parabens in water samples (surface water and groundwater) are presented in Table 4. The Kaiser-Meyer-Olkin (KMO) measurements were ≥0.700, and the PCA results passed the Bartlett sphericity tests ($P < 0.001$), indicating the suitability of the data for structure detection. Two principal components (PC1 and PC2) were extracted representing 79.8% of the total variances of the studied parabens in surface water.

The principal components (PC1 and PC2) are the axes of the principal components analysis, PC1 representing the dominant variance. Two or more parabens are known to be used as preservatives in cosmetics, pharmaceuticals and food to improve their antimicrobial activity (Błędzka et al., 2014; Gasperi et al., 2014; Guo et al., 2014). To understand their correlation, PCA was conducted for surface water samples in this study. Results obtained suggest that there is a strong association between MeP and EtP in PC 1 (separated by a small distance in the 3-D PCA loading plot as shown in Fig. 3), contributing 47.21% of the total variance, with high loadings of 0.90 and 0.91 respectively. The strong association between MeP and EtP in the water samples is further supported by an overlap of the two contaminants as shown in the rotated matrix dot plot for paraben concentrations in surface water samples (Fig. 4). The same PCA shows a less strong association between PrP and BuP in PC 2, contributing 32.63% of the total variance, with high loadings of 0.89 and 0.83 respectively. This is supported by the rotated matrix dot plot in Fig. 4. On the contrary, weak associations exist between MeP, PrP and BuP which is evident from the larger distance between them in Figs. 3–4.

Table 4
Rotated component matrix of principal component analysis (PCA) for variables in groundwater and surface water samples.

Parameter	Surface water		Groundwater
	Component		Component
	1	2	1
MeP	**0.90**	0.06	**0.92**
EtP	**0.91**	0.14	**0.90**
PrP	−0.42	**0.89**	**0.91**
BuP	0.26	**0.83**	0.78
Eigenvalues	1.89	1.31	
% Total variance	47.2	32.6	
Cumulative %	47.2	79.8	

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser (Bold figures indicate values ≥ 0.8).

For groundwater samples, only one principal component dominated the PCA analysis with high loadings for all the studied parabens except BuP (Table 4). The BuP loading (0.78) for groundwater samples is not as high as that of other parabens, suggesting a quasi-independent behaviour within the group that may link the contribution of a variety of sources to its presence in water. However, MeP, EtP and PrP have close associations with higher loadings of 0.92, 0.90 and 0.91 respectively, indicating that their presence in groundwater around sites used for this study can be linked to similar sources.

While these PCA results suggests that similar factors are responsible for the presence of these pair of parabens in surface water, there is also the concern that with increasing concentration of these pair of parabens in humans, there is the risk of falling ill with estrogenicity-related diseases (Sun et al., 2016).

In addition, there is strong association among the parabens shown in the correlation matrix for concentration of parabens in groundwater (Table 5). Significant correlation was observed among the concentration of MeP, EtP, PrP and BuP. However, closer association was observed with MeP, EtP and PrP, this agrees with the result of PCA for groundwater (Table 4) indicating they are from similar sources.

3.3. Risk assessment

The ecological risk assessment of methyl-, ethyl-, propyl-, and butylparaben, computed based on the risk quotient for minimum and maximum measured environmental concentrations obtained from this study, are presented in Table 6. Acute and chronic risk of the four parabens to algae, daphnia and fish was calculated for groundwater and surface water. All the parabens in groundwater samples (except MeP) posed a high risk to daphnia at the maximum concentration. The risk quotient (RQ) values for daphnia were as high as 2.8 (EtP), 10.9 (PrP), 15.4 (BuP) while MeP was less than 1.0 in groundwater samples. In the surface water, all the four parabens showed a high risk to daphnia with RQ > 1 observed for the worst-case scenario (at maximum concentration). All parabens, aside BuP, showed a lower risk to algae in both groundwater and surface water samples as indicated by their RQ values which are below 1.0 (0.03–0.7) while BuP has RQ value of up to 3.7. Also, fish are susceptible to these parabens having a maximum RQ value of 9.7 and 9.4 in groundwater and surface water respectively. It is observed that daphnia was the most sensitive taxonomic group to the parabens with the highest RQ values of 15.4 in groundwater (BuP) and 14.9 in surface water (BuP). The potential risks to these organisms were in the order algae < fish < daphnia, with BuP and PrP showing the highest risk and MeP posing the lowest risk. It has been reported that toxicity of parabens could increase with increasing alkyl chain length (Terasaki et al., 2015) and that MeP was least acutely toxic (Dobbins et al., 2009). Nagar et al. (Nagar et al., 2020) also observed that toxicity of paraben was in the order BuP > PrP > EtP > MeP. The higher risk observed is due to the higher concentration of parabens recorded in this study and by extension, could have an impact on the environment and human health.

It is important to note that, although the risk quotient was calculated for individual paraben in this study, this could increase when parabens occur simultaneously in the environment. Simultaneous presence of parabens could increase their toxicity. Lee et al. (2018) reported that toxicity was stronger in the presence of mixed parabens than single parabens.

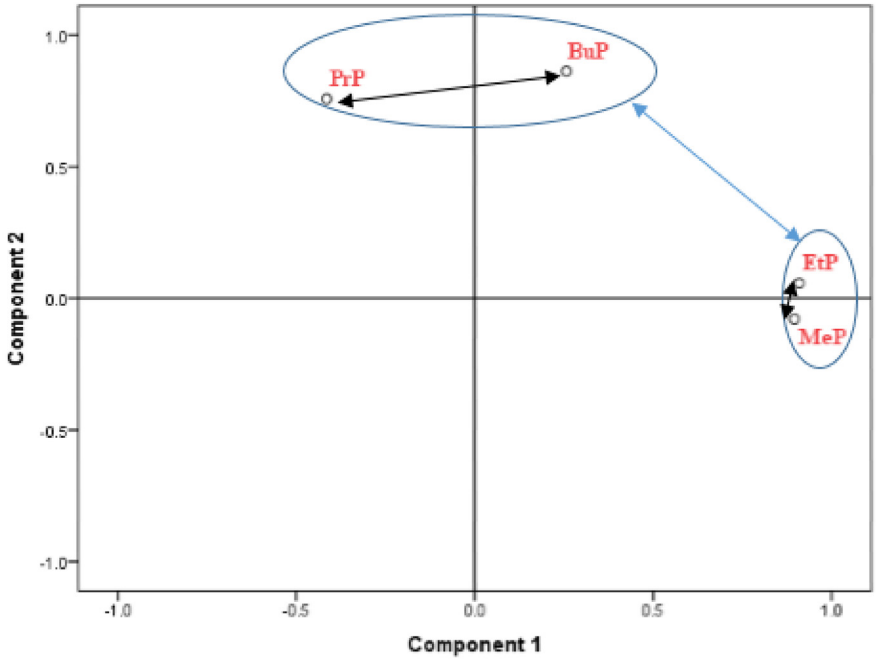

Fig. 3. 3-D plot of principal component analysis (PCA) loading (PC 1 vs PC 2) for parabens in surface water samples.

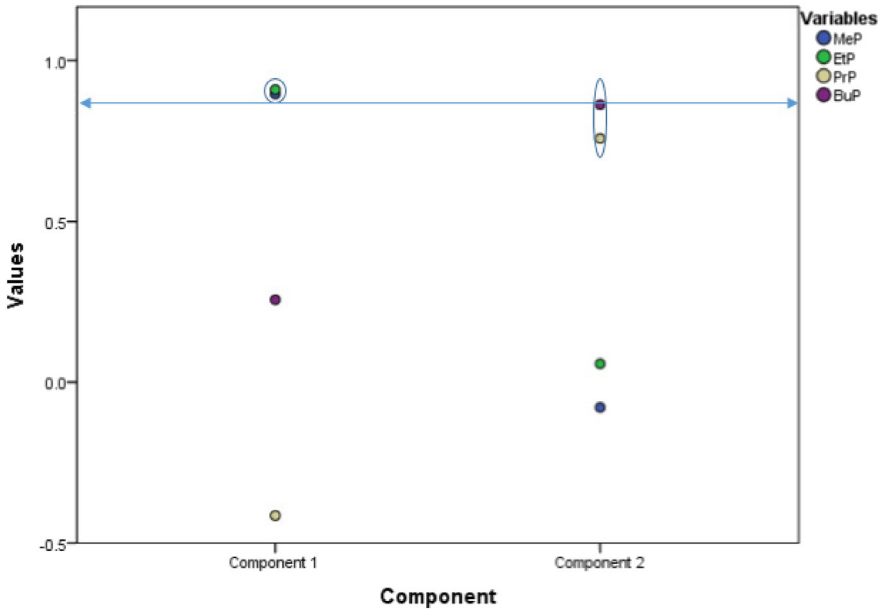

Fig. 4. Rotated component matrix dot plot of principal component analysis for parabens in surface water samples.

3.4. Human exposure assessment

Assessing human exposure to parabens via water ingestion is important because groundwater and even surface water serve as drinking water sources to over 80% of the population in Osun State. The human exposure to parabens was assessed using the estimated daily intake (EDI; μg kg^{-1} bw day^{-1}) based on the United States Exposure Factors Handbook (USEPA, 2011). The population was grouped into infants (<1), toddlers (1–3), children (4–11), teenagers (12 − 21) and adults (≥21).

Table 5
Correlation matrix for concentrations of parabens in groundwater samples.

	MeP	EtP	PrP	BuP
MeP	1			
EtP	0.895**	1		
PrP	0.775**	0.696**	1	
BuP	0.538**	0.524**	0.723**	1

** Correlation is significant at $P \leq 0.01$.

$$\text{EDI water } \left(\mu g\ kg^{-1}\ bw\ day^{-1}\right) = (C \times D)/BW$$

where C is the concentration of the analyte in water (μg L^{-1}), D is the daily water consumption rate (L Day^{-1}) and BW is the body weight (kg). The median and the maximum concentration were used to calculate the EDI. The daily water consumption rate (D) and body weight used for

Table 6
Acute and chronic risk quotient of target analyte in groundwater and surface water samples.

Analytes	Taxonomic group	$PNEC_{acute}$ (μg/L)	$PNEC_{chronic}$ (μg/L)	MEC (μg/L)	RQ_{acute}	$RQ_{chronic}$
Groundwater						
MeP	Algae	800	2100	50–211	0.06–0.3	0.02–0.1
	Daphnia	340	240		0.2–0.6	0.2–0.9
	Fish	630	160		0.08–0.3	0.3–1.3
EtP	Algae	520	1800	98–210	0.2–0.4	0.05–0.1
	Daphnia	74	160		1.3–2.8	0.6–1.3
	Fish	140	80		0.7–1.5	1.2–2.6
PrP	Algae	360	740	32–217	0.09–0.6	0.04–0.3
	Daphnia	20	110		1.6–10.9	0.3–2.0
	Fish	49	40		0.7–4.4	0.8–5.4
BuP	Algae	95	80	45–293	0.5–3.1	0.6–3.7
	Daphnia	19	80		2.4–15.4	0.6–3.7
	Fish	31	30		1.5–9.5	1.5–9.7
Surface water						
MeP	Algae	800	2100	67–527	0.08–0.7	0.03–0.3
	Daphnia	340	240		0.2–1.6	0.3–2.2
	Fish	630	160		0.1–0.8	0.4–3.3
EtP	Algae	520	1800	67–377	0.1–0.7	0.04–0.2
	Daphnia	74	160		0.9–5.1	0.4–2.4
	Fish	140	80		0.5–2.7	0.8–4.7
PrP	Algae	360	740	65–229	0.2–0.6	0.09–0.3
	Daphnia	20	110		3.3–11.5	0.6–2.1
	Fish	49	40		1.3–4.7	1.6–5.7
BuP	Algae	95	80	40–284	0.4–3.0	0.5–3.6
	Daphnia	19	80		2.1–14.9	0.5–3.6
	Fish	31	30		1.3–9.2	1.3–9.5

calculating the EDI was: infants (1 L day^{-1}, 9.2 kg), toddlers (0.9 L Day^{-1}, 13.8 kg), children (1.3 L Day^{-1}, 31.8 kg), teenagers (2.4 L Day^{-1}, 71.6 kg) and adults (3.1 L Day^{-1}, 80 kg) respectively (USEPA, 2011). The median and maximum concentration for surface water was: MeP (127 μg L^{-1}, 527 μg L^{-1}); EtP (82 μg L^{-1}, 377 μg L^{-1}); PrP (10 μg L^{-1}, 229 μg L^{-1}); and BuP (33 μg L^{-1}, 283 μg L^{-1}) respectively. The median and maximum concentration for groundwater was: MeP (12 μg L^{-1}, 211 μg L^{-1}); EtP (0 μg L^{-1}, 210 μg L^{-1}); PrP (0 μg L^{-1}, 217 μg L^{-1}); and BuP (4 μg L^{-1}, 293 μg L^{-1}) respectively.

The estimated daily intake of the analytes via water ingestion is presented in Table 7. The observed median EDI of MeP, EtP, PrP and BuP ranged from 0.38–13.8 μg kg^{-1} bw day^{-1}, 0–9.02 μg kg^{-1} bw day^{-1}, 0–1.08 μg kg^{-1} bw day^{-1} and 0.13–3.60 μg kg^{-1} bw day^{-1} respectively in both groundwater and surface water. Higher overall median EDI values for groundwater were observed for infants (1.71 μg kg^{-1} bw day^{-1}, ΣPBs) compared to others, which is about 2–3 times higher than for toddlers (1.03 μg kg^{-1} bw day^{-1}, ΣPBs), children (0.64 μg kg^{-1} bw day^{-1}, ΣPBs), teenagers (0.51 μg kg^{-1} bw day^{-1}, ΣPBs) and adults (0.62 μg kg^{-1} bw day^{-1}, ΣPBs). A similar trend was also observed for overall median EDI for surface water, with values of 27.5, 16.5, 10.4, 8.10 and 9.81 μg kg^{-1} bw day^{-1} for infants, toddlers, children, teenagers and adults respectively. For the worst-case scenario (using the maximum concentrations of parabens found in both surface and groundwater), the EDI values of the population groups ranged from 22.8–57.3 μg kg^{-1} bw day^{-1} for infant, 13.7–34.4 μg kg^{-1} bw day^{-1} in toddlers, 8.60–21.5 μg kg^{-1} bw day^{-1} in children, 7.04–17.7 μg kg^{-1} bw day^{-1} in teenagers and 8.14–20.4 μg kg^{-1} bw day^{-1} in adults. The population groups are more exposed to MeP in both groundwater and surface water as indicated by the higher EDI values of MeP with respect to other parabens in this study (Table 7). It has been reported that EtP, PrP and BuP can be biodegraded to MeP which may explain why its concentration and exposure risk are higher than that of other parabens.

However, the overall maximum EDI values for all the population groups for groundwater (range: 31.2–101.1 μg kg^{-1} bw day^{-1}, ΣPBs) and surface water (range: 47.5–154 μg kg^{-1} bw day^{-1}, ΣPBs) was quite lower than the acceptable daily intake (ADI) of 10 mg kg^{-1} bw day^{-1} for MeP and EtP set by the European Food Safety Authority (EFSA) (EFSA, 2004). Also, the sum of paraben exposure assessment values for groundwater is considerably lower than the 1.25 mg kg^{-1} bw day^{-1} limit set by the European Medicines Agency (EMA) (EPMAR, 2015), where evidence of adverse health effects was observed.

4. Conclusion

This study presents a report on the presence of parabens (an emerging contaminant) in Nigeria waters. This is the first study from Nigeria to report the presence methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP) and butyl paraben (BuP) in both surface and ground water which serve as sources of potable water for millions of Nigerians. The concentration of parabens in this study was relatively higher than in previously reported studies. MeP was the most dominant among the parabens with detection frequency of (88, 50%) while BuP (69, 50%), PrP (63, 43%), and EtP (63, 36%) for surface water and groundwater respectively. Also, MeP had the highest concentration (527 μg L^{-1}) in samples used for this study, EtP (377 μg L^{-1}), PrP (229 μg L^{-1}) and BuP (293 μg L^{-1}). The Principal Component Analaysis (PCA) of data obtained showed that there was a strong correlation between the concentrations of MeP and EtP in surface water samples which suggests that MeP and EtP in the water samples are from similar sources. This similarity in source was also corroborated by statistical results from PCA, confirming that similar factors are responsible for the presence of these pair of parabens in surface water. Although, the concentrations of parabens in groundwater samples were higher in urban areas than in rural areas, statistical analysis showed that there was no significant difference ($p < 0.05$) in these concentrations, suggesting that persons living in both sites (urban and rural areas) are equally exposed to any potential risk resulting from elevated concentrations of these parabens in water.

Table 7
Human exposure assessment to parabens in water samples (μg kg^{-1} bw day^{-1}).

	Median (groundwater)					Maximum (groundwater)				
	Infant	Toddlers	Children	Teenagers	Adults	Infant	Toddlers	Children	Teenagers	Adults
MeP	1.28	0.77	0.48	0.38	0.46	23.0	13.8	8.64	7.08	8.19
EtP	–	–	–	–	–	22.8	13.7	8.59	7.04	8.14
PrP	–	–	–	–	–	23.5	14.1	8.85	7.26	8.39
BuP	0.43	0.26	0.16	0.13	0.16	31.8	19.1	12.0	9.82	11.4
ΣPBs	1.71	1.03	0.64	0.51	0.62	101.1	60.7	38.1	31.2	36.1
	Median (surface water)					Maximum (surface water)				
	Infant	Toddlers	Children	Teenagers	Adults	Infant	Toddlers	Children	Teenagers	Adults
MeP	13.8	8.30	5.20	4.07	4.93	57.3	34.4	21.5	17.7	20.4
EtP	9.02	5.41	3.39	2.65	3.21	41.0	24.6	15.4	12.6	14.6
PrP	1.08	0.65	0.41	0.32	0.39	24.9	14.9	9.36	7.68	8.88
BuP	3.60	2.16	1.35	1.06	1.28	30.9	18.4	11.6	9.47	11.0
ΣPBs	27.5	16.5	10.4	8.10	9.81	154	92.3	57.9	47.5	54.9

The risk assessment showed that parabens in these water samples, if ingested raw, could be harmful to aquatic organisms at the levels found in this study. Although, the sum of the estimated daily intake for all parabens in this study is quite lower than the acceptable daily intake (ADI), continuous exposure could pose risk to human health. Hence, practices like discharge of untreated sewage, hospital and industrial waste and poor sanitation practices that contribute to the occurrence of these contaminants in the environment should be prohibited. Furthermore, water treatment professionals should include parabens as one of the target contaminants for removal in drinking water. Besides, more funding should be provided by government and funding agencies to carry out further studies on these contaminants of emerging concern with a view to understanding a bit more of their role in human health and how best to mitigate their presence in the environment. This will ultimately encourage the development of policies and regulations that will prevent their discharge into the environment as well as mitigate their presence in the environment especially drinking water.

CRediT authorship contribution statement

Nathaniel B. Bolujoko: Conceptualization, Investigation, Writing – original draft, Formal analysis, Writing – review & editing, Methodology. **Olumuyiwa O. Ogunlaja:** Funding acquisition, Investigation, Supervision, Writing – review & editing, Methodology, Formal analysis. **Moses O. Alfred:** Supervision, Resources, Formal analysis, Validation, Writing – original draft. **Dorcas M. Okewole:** Validation, Methodology, Formal analysis. **Aemere Ogunlaja:** Funding acquisition, Supervision, Resources. **Olumide D. Olukanni:** Funding acquisition, Supervision, Resources. **Titus A.M. Msagati:** Writing – review & editing, Writing – original draft, Methodology. **Emmanuel I. Unuabonah:** Funding acquisition, Conceptualization, Investigation, Resources, Project administration, Methodology, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

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