Ecological and Human Health Risk Assessment of Alkylphenols and Alkylphenol Ethoxylates in Surface Water and Sediment from River Benue, Central Nigeria

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ABSTRACT

Alkylphenols (APs) and Alkylphenol Ethoxylates (APEs) are endocrine disrupting chemicals of global environmental concern, yet, there is paucity of data, and no regulation on these chemicals on the Nigerian environment, and the rest of African continent. This study determined occurrence and baseline risks of APs and APEs in water and sediment from River Benue, central Nigeria, using Gas Chromatography-mass Spectrometry (GC-MS). Sum of twenty APs ($\sum_{20}$APs) in water ranged from ND-38.0 ngL^{-1} during rainy season, and range during dry season was 1.02-5.03 ngL^{-1}. Sum of four APEs ($\sum_{4}$APEs) in water during rainy season ranged from ND-11.1 ngL^{-1}, with the range of ND-1.33 ngL^{-1} during dry season respectively. $\sum_{20}$APs in sediment ranged from ND-11.98 ngg^{-1} d wt during rainy season, with the range of ND-34.4 ngg^{-1} during dry season. $\sum_{4}$APEs in sediment occurred in range of ND-0.91 ngg^{-1} d wt during rainy season, while the dry season APEs occurred in range of ND-8.23 ngg^{-1} d wt. Risks estimate of APs and APEs in water and sediment were consistently lower than the global ecological and human health risks guidelines, suggesting no immediate threat to the ecosystem or humans. This study provides comprehensive baseline data on the levels and risk assessment of APs and APEs in water and sediment from River Benue (second biggest river in Nigeria) in order to guide regulatory authorities, and intending researchers, hereafter.

Keywords: Ecological, Human health risk, Alkylphenols, Alkylphenol ethoxylates, River Benue

INTRODUCTION

Akylphenols (APs) are phenols in which at least one of the hydrogen atoms is substituted by an alkyl group, while Alkylphenol ethoxylates (APEs) are non-ionic surfactants which are obtained by ethoxylation of APs under certain conditions (Thu *et al*., 2024). APs of greatest commercial importance have alkyl groups ranging in size from one (methyl) to twelve carbons (dodecyl) (Allan and Frans, 2013). APEs are among the world most widely used surfactants, having annual global production of about 600, 000 tons (Heemken and Amann, 2023), with octylphenol ethoxylates (OPEs) and nonylphenol ethoxylates (NPEs) contributing about 20% and 80% of the total commercial APEs surfactants (Xie *et al*., 2020). For example, the annual use of NPE in the United States of America as at 2010 was estimated at between 123, 000 and 168, 000 metric tons (Lindborg, 2021). These compounds have wide application as wetting agents, emulsifiers, pesticides adjuvants, industrial cleaning agents and domestic soaps (Mahalakshmi *et al*., 2020; De Bruin *et al*., 2019; Thu *et al*., 2024). These group of chemicals have been classified as ubiquitous, emerging environmental contaminants and endocrine disruptors (EDs), which induce reproductive, and other adverse health disorders on the environmental ecosystem (Macedo *et al*., 2023; Lalonde and Garron, 2024). Due to environmental toxicity of APs and APEs, the German government pronounced ban on the use of APEs in detergent (Tongu *et al*., 2018), while the Directive 2000/60/EC included 4-nonylphenol (4-NP) and 4-octylphenol (4-OP) in the list priority hazardous substances (Lalonde and Garron, 2024; Thu *et al*., 2024).

The aquatic ecosystem receives about 60 % of the total surfactants produced through routes such as urban

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surface runoff, atmospheric deposition, discharge from sewage sludge and/or wastewater treatment plants (Sun *et al*., 2014; Profita *et al*., 2024). On entering the aquatic environment, these group of pollutants bind on solid surfaces such as sediments and biodegrade slowly into lower metabolites (mono- tri-ethoxylates), which turn out to be more persistent, lipophilic, and toxic than their parent compounds (Syakti *et al*., 2023). Anaerobic biodegradation is the major source of metabolites of lower APs in aquatic environment (Xie *et al*., 2020; Hong *et al*., 2020).

Rivers play a key role by supplying water and aquatic resources for the benefit of mankind; therefore, it is important to monitor the quality of river waters to understand their impact on biota and human health, since humans depend on these resources for their various needs (Mahmoud *et al*., 2024). While there are regulations on these pollutants in Europe and America (Acir and Guenther, 2018), we are not aware of any such regulations or restrictions on the African continent, and this may be attributed to the paucity of data on their occurrence and distribution its environment (Acir and Guenther, 2018). Several studies have been conducted on APs and APEs in some parts of Nigeria: (Taylor *et al*., 2001; Arukwe *et al*., 2012; Inam *et al*., 2019; Adeyi, 2020; Adebesin *et al*., 2023), however, to the best of our knowledge, only (Tongu *et al*., 2018) has so far published data on these pollutants in the River Benue in Central Nigeria. Thus, this study was aimed at generating additional baseline data on the occurrence, concentrations and associated ecological and human health risks of residual alkylphenols and alkylphenol ethoxylates in water and sediment from the River Benue ecosystem.

MATERIALS AND METHODS

The Study Area and Sampling Sites

River Benue, the second major river in Nigeria originates in the Adamawa mountains in the Republic of Cameroon, and flows westward for about 1,400 km, passing through Garoua (in Cameroon), Yola and Makurdi until it meets the River Niger at Lokoja in, Nigeria (Tongu *et al*., 2023), as in Fig. 1. For this study, sampling sites were located as indicated in Fig. 2 and Table 1, respectively along its course within Benue State in Central Nigeria.

Fig. 1: Map Showing the River Benue drainage basin across Chad, Cameroon and Nigeria. (Source : Karl Musser -Elevation data from SRTM; drainage basin from GTOPO. All other features from Vector Map.CC BY-SA 3.0 File: Benuerivermap.png. Created: 1 April 2010. Uploaded: 8 October 2010 (Used with KM's permission).

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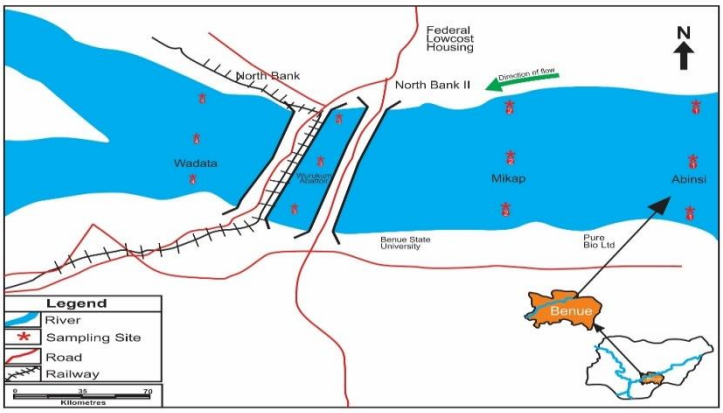

Fig. 2 Sketch map of River Benue showing sampling points in the study area

Table 1: Description of sampling sites in river Benue

		GPS Co-ordinates		
Site No.	Site Name	Latitude	Longitude	Location, characteristics and activities
1	Abinsi	7º 76.060ʿN	8º 72.610 ʿE	Located behind Abinsi open-air market. effluence by drains, fishing, laundry; source of water for domestic activities, boat station, sand dredging, riverbank commerce.
2	Mikap Miva Rice Mills	7º 43.649'N	8º 35.302'E	Located behind Miva Rice Mills Ltd; downstream Pure Bio Ethanol Company Ltd and Benue Brewery Nigeria Ltd. Effluence by factory and city drains. Fishing and sand dredging.
3	Wuruk Abattoir um	7º 44.076'N	8º 32.840'E	Located behind Wurukum Abattior and Wurukum Rice Mills. Effluence by city and Rice Mill drains. Runoff from illegal open-air incineration of vehicle tyres. fishing and sand dredging.
4	Wadata	7º 44.789'N	8º 30.624'E	Located behind Wadata open Market, and downstream the Greater Markudi Water works. Illegal waste dump site, boat station, laundry, fishing, sand dredging, and a source of water for domestic use.

Sample Collection

Collection of water and sediment samples were a one cycle seasonal event, carried out as reported elsewhere (Chokwe *et al*., 2016; Tonugu *et al*., 2018). Briefly, water samples were collected at the same spot with sediments across each sampling point at the depth of about 5 cm below the surface, homogenized, and put into pre-cleaned and labelled 2.5 L amber brown bottles, and about 10 mL of concentrated sulphuric acid added for preservation, tightly sealed, and taken to the laboratories of Joseph Sarwuan Tarka University, Makurdi, where they were stored in a refrigerator at about 4 °C till the time of extraction. A total of 16 water samples were collected during the sampling event.

Sediment samples were collected at about the depth of 0 cm to 5 cm benthic level, using stainless steel grab sampler, placed into pre-labelled 500 mL wide-mouth brown glass sample bottles and tightly closed, then taken to the laboratories of Chemistry Department, Joseph Sarwuan Tarka University, Makurdi. The sediments were placed in wash glasses, allowed to air dry at ambient temperature in a dark cupboard for 5 – 6 days, then, ground with pestle and mortar, sieved through a 500 µm mesh and stored in 500 mL wide-mouth brown glass sample

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bottles at 4 ^{o}C until the time of extraction. A total of 16 sediment samples were collected during the sampling period.

Sample Extraction, Clean-up and Derivatization

Solid phase and Soxhlet extraction procedures were employed to treat water and sediment samples as described elsewhere (Tongu *et al*., 2018), with slight modifications as follows.

One thousand millilitres (1000 mL) water sample was extracted using SPE column under gentle suction in column, plugged with glass wool at the base and 0.5 g C_{18}-reversed phase silica gel placed on top of the wool, conditioned using 6 mL (4:1 v/v) hexane/acetone followed by deionized water. Sample was passed through the column at the rate of 10 mL min^{-1}, after which column was dried under gentle suction for about 15 minutes, and its content eluted with 6 mL (4:1 v/v) dichloromethane (DCM)/hexane. The eluate was then passed through a packed column containing 0.2 g anhydrous sodium sulphate, collected and reduced to incipient dryness with a stream of nitrogen gas. Ten-gram (10 g) of sediment sample was weighed and thoroughly blended with anhydrous sodium sulphate (1:2 w/w) to free flowing using mortar and pestle, then extracted with 300 mL (4:1v/v) hexane/acetone at 55 ^{o}C for 12 hours in 500 mL round bottom flask. The resulting extract was reduced to 5 mL by rotary evaporation at 55 ^{o}C before subjecting it to SPE as described previously.

Derivatization of APs and APEs was carried out according to Chokwe *et al*., 2016), after reconstituting residues with 0.1 mL hexane in a Pyrex tube shaken with 40 µL of 0.1 M triethylamine (TEA) and 4 µL heptafluorobutyric anhydride (HFBA).

Instrumental Analysis

The derivatized extracts were analysed by Agilent 6890 GC equipped with 5975 Mass Selective Detector (MSD), and Agilent autosampler A673, comprising of capillary column (Restek RTx1614; film thickness = 0.10 µm, 15 m x 0.25 mm I.D.). The GC/MS operational conditions were as follows: linear velocity = 40 cm/s; ion source = 150 °C; injector temperature = 280 °C; transfer line temperature = 300°C; carrier gas = Helium; GC initial temperature = 50 °C, heated to 120 °C by a temperature ramp of 7.5 °C/min, then 275 °C by a temperature ramp of 15 °C/min, and finally heated to 300 °C (held for 2 min) by a temperature ramp of 25 °C/min.

Quality Assurance and Statistical Analysis

Quality assurance of the entire analytical process consisted of homogenizing sub-samples in order to obtain a single field sample, transporting samples in ice-box, duplicate analysis of the samples, gentle and incipient drying of extracts, monitoring chromatographic conditions in order to check variations during analysis, running blanks at interval of five samples. Analytes with concentrations below limit of detection (ND) were assigned numerical value of zero for ease of computation. All data were analysed using Microsoft excel, windows 2019 version.

Ecological Risk Assessment

Toxic equivalence (TEQ) approach is used to characterize the toxicity of a mixture of related compounds to aquatic life by expressing the toxicities of each individual compound in common terms and summing them. Application of the TEQ approach requires that all components of a mixture have a common mode of toxicity such that their effects are additive, APs and APEs meet these criteria. At typical environmental concentrations and for conventional toxicity endpoints, the mode of toxicity for APs and APEs homologues is narcosis; hence additivity of their effect is most likely (CCME, 2002). Due to availability of toxic equivalence factors (TEFs) for nonylphenol (NP), nonylphenol ethoxylates (NPEs), octylphenol (OP), and octylphenol ethoxylates (OPEs), they were selected for determination of their total TEQs on the aquatic life of River Benue according to (CCME, 2002) and (Tongu *et al*., 2023) as shown in equation (1).

$$\text{Total TEQ} = \sum_{m=1}^{n}(C_m \text{ x } TEF_m) \quad (1)$$

were,

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TEQ = concentration of the mixture of the APs and APEs, expressed in terms of NP,

n = number of APs and APEs homologues,

m = 1, 2, 3, …, n,

C_m = concentration of compound m,

TEF_m = toxic equivalence factor for the compound *m*.

The sum of TEQ concentrations is then compared with the interim quality guidelines (IQGs) values of 1000 ngL^{-1} and 1400 ngg^{-1} for water and sediment. Toxic equivalence factor value of 1 for NP and OP, while the value of 0.5 for NPE1, NPE2, OPE1 and OPE2 were employed for the computation of TEQs for ecological risk assessment of APs and APEs homologues mentioned above in water and sediment matrices from river Benue during (CCME, 2002).

Human Health Risk Assessment

There is paucity of data indicating the carcinogenic potential of APs ad APEs, thus, the non-cancer hazard quotient (HQ) proposed by the United States Environmental Protection Agency (USEPA) 1989 was adopted from Lee *et al*. (2015) to characterize the health risk posed by NP, NPE, OP, OPE and 4t-BP in water and sediment from river Benue as follows:

$$HQ = \frac{ADD}{RfD} \quad (2)$$

$$ADD = \frac{(Ci\ X\ IR)}{BW} \quad (3)$$

where ADD is the average daily intake of a chemical ($\mu gkg^{-1}BWday^{-1}$), and RfD is the daily intake reference dose ($\mu gkg^{-1}BWday^{-1}$). The tolerable daily intake (TDI) of NP and NPE used as RfD as there is no RfD for these compounds yet. The TDI for NP was 5000 $ngkg^{-1}$ $BWday^{-1}$, and 13000 $ngkg^{-1}$ $BWday^{-1}$ for NPE as proposed by the Danish Institute of Safety and Toxicology (Nielsen *et al*., 2000). The United States Environmental Protection Agency (USEPA) sets a RfD for phenol at 300 000 $ngkg^{-1}BWday^{-1}$ (EFSA, 2013). This RfD value was adopted as the RfD of OP, OPE and 4-tert-butylphrnol for evaluation of their HQ evaluation in water and sediment from River Benue as the RfD of these APs and APEs homologues are yet reported in literature. C_i is the chemical concentration in water and sediment (μgkg^{-1} w/w). IR is the ingestion rate of water (2 L for adult, 1 L for children), and sediment (100 for adult, 200 for children) per day. The above parameters were obtained from (Ukoha *et al*., 2014; Tesi and Iniaghe, 2020; Chen *et al*., 2020; Lee *et al*., 2015). An HQ > 1 indicates that there may be concern for potential human health effects, and vice versa.

RESULTS AND DISCUSSION

Alkylphenols and Alkylphenol Ethoxylates in Water from River Benue

Concentrations of twenty APs isomers ($\sum_{20}$APs) detected in water ranged from ND-38.0 ngL^{-1}, with total and mean±SD concentrations of 96.2 and 12.0±23.4 ngL^{-1}, respectively during rainy season, whereas the range of concentration recorded during dry season was 1.02-5.03 ngL^{-1}, with the total and mean±SD concentrations of 18.4 and 2.30±2.22 ngL^{-1} (Table 2). Levels of APs also varied according to chain length as previously observed by (Acir and Guenther, 2018). The concentrations of nine short chain length APs ($\sum_{9}$SCAPs) detected during this study ranged from ND-38.0 ngL^{-1}, sum of 41.2 ngL^{-1}, and mean±SD of 5.15±21.3 ngL^{-1} during rainy season, then, the range of ND-2.77 ngL^{-1}, sum and mean±SD of 4.1 ngL^{-1} and 0.51±0.73 ngL^{-1} were obtained during dry season respectively. Levels of SCAPs isomers also varied across the seasons, with total of three propylphenol isomers ($\sum_{3}$PP) having the highest concentration across seasons, and also the highest detection frequency of 13% followed by total of three ethylphenol isomers ($\sum_{3}$EP**)**, having the detection frequency of 8% respectively. Concentrations of methylphenol across seasons were below the detection limit of our instrument (Table 2). Levels of total of eleven long chain APs isomers ($\sum_{11}$LCAPs) detected during this study varied in the order:

range = ND-22.6 ngL^{-1}; sum = 55.0 ngL^{-1}, and mean±SD = 6.88±9.85 ngL^{-1} during rainy season, whereas, the concentrations of these pollutants varied in the dry season as follow: range = ND-7.42 ngl^{-1}, sum = 14.3 ngL^{-1}, and mean±SD = 1.79±2.55 ngL^{-1} respectively. 2-EP was the most frequently detected of all the SCAPs reported in water from River Benue (Table 2). Sum of concentrations of $\sum_{11}$LCAPs homologues equally varied in the following order across seasons: $\sum_2$HxP > $\sum_2$BP > 4-HP > $\sum_3$OP > $\sum_2$PnP > 4-NP during rainy season, while the order: $\sum_3$OPs > 4-NP > $\sum_2$BP > $\sum_2$HxP > $\sum_2$PnP and 4-HP was obeyed during dry season, with their respective frequency of detection shown in Table 2. Hong *et al*. (2023) reported detection frequencies of APs to decrease in the sequence: 4-NP > 4-OP > 2-PP > 4t-BP > 4-PnP > 4-EP > 4-HP > 4-HxP respectively, but Lei *et al*. (2021) published highest detection frequency of 4-NP, which is in line with our study. 2-ethylphenol is used as a raw material for manufacture of indene-coumarone resins. This resin is an important ingredient in production of paints, glues and rubber applications to increase solid content, improve the gloss, abrasion resistance, and protect against corrosion (Vinu *et al*., 2005).

NPE is widely used in the pulp and paper making, textile manufacturing, agriculture, metal and plastic manufacturing, and oil refining industries. Products containing NP include detergents, emulsifiers, wetting and dispersing agents, antistatic and emulsifying agents, and solubilizers, which are used in a wide range of industrial, institutional, commercial, and domestic applications (Crini *et al*., 2022; Lalonde and Garron, 2024). NPE as an important component of these products, enters water bodies in various ways, where it is easily degraded to NP, with a more stable chemical structure under the combined actions of various environmental factors (Hong *et al*., 2023; Lalonde and Garron, 2024). Due to recent rapid urbanization, modernization, and industrialization, large amounts of NP have entered rivers, lakes, and reservoirs. It is estimated that approximately 60% of the NP (and its derivatives) produced in the world has been introduced into water resources (Hong *et al*., 2023). Therefore, the abundance of 2-EP and 4-NP in water over other APs homologues could be attributed to point sources of these pollutants around the sites, which calls for further research in the future.

Mean percentage ratio for emission of $\sum_{20}$APs across seasons were found to be 30 %: 70 % for $\sum_9$APs to $\sum_{11}$APEs during rainy season, whereas, the ratio of 5 : 95 % $\sum_9$APs to $\sum_{11}$APEs was observed during dry season respectively (Table 2). Similarly, total concentration of four APEs isomers ($\sum_4$APEs) ranged from ND-11.1 ngL^{-1}, with sum and mean±SD values of 16.0 and 2.00±7.72 ngL^{-1} respectively during rainy season, then the range of ND-1.33 ngL^{-1}, sum and mean±SD of 2.59 and 0.32±0.91 ngL^{-1} were equally obtained during dry season. Concentration and detection frequencies of total of two octyl phenol ethoxylate isomers ($\sum_2$OPEs) were lower than concentration of total of two nonylphenol ethoxylate isomers ($\sum_2$NPEs) across seasons. Similarly, OPE1 isomers were more abundant over those of NPE1 across seasons.

Table 2: Trend APs and APEs in water (ngL^{-1}) from River Benue across seasons

	Rainy Season			Dry Season			
Analyte	Sum	Range	Mean	Sum	Range	Mean	FD
2-MP	ND	ND	ND	ND	ND	ND	**0**
3-MP	ND	ND	ND	ND	ND	ND	0
4-MP	ND	ND	ND	ND	ND	ND	0
$\sum_3$MP	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**0**
2-EP	2.23	ND-1.95	0.28±0.68	2.77	ND-1.75	0.35±0.67	25
3-EP	ND	ND	ND	ND	ND	ND	0
4-EP	ND	ND	ND	ND	ND	ND	0
$\sum_3$EP	**2.23**	**ND-2.23**	**0.28**±0.68	**2.77**	**ND-2.77**	**0.17±0.67**	**8**
2-PP	1.02	ND-1.02	0.13±0.36	ND	ND	ND	0
3-PP	ND	ND	ND	ND	ND	ND	0
4-PP	38.0	ND-23.8	4.74±8.15	1.33	ND-1.33	0.17±0.47	11
$\sum_3$PP	**39.0**	**ND-38.0**	**4.87**±8.08	**1.33**	**ND-1.33**	**0.17**±0.47	**13**
$\sum_9$SCAPs	**41.2**	**ND-38.0**	**5.15**±21.3	**4.10**	**ND-2.77**	**0.51**±0.73	**7**
4-BP	0.64	ND-0.64	0.08±0.23	4.01	ND-4.01	0.50±1.42	13
4t-BP	11.80	ND-7.85	1.47±2.92	ND	ND	ND	13
$\sum$2BP	**12.4**	**0.64-11.8**	**1.55**±2.89	**4.01**	**ND-4.01**	**0.50**±1.42	**13**
2-PnP	ND	ND	ND	ND	ND	ND	0
4-PnP	3.67	ND-3.67	0.46±1.30	ND	ND	ND	6
$\sum_2$PnP	**3.67**	**ND-3.67**	**0.46**±1.20	**ND**	**ND**	**ND**	**3**
2-HxP	ND	ND	ND	0.43	ND-0.43	0.05±0.15	6
4-HxP	22.6	ND-22.6	2.83±8.00	0.90	ND-0.90	0.11±0.32	13
$\sum_2$HxP	**22.6**	**ND-22.6**	**2.83**±8.00	**1.33**	**ND-0.90**	**0.17**±0.33	**9**
4-HP	10.7	ND-9.90	1.36±3.48	ND	ND	ND	13
2-OP	0.2	ND-0.20	0.02±0.07	1.66	ND-1.07	0.21±0.40	19
4-OP	3.73	ND-1.51	0.46±1.23	1.54	ND-1.54	0.19±0.53	19
4t-OP	ND	ND	ND	0.76	ND-0.76	0.20±0.27	6
$\sum_3$OPs	**3.93**	**ND-3.73**	**0.49**±1.23	**3.96**	**ND-1.66**	**1.12**±0.91	**15**
4-NP	1.53	ND-1.53	0.19±0.54	5.03	ND-3.41	0.63±1.20	25
$\sum_{11}$LCAPs	**55.0**	**ND-22.6**	**6.88**±9.85	**14.3**	**ND-7.42**	**1.79**±2.55	**12**
$\sum_{20}$APs	**96.2**	**ND-38.0**	**12.0**±23.4	**18.4**	**1.02-5.03**	**2.30**±2.22	**10**
OPE1	11.1	ND-5.69	1.39±2.02	1.33	ND-1.33	0.17±0.47	25
OPE2	ND	ND	ND	ND	ND	ND	ND
$\sum_2$OPEs	**11.1**	**ND-11.1**	**1.39**±2.02	**1.33**	**ND-1.33**	**0.17**±0.47	**13**
NPE1	ND	ND	ND	ND	ND	ND	0
NPE2	4.87	ND-4.59	0.61±1.61	1.26	ND-1.26	0.16±0.44	19
$\sum$2NPEs	**4.87**	**ND-4.87**	**0.61**±1.61	**1.26**	**ND-1.26**	**0.16**±0.44	**9**
$\sum_4$APEs	**16.0**	**ND-11.1**	**2.00**±7.72	**2.59**	**ND-1.33**	**0.32**±0.91	**11**

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$\sum_3$MP = 2-MP + 3-MP + 4-MP. $\sum_3$PP = 2-PP + 3-PP + 4-PP. $\sum_9$SCAPs = $\sum_3$MP + $\sum_3$EP + $\sum_3$PP. $\sum_2$BP = 4-BP + 4t-BP. $\sum_2$PnP = 2-PnP + 4-PnP. $\sum_2$HxP = 2-HxP + 4-HxP. $\sum_3$OPs = 2-OP + 4-OP+ 4t-OP. $\sum_{11}$LCAP = $\sum_2$BP + $\sum_2$PnP + 4-HP + $\sum_2$HxP + $\sum_3$OPs + 4-NP. $\sum$20APs = $\sum_9$SCAPs +$\sum_{11}$LCAP + 4-HP + 4.NP. $\sum_2$OPEs = OPE1 + OPE2. $\sum_2$NPEs + NEP1 + NPE2. ND = Not Detected. Analytes with ND were assigned numerical value of zero for ease of data computation.

Concentrations of APs and APEs from River Benue were consistently higher during rainy season than dry season, which agreed with the research reports of (Tongu *et al*., 2018; Vinu *et al*., 2005). Higher APs and APEs load recorded in this study during rainy season than dry season might be the consequence of runoff from farm lands, drains and storm water into the studied sites during rainy season. APs and APEs are applicable for the production of diverse categories of substances including pesticides (Crini *et al*., 2022; Brenkus *et al*., 2024), and application of the pesticides on farm lands and/or crops for control of pests leaves residues of these chemicals which might enter aquatic environment through fate processes such as runoff and wet deposition, given higher load of these pollutants during rainy season than dry season. Drains have been reported to serve as conveyor belt for pollutants into receiving water bodies such as rivers, lakes and ponds (Tongu *et al*., 2023).

When compared with similar other studies, levels of APs and APEs in water from this study were in range with the reports of (Tongu *et al*., 2018) from river Benue, Nigeria; Adeyi (2020) from Lagos Lagoon, Nigeria; Janousek et al. (2020) from Waste Water Treatment Plant (WWTP), Germany, and Chokwe *et al*. (2012) from WWTP, South Africa respectively. Sibali *et al*. (2010), Liu *et al*. (2016), Li *et al.* (2003) and Xie *et al*. (2020) reported higher APs and APE values in water from Major rivers in Lagos, Nigeria; Jukskei river Catchment, South Africa; Taihu Lake China, and Pearl river Networks, South China respectively.

Total and sum of mean emission of pollutants in water were consistent per site and decreased in the sequence: site 4 > site 2 > site 3> site 1 during rainy season, and site 1 > site 4 > site 2 > site 3 during dry season respectively (Fig. 3). Variation in anthropogenic activities around the sites coupled with runoff and non-point source emission of APs and APEs might account for the site differences in the pollutants load during this study (Table 1). The city of Makurdi reportedly has poor waste management practices, and as such, waste of various compositions is illegally dumped on sites, which serve as potential sources of pollutants in and around the city (Sha'Ato *et al*., 2007). The impact of drains and other anthropogenic activities on the emission of APs and APEs were previously reported in literature (Tongu *et al*., 2023; Brenkus *et al*., 2024; Crini *et al*., 2022; Lalonde and Garron, 2024).

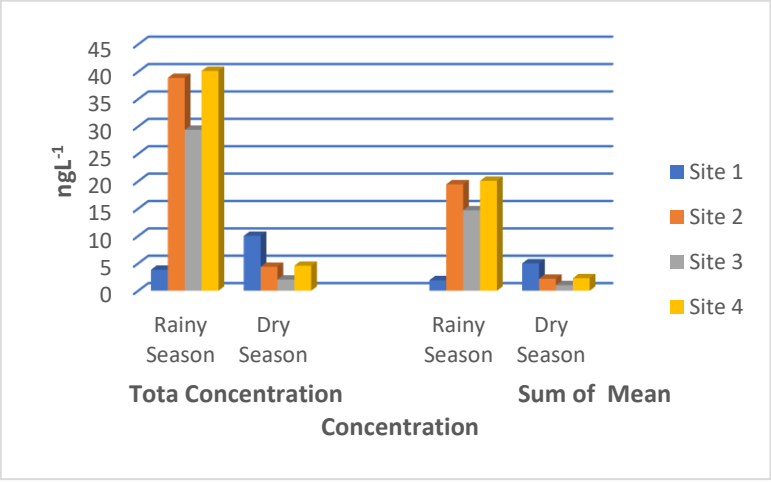

Fig. 3 Variation of total and sum of mean pollutants in water from River Benue

Alkylphenols and Alkylphenol Ethoxylates in Sediment from River Benue

Concentrations of twenty APs isomers ($\sum_{20}$AP) obtained in sediment from River Benue ranged from ND-11.98 ngg^{-1} d wt, with total and mean±SD concentrations of 44.8 ngg^{-1} d wt, and 5.60±4.52 ngg^{-1} d wt during rainy season, while the range, total and mean±SD of ND-34.4 ngg^{-1}, 116 ngg^{-1} d wt, and 14.5±13.37 ngg^{-1} d wt respectively were recorded during dry season (Table 3).

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Trend of emission of $\sum_9$SCAP was equally observed during this study: range of ND-7.60 ngg^{-1} d wt, total and mean±SD concentrations of 14.3 ngg^{-1} d wt and 1.79±2.32 ngg $^{-1}$ d wt respectively during rainy season, whereas, the range of ND-22.2 ngg^{-1} d wt, total and mean±SD concentrations of 44.1 ngg^{-1} d wt, and 5.50±7.59 ngg^{-1} d wt respectively were noted during dry season. The scenario of of eleven long chain APs isomers ($\sum_{11}$LCAPs) in sediment from river Benue was considered as well. Concentrations of $\sum_{11}$LCAPs varied with the range of ND-12.0 ngg^{-1} d wt, total of 30.5 ngg^{-1} d wt, and mean±SD of 3.81±4.71 ngg^{-1} d wt during rainy season, while variation in the range of ND-34.4 ngg^{-1} d wt, total and mean±SD of 71.7 ngg^{-1} d wt, and 8.96±10.3 ngg^{-1} d wt respectively during dry season (Table 3). Among the APs detected during this study, $\sum_9$SCAP contributed mean concentration ratios of 31.96 % and 38.04 % during rainy and dry seasons, while $\sum_{11}$LCAPs contributed the ratios of 68.04 % and 61.96 % during rainy and dry seasons respectively. The abundance of LCAPs over SCAPs during this study could be attributed to non-point source emissions especially through runoff from illegal waste dump sites as the city of Makurdi has a history of poor waste management practices (Sha'Ato *et al*., 2007). The studied sites were also surrounded with agricultural lands which could equally serve as point source for these pollutants.

Concentrations of four APEs isomers ($\sum_4$APEs) detected in sediment also varied across seasons. The range, sum and mean±SD of $\sum_4$APEs during rainy season were ND-0.91 ngg^{-1} d wt, 1.45 ngg^{-1} d wt, and 0.11±0.35 ngg^{-1} d wt, then, the concentrations in the range of ND-8.23 ngg^{-1} d wt, sum and mean±SD of 8.23 ngg^{-1} d wt and 1.03±±1.94 ngg^{-1} d wt were recorded during dry season respectively (Table 3). The detection frequency of APs and APEs in sediment from this study was observed in the order: $\sum_9$SCAP > $\sum_{11}$LCAPs > $\sum_4$APEs (Table 3). Frequency of detection for the SCAP group of APs was found to follow the pattern: $\sum_3$PP > $\sum_3$EP > $\sum_3$MP, and among which 2-PP was most abundant. Hong *et al*. (2022) reported 100% abundance of 2-PP from the Beiyun river. 2-PP is used as food additive and fragrance, and as such, its high abundance in sediment from this study suggested strong emission source(s) for this chemical, hence the need to investigate in future research. The trend of abundance of sum of LCAPs across seasons were equally observed to follow the pattern: $\sum_3$OPs > $\sum_2$BP > $\sum_2$HxP > 4.NP > 4-HP during rainy season, while the trend: 4-NP > $\sum_2$BP > $\sum_2$HxP > $\sum_3$OP > $\sum_2$PnP > 4-HP was noted during dry season, with detection frequencies of their various homologues shown in Table 3. The trend of abundance of APs found in sediment in this study suggested variation in emission sources for these chemicals. 4-NP and 4t-BP had the highest detection frequency (38 %) among all APs detected in sediment, while the detection frequency of MP, 4-PnP, 4-HP and 2-OP were zero. NPE2 had the highest detection frequency (6 %) among all APE studied. Mahalakshmi *et al*. (2020) detected 100% NP in tannery sediment from Tamil Nadu, India. The low level of APEs detected during this study could be attributed to low sources of these pollutants, hence further investigation is necessary for future research.

Concentrations of APs and APEs from River Benue was consistently higher during dry season than rainy season, and this agreed with the reports of (Tongu *et al*., 2018; Li *et al*., 2004; Shiu *et al*., 2019). Higher concentrations of APs and APEs recorded during dry season might be the consequence of dilution during rainy season and/or higher water current which stimulates resuspension of these chemicals from sediment into surface water, reducing the sediment concentration of these chemicals during rainy season, or longer resident time of the pollutants in sediment during dry season, increasing their availability in the matrix. The effects of dilution, turbulence due to water current, and longer resident time on accumulation of pollutants on sediment were reported earlier in literature (Shiu *et al*., 2019; Lalonde and Garron, 2024). Long chain APEs could degrade into short chain metabolites such as OPE1, OPE2, NPE1 and/or NPE2 respectively. Degradation of APEs is influenced by temperature, microorganisms, and photolysis (Shiu *et al*., 2019; Botha *et al*., 2023). The higher levels of APs metabolites obtained in sediment during dry season could be the consequence of photodegradation of APEs as the study area is characterized with high intensity of sun light during dry season, although the impact of microorganisms on degradation of APEs into APs should equally be thoughtful, hence, the necessity for a comprehensive and systematic consideration of this scenario for future research.

Total concentrations of APs and APEs in sediment were in range with the study of Tongu *et al*. (2018), Adeyi (2020), Ying (2006), Liu *et al*. (2016), Lalonde and Garron (2024), while Brenkus *et al*. (2024); Hong *et al*. (2022), Sibali *et al*. (2010), McLaren and Rawlins (2022) and Lee *et al*. (2020) reported higher sedimentary values of APs and APEs. APs and APEs posed total and sum of mean variations in sediment per site across seasons (Fig. 4). Total concentrations of these pollutants in sediment from this study were consistent across seasons, and decreased in the sequence: site 3 > site 2 > site 4 > site 1. Conversely, sum of mean concentration

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of APs and APEs followed the pattern: site 3 > site 2 site 1 > site 4 during rainy season, while the order: site 2 > site 3 > site 4 > site 1 were obeyed during dry season. Variation in site specific emission sources for the APs and APEs might account for this trend of emission of the pollutants in the studied sites, and this calls for further investigation in future research.

Table 3 Trend of APs and APEs (ngg^{-1} d wt) and Total Organic Carbon (TOC) (%) in sediment from River Benue

	Rainy Season			Dry Season			
Analyte	Sum	Range	Mean	Sum	Range	Mean	FD
2-MP	ND	ND	ND	ND	ND	ND	0
3-MP	ND	ND	ND	ND	ND	ND	0
4-MP	ND	ND	ND	ND	ND	ND	0
$\sum_3$MP	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**0**
2-EP	0.91	ND-0.53	0.11±0.21	1.22	ND-1.22	0.15±0.43	19
3-EP	ND	ND	ND	1.28	ND-1.28	0.16±0.45	6
4-EP	0.54	ND-0.54	0.068±0.19	22.20	ND-19.3	2.76±6.75	19
$\sum_3$EP	**1.45**	**ND-0.91**	**0.18±0.19**	**24.70**	**ND-22.2**	**3.07**±7.62	**15**
2-PP	7.60	ND-2.63	0.95±1.31	5.36	ND-3.91	0.67±1.40	31
3-PP	ND	ND	ND	6.16	ND-3.26	0.77±1.43	13
4-PP	5.23	ND-3.20	0.65±1.38	7.87	ND-7.87	0.98±2.78	25
$\sum_3$PP	**12.8**	**ND-5.23**	**1.6±1.38**	**19.39**	**ND-7.87**	**2.42**±3.78	**23**
$\sum_9$SCAP	**14.3**	**ND-7.60**	**1.79±2.32**	**44.09**	**ND-22.2**	**5.50±7.59**	**13**
4-BP	11.2	ND-10.7	1.4±3.77	15.14	ND-4.42	1.89±2.06	38
4t-BP	ND	ND	ND	4.46	ND-3.14	0.56±1.14	13
$\sum_2$BP	**11.2**	**ND-11.2**	**1.4±3.77**	**19.60**	**ND-15.1**	**2.45**±2.50	**25**
2-PnP	1.32	ND-1.32	0.17±0.47	ND	ND	ND	6
4-PnP	ND	ND	ND	ND	ND	ND	0
$\sum_2$PnP	**1.32**	**ND-1.32**	**0.17±0.47**	**ND**	**ND**	**ND**	**3**
2-HxP	ND	ND	ND	11.52	ND-11.5	1.44±4.07	6
4-HxP	3.92	ND-3.92	0.49±1.39	0.81	ND-0.81	0.11±0.29	13
$\sum_2$HxP	**3.92**	**ND-3.92**	**0.49±1.39**	**12.33**	**ND-11.5**	**1.54**±4.36	**9**

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4-HP	ND	ND	ND	ND	ND	ND	0
2-OP	ND	ND	ND	ND	ND	ND	0
4-OP	12.0	6.99	1.5±2.82	0.91	ND-0.91	0.11±0.32	19
4t-OP	ND	ND	ND	4.43	ND-4.43	0.55±1.57	6
$\sum_3$Ops	**12.0**	**ND-12.0**	**1.5±2.82**	**5.34**	**ND-4.43**	**0.67**±1.55	**8**
4-NP	2.08	ND-2.08	0.26±0.74	34.41	ND-19.1	4.3±6.27	38
$\sum_{11}$LCAPs	**30.5**	**ND-12.0**	**3.81±4.71**	**71.67**	**34.4**	**8.96**±10.3	**11**
$\sum_{20}$APs	**44.8**	**ND-11.98**	**5.60±4.52**	**115.77**	**ND-34.4**	**14.5±13.37**	**13**
OPE1	0.54	ND-0.54	0.07±0.19	8.23	ND-4.80	1.03±1.94	19
OPE2	ND	ND	ND	ND	ND	ND	0
$\sum_2$OPEs	**0.54**	**ND-0.54**	**0.07±0.19**	**8.23**	**ND-8.23**	**1.03±1.94**	**9**
NPE1	ND	ND	ND	ND	ND	ND	0
NPE2	0.91	ND-0.91	0.11±0.32	ND	ND	ND	6
$\sum_2$NPEs	**0.91**	**ND-0.91**	**0.11±0.32**	**ND**	**ND**	**ND**	**3**
$\sum_4$APEs	**1.45**	**ND-0.91**	**0.11±0.35**	**8.23**	**ND-8.23**	**1.03±±1.94**	**6**
TOC	**64.9**	**15.97-22.08**	**16.2**	**705.06**	**88.84-285.11**	**176.27**±1.94	

Concentrations of total organic carbon (TOC) was consistent with the levels of APs and APEs in sediment from river Benue across seasons (Table 3). Levels of TOC ranged from 16.0-22.1 %, total and mean±SD of 64.9 % and 16.2±4.80 % during rainy season, whereas, the range, total and mean±SD concentrations of 88.8-285 %, 705 % and 176±81.7 % respectively were recorded during dry season (Table 3).

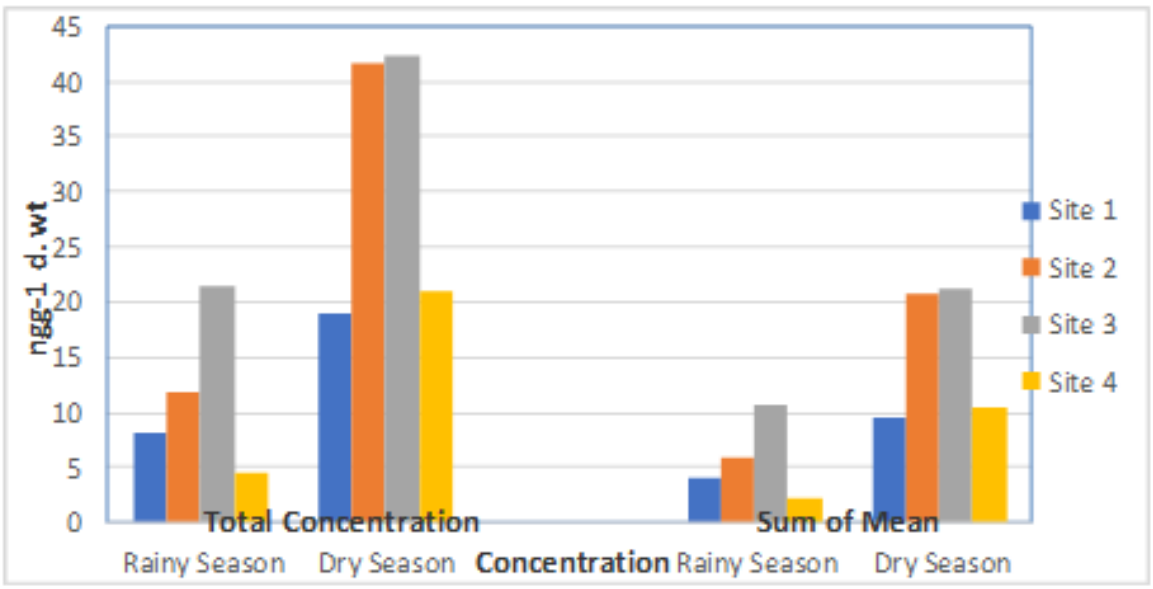

Fig. 4 Variation of total and sum of mean pollutants in sediment from River Benue

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Levels of APs and APEs in sediment from River Benue correlated weakly (rs = 0.19) with TOC during rainy season, while very strong correlation (rs = 0.78) of these pollutants with TOC was recorded during dry season This scenario confirmed the earlier report that accumulation of pollutants in soils and/or sediment is a function of TOC as the two exist in direct proportion to each other (Schumacher, 2002). The relationship between TOC and sediment accumulation of APs and APEs also affirmed the reason for the high affinity of these compounds to sediment The higher levels of TOC obtained from this study during dry season over rainy season might be the consequence of dilution due to large volume of water during rainy season, turbulence due to water current which might result into resuspension of the pollutants rich sediment into surface waters, hence reducing their concentrations in the sediment during rainy season. Dry season is generally characterized with low water volume (high pollutant concentration), less water current (low turbulence) and longer resident time for compounds in sediment, and these favour accumulation of pollutants during this season.

Risk Assessment of APs and APEs in Water and Sediment from River Benue

Risk assessment is a tool developed by regulatory agents in order to evaluate the hazard of pollutants to ecology and humans (Huang *et al*., 2014). An organism could be exposed to pollutants through ingestion, dermal absorption and/or inhalation (Chen *et al*., 2020). In this study, ecological and human health risks assessment were carries out on surface water and sediment to assess the impact of APs and APEs on these matrices.

Ecological Risk Assessment of APs and APEs in Water from River Benue

Regulatory guidelines developed by USEPA (Sauter and Licha, 2002; USEPA, 2005), Netherlands (Nielsen *et al*., 2000), Europe (Janousek *et al*., 2020), and Canada (CCME, 2002) were adopted for the ecological risk assessment of APs and APEs in water from river Benue during the period of this study since there is no such regulation in Nigeria yet. Referred to Table 4, concentrations of APs and APEs in water from river Benue were lower than all regulatory guidelines considered for the risk evaluation across sites, with ∑PP having the highest value (sum = 27.092 ngL^{-1}, mean = 6.77 ngL^{-1}), while ∑MP was not detected in any of the sites. 4t-OP and 4-NP were reported to cause sex differentiation and vitellogenin induction during the early life stage in Medaka (*Oryzias latipes*) at concentrations of 11400 ngL^{-1} and 11600 ngL^{-1} (Seki *et al*., 2002). Cui *et al*. (2022) reported that 4t-BP-exposure ultimately induced ferroptosis in hepatocytes through oxidative stress, iron overload, SLC7A11/GSH/GPX4 axis, and ATF4/HSPA5/GPX4 axis. According to (Barse *et al*., 2006), $i/10^{th}$ dose (690000 ngL^{-1}) of the 96^{th} h LC_{50} (6900000 ngL^{-1}) of 4t-BP causes endocrine disruption and metabolic changes in *Cyprinus carpio*. The values of 4t-OP, 4-NP and 4t-BP obtained from this study were lower than the literature values reported by (Seki *et al*. (2002), Cui *et al.* (2022) and Barse *et al*. (2006) respectively. Concentrations of 4-EP, 2-PP, 4-PnP, 4-HxP, 4-HP and 4-OP recorded in water from were lower than the predicted toxicity values of APs developed by the QSAR model for aquatic species (Hong *et al*., 2022). Predicted no-effect concentration (PNEC) is the concentration threshold at which no adverse effects are likely to occur to an ecological organism. PNEC is one of the important tools in ecological risk assessment because it helps to determine the short-term and long-term water quality criteria for detecting levels of pollutants to protect certain ecosystems. For instance, the European Union had established a toxicity threshold of 330 ng^{-1} with species sensitivity distribution based on the potential toxic effect of nonylphenol on freshwater fish (Hong *et al*., 2020). Values of 4-NP obtained in water from this study were 66 to 1737 times lower than the threshold set by the European Union.

Toxic Equivalence of APs and APEs in Water from River Benue

The toxic equivalence quotient (TEQ) was applied in order to determine the risk of selected APs and APEs in water from river Benue during this study. An organism might be affected by a mixture of APs and/or APEs in a given ecology (Servos *et al*., 2003). Total concentrations of APs and APEs homologues in water ($\sum_{hono}$TEQ) ranged from 0.031-10.852 ngL^{-1}TEQ, with sum and mean of 33.02 ngL^{-1} TEQ and 5.512 ngL^{-1}TEQ. Levels of TEQ per site ($\sum_{site}$TEQ) follows the pattern: Abattoir > Abinsi > Wadata > Mikap respectively (Table 5). Total TEQs for APs and APEs homologues studied in this research also varied in the order: 2-OP > 4-NP > 4-OP > OPE1 > 4t-OP > NPE2 respectively (Table 5). When compared with interim guidelines of 1000 ngL^{-1} developed by the CCME (2002), levels of TEQ in water from this study were lower than this guideline value. In comparison with similar other studies, Lalonde and Garron (2021), Shah and Smyth 2013) reported higher TEQ values for APs and APEs than our study.

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Human Health Risk Assessment of APs and APEs in Water from River Benue

Ingestion of contaminated water has been established to be one of the important routes which humans are exposed to emergent contaminants, and its impact depends on physicochemical and biotic metabolic characteristics of the contaminants themselves (Chokwe *et al*., 2017). Due to paucity of data on carcinogenicity of APs and APEs, the non-carcinogenic hazard quotient (HQ) is usually adopted for evaluating the risk of exposure of an organism to APs and APEs (Lee *et al*., 2015; Lee *et al*., 2020). The HQ due to ingestion of water contaminated with AP and APEs from River Benue as stated in Table 6 indicated that no risk was expected for adult and children who drank it as HQ < 1 for all the pollutants across sites. Sum and mean HQ values were consistent for adult and children, and decreased in the sequence: 4-NP > 4t-BP > 4t-OP.

According to USEPA (1989), an organism might be affected by a mixture of pollutants through a single dietary component, and as such, evaluation of sum of hazard quotient (∑HQ) became necessary. ∑HQ values for ingestion of APs and APEs in water by adult and children during this research were reported as shown in Table 6 were consistently higher in children than adult, which connotes higher risk of exposure exposure for children than adult, even as the ∑HQ values were less than 1 for the two groups. Although children consume less water (1 $Lday^{-1}$) than adult (2 $Lday^{-1}$), their low body weight and their body sensitivity might account for their higher body burden of these pollutants than adult. The order of ∑HQ for adult and children decreased in the sequence: Abinsi > Abattoir > Wadata > Mikap. This trend might be attributed to variation in emission sources of the pollutants at the various sites, thus risk due to source specific emission of APs and APEs from River Benue should be considered for further research.

Based on the levels of APs and APEs in water obtained from this study, River Benue water is adjudged to be minimally contaminated with these chemicals, hence, potentially safe for aquatic and human life.

Table 4: Comparison of APs and APEs (ngL^{-1}) in water from River Benue with regulatory standards

Analyte	Abinsi Sum	Mean	Mikap Sum	Mean	Abattior Sum	Mean	Wadata Sum	Mean		Regulatory	Agent and Standard (ngL-1)
									USEPA: Sauter and Licha (2002)	Netherlands: Nielsen et al. (2000)	USEPA: Europe: Canada:
											USEPA (2005): Janousek et al. (2020): CCME (2002)
∑MP	ND	ND	ND	ND	ND	ND	ND	ND	20	-	- - -
∑EP	ND	ND	1.95	0.49	1.02	0.26	2.03	0.51	20	-	- - -
∑PP	ND	ND	27.09	6.77	5.63	1.41	7.59	1.9	20	-	- - -
4t-BP	ND	ND	3.95	0.99	7.85	1.96	ND	ND	-	-	- 73000 -
4t-OP	ND	ND	ND	ND	ND	ND	0.76	0.19	-	-	- 6000 -
4-NP	3.41	0.85	0.46	0.12	1.53	0.38	1.16	0.29	-	500	6600

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											25000 1000
NPE1	ND	ND	ND	ND	ND	ND	ND	ND	-	500	- - -
NPE2	ND	ND	5.85	1.46	ND	ND	0.28	0.07	-	500	- - -

Table 5: Toxic equivalence quotient (ngL^{-1}TEQ) of APs and APEs in surface water from River Benue

Site	2-OP	4-OP	4t-OP	4-NP	OPE1	NPE2	$\sum_{site}$TEQ	Range	Mean±SD
Abinsi	1.264	1.734	NA	3.412	0.014	ND	6.424	ND-3.412	1.071±1.41
Mikap	NA	NA	NA	0.460	1.521	0.029	2.010	ND-1.521	0.335±0.77
Abattoir	9.588	3.514	NA	1.530	0.470	ND	15.102	ND-9.588	2.517±4.08
Wadata	NA	NA	0.764	1.156	2.846	0.001	4.767	ND-2.846	0.794±1.20
$\sum_{hono}$TEQ	10.852	5.248	0.764	6.558	4.851	0.030	33.020	0.031-10.852	5.512±3.97

Interim Quality Guideline (IQG) = 1000 ng L^{-1}. Source: CCME (2002). $\sum_{sites}$TEQ = site 1 TEQ + site 2 TEQ + site 3 TEQ + site 4 TEQ. $\sum_{homo}$TEQ = 2-OP TEQ + 4-OP TEQ + 4t-OP TEQ + 4-NP TEQ + OPE1 TEQ + NPE2 TEQ. NA = not applicable as concentration of analyte was ND

Table 6: Hazard quotient (ngL^{-1}) for ingestion of APs and APEs in water from River Benue by adult and children

	Abinsi		Mikap		Abattoir		Wadata		Adult		Children	
Analyte	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Sum	Mean	Sum	Mean
4t-BP	ND	ND	3.76E-07	8.22E-07	7.48E-07	1.64E-06	ND	ND	1.12E-06	2.81E-07	2.46E-06	6.16E-07
4t-OP	ND	ND	ND	ND	ND	ND	7.28E-08	1.59E-07	7.28E-08	1.82E-08	1.59E-07	3.98E-08
4-NP	1.95E-05	4.27E-05	2.63E-06	5.75E-06	8.75E-06	1.92E-05	7.11E-06	1.44E-05	3.80E-05	9.50E-06	8.21E-05	2.05E-05
∑HQ	1.95E-05	4.27E-05	3.01E-06	6.57E-06	9.50E-06	2.08E-05	7.18E-06	1.46E-05	3.92E-05	9.80E-06	8.47E-05	2.12E-05

Ecological Risk Assessment of APs and APEs in Surface Sediment from River Benue

It is worth noting once again that APs and APEs such as NP and the short chain NPEs (NPE1 and NPE2) are persistent, moderately bioaccumulative, and extremely toxic to aquatic organisms, and due to reports on multiple estrogenic responses on aquatic organisms, they have been classified as EDs. Biodegradation of APEs has been proven to be the main source of 4-OP and 4-NP environmental contamination (Acir and Guenther, 2018).

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Degraded product of NP is said to be tenfold more estrogenic than its parent NPE and is the highly recalcitrant

derivative of the APE surfactants (Mahalakshmi *et al*., 2020). Concentrations of sum of 4-NP obtained in sediment from this study during rainy season (Table 3) was 67 times lower than the guideline value of 1400 ngg^{-1} d wt set by the CCME (2002), while the value of the chemical recorded in this study during dry season was 14 times lower than this guideline values (CCME, 2002). Concentration of 4t-OP recorded in sediment from this study during rainy season was less than the limit of detection of the instrument used for analysis of APs and APEs in this study, and levels of this compound obtained during dry season was about 26 times lower than the PNEC guideline value of 100 ngg^{-1} d wt set by CSL (2022). Similarly, sediment concentration of 4-NP during rainy and dry seasons were about 19 times lower, and 5 ngg^{-1} d wt less than the PNEC guideline value of 39 ngg^{-1} d wt set by the European Commission (Mahalakshmi *et al*., 2020). The EU also set PNEC guideline value of 250 ngg^{-1} d wt for NPE2 in sediment (Mahalakshmi *et al*., 2020), and this guideline value was 275 times higher than the concentration of NPE2 recorded from this study (Table 3**).**

Total TEQ for APs and APEs homologues ($\sum_{hom}$ranged from 0.46-36.49 ngg^{-1}TEQ with sum and mean concentrations of 58.66 ngg^{-1}TEQ and 11.73 ngg^{-1}TEQ respectively. It is worthy to note that an organism might be affected by a variety of APs and APEs homologues at a given environment, hence the need to evaluate the $\sum_{homo}$TEQ in this study. Concentrations of APs and APEs homologues decreased in the order: 4-NP > 4-OP > 4t-OP > OPE1 > NPE2, while site variation of these pollutants followed the sequence: Mikap > Abattoir > Wadata > Abinsi respectively (Table 7). Concentrations of TEQs in sediment from river Benue were lower when compared with interim guidelines value of 1400 ngg^{-1}TEQ set by CCME (2002).

Table 7: Toxic equivalence (ngg^{-1} d wt TEQ) of APs and APEs in sediment from river Benu**e**

Site	4-OP	4t-OP	4-NP	OPE1	NPE2	$\sum_{site}$TEQ	Range	Mean
Abinsi	0.90	ND	3.87	2.40	0.46	7.63	ND-3.87	1.53±1.59
Mikap	6.99	ND	23.6	0.27	ND	30.9	ND-23.6	6.17±10.2
Abattoir	5.00	ND	5.39	1.72	ND	12.1	ND-5.39	2.42±2.63
Wadata	ND	4.43	3.64	ND	ND	8.07	ND-4.43	1.61±2.23
$\sum_{hono}$TEQ	12.89	4.43	36.5	4.39	0.46	58.7	0.46-36.5	11.7±14.6

IQG = 1400 ngg^{-1}

Human Health Risk Assessment for Ingestion of Sediment from River Benue

In this study, the human health risk assessment focused on 4t-BP, 4t-OP and 4-NP because of their reported endocrine disruption potentials (Beck *et al*., 2006; Genthe and Steyn, 2008; Sauter and Licha, 2002; Barse *et al*., 2006; Kroll, 2005). Sum of mean hazard quotient (∑HQ) for accidental ingestion of 4t-BP, 4t-OP and 4-NP in sediment from river Benue by adult during this study were 1.05E-02 and 2.63E-03, while the ∑HQ values for children were 9.17E-02 and 2.29E-02 respectively. Concentrations of AP and APEs homologues also varied consistently following the pattern: 4-NP > 4t-BP > 4t-OP for adult and children during this study. Concentrations of ∑HQ for accidental ingestion of pollutants in sediment per site by adult and children were consistent and decreased in the sequence: Mikap > Abattoir > Abinsi > Wadata (Table 8). Levels of hazard quotient due to accidental ingestion of pollutants in sediment from river Benue by adult and children during this study indicated no harm as HQ < 1, and risk was higher in children than adult for the APs and APEs selected for this study. The higher risk recorded by children than adult could be the consequence of children's low body weight, and their characteristic hand to mouth activity. Although HQ in sediment from this study indicated no harm, their accumulation in humans over a given period might become harmful because of bioaccumulation, thus, routine evaluation of the pollutants is important for future research.

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Table 8: Hazard quotient for ingestion of APs and APEs (ngg^{-1}) in sediment from River Benue by adult and children

	Abinsi		Mikap		Abattoir		Wadata		Adult		Children	
Analyte	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Sum	Mean	Sum	Mean
4t-BP	ND	ND	6.29 E-06	5.51E-05	4.50E-05	1.31E-04	0.00E+00	0.00E+00	5.13 E-05	1.28 E-05	1.86 E-04	4.65 E-05
4t-OP	0.00E+00	0.00E+00	ND	ND	0.00E+00	0.00E+00	2.11E-05	1.85-04	2.11 E-05	5.28 E-06	1.85 E-04	4.63 E-05
4-NP	1.11E-03	9.69E-03	6.74 E-03	5.90E-02	1.54E-03	1.35E-02	1.04E-03	9.09E-03	1.04 E-02	2.61 E-03	9.13 E-02	2.28 E-02
∑HQ	1.11E-03	9.68E-03	6.75 E-03	5.91E-02	1.59E-03	1.36E-02	1.06E-03	9.09E-03	1.05 E-02	2.63 E-03	9.17 E-02	2.29 E-02

CONCLUSION

Baseline data on the occurrence, levels and associated ecological and human health risks of APs and APEs in water and sediment from River Benue were generated during this study. The data revealed higher load of the detected pollutants in surface water during rainy season than dry season, but higher load of the compounds in the surface sediment during dry season than rainy season, with corresponding variation in ecological and human health risks of the chemicals accordingly. The non-carcinogenic hazard quotient for ingestion of the surface water and sediment by adult and children suggested that no adverse effects were expected as HQ < 1 for the two groups during this study. Comparison of data with various regulatory standards indicated that the surface water and sediment from River Benue during this study were less contaminated by APs and APEs, hence, it is potentially safe for ecology and human life. Results of this research revealed that the surface water and sediment from river Benue were less contaminated by APs and APEs than some other rivers selected for comparison, nevertheless, routine monitoring is necessary before harm would be recorded, since these chemicals are persistent, and could bioaccumulate stepwise in food chain.

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Data availability Data generated during this research shall be made available by the corresponding author on request.

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