

## Seasonal distribution, source apportionment and risk assessment of polycyclic aromatic hydrocarbons in groundwaters in Owo, Southwestern Nigeria

Odunayo T. Ore <sup>a,b,\*</sup>, Ajibola A. Bayode <sup>c</sup>, Hamza Badamasi <sup>d</sup>, Johnson Adedeji Olusola <sup>e,f</sup>, Solomon S. Durodola <sup>a</sup>, Olaniran K. Akeremale <sup>g</sup> and Morenike O. Adesina <sup>h</sup>

<sup>a</sup> Department of Chemistry, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

<sup>b</sup> Department of Chemical Sciences, Achievers University, P.M.B. 1030, Owo, Nigeria

<sup>c</sup> Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, P.M.B. 230, 232101, Ede, Nigeria

<sup>d</sup> Department of Chemistry, Federal University Dutse, Dutse, Jigawa State, Nigeria

<sup>e</sup> Department of Geography and Planning Science, Ekiti State University, Ado Ekiti, Ekiti State, Nigeria

<sup>f</sup> Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

<sup>g</sup> Department of Science and Technology Education, Bayero University, Kano 3011, Nigeria

<sup>h</sup> Department of Chemical Sciences, Lead City University, Ibadan, Oyo State 200255, Nigeria

\*Corresponding author. E-mail: oreodunayo@yahoo.com

 OTO, 0000-0002-5529-1509; AAB, 0000-0003-2461-6208; HB, 0000-0001-5339-1111; JAO, 0000-0003-4403-4475; SSD, 0000-0003-0097-1272; OKA, 0000-0002-7677-9589; MOA, 0000-0002-9329-0072

### ABSTRACT

The study focused on evaluating the seasonal distribution, source apportionment, and probabilistic risk assessment of polycyclic aromatic hydrocarbons (PAHs) in groundwater. Groundwater samples were obtained from Owo, southwestern Nigeria and subjected to liquid–liquid extraction and quantified using gas chromatography–mass spectrometry. Total PAH concentrations varied from about 180 to 23,600 ng/L during the dry season. The wet season, on the other hand, exhibited a wider range, from about 1,550 to 150,000 ng/L. Seasonal variations were also found in PAH types and concentrations, with relatively higher concentrations recorded during the wet season. Diagnostic ratios and positive matrix factorization indicated that coal/biomass combustion and traffic-related vehicular emissions were the prevalent sources of PAHs in groundwater. Health risk assessment indicated potential carcinogenic risks (incremental lifetime cancer risk (ILCR) > 1E – 04), while ecological assessment suggested medium ( $RQ_{NC} < 800$  and  $RQ_{MPC} \geq 1$ ) and high ecological risks ( $RQ_{NC} \geq 800$  and  $RQ_{MPC} \geq 1$ ). The study reflected the need for effective mitigation strategies.

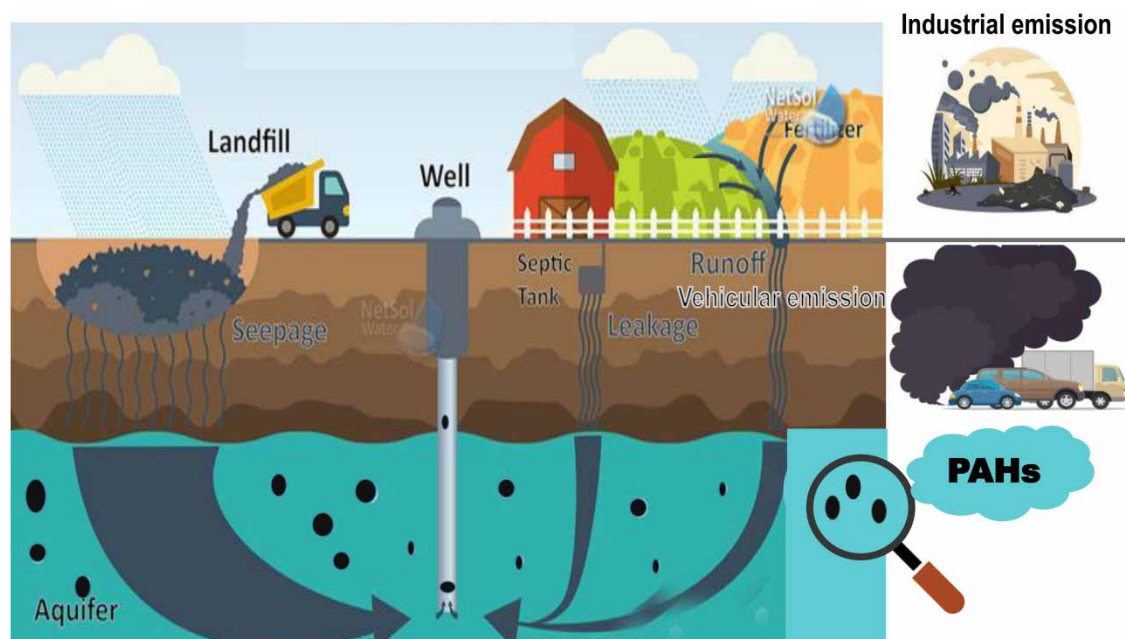
**Key words:** environment, polycyclic aromatic hydrocarbons, potable water, risk assessment, sustainability

### HIGHLIGHTS

- The study examined the risk assessment of PAHs in groundwater.
- PAH concentrations were relatively higher in the wet season.
- Coal/biomass combustion and vehicular emissions were the sources of PAHs.
- Carcinogenic risks and medium to high ecological risks were associated with the water quality.

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic molecules composed of several carbon rings. They emanate from natural and anthropogenic processes including incomplete combustion of organic matter (Adekunle *et al.* 2017). They are found all over the environment and have been the focus of much investigation due to the harm they might do to human health and/or the natural world (Balcioglu 2016). Most PAHs are discharged into the environment as a result of human activities including fossil fuel combustion, industrial operations, and waste disposal (Li *et al.* 2015; Varjani *et al.* 2018). Because they are persistent, many accumulate in living beings and have been linked to cancer, and their prevalence in different aspects of the environment, including groundwater, is worrisome (Ali *et al.* 2021).

Groundwater is a vital drinking water resource for millions of people worldwide (Mishra 2023). It can represent a major hazard to both the environment and public health if it becomes polluted with PAHs (Hojjati-Najafabadi *et al.* 2022). It is critical to understand how PAHs are dispersed in groundwater, where they come from, and what hazards they represent, to control pollution properly and safeguard human health, as well as develop strategies for cleaning up contaminated groundwater and preventing further pollution.

The prevalence of PAHs in groundwater is influenced by several variables, including climate, geology, and land use (Burri *et al.* 2019). Seasonal variations can also have a substantial influence. Changes in rainfall, temperature, and the pace of groundwater recharge, for example, can all affect contaminant movement (Saravanan *et al.* 2021). PAHs can be washed out of contaminated soil and transferred to groundwater during wet seasons when there is more rainfall. Raised water levels may also result in increased subsurface water flow, potentially distributing PAHs to new regions (Jiang *et al.* 2022). During dry seasons, however, when groundwater levels are lower and water moves more slowly, PAHs may linger in the ground for extended periods, resulting in increased concentrations. Temperature fluctuations can also influence PAH levels in groundwater by changing the activity of soil bacteria (Alegbeye *et al.* 2017). PAHs may be broken down by microbes, reducing their concentrations in groundwater (Padhan *et al.* 2021). When temperatures rise, microbial activity increases, resulting in quicker PAH degradation, suggesting that PAH concentrations in groundwater may decline more quickly in warmer seasons due to greater microbial breakdown (Logeshwaran *et al.* 2018; Adetunji & Anani 2021).

In order to minimize pollution and clean it up, it is critical to identify the sources of PAH contamination. PAHs can be found in both man-made and natural environments, and anthropogenic sources include automobile exhaust, industrial pollution, and inappropriate garbage disposal. These PAHs are released into the atmosphere, from where they can settle on the ground and eventually enter groundwater (Kozak *et al.* 2017; Li *et al.* 2021). However, in many situations, PAH pollution of groundwater results primarily from human activity (Ren *et al.*

2021). Profiles can be constructed to assist in pinpointing pollution sources by analyzing the precise types and concentrations of PAHs found.

Many PAHs are known or suspected causes of cancer, and being exposed to excessive quantities of them by drinking water or skin contact can be harmful. PAHs can also accumulate in aquatic creatures, altering ecosystems, and potentially entering the food chain (Okechukwu *et al.* 2021; Oyekunle *et al.* 2023; Vijayanand *et al.* 2023). PAH mobility in the environment is influenced by factors such as geology, how easily they adhere to soil particles, and how rapidly they degrade. Understanding how PAHs migrate makes it possible to forecast whether they will end up in sensitive places such as wells or bodies of surface water (Adeola & Forbes 2021a, 2021b).

Therefore, effective water resource management depends on PAH source identification and risk evaluation (Li *et al.* 2017). Many recent studies have been carried out on PAH seasonal distribution, source identification, and risk assessment in water resources (Apata *et al.* 2022; Aralu *et al.* 2023; Areguamen *et al.* 2023; Ogunbisi *et al.* 2023; Ololade *et al.* 2023). However, this study is the first known attempt at evaluating groundwater, the predominant water resource in the study area.

## 2. MATERIALS AND METHODS

### 2.1. Sample collection and preparation

Water samples were collected from randomly selected wells around dumpsites in Owo, southwestern Nigeria, during the dry and wet seasons in 2021. Prior to analysis, the samples were pretreated with 20 mL chloroform and refrigerated, to inhibit microbial action.

### 2.2. Reagents

All reagents were of analytical grade and were obtained in Nigeria. They included chloroform, acetone, and methanol (BDH Poole House, England), dichloromethane and nitric acid (Sigma-Aldrich), anhydrous sodium sulfate (BDH Poole House, England), and silica gel 60-200 PF<sub>254</sub> (MERK, Germany).

### 2.3. PAH extraction

Sample aliquots of 100 mL were measured into a 500 mL separatory funnel to determine their PAH content. The samples were extracted in triplicate with 200 mL of dichloromethane, before being mixed in an amber-colored vial, which was kept at 4 °C in preparation for further clean-up. This method provides for precise determination of PAH levels in water samples.

### 2.4. Clean-up

Clean-up was based on chromatography and involved mixing stationary (silica gel) and mobile phases (1:2:2 acetone–dichloromethane–ethanol). A small quantity of glass wool was used as a plug to prevent the loss of the stationary phase before the addition of silica gel. Anhydrous sodium sulphate was added on top of the silica gel. The solvent mixture was introduced first into the packed column to prevent contaminant interference.

Clean-up is essential to remove or reduce impurities that might be present in the eluate. The eluate was left to dry completely, then reconstituted with 1 mL of dichloromethane and stored in amber-colored vials prior to GC-MS determination.

### 2.5. Recovery

The recovery experiments were carried out by introducing 20 ng/L of the available PAHs – i.e., chrysene, phenanthrene, anthracene, and fluorene – into a known volume of the groundwater sample while the same quantity was left unspiked. The two samples were then subjected to the same liquid–liquid extraction process adopted for PAH extraction and clean-up as described above. The proportional recovery was calculated using the following equation:

$$\%R = \frac{C - D}{20} \times 100 \quad (1)$$

where  $C$  is the concentration in the spiked sample and  $D$  is the concentration in the un-spiked sample.

The recovery analysis result is presented in Table 1. The proportional recoveries ranged between 89 and 108%, well within the 70–110% recovery range stipulated, for instance, by the European Union (2006).

**Table 1** | PAH recovery analysis

PAHs	Amount in spiked sample (ng/L)	Amount in unspiked sample (ng/L)	%R
Chrysene	92.8	75	89
Phenanthrene	91.4	72.6	94
Anthracene	82.6	63.6	95
Fluorene	70.3	48.7	108

## 2.6. Gas chromatography

The PAHs were determined by a gas chromatograph (Agilent Model 7890B) coupled with a Pegasus 4D mass spectrometer (GC-MS). An Agilent DB-7890 capillary GC column, 30 m × 0.25 mm id × 0.25 μm film thickness, was used at 340 °C. The operating conditions were: splitless (1 μL) injection, injector temperature 250 °C, helium carrier gas (99.99% purity) flowing at 0.9 mL min<sup>-1</sup> with column head pressure 7.4 psi. The oven temperature was kept at 70 °C for 2 min, and then programmed to rise to 130 °C at 25 °C min<sup>-1</sup>, and on to 220 °C at 2 °C min<sup>-1</sup>, and finally to 280 °C at 10 °C min<sup>-1</sup>. The final temperature was maintained for 4.6 min.

The MS settings were electron impact ionization mode with 70 eV electron energy, scan mass range 100–400 at 0.62 s/cycle, ion source temperature 230 °C, MS quad temperature 150 °C, EM voltage 1450, and solvent delay 4 min. The MS system was routinely operated in selective ion monitoring (SIM) mode with electron ionization. The PAH compounds were identified on the basis of a comparison of peak retention times with those of standard PAHs, after which an internal standard method was used for PAH quantification (Oyekunle *et al.* 2022).

## 2.7. Data analysis

Data were processed using Microsoft Excel and Origin software and source identification was estimated using EPA-PMF (version 5) (Ambade *et al.* 2023). Health risk was assessed using the method developed by USEPA to calculate the incremental lifetime cancer risk (ILCR) associated with groundwater ingestion – Equation (2) as well as the toxic equivalent quantity (TEQ) – Equation (3):

$$\text{ILCR} = \frac{\text{TEQ} \times \text{DR} \times \text{CSF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (2)$$

$$\text{TEQ} = C \times \text{TEF} \quad (3)$$

where  $C$  is the concentration of PAH, TEF is the toxic equivalent factor, DR is the daily water intake (L/day), CSF is the carcinogenic slope coefficient of BaP (10 (kg day)/mg), EF is the number of days of exposure per year (set to 365 days), ED is the exposure duration (years), BW is the body weight (kg), and AT is the averaging time for life (day) (Ambade *et al.* 2021).

The ecological risk was assessed using the risk quotient, which was subdivided into two categories – maximum permissible concentrations (MPCs) and negligible concentrations (NCs). They were estimated using the following equations

$$\text{RQ} = \frac{C_{\text{PAH}}}{C_{\text{QV}}} \quad (4)$$

$$\text{RQ}_{\text{MPCs}} = \frac{C_{\text{PAH}}}{C_{\text{QV(MPCs)}}} \quad (5)$$

$$\text{RQ}_{\text{NCs}} = \frac{C_{\text{PAH}}}{C_{\text{QV(NCs)}}} \quad (6)$$

where  $C_{\text{PAHs}}$  is the PAH concentration in water (ng/L),  $C_{\text{QV}}$  is the corresponding PAH risk standard value (ng/L),  $C_{\text{QV(MPCs)}}$  is the PAH MPC value,  $C_{\text{QV(NCs)}}$  is the PAH NC value (ng/L), and RQ the PAH ecological risk quotient.

### 3. RESULTS AND DISCUSSION

#### 3.1. Seasonal PAH distribution in groundwater

The descriptive seasonal distribution statistics of the PAHs in the groundwater in the dry and wet seasons are presented in Table 2. During the dry season, total PAH concentrations ranged from 182 to  $2.36 \times 10^4$  ng/L. However, total PAH concentrations during the wet season ranged from  $1.55 \times 10^3$  to  $1.49 \times 10^5$  ng/L.

The PAHs exhibited different compositional profiles in the dry and wet seasons. While acenaphthylene had the highest concentration ( $3.79 \times 10^3$  ng/L) in the dry season, benzo[a]pyrene had the highest ( $3.69 \times 10^4$  ng/L) in the wet season. Apart from fluoranthene, the concentrations of the other PAHs in the groundwater were relatively higher in the wet than in the dry season. One-way analysis of variance (Table 3) indicated that the concentrations of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, benzo[g,h,i]perylene, and indeno[1,3,3-cd]pyrene were significantly higher ( $p < 0.05$ ) in the wet season than the dry one. The increased wet season PAH concentrations could be due to the promotion of soil permeability by rainfall when PAHs in soils are dissolved and subsequently migrate into groundwater (Yang *et al.* 2012; Sun *et al.* 2019). In essence, the difficulty associated with the migration of these PAHs during the dry season might explain why their concentrations are relatively lower then (Perrette *et al.* 2013), as the relative increase in soil moisture during the wet season ensures the carriage of PAHs into groundwater by colloids and dissolved organic matter (Schwarz *et al.* 2011).

Unsurprisingly, in both dry and wet seasons, lower molecular weight PAHs were predominant. This has a direct link with PAH physical and chemical properties, as these relatively light molecules have low hydrophobicity and high-water solubility, while the heavier PAHs are relatively more resistant to degradation (Montuori *et al.* 2016; Li *et al.* 2017; He *et al.* 2020). The PAH concentrations found in this study are relatively higher than those reported elsewhere (López-Macias *et al.* 2019; Ibigami *et al.* 2022).

#### 3.2. PAH source identification

The PAH source apportionment in groundwater was estimated using diagnostic ratios and positive matrix factorization. The diagnostic ratio is a qualitative determination through a comparison of the concentration ratios of PAH isomers in a particular sample with those ascribed to specific pollution sources (Jiang *et al.* 2022). The PAH diagnostic ratios used in this study comprise Ant/(Ant + Phe), Fla/(Fla + Pyr), BaA/(BaA + Chr), and InP/(InP + BPY) – Figure 1. Ant/(Ant + Phe) ratios  $< 0.1$  and  $> 0.1$  indicate petroleum and combustion sources, respectively. Fla/(Fla + Pyr) ratios of  $> 0.5$ , 0.4 to 0.5, and  $< 0.4$  correspond to coal/biomass combustion, petroleum combustion, and petroleum sources, respectively. BaA/(BaA + Chr) ratios of  $> 0.35$ , 0.2 to 0.35, and  $< 0.2$  suggest coal/biomass combustion, mixed, and petroleum sources, respectively, while InP/(InP + BPY) ratios of  $> 0.5$ , 0.2 to 0.5, and  $< 0.2$  indicate coal/biomass combustion, petroleum combustion, and petroleum sources, respectively (Deng *et al.* 2013; Cai *et al.* 2017). The estimated groundwater-PAH diagnostic ratios in this study indicate that the PAHs originate predominantly from coal/biomass combustion and petroleum.

PMF was also used to assess possible PAH sources in groundwater. Three factors were identified – Figure 2. Factor 1 accounted for about 31% of data variance, with significant loadings from naphthalene, fluorene, fluoranthene, and pyrene, and was widely characterized by low molecular weight PAHs probably emanating from oil spills (Friesen *et al.* 2007).

Factor 2 accounted for 40% of data variance, with high factor loadings from benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and benzo[g,h,i]perylene. It comprises PAHs with 4–6 aromatic rings, which are predominantly fossil fuel combustion products (Tian *et al.* 2019) and can be ascribed to traffic-related vehicular emissions.

Factor 3 had the lowest data variance contribution – 29% – and arose from predominant loadings from acenaphthylene, anthracene, benzo[b]fluoranthene, dibenzo[a,h]anthracene, and indeno[1,3,3-cd]pyrene, high molecular weight PAHs implicated as tracers of incomplete PAH combustion from internal combustion engines and biomass (Li *et al.* 2017). Based on the foregoing, it is clear that the combustion of coal/biomass and petroleum are the chief PAH sources in the groundwater.

#### 3.3. Risk assessment of PAHs in groundwater

The possible health risks associated with PAH ingestion through drinking groundwater were assessed. The estimated ILCR and risk index (RI) for adults and children are presented in Table 4. In both dry and wet seasons, the carcinogenic PAH ILCRs were relatively higher for children than adults, except for chrysene. Regardless of

**Table 2** | Descriptive statistics of PAHs in groundwater (ng/L) during dry and wet season

Type	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	DbA	BPy	InP	Σ PAH
Dry season																	
Min	1.15	19.1	29.3	125	ND	7.84	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	182
Max	$2.51 \times 10^3$	$3.79 \times 10^3$	$3.45 \times 10^3$	$3.36 \times 10^3$	$2.31 \times 10^3$	258	$2.63 \times 10^3$	195	88.4	412	$1.79 \times 10^3$	529	$1.81 \times 10^3$	316	30.8	165	$2.36 \times 10^4$
Wet season																	
Min	138	526	301	355	158	12.4	ND	ND	ND	2.45	10.1	39.8	ND	2.62	ND	3.99	$1.55 \times 10^5$
Max	$3.43 \times 10^3$	$1.42 \times 10^4$	$2.82 \times 10^4$	$7.74 \times 10^3$	$8.30 \times 10^3$	$2.36 \times 10^3$	$1.42 \times 10^3$	482	$3.02 \times 10^3$	$6.24 \times 10^3$	$2.12 \times 10^4$	$1.49 \times 10^4$	$3.69 \times 10^4$	273	640	626	$1.49 \times 10^5$

Nap, naphthalene; Acy, acenaphthylene; Ace, acenaphthene; Flu, fluorene; Phe, phenanthrene; Ant, anthracene; Fla, fluoranthene; Pyr, pyrene; BaA, benz [a] anthracene; Chr, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; DbA, dibenzo[a,h]anthracene; BPy, benzo[g,h,i]perylene; InP, indeno[1,3,3-cd]pyrene; Min, minimum; Max, maximum; ND, not detected.



**Table 3** | One-way analysis of variance – ANOVA – showing the significant PAH concentration differences in groundwater during the dry and wet seasons

		Sum of squares	df	Mean square	F	Sig.
Nap	Between groups	16.935	1	16.935	25.801	0.000
	Within groups	11.815	18	0.656		
	Total	28.750	19			
Acy	Between groups	109.319	1	109.319	12.959	0.002
	Within groups	151.848	18	8.436		
	Total	261.167	19			
Ace	Between groups	821.085	1	821.085	16.417	0.001
	Within groups	900.237	18	50.013		
	Total	1,721.322	19			
Flu	Between groups	55.395	1	55.395	14.945	0.001
	Within groups	66.717	18	3.707		
	Total	122.112	19			
Phe	Between groups	34.428	1	34.428	12.979	0.002
	Within groups	47.748	18	2.653		
	Total	82.176	19			
Ant	Between groups	1.685	1	1.685	5.575	0.030
	Within groups	5.440	18	0.302		
	Total	7.124	19			
Fla	Between groups	0.037	1	0.037	0.086	0.772
	Within groups	7.796	18	0.433		
	Total	7.834	19			
Pyr	Between groups	0.013	1	0.013	0.983	0.335
	Within groups	0.237	18	0.013		
	Total	0.250	19			
BaA	Between groups	0.514	1	0.514	1.146	0.299
	Within groups	8.077	18	0.449		
	Total	8.591	19			
Chr	Between groups	2.760	1	2.760	1.467	0.242
	Within groups	33.874	18	1.882		
	Total	36.634	19			
BbF	Between groups	26.033	1	26.033	1.202	0.287
	Within groups	389.758	18	21.653		
	Total	415.791	19			
BkF	Between groups	20.698	1	20.698	1.933	0.181
	Within groups	192.727	18	10.707		
	Total	213.425	19			
BaP	Between groups	66.264	1	66.264	0.975	0.337
	Within groups	1,223.341	18	67.963		
	Total	1,289.605	19			
DbA	Between groups	0.005	1	0.005	0.602	0.448
	Within groups	0.147	18	0.008		
	Total	0.152	19			
BPy	Between groups	0.106	1	0.106	4.843	0.041
	Within groups	0.396	18	0.022		
	Total	0.502	19			
InP	Between groups	0.268	1	0.268	10.305	0.005
	Within groups	0.469	18	0.026		
	Total	0.737	19			

season, benzo[a]pyrene contributed the greatest risk of cancer and chrysene the least. ILCR values  $\leq 1 \times 10^{-6}$  have been classified as acceptable, while those  $\geq 1 \times 10^{-4}$  have been described as indicating high risk (Huang *et al.* 2016). Most ILCRs exceeded the USEPA's acceptable level ( $1 \times 10^{-4}$ ), indicating that drinking groundwater carries potential carcinogenic risk (Qiao *et al.* 2021).

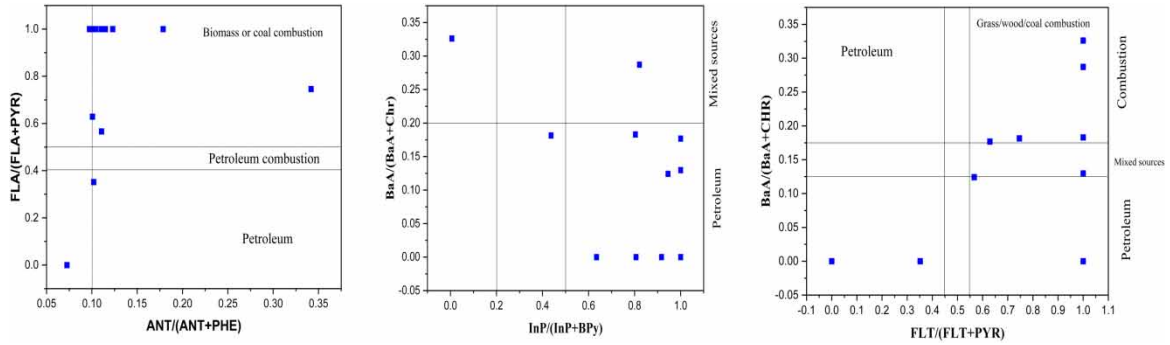


Figure 1 | PAH diagnostic ratios in groundwater.

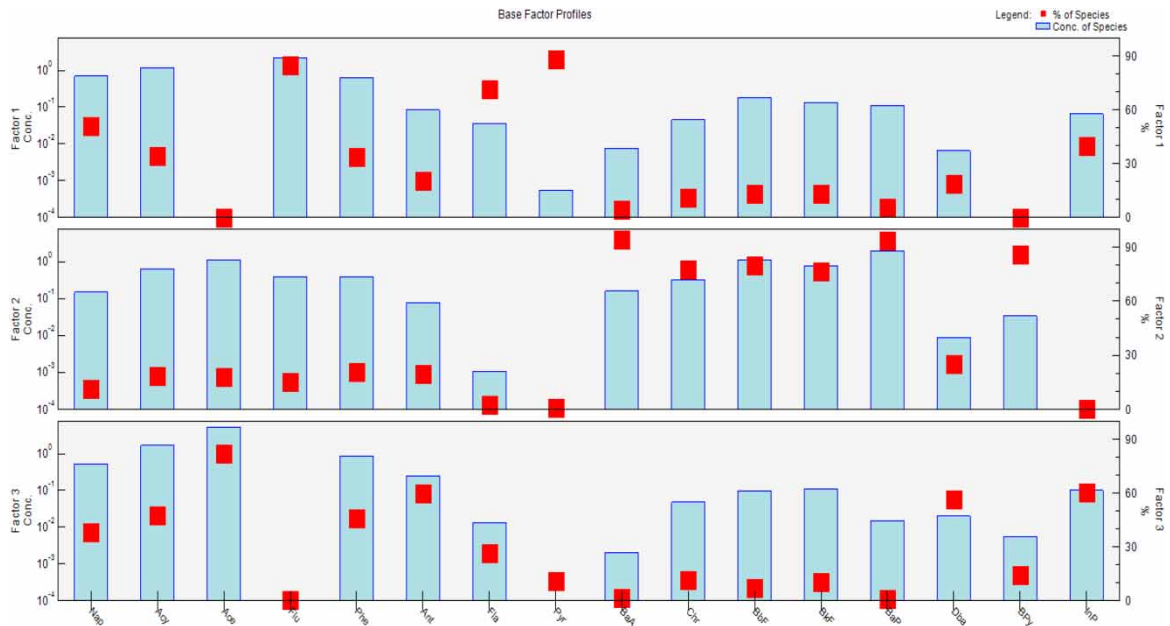


Figure 2 | Factor profiles and PAH contributions in groundwater using PMF.

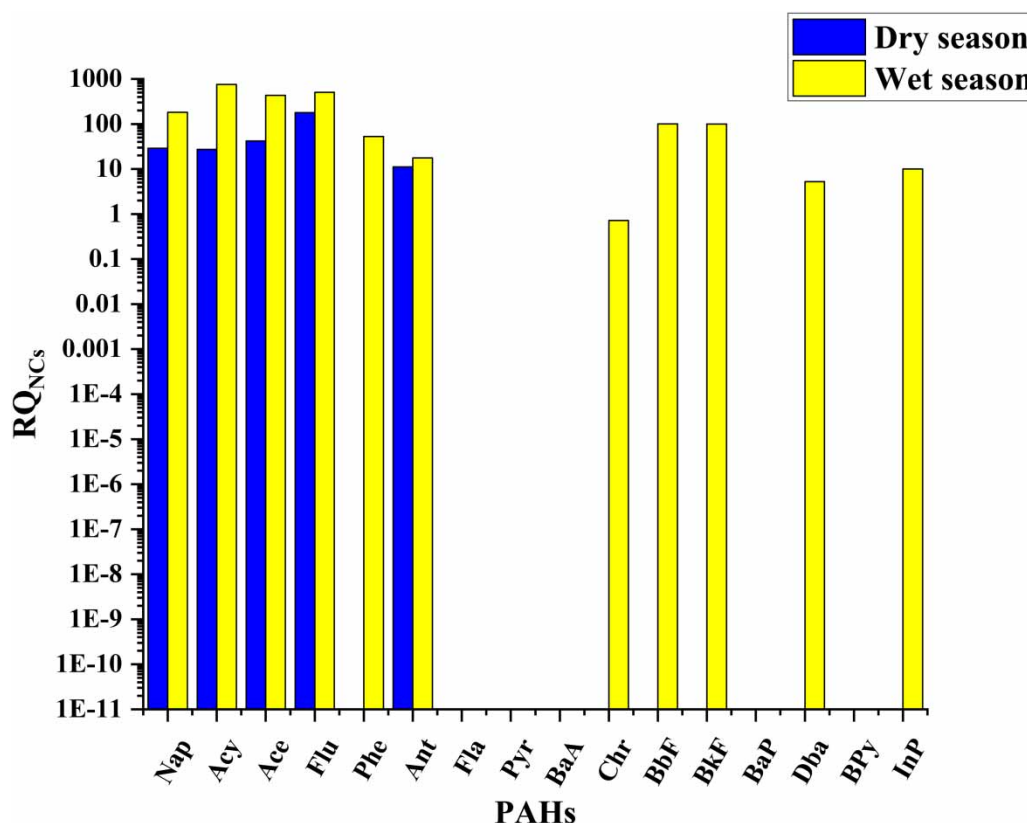
Table 4 | ILCR and RI of carcinogenic PAHs in groundwater

PAHs	Dry season			Wet season		
	TEQ	ILCR		TEQ	ILCR	
Carcinogenic PAHs		Adults	Children		Adults	Children
BaA	1.24	0.24	0.01	33.31	6.66	13.30
Chr	0.04	0.09	$2.96 \times 10^{-4}$	0.79	1.58	0.07
BbF	27.47	5.49	9.05	255.65	51.13	783.43
BkF	9.03	1.80	0.97	212.48	42.49	541.20
BaP	185.74	37.14	413.53	3,826.19	765.23	175,476.40
DbA	60.15	12.03	43.37	91.56	18.31	100.50
InP	3.06	0.61	0.11	26.23	5.24	8.24
RI		57.44	467.07		890.67	176,923.20

TEQ, toxic equivalent quantity.



The PAH ecological risk was evaluated using the NCs and MPCs, which are presented in Figures 3 and 4, respectively. NCs indicate that PAH concentrations below this level are likely to have negligible negative impact, while MPCs indicate that negative impacts on the ecosystem are likely to be severe if PAH concentrations exceed them (Chen *et al.* 2019). Consonant with trends in this study,  $RQ_{NC}$  and  $RQ_{MPC}$  values were relatively higher in the wet than the dry season. Apart from chrysene –  $RQ_{NC}$  0.72 – during the wet season, all other PAHs had  $RQ_{NC}$  values exceeding 1, indicating that the ecological risk posed by them is not negligible. The PAH  $RQ_{MPC}$  values are below 1 in some cases. The PAH cumulative  $RQ_{NC}$  and  $RQ_{MPC}$  suggested that total PAHs posed a medium ecological risk in the dry season, but, in the wet season, it indicated that they posed a high ecological risk (Chen *et al.* 2019).



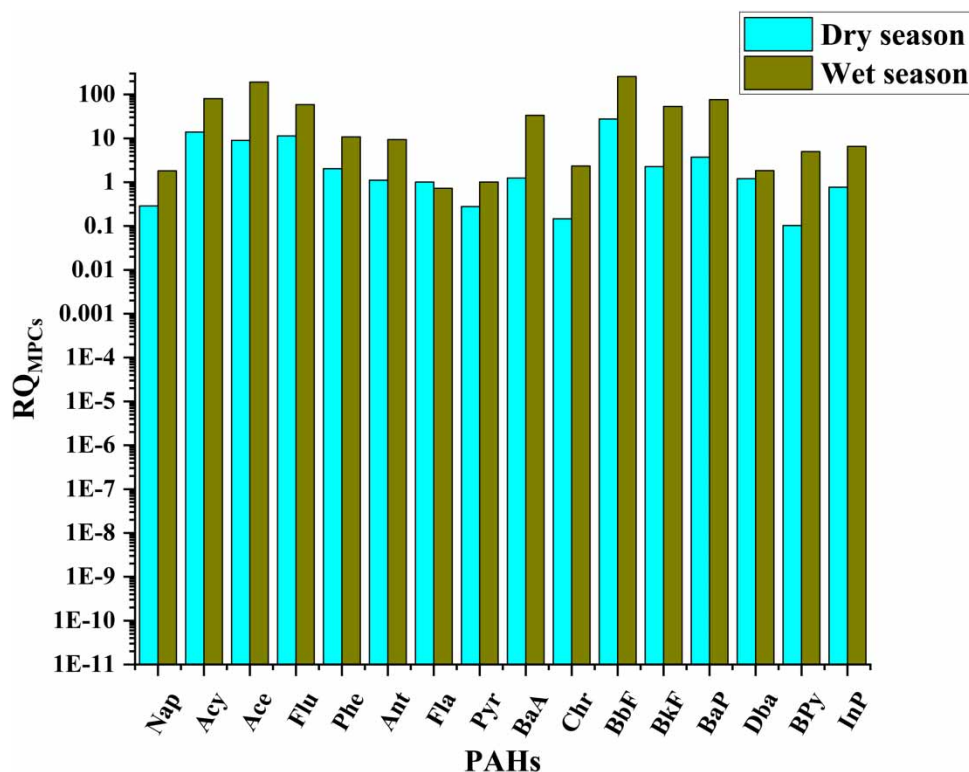
**Figure 3** | Ecological risk assessment of PAH NCs in groundwater.

#### 4. CONCLUSIONS

The study's aim was to investigate the seasonal distribution and likely sources of 16 PAHs in groundwater. There were considerable changes in PAH concentrations between the dry and rainy seasons. The major influence of seasonal fluctuations on PAH concentrations was produced by rainfall, with higher PAH concentrations found during the wet season due to increased soil permeability, which allows PAHs to migrate into groundwater.

The study also showed that the PAH mix differed between the dry and rainy seasons. Because of their relatively low hydrophobicity and higher water solubility, lower molecular weight PAHs were more abundant than those with higher molecular weights in both seasons.

Diagnostic ratios and PMF were used to identify PAH origins in groundwater. The diagnostic ratios indicated that coal/biomass combustion and petroleum were the primary PAH sources. PMF identified three sources: low molecular weight PAHs from oil spills, higher molecular weight PAHs from car emissions, and another source associated with incomplete combustion from internal combustion engines and biomass. This emphasizes the need to consider both temporal fluctuations and probable sources when assessing PAH contamination in groundwater.



**Figure 4** | Ecological risk assessment of PAH MPCs in groundwater.

Risk assessment indicated the potential for cancer risks from drinking groundwater, as well as potential medium and high ecological risks. The findings have human health and environmental consequences, emphasizing the need for focused initiatives to minimize the effects of PAH pollution, particularly during rainy seasons.

#### ACKNOWLEDGEMENT

The authors sincerely acknowledge the management of their respective institutions for providing an enabling environment for the research.

#### CONSENT FOR PUBLICATION

All authors have approved the final version of the manuscript for publication.

#### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

#### CONFLICT OF INTEREST

The authors declare there is no conflict.

#### REFERENCES

- Adekunle, A. S., Oyekunle, J. A. O., Ojo, O. S., Maxakato, N. W., Olutona, G. O. & Obisesan, O. R. 2017 Determination of polycyclic aromatic hydrocarbon levels of groundwater in Ife north local government area of Osun state, Nigeria. *Toxicology Reports* **4**, 39–48.
- Adeola, A. O. & Forbes, P. B. 2021a Advances in water treatment technologies for removal of polycyclic aromatic hydrocarbons: Existing concepts, emerging trends, and future prospects. *Water Environment Research* **93**(3), 343–359.
- Adeola, A. O. & Forbes, P. B. 2021b Influence of natural organic matter fractions on PAH sorption by stream sediments and a synthetic graphene wool adsorbent. *Environmental Technology & Innovation* **21**, 101202.
- Adetunji, C. O. & Anani, O. A. 2021 Bioaugmentation: A powerful biotechnological techniques for sustainable Ecorestoration of soil and groundwater contaminants. *Microbial Rejuvenation of Polluted Environment* **1**, 373–398.

- Alegbeleye, O. O., Opeolu, B. O. & Jackson, V. A. 2017 Polycyclic aromatic hydrocarbons: A critical review of environmental occurrence and bioremediation. *Environmental Management* **60**, 758–783.
- Ali, M. U., Siyi, L., Yousaf, B., Abbas, Q., Hameed, R., Zheng, C., Kuang, X. & Wong, M. H. 2021 Emission sources and full spectrum of health impacts of black carbon associated polycyclic aromatic hydrocarbons (PAHs) in urban environment: A review. *Critical Reviews in Environmental Science and Technology* **51**(9), 857–896.
- Ambade, B., Sethi, S. S., Kumar, A., Sankar, T. K. & Kurwadkar, S. 2021 Health risk assessment, composition, and distribution of polycyclic aromatic hydrocarbons (PAHs) in drinking water of Southern Jharkhand, East India. *Archives of Environmental Contamination and Toxicology* **80**, 120–133.
- Ambade, B., Sethi, S. S. & Chintalacheruvu, M. R. 2023 Distribution, risk assessment, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) using positive matrix factorization (PMF) in urban soils of East India. *Environmental Geochemistry and Health* **45**(2), 491–505.
- Apata, A., Ololade, I. A., Oladoja, N. A., Alabi, B. A. & Ololade, O. O. 2022 Polycyclic aromatic hydrocarbons in selected rivers in southwestern Nigeria: Seasonal distribution, source apportionment and potential risk assessment. *Regional Studies in Marine Science* **52**, 102318.
- Aralu, C. C., Okoye, P.-A. C., Abugu, H. O., Eboagu, N. C. & Eze, V. C. 2023 Characterization, sources, and risk assessment of PAHs in borehole water from the vicinity of an unlined dumpsite in Awka, Nigeria. *Scientific Reports* **13**(1), 1–15.
- Areguamen, O. I., Calvin, N. N., Gimba, C. E., Okunola, O. J. & Elebo, A. 2023 Seasonal assessment of the distribution, source apportionment, and risk of water-contaminated polycyclic aromatic hydrocarbons (PAHs). *Environmental Geochemistry and Health* **45**, 5415–5439.
- Balcioglu, E. B. 2016 Potential effects of polycyclic aromatic hydrocarbons (PAHs) in marine foods on human health: A critical review. *Toxin Reviews* **35**(3–4), 98–105.
- Burri, N. M., Weatherl, R., Moeck, C. & Schirmer, M. 2019 A review of threats to groundwater quality in the anthropocene. *Science of the Total Environment* **684**, 136–154.
- Cai, C., Li, J., Wu, D., Wang, X., Tsang, D. C., Li, X., Sun, J., Zhu, L., Shen, H. & Tao, S. 2017 Spatial distribution, emission source and health risk of parent PAHs and derivatives in surface soils from the Yangtze River Delta, Eastern China. *Chemosphere* **178**, 301–308.
- Chen, D., Feng, Q., Liang, H., Gao, B. & Alam, E. 2019 Distribution characteristics and ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in underground coal mining environment of Xuzhou. *Human and Ecological Risk Assessment: An International Journal* **25**(6), 1564–1578.
- Deng, W., Li, X. G., Li, S. Y. & Ma, Y. Y. 2013 Source apportionment of polycyclic aromatic hydrocarbons in surface sediment of mud areas in the East China Sea using diagnostic ratios and factor analysis. *Marine Pollution Bulletin* **70**(1–2), 266–273.
- European Union 2006 Directive 2002/32/EC of the European Parliament and the council. <http://eur-lex.europa.eu/LexUriServ/site/en/consol> Accessed 5 Nov 2023.
- Friesen, M. C., Demers, P. A., Spinelli, J. J. & Le, N. D. 2007 Adequacy of benzo (a) pyrene and benzene soluble materials as indicators of exposure to polycyclic aromatic hydrocarbons in a Söderberg aluminum smelter. *Journal of Occupational and Environmental Hygiene* **5**(1), 6–14.
- He, Y., Yang, C., He, W. & Xu, F. 2020 Nationwide health risk assessment of juvenile exposure to polycyclic aromatic hydrocarbons (PAHs) in the water body of Chinese lakes. *Science of the Total Environment* **723**, 138099.
- Hojjati-Najafabadi, A., Mansoorianfar, M., Liang, T., Shahin, K. & Karimi-Maleh, H. 2022 A review on magnetic sensors for monitoring of hazardous pollutants in water resources. *Science of the Total Environment* **824**, 153844.
- Huang, H. F., Xing, X. L., Zhang, Z. Z., Qi, S. H., Yang, D., Yuen, D. A., Sandy, E. H., Zhou, A. G. & Li, X. Q. 2016 Polycyclic aromatic hydrocarbons (PAHs) in multimedia environment of Heshan coal district, Guangxi: distribution, source diagnosis and health risk assessment. *Environmental geochemistry and health*. **38**, 1169–1181.
- Ibigbami, O. A., Adeyeye, E. I. & Adelodun, A. A. 2022 Polychlorinated biphenyls and polycyclic aromatic hydrocarbons in groundwater of fuel-impacted areas in Ado-Ekiti, Nigeria. *Polycyclic Aromatic Compounds* **42**(5), 2433–2446.
- Jiang, C., Zhao, D., Chen, X., Zheng, L., Li, C. & Ren, M. 2022 Distribution, source and ecological risk assessment of polycyclic aromatic hydrocarbons in groundwater in a coal mining area, China. *Ecological Indicators* **136**, 108683.
- Kozak, K., Ruman, M., Kosek, K., Karasiński, G., Stachnik, Ł. & Polkowska, Ż. 2017 Impact of volcanic eruptions on the occurrence of PAHs compounds in the aquatic ecosystem of the southern part of West Spitsbergen (Hornsund Fjord, Svalbard). *Water* **9**(1), 42.
- Li, P., Xue, R., Wang, Y., Zhang, R. & Zhang, G. 2015 Influence of anthropogenic activities on PAHs in sediments in a significant gulf of low-latitude developing regions, the Beibu Gulf, South China Sea: Distribution, sources, inventory and probability risk. *Marine Pollution Bulletin* **90**(1–2), 218–226.
- Li, J., Li, F. & Liu, Q. 2017 PAHs behavior in surface water and groundwater of the Yellow River estuary: Evidence from isotopes and hydrochemistry. *Chemosphere* **178**, 143–153.
- Li, Y., Zang, S., Zhang, K., Sun, D. & Sun, L. 2021 Occurrence, sources and potential risks of polycyclic aromatic hydrocarbons in a permafrost soil core, northeast China. *Ecotoxicology* **30**, 1315–1324.
- Logeshwaran, P., Megharaj, M., Chadalavada, S., Bowman, M. & Naidu, R. 2018 Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches. *Environmental Technology & Innovation* **10**, 175–193.

- López-Macias, R., Cobos-Gasca, V., Cabañas-Vargas, D. & Rendón von Osten, J. 2019 Presence and spatial distribution of polynuclear aromatic hydrocarbons (PAHs) in groundwater of Merida City, Yucatan, Mexico. *Bulletin of Environmental Contamination and Toxicology* **102**, 538–543.
- Mishra, R. K. 2023 Fresh water availability and its global challenge. *British Journal of Multidisciplinary and Advanced Studies* **4**(3), 1–78.
- Montuori, P., Aurino, S., Garzonio, F., Sarnacchiaro, P., Nardone, A. & Triassi, M. 2016 Distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in water and sediments from Tiber River and estuary, Italy. *Science of the Total Environment* **566**, 1254–1267.
- Ogunbisi, M., Olujimi, O., Sojinu, O., Xian, Q. & Arowolo, T. 2023 Occurrence, source and risk assessment of polycyclic aromatic hydrocarbons in Ogun River and Lagos Lagoon, Southwest, Nigeria. *International Journal of Environmental Science and Technology* **20**(4), 4391–4404.
- Okechukwu, V. U., Omokpariola, D. O., Onwukeme, V. I., Nweke, E. N. & Omokpariola, P. L. 2021 Pollution investigation and risk assessment of polycyclic aromatic hydrocarbons in soil and water from selected dumpsite locations in rivers and Bayelsa State, Nigeria. *Environmental Analysis, Health and Toxicology* **36**(4), e2021023.
- Ololade, I., Apata, A., Oladoja, N., Alabi, B. & Ololade, O. 2023 Polycyclic aromatic hydrocarbons in rivers and health risk consequences of human exposure: A Nigerian case study. *International Journal of Energy and Water Resources* 1–18.
- Oyekunle, J., Falodun, I., Ore, O. & Fakoya, T. 2022 Effects of different activation methods on the capacity of an agro-waste adsorbent in the removal of organochlorine pesticides and heavy metals contaminants from wastewater. *Ife Journal of Science and Technology* **6**(1), 78–95.
- Oyekunle, J. A., Inalegwu, S. A., Fagbuyi, A., Adekunle, A. S. & Ore, O. T. 2023 Evaluation of polycyclic aromatic hydrocarbons and potentially toxic metals in commonly consumed pasta products available in the Nigerian Markets. *Journal of Trace Elements and Minerals* **4**, 100077.
- Padhan, D., Rout, P. P., Kundu, R., Adhikary, S. & Padhi, P. P. 2021 Bioremediation of heavy metals and other toxic substances by microorganisms. *Soil Bioremediation: An Approach Towards Sustainable Technology* 285–329.
- Perrette, Y., Poulenard, J., Durand, A., Quiers, M., Malet, E., Fanget, B. & Naffrechoux, E. 2013 Atmospheric sources and soil filtering of PAH content in karst seepage waters. *Organic Geochemistry* **65**, 37–45.
- Qiao, X., Zheng, B., Li, X., Zhao, X., Dionysiou, D. D. & Liu, Y. 2021 Influencing factors and health risk assessment of polycyclic aromatic hydrocarbons in groundwater in China. *Journal of Hazardous Materials* **402**, 123419.
- Ren, C., Zhang, Q., Wang, H. & Wang, Y. 2021 Characteristics and source apportionment of polycyclic aromatic hydrocarbons of groundwater in Hutuo River alluvial-pluvial fan, China, based on PMF model. *Environmental Science and Pollution Research* **28**, 9647–9656.
- Saravanan, S., Saranya, T., Abijith, D., Jacinth, J. J. & Singh, L. 2021 Delineation of groundwater potential zones for Arkavathi sub-watershed, Karnataka, India using remote sensing and GIS. *Environmental Challenges* **5**, 100380.
- Schwarz, K., Gocht, T. & Grathwohl, P. 2011 Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. *Environmental Pollution* **159**(1), 133–139.
- Sun, Y., Zhang, S., Lan, J., Xie, Z., Pu, J., Yuan, D., Yang, H. & Xing, B. 2019 Vertical migration from surface soils to groundwater and source appointment of polycyclic aromatic hydrocarbons in epikarst spring systems, southwest China. *Chemosphere* **230**, 616–627.
- Tian, D.-N., Dang, L.-H., Ding, R.-M., Cai, Q., Zhang, P.-J., Wang, L. & Yang, H.-F. 2019 Distribution, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in the surface waters of the Yinchuan Wetlands. *Huan Jing ke Xue = Huanjing Kexue* **40**(7), 3068–3077.
- Varjani, S. J., Joshi, R. R., Senthil Kumar, P., Srivastava, V. K., Kumar, V., Banerjee, C. & Praveen Kumar, R. 2018 Polycyclic aromatic hydrocarbons from petroleum oil industry activities: Effect on human health and their biodegradation. *Waste bioremediation* 185–199.
- Vijayanand, M., Ramakrishnan, A., Subramanian, R., Issac, P. K., Nasr, M., Khoo, K., Rajagopal, R., Greff, B., Azelee, N. I. W. & Jeon, B.-H. 2023 Polyaromatic hydrocarbons (PAHs) in the water environment: A review on toxicity, microbial biodegradation, systematic biological advancements, and environmental fate. *Environmental research* **227**, 115716.
- Yang, R., Liu, Z., Zeng, C. & Zhao, M. 2012 Response of epikarst hydrochemical changes to soil CO<sub>2</sub> and weather conditions at Chenqi, Puding, SW China. *Journal of Hydrology* **468**, 151–158.

First received 6 September 2023; accepted in revised form 22 November 2023. Available online 1 December 2023