



## Research article

# Human and ecological risk assessments of potentially toxic elements in sediments around a pharmaceutical industry

Hussein K. Okoro<sup>a,\*,\*\*</sup>, Muyiwa M. Orosun<sup>b,\*</sup>, Salman A. Umar<sup>a</sup>,  
Khursheed Muzammil<sup>c</sup>, Clement O. Ogunkunle<sup>d</sup>, Kingsley O. Iwuozor<sup>a,e</sup>, Ebuka  
Chizitere Emenike<sup>a,e</sup>, Saiful Islam<sup>f</sup>, Jane C. Ngila<sup>g</sup>, Caliphs Zvinowanda<sup>g</sup>

<sup>a</sup> Environmental-Analytical & Material Research Group, Department of Industrial Chemistry, University of Ilorin, P. M. B. 1515, Ilorin, Nigeria

<sup>b</sup> Department of Physics, University of Ilorin, P. M. B. 1515, Ilorin, Nigeria

<sup>c</sup> Department of Public Health, College of Applied Medical Sciences, Khamis Mushait Campus, King Khalid University, Abha, Saudi Arabia

<sup>d</sup> Department of Plant Biology, University of Ilorin, Ilorin, Nigeria

<sup>e</sup> Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Nigeria

<sup>f</sup> Civil Engineering Department, College of Engineering, King Khalid University, Abha 61421, Saudi Arabia

<sup>g</sup> Department of Chemical Sciences, University of Johannesburg, South Africa

## ARTICLE INFO

## Keywords:

Pharmaceutical

Hazard index

Sediments

Potential toxic elements

Risk assessment

## ABSTRACT

Potentially toxic elements (PTEs) in sediment can be highly hazardous to the environment and public health. This study aimed to assess the human and ecological risks of PTEs in sediments around a pharmaceutical industry in Ilorin, Nigeria. Physicochemical parameters and the concentrations of lead (Pb), chromium (Cr), cadmium (Cd), cobalt (Co), arsenic (As), and nickel (Ni) were analyzed in sediment samples collected from seven locations in the wet and dry seasons. Standard two-dimensional principal component analysis (PCA) and risk assessments were also conducted. The concentrations of Pb, Co, Ni, Cr, Cd, and As in the sediments ranged from 0.001 to 0.031 mg/kg, 0–0.005 mg/kg, 0.005–0.012 mg/kg, 0.001–0.014 mg/kg, 0.005–0.024 mg/kg, and 0.001–0.012 mg/kg, respectively. The mean concentrations of the total PTEs content were found in decreasing order of concentration: Pb > Cd > Ni > Cr > As > Co. PCA showed that some of the PTEs were highly concentrated in samples obtained at other locations as well as at the discharge point. The Hazard Index was mostly <1 across locations, indicating little to no probable non-carcinogenic effect. However, the incremental lifetime cancer risk for arsenic and nickel was high and required attention. The ecological risk assessment showed that lead and arsenic were the major PTEs pollutants in all locations. The study identifies PTEs profiles in sediments and emphasises the necessity of continual monitoring and action to stop long-term negative impacts on the local environment and public health.

## 1. Introduction

Potentially toxic elements (PTEs) are naturally occurring or anthropogenic elements that have the potential to cause adverse health

\* Corresponding author. 1.

\*\* Corresponding author. 2.

E-mail addresses: [okoro.hk@unilorin.edu.ng](mailto:okoro.hk@unilorin.edu.ng) (H.K. Okoro), [orosun.mm@unilorin.edu.ng](mailto:orosun.mm@unilorin.edu.ng) (M.M. Orosun).

<https://doi.org/10.1016/j.heliyon.2024.e31685>

Received 4 November 2023; Received in revised form 28 March 2024; Accepted 20 May 2024

Available online 23 May 2024

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effects in humans and ecological systems [1,2]. Examples of PTEs include arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), nickel (Ni), lead (Pb), mercury (Hg), and many others [3]. These elements can enter the environment through various anthropogenic activities, such as industrial processes, mining, and agricultural practices, or natural processes like weathering and erosion [4]. Once released into the environment, PTEs can accumulate in soil, water, and sediments and be taken up by plants and animals, leading to potential human health and ecological risks [5,6]. PTEs can also persist in the environment for long periods, making them a significant concern for environmental management and public health. The adverse effects of PTEs on human health can range from mild to severe, depending on the type and amount of exposure [7]. Acute exposure to high levels of PTEs can result in severe poisoning, while chronic exposure to low levels can lead to long-term health effects such as cancer, reproductive problems, and developmental disorders [8–11]. In ecological systems, PTEs can disrupt the balance of ecosystems, leading to biodiversity loss and ecosystem degradation [12,13].

One of the major sources of PTEs in the environment is the discharge of effluents from industries. The pharmaceutical industry, in particular, is known to produce a range of PTEs that can accumulate in sediments, posing a potential risk to human health and the environment [14]. Prior research on the impact of the pharmaceutical industry on sediments in Nigeria primarily concentrated on the distribution and pollution indices of PTEs [15–17], with limited consideration given to the associated human health risks, even though the pharmaceutical industry is a significant contributor to the country's economy. The human and ecological risks associated with PTEs pollution in sediments have been widely studied in different parts of the world. For example, Satapathy and Panda [18] identified the sources and assessed the health and environmental risks of some toxic elements present in the sediment of an Indian coastal industrial environment. El Zrelli et al. [19] investigated the heavy metal pollution and ecological risk assessment in sediment samples obtained from the surroundings of a Tunisian industrial coastal complex. In another study, the health risk assessment of potentially toxic elements in soil and sediment samples around a petrochemical company was studied by Relić et al. [20]. However, there is a lack of data on the levels of PTEs in sediments around pharmaceutical industries in Nigeria.

Previous studies have identified various PTEs present in sediment samples obtained around Ilorin metropolis [15,21]. However, there is yet to be any study that examined the human and ecological risks posed by these contaminants. This is a knowledge gap that this study bridges. This study addresses the health risks associated with PTEs in sediment samples obtained around a prominent pharmaceutical industry in Ilorin, Nigeria. The specific objectives encompass determining the total concentrations and spatial distribution of PTEs within sediment samples in both the rainy and dry climatic seasons, assessing pollution and environmental risks along with their causes, and evaluating potential non-carcinogenic and carcinogenic human health risks linked to PTEs in the sediments. The novelty of this study is that it examined the human and ecological risks being posed by PTEs in sediments obtained from Ilorin metropolis. The selection of As, cadmium, chromium, lead, cobalt, and nickel as potentially toxic elements (PTEs) for this study was driven by their recognized environmental significance, potential health risks, well-established toxicity, and use in industrial processes, particularly pharmaceutical manufacturing, ensuring a comprehensive evaluation of diverse exposure pathways and environmental impacts [6,8,22,23].

The assessment of PTEs in sediments is crucial, as sediments are known to act as a long-term sink for contaminants in aquatic ecosystems, leading to bioaccumulation and biomagnification in the food chain [24]. Additionally, the sediment-bound PTEs can be re-suspended and transported to other areas through natural processes such as erosion and flooding, leading to further contamination of the environment [25]. The decision to conduct sampling during distinct climatic periods stemmed from the recognition that environmental factors, such as precipitation patterns, can significantly influence the transport, deposition, and accumulation of pollutants in aquatic ecosystems. The rainy season, characterized by increased rainfall and surface runoff, may result in the mobilization and transport of contaminants from terrestrial sources into nearby water bodies, potentially leading to elevated PTEs concentrations in sedimentary deposits. Conversely, the dry season, characterized by reduced precipitation and lower water levels, may facilitate the concentration and accumulation of PTEs in sedimentary matrices due to decreased dilution and enhanced sedimentation processes. It is expected that this study will provide important information that can be used to develop appropriate risk management strategies and environmental policies aimed at reducing the discharge of PTEs from the pharmaceutical industry and protecting human health and the environment.

## 2. Methodology

### 2.1. The study area

The pharmaceutical industry under investigation is situated at New-Yidi Road, Ilorin South local government area, Kwara State, Nigeria, with geographical coordinates of latitude 8°28'33.20" N and longitude 4°33'08.20" E, as shown in Table 1 and Fig. 1. The

**Table 1**  
Table showing the sampling points.

| Locations                         | Coordinates             | Depth | Activities                        |
|-----------------------------------|-------------------------|-------|-----------------------------------|
| <b>Location 1</b>                 | 8°28'33.2"N 4°33'08.2"E | 13 cm | Industry discharge point          |
| <b>Location 2</b>                 | 8°28'33.4"N 4°33'09.7"E | 13 cm | Close to industry discharge point |
| <b>Location 3</b>                 | 8°28'35.0"N 4°33'11.2"E | 10 cm | Farming, Irrigation, Fishing      |
| <b>Location 4</b>                 | 8°28'35.3"N 4°33'11.7"E | 10 cm | Farming, Irrigation, Fishing      |
| <b>Location 5</b>                 | 8°28'37.7"N 4°33'17.0"E | 8 cm  | Urban runoff, Dump site           |
| <b>Location 6</b>                 | 8°28'37.9"N 4°33'18.1"E | 8 cm  | Urban runoff, Local laundry site  |
| <b>Location 7 (Control Point)</b> | 8°26'29.4"N 4°33'21.9"E | 10 cm | Dam site, Farming                 |

industry serves as a drug supplier for the entire country. Adjacent to the industry, a river flows through a residential area and receives waste discharge from the depot. In the event of contamination, this river could pose a significant risk to human health and aquatic organisms in the surrounding area of New-Yidi Road, Ilorin. Fishing and farming activities like irrigation are taking place within the

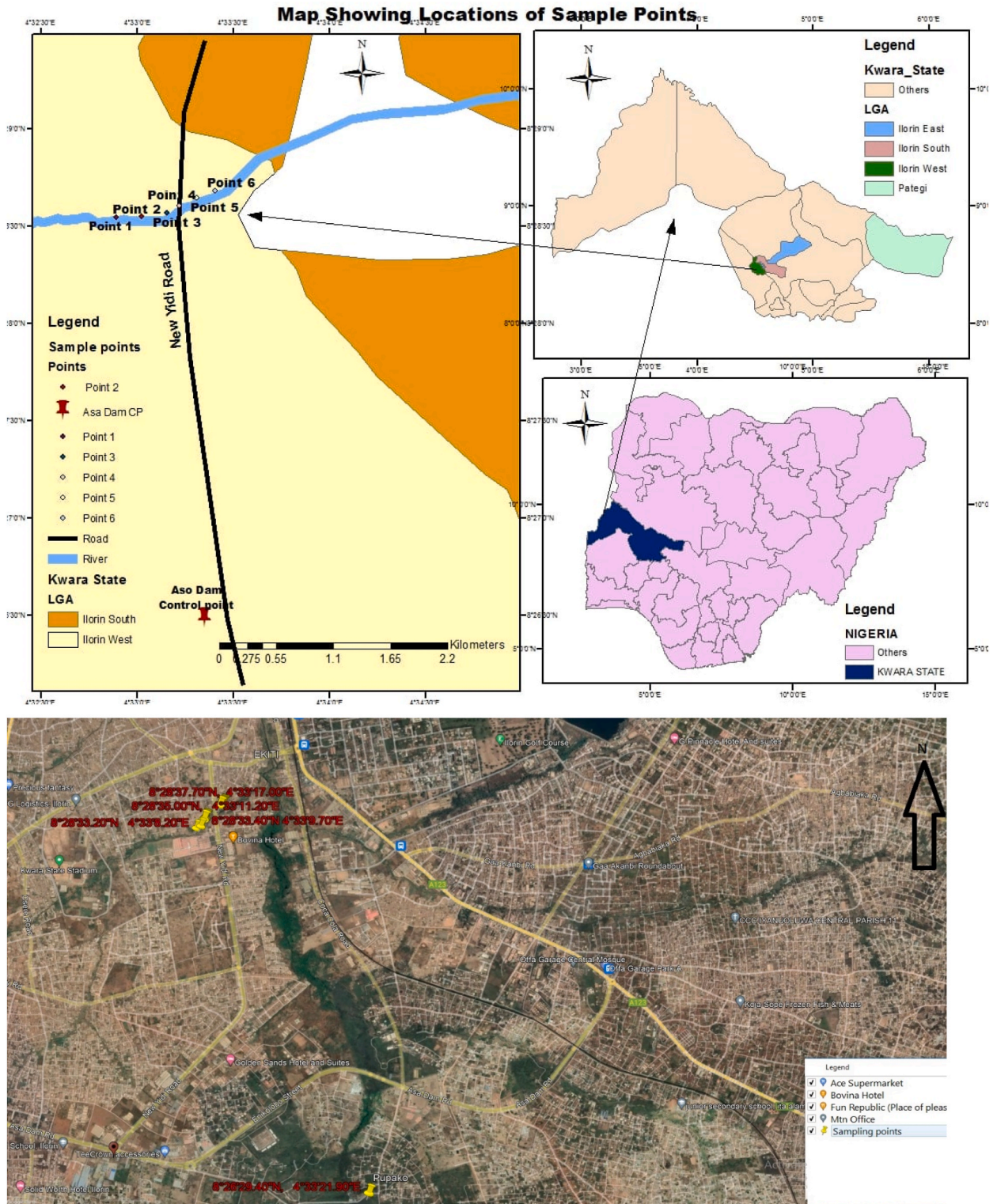


Fig. 1. Map of study area and sampling points along the pharmaceutical area.

river, while some residents often use the water for laundry [26]. The sediment samples were collected at the same locations in the months of January (dry season) and June (rainy season) to assess potential variations in PTEs levels under different climatic conditions.

## 2.2. Reagents, sample collection and preparation

The reagents used for this study,  $\text{HNO}_3$  (68 % purity) and  $\text{HCl}$  (35 % purity), both of AnalaR grade (manufactured by British Drug Houses Limited in London, United Kingdom), were used as received without further purification. Six sediment samples were systematically collected from various locations surrounding the industrial area, as detailed in Table 1. Additionally, a control sample was randomly obtained from a site several kilometers away, chosen for its presumed lack of pollution. The sampling process was conducted during both the rainy and dry seasons to capture potential seasonal variations. Utilizing a soil auger and specialized polyethylene test containers, each with a volume of approximately  $10 \text{ cm}^3$ , meticulous care was taken during the collection process to ensure representative and accurate sediment samples were obtained for subsequent analysis. Thereafter, some visible impurities, such as stones, plastic rubbers, glass, animal and plant matter, and other significant particles, were removed. Afterward, the samples were air-dried at room temperature in the lab for a period of 14 days to reduce the overall water content and prevent any chemical reactions. The sediments were fragmented into smaller pieces using an agate mortar, passed through a filter featuring a 1 mm mesh size, and then placed into plastic containers with suitable labeling for the digestion process [27].

For the digestion of samples, the aqua regia method was used. The sample bottles were soaked with 10 % nitric acid for 24 h before thorough washing and rinsing with distilled water. A clean digestion flask was used to measure 1.0 g of sediment samples. Then, 3 ml of concentrated  $\text{HNO}_3$  and 9 ml of concentrated hydrochloric acid were added to each sample in the flask. The mixtures were heated using an electric hot plate until they stopped releasing brown fumes, indicating the release of nitrogenous compounds and completion of the digestion process. Once cooled, a few drops of distilled water were added, and the mixture was filtered into a 50-ml standard flask and transferred into plastic reagent bottles [27].

## 2.3. Analytical methods and quality assurance and control analysis (QA/QC)

After digestion, the concentration of the PTEs of interest in the samples was quantitatively determined using an inductively coupled plasma optical emission spectrophotometer (ICP-OES) (model Agilent 5800, by Agilent Technologies, USA) and an atomic absorption spectrophotometer (AAS) (model 210 VGP, Buck Scientific, E. Norwalk, CT, USA). The concentrations of chromium, cobalt, cadmium, nickel, and lead were obtained using the AAS equipment, while the concentration of nickel was determined using the ICP-OES equipment.

In ensuring the quality control and quality assurance (QA/QC) of the analysis of PTEs in the sediment samples, calibration of the analysis equipment was conducted in accordance with the IAEA-Soil 7 standards, and blank reagents were utilized. At regular intervals, blank and standard solutions were analyzed. A series of standard solutions containing the following concentrations of Pb, Co, Ni, Cr, Cd, and As ions were prepared using deionized distilled water and standard certified solutions (1000 ppm): 0.00, 0.25, 0.50, 1.00, 1.50, 2.00, 3.00, and 4.00 ppm. To obtain accurate quantitative data, the regression coefficient of the standard calibration curve for each PTEs was greater than 0.9960. The analytical data was derived by averaging the results of three replicates [28]. Precision assessment involved the use of three internal replicas and two blind replicas. The formula documented by Reyes et al. [29] for calculating the accuracy of the acquired data was utilized.

For calculating the electrical conductivity (EC), pH, and total dissolved solids (TDS) of the sediment samples, 10 g of each sample from the various locations was weighed and mixed with 100 ml of distilled water. The mixture was stirred and allowed to settle. A multi-functional pH meter (model HI-98130, Hanna Instruments, Woonsocket, Rhode Island, USA) coupled with both an EC and TDS meter was used to measure all the various parameters by dipping the electrode in each sample.

## 2.4. Health risk assessment

The procedure of determining the potential health impacts of vulnerability to both carcinogenic and non-carcinogenic compounds is known as “human health risk assessment.” The risk assessment process includes four fundamental stages: identifying potential hazards, evaluating exposure levels, assessing toxicity and dose-response relationships, and characterizing the overall risk posed by the hazard.

The risk assessment method consists of four basic steps: hazard identification, exposure assessment, toxicity and dose-response assessment, and risk characterization [30]. In essence, hazard identification looks at the contaminants that are present, their concentrations, and their geographical dispersion in a given area. Assessing exposure levels is a crucial approach for determining how frequently, for how long, and how strongly individuals come into contact with contaminants such as PTEs. To measure exposure in this study, the authors calculated the average daily intake (ADI) of PTEs resulting from ingestion, inhalation, and skin contact by the general population. A dose-response study assesses the toxicity resulting from PTE exposure intensities. There are two main measures of toxicity that are commonly utilized: the cancer slope factor (SF), which indicates the potency of a carcinogen, and the reference dose (RfD), which indicates the non-carcinogenic threshold. Risk classification combines various data to create numerical estimates of cancer risks and hazard indices. This process aids in predicting potential health risks, both cancerous and non-cancerous, to the population in the study region who may have been exposed. To calculate the ADI for non-carcinogenic transmission via ingestion, inhalation, and skin contact exposure, Equations (1)–(3) were employed [27]. The ADI is measured in milligrams per kilogram per day.

For ingestion pathway,

$$ADI_{ing} = \frac{Cs \times IngRs \times EF \times ED}{BW \times AT} \quad (1)$$

The  $ADI_{ing}$  calculates the mean daily intake of PTEs through the ingestion of sediment. The equation involves several variables, including  $Cs$ , which is the PTE concentration in the sediment sample in mg/kg;  $BW$ , the body weight of the at-risk individual assumed to be 70 kg;  $ED$ , which represents the annual duration of exposure assumed to be 55 years;  $IngRs$ , the rate of sediment particle ingestion (100 mg/day);  $EF$ , the frequency of exposure (365 days per year); and  $AT$ , which is the duration over which the dose is averaged ( $ED \times 365$  days).

For the inhalation pathway,

$$ADI_{inh} = \frac{Cs \times InhRs \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

In equation (2), “PEF” refers to the particle emission factor and is expressed in cubic meters per kilogram (i.e.  $1.36 \times 10^9 \text{ m}^3/\text{kg}$ ). The inhalation rate (InhR) is taken as  $20 \text{ m}^3/\text{day}$ .

For the Dermal pathway,

$$ADI_{derm} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (3)$$

In equation (3), “SA” represents the area of the skin that is exposed and is measured in square centimeters (i.e.  $5700 \text{ cm}^2$ ), while “ABS” refers to the skin absorption factor (0.001) and Adherence factor (AF) is assumed to be  $0.07 \text{ mg}/\text{cm}^2\text{-day}$ .

#### 2.4.1. The non-carcinogenic risk assessment

To evaluate the non-carcinogenic risk, the Target Hazard Quotient (THQ) was utilized by dividing the extended average daily intake (ADI) by the reference dose (RfD) of a particular potentially toxic element (PTE), as shown in equation (4) [31]. The THQ utilizes a daily absorption rate, also referred to as the level of exposure, which is expected to have negligible health risks over the course of approximately 70 years [27].

$$THQ = \frac{ADI}{RfD} \quad (4)$$

There is a high possibility that the exposed population will have negative health impacts if the THQ is greater than 1. However, there are fewer chances of negative health impacts if the THQ is less than 1. The sum of the THQs obtained from various pathways, as outlined in Equation (5), is the total hazard quotient (HI). The hazard index (HI) is used to evaluate the potential risks to human health posed by multiple potentially toxic elements (PTEs) [32]. The oral (ingestion) reference doses for the PTEs are  $3.50 \times 10^{-3}$ ,  $2.00 \times 10^{-2}$ ,  $3.00 \times 10^{-3}$ ,  $1.00 \times 10^{-3}$ ,  $3.00 \times 10^{-3}$ , and  $2.00 \times 10^{-2} \text{ mg}/\text{kg}/\text{day}$  for Pb, Ni, Cr, Cd, As and Co, respectively. The inhalation reference doses for the PTEs are  $3.25 \times 10^{-3}$ ,  $5.40 \times 10^{-3}$ ,  $2.86 \times 10^{-5}$ ,  $5.70 \times 10^{-5}$ ,  $3.01 \times 10^{-4}$  and  $5.71 \times 10^{-6} \text{ mg}/\text{kg}/\text{day}$  for Pb, Ni, Cr, Cd, As and Co, respectively. The dermal reference doses for the PTEs in  $\text{mg}/\text{kg}/\text{day}$  are Cr ( $6.00 \times 10^{-5}$ ), Cd ( $5.00 \times 10^{-4}$ ), Ni ( $5.40 \times 10^{-3}$ ), Co ( $1.60 \times 10^{-2}$ ), Pb ( $5.25 \times 10^{-4}$ ), and As ( $1.23 \times 10^{-4}$ ).

$$HI = \sum THQ \quad (5)$$

#### 2.4.2. The carcinogenic risk assessment

Carcinogenic risk assessment is utilized to evaluate and determine the probability of a population developing any type of cancer due to exposure to a carcinogen. The incremental lifetime cancer risk (ILCR) is the increased probability of an individual developing cancer over time as a result of exposure to potentially toxic elements (PTEs) [33]. Mathematically, it is represented as:

$$ILCR = ADI \times SF \quad (6)$$

The incremental lifetime cancer risk (ILCR) indicates the likelihood of an individual developing cancer due to exposure to carcinogenic potentially toxic elements (PTEs). The carcinogenic slope factor (SF) and average daily intake (ADI) are measured in  $\text{mg}/\text{kg}/\text{day}$ . Only the known human carcinogens, including Co, As, Pb, Cr, Cd, and Ni, were considered when assessing cancer risk. The permissible range is between  $1 \times 10^{-4}$  and  $1 \times 10^{-6}$ , with values lower than  $1 \times 10^{-6}$  indicating no significant cancer risk. Cancer risks exceeding  $1 \times 10^{-4}$  are significantly high and pose a greater risk of developing cancer. Haque et al. [34] and Orosun et al. [27] classified risk values into seven tiers using the Delphi approach. The values of exposure used for calculating the human health risks in this study were obtained from Isinkaye [35]. The cancer slope factors are: Ingestion slope factors, As (1.5), Pb ( $8.5 \times 10^{-3}$ ), Cr (0.5), Cd (0.38); Inhalation slope factors, Cr ( $4.20 \times 10^{-1}$ ), Cd (6.30), Ni ( $8.40 \times 10^{-1}$ ), As ( $1.51 \times 10^{-1}$ ) and Dermal slope factor As (3.66).

#### 2.4.3. Ecological risk assessment

The accumulation coefficients of potentially toxic elements (PTEs) in sediment samples from each site were determined by calculating the accumulation coefficients from six different locations and a control point. The following equation was employed to determine the accumulation coefficient  $C_f^i$ :

**Table 2**  
Seasonal mean concentrations of the PTEs at different locations.

| PTEs            | Location    | Rainy season (mg/kg) | Dry season (mg/kg) | Mean concentrations (mg/kg) |
|-----------------|-------------|----------------------|--------------------|-----------------------------|
| <b>Lead</b>     | Location 1  | 0.021 ± 0.016        | 0.019 ± 0.005      | 0.019 ± 0.010               |
|                 | Location 2  | 0.023 ± 0.005        | 0.029 ± 0.002      | 0.025 ± 0.005               |
|                 | Location 3  | 0.034 ± 0.009        | 0.028 ± 0.004      | 0.031 ± 0.007               |
|                 | Location 4  | 0.022 ± 0.013        | 0.037 ± 0.007      | 0.029 ± 0.013               |
|                 | Location 5  | 0.015 ± 0.007        | 0.018 ± 0.001      | 0.016 ± 0.004               |
|                 | Location 6  | 0.018 ± 0.016        | 0.005 ± 0.001      | 0.011 ± 0.012               |
|                 | Location 7  | 0.002 ± 0.001        | 0.000 ± 0.000      | 0.001 ± 0.001               |
|                 | Mean Season | 0.019 ± 0.012        | 0.019 ± 0.0131     | –                           |
|                 | CV%         | –                    | 77.3               | –                           |
|                 | p ≤ 0.05    | –                    | NS                 | –                           |
|                 | Interaction | –                    | NS                 | –                           |
| <b>Cobalt</b>   | Location 1  | 0.001 ± 0.001        | 0.003 ± 0.001      | 0.002 ± 0.002               |
|                 | Location 2  | 0.002 ± 0.000        | 0.003 ± 0.000      | 0.002 ± 0.000               |
|                 | Location 3  | 0.004 ± 0.004        | 0.006 ± 0.002      | 0.005 ± 0.002               |
|                 | Location 4  | 0.001 ± 0.002        | 0.000 ± 0.000      | 0.001 ± 0.001               |
|                 | Location 5  | 0.002 ± 0.002        | 0.001 ± 0.000      | 0.002 ± 0.002               |
|                 | Location 6  | 0.000 ± 0.000        | 0.001 ± 0.001      | 0.000 ± 0.001               |
|                 | Location 7  | 0.001 ± 0.001        | 0.000 ± 0.000      | 0.001 ± 0.001               |
|                 | Mean Season | 0.016 ± 0.001        | 0.002 ± 0.002      | –                           |
|                 | CV%         | –                    | 77.0               | –                           |
|                 | p ≤ 0.05    | –                    | NS                 | –                           |
|                 | Interaction | –                    | NS                 | –                           |
| <b>Nickel</b>   | Location 1  | 0.018 ± 0.003        | 0.005 ± 0.000      | 0.012 ± 0.008               |
|                 | Location 2  | 0.021 ± 0.002        | 0.002 ± 0.000      | 0.011 ± 0.011               |
|                 | Location 3  | 0.006 ± 0.002        | 0.009 ± 0.001      | 0.008 ± 0.002               |
|                 | Location 4  | 0.011 ± 0.003        | 0.002 ± 0.000      | 0.006 ± 0.006               |
|                 | Location 5  | 0.013 ± 0.004        | 0.006 ± 0.000      | 0.009 ± 0.005               |
|                 | Location 6  | 0.007 ± 0.001        | 0.003 ± 0.000      | 0.005 ± 0.003               |
|                 | Location 7  | –                    | –                  | –                           |
|                 | Mean Season | 0.011 ± 0.007        | 0.004 ± 0.003      | –                           |
|                 | CV%         | –                    | 95.8               | –                           |
|                 | p ≤ 0.05    | –                    | –                  | –                           |
|                 | Interaction | –                    | –                  | –                           |
| <b>Chromium</b> | Location 1  | 0.006 ± 0.002        | 0.019 ± 0.005      | 0.012 ± 0.008               |
|                 | Location 2  | –                    | 0.002 ± 0.001      | 0.001 ± 0.001               |
|                 | Location 3  | 0.012 ± 0.005        | 0.014 ± 0.017      | 0.013 ± 0.010               |
|                 | Location 4  | 0.005 ± 0.002        | 0.005 ± 0.001      | 0.005 ± 0.001               |
|                 | Location 5  | –                    | 0.001 ± 0.000      | 0.001 ± 0.000               |
|                 | Location 6  | 0.013 ± 0.004        | 0.015 ± 0.001      | 0.014 ± 0.003               |
|                 | Location 7  | 0.004 ± 0.002        | 0.000 ± 0.000      | 0.002 ± 0.002               |
|                 | Mean Season | 0.005 ± 0.005        | 0.008 ± 0.009      | –                           |
|                 | CV%         | –                    | 73.4               | –                           |
|                 | p ≤ 0.05    | –                    | NS                 | –                           |
|                 | Interaction | –                    | NS                 | –                           |
| <b>Cadmium</b>  | Location 1  | 0.020 ± 0.009        | 0.020 ± 0.002      | 0.020 ± 0.005               |
|                 | Location 2  | 0.016 ± 0.002        | 0.018 ± 0.002      | 0.017 ± 0.002               |
|                 | Location 3  | 0.022 ± 0.001        | 0.026 ± 0.006      | 0.024 ± 0.007               |
|                 | Location 4  | –                    | –                  | –                           |
|                 | Location 5  | 0.008 ± 0.002        | 0.012 ± 0.005      | 0.010 ± 0.004               |
|                 | Location 6  | 0.006 ± 0.002        | 0.003 ± 0.003      | 0.005 ± 0.003               |
|                 | Location 7  | –                    | –                  | –                           |
|                 | Mean Season | 0.010 ± 0.001        | 0.011 ± 0.010      | –                           |
|                 | CV%         | –                    | 89.5               | –                           |
|                 | p ≤ 0.05    | –                    | NS                 | –                           |
|                 | Interaction | –                    | NS                 | –                           |
| <b>Arsenic</b>  | Location 1  | 0.017 ± 0.020        | 0.007 ± 0.000      | 0.012 ± 0.013               |
|                 | Location 2  | 0.001 ± 0.000        | –                  | 0.001 ± 0.001               |
|                 | Location 3  | 0.014 ± 0.010        | 0.002 ± 0.001      | 0.008 ± 0.008               |
|                 | Location 4  | 0.004 ± 0.005        | 0.010 ± 0.004      | 0.007 ± 0.005               |
|                 | Location 5  | 0.019 ± 0.020        | –                  | 0.009 ± 0.016               |
|                 | Location 6  | 0.001 ± 0.000        | 0.007 ± 0.001      | 0.004 ± 0.004               |
|                 | Location 7  | 0.001 ± 0.001        | –                  | 0.000 ± 0.001               |
|                 | Mean Season | 0.008 ± 0.011        | 0.004 ± 0.004      | –                           |
|                 | CV%         | –                    | 56.8               | –                           |
|                 | p ≤ 0.05    | –                    | NS                 | NS                          |
|                 | Interaction | –                    | NS                 | –                           |

\*NS = not significant; CV% = coefficient of variation; p ≤ 0.05 = significance level at 5 %.

$$C_f^i = C_m^i / C_n^i \quad (7)$$

The accumulation coefficient was calculated using the PTEs concentration of the sediment samples denoted as  $C_m^i$  and the control values of sediments indicated as  $C_n^i$  both measured in mg/kg [36]. The potential ecological risk index ( $Ri$ ) neglects chemical speciation while taking into account both the toxicities and total concentrations of the PTEs. In this study, the possible ecological risk index methodology created by Hakanson [37] was used. Equations (8) and (9) were used to calculate the potential ecological risk coefficient  $E_r^i$  of a single element and the potential ecological risk index  $Ri$  of a multi-element system [38]:

$$E_r^i = T_f^i \times C_f^i \quad (8)$$

$$Ri = \sum_{i=1}^n E_r^i \quad (9)$$

According to the equations,  $C_f^i$  represents the accumulation coefficient of element  $i$ , while  $T_f^i$  denotes the toxic-response factor of element  $i$ . The toxic-response factor reflects the sensitivity of bio-organisms and the toxicity levels of the element. The toxic-response factors for widely known PTEs, including Pb, Cd, As, Co, Cr, and Ni, are 5, 30, 10, 5, 2, and 5, respectively [38].

## 2.5. Statistics analysis of data

The IBM SPSS Statistics for Windows, version XXVI (2019), software was employed to treat the collected data and investigate the varying amounts of potential toxic elements present in each sediment sample so as to establish the relationship between their abundance. The two-way analysis of variance (ANOVA) was used to compare PTEs concentrations across different locations and seasons.

## 3. Results and discussions

### 3.1. Analysis of PTEs concentrations at different locations

As shown in Table 2, lead concentration (mean) at all locations ranged from  $0.001 \pm 0.001$  mg/kg (minimum) to  $0.031 \pm 0.007$  mg/kg (maximum) in location 7 and location 3, respectively. This shows that the concentration of Pb is lowest in the control sample. The implication of this is that there could have been other sources of lead emission either from the industry or other sources. However, the mean concentration of lead at the industry discharge point (location 1) was observed to be lower than in location 2, 3, and 4. This means that the residual lead could have emanated from other anthropogenic activities such as the wash-off of residual fertilizer from farm lands. The highest concentration value for Pb was recorded in the dry season (location 4), with a mean and standard deviation of  $0.037 \pm 0.007$  mg/kg, which could have been as a result of the reasons stated above. The result obtained is lower than that obtained by Ajala et al. [39], Akintade et al. [21], and Akintade et al. [15] for sediments obtained from different locations in Ilorin. The order of increasing seasonal values is rainy < dry, as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) was 77.3 %. The concentration of Pb from the result across all locations falls below 0.1 mg/kg, which is within the WHO acceptable limit for soil and sediment [40]. The low values recorded show that there is less emission of Pb into the river. Pb is a natural constituent of the earth's crust, and it cannot be easily degraded or destroyed. Pb is generally dangerous because it tends to bioaccumulate and bio-magnify [41].

The mean cobalt concentration at all locations ranged from  $0.000 \pm 0.001$  mg/kg (minimum) to  $0.005 \pm 0.002$  mg/kg (maximum) in location 6 and location 3, respectively (Table 2). Just like the concentration of lead obtained, the mean concentration of cobalt was observed to be relatively same in the samples obtained at the industry discharge point, few meters away from the discharge point and at an urban runoff point. This implies that the concentration of cobalt in the sediment is not spiked from the activities of the pharmaceutical industry. The highest concentration value for Co was recorded in the dry season, with a mean and standard deviation of  $0.006 \pm 0.002$  mg/kg (location 3). The result obtained in this study is lower than that obtained by Akintade et al. [21] and Akintade et al. [15] for sediments obtained from different locations in Ilorin. The tolerable limit of cobalt in sediment is 0.2–0.5 mg/kg, as stipulated by the USEPA [42], which implies that the Co concentration obtained in this study is within the range of acceptable limits. The order of increasing seasonal values is dry < rainy as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) is 77.0 %. The buildup of PTEs, particularly Co, in agricultural areas and water bodies as a result of anthropogenic and natural processes is of great concern. Despite being a crucial component of vitamin B12, its increased exposure has a major impact on agricultural plants. Co intake by humans via food is around 5–40 µg/day [43]. 5–30 % of cobalt is included in cement carbide [42].

The mean nickel concentration at all locations ranged from  $0.005 \pm 0.003$  mg/kg (minimum) to  $0.012 \pm 0.008$  mg/kg (maximum) in location 6 and location 1, respectively (Table 2). Unlike the observation made for lead and cobalt, the concentration of Nickel was highest at the industry discharge point followed by the point close to the discharge point. This implies that the sediments at such point had served as a sink for the relatively high nickel concentration of the effluent discharged. The highest concentration of Ni was recorded in the rainy season, with a mean and standard deviation of  $0.021 \pm 0.002$  mg/kg (location 2). The concentrations obtained are within the World Health Organization (WHO) acceptable limit of 0.5 mg/kg [40]. No value was recorded at location 7, which is due

to low anthropogenic activities in the area. The order of increasing seasonal values is dry < rainy as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) is 95.8 %. Findings from the research conducted by Enuneku and Ineh [44] obtained a mean nickel concentration of 1.289 mg/kg, which implies that the Ikpoba River in Benin City is polluted from impacted soil erosion. The values recorded are higher than those obtained in this study. Also, research carried out by Aendo et al. [45] in Central Thailand recorded a high mean concentration of Ni ( $9.9 \pm 0.99$  mg/kg), which is also not in agreement with the value recorded in this study.

The mean chromium concentration at all locations ranged from 0.001 mg/kg (minimum) to  $0.014 \pm 0.003$  mg/kg (maximum) in location 5 and location 6, respectively (Table 2). The highest concentration value for Cr was observed in the dry season, with a mean and standard deviation of  $0.019 \pm 0.005$  mg/kg (location 1). This means that the sediment at the industry discharge point serves as a sink for chromium accumulation due to the industrial discharge. However, it was observed that even though the presence of chromium was detected in the samples 2 and 5 during the dry season, it was undetected in the rainy season. This could have been as a result of the wash-off of the element from the sediment that had occurred. The result obtained in this study is lower than that obtained by Akintade et al. [21] and Akintade et al. [15] for sediments obtained from different locations in Ilorin. The order of increasing seasonal values is rainy < dry, as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) is 73.4 %. The concentrations of Cr recorded in all locations were within the acceptable limit of 0.1 mg/kg set by the WHO [40]. Notwithstanding, a lot of Cr is released into the soil, groundwater, and air by the chemical, metallurgical, and refractory sectors, which affects the health of people, animals, and marine life [46].

The mean cadmium concentration at all locations ranged from  $0.005 \pm 0.003$  mg/kg (minimum) to  $0.024 \pm 0.007$  mg/kg (maximum) in location 6 and location 3 (Table 2). The highest concentration value for Cd was recorded in the dry season, with a mean and standard deviation of  $0.026 \pm 0.006$  mg/kg (location 3). The relatively high concentration of cadmium in the sample obtained from the farming, irrigation, and fishing point does not show a direct link with that from the industry discharge point. No value was recorded at location 4 in the rainy season and location 7, which is due to low anthropogenic activities in the area [40]. The order of increasing seasonal values is rainy < dry, as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) is 89.5 %. The cadmium concentrations recorded across all locations are within the acceptable value of 0.48 mg/kg set by USEPA. However, the value set by WHO is 0.003 mg/kg. Concentrations in locations 4 and 6 are within the WHO acceptable limit, while in the other locations they exceed it. The high concentration of Cd found in these locations is consistent with previous reports by Okoro et al. [47], Okoro et al. [48], Okoro and Jimoh [49], Okoro et al. [50], and Orosun et al. [27], all of which also showed levels above the WHO limit. The increase in Cd concentration in these locations may be due to anthropogenic activities such as farming, refuse disposal, and irrigation.

The mean concentration of arsenic at all locations ranged from  $0.001 \pm 0.001$  mg/kg (minimum) to  $0.012 \pm 0.013$  mg/kg (maximum) in location 2 and location 1, respectively (Table 2). The highest concentration value of As was recorded in the rainy season at location 5, with a mean and standard deviation of  $0.019 \pm 0.020$  mg/kg. This may be due to urban runoff and refuse dumping on the site. The recorded concentrations of As at all locations are within the acceptable limit set by the USEPA for sediment of 5–20 mg/kg [27]. The order of increasing seasonal values is dry < rainy as summarized in Table 2. Furthermore, from the two-way analysis of variance computed, there was no significance difference in seasonal or interaction effects. The coefficient of variation (CV) is 56.8 %. As recorded in a study by Okoro et al. [51], the predominant natural occurrences are due to volcanic eruptions and biological activities. The contribution from volcanic eruptions and biological activities is very small compared to the anthropogenic inputs, such as

**Table 3**  
Correlation analysis of concentrations of PTEs in all location.

| PTEs |                     | Pb     | Co      | Ni     | Cr     | Cd      | As     |
|------|---------------------|--------|---------|--------|--------|---------|--------|
| Pb   | Pearson Correlation | 1      | 0.209   | 0.270  | 0.027  | 0.423*  | −0.001 |
|      | Sig. (2-tailed)     | –      | 0.285   | 0.165  | 0.890  | 0.025   | 0.994  |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |
| Co   | Pearson Correlation | 0.209  | 1       | 0.079  | 0.389* | 0.662** | 0.157  |
|      | Sig. (2-tailed)     | 0.285  | 0.690   | 0.041  | 0.000  | 0.000   | 0.424  |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |
| Ni   | Pearson Correlation | 0.270  | 0.079   | 1      | −0.158 | 0.384*  | 0.179  |
|      | Sig. (2-tailed)     | 0.165  | 0.690   | –      | 0.421  | 0.043   | 0.363  |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |
| Cr   | Pearson Correlation | 0.027  | 0.389*  | −0.158 | 1      | 0.181   | 0.092  |
|      | Sig. (2-tailed)     | 0.890  | 0.041   | 0.421  | –      | 0.357   | 0.642  |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |
| Cd   | Pearson Correlation | 0.423* | 0.662** | 0.384* | 0.181  | 1       | 0.145  |
|      | Sig. (2-tailed)     | 0.025  | 0.000   | 0.043  | 0.357  | –       | 0.462  |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |
| As   | Pearson Correlation | −0.001 | 0.157   | 0.179  | 0.092  | 0.145   | 1      |
|      | Sig. (2-tailed)     | 0.994  | 0.424   | 0.363  | 0.642  | 0.462   | –      |
|      | N                   | 28     | 28      | 28     | 28     | 28      | 28     |

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level (2-tailed).

\*Pb = lead; Co = Cobalt; Ni = Nickel; Cr = Chromium, Cd = Cadmium; As = Arsenic; N = sample size.



agricultural chemicals or the smelting of ores. As readily enters the atmosphere because of its relative volatility (Arsenic emissions inevitably yield relatively high residues during the rainy season) [51]. This is in agreement with the data collected in this study. However, a study by Orosun et al. [27] recorded that the concentration of As (42.48 mg/kg) is much greater than the value recorded in this study and is above the acceptable limit of the USEPA. The study further disclosed that significant quantities of As arise from lithogenic sources of pollution rather than anthropogenic sources.

Findings by Okoro et al. [51] also reported that metal pollution sites, such as agricultural land, landfill sites, and sewage treatment plants, could be another source of Pb in the environment. However, a number of human activities, such as the exploitation of mineral resources, the production of metals, the smelting and processing of metals, industrial emissions, the use of pesticides and fertilizers, and atmospheric transportation, can result in an increase in the concentration of lead and other potentially toxic elements in the aquatic environment. They can move through a carrier and eventually get absorbed by micro-mineral particles in soil and sediment, which contaminate aquatic ecosystems. This may result in significant harm to the aquatic ecology and to people's health [44]. Table 3 demonstrates significant relationships between different PTEs concentrations. A single asterisk indicates a significant correlation at a 5 % level of significance, while a double asterisk represents a significant relationship at a 1 % level. Furthermore, a negative relationship was discovered between lead and arsenic, as well as between nickel and chromium. Such negative correlations suggest potential antagonistic interactions or contrasting sources of contamination within the study area. Lead and arsenic are commonly associated with anthropogenic activities such as industrial emissions and urban runoff, yet their negative relationship may indicate differences in their sources or mobility in the environment. Similarly, nickel and chromium are often found together in industrial processes, yet their negative correlation could reflect variations in their geochemical behavior or differential transport mechanisms in the aquatic ecosystem [2,52,53].

### 3.2. Factor and cluster analysis of concentration of the PTEs

Fig. 2a displays the standard two-dimensional Principal Component Analysis (PCA) for six PTEs (Pb, Co, Ni, Cr, Cd, and As) evaluated at the seven locations in Ilorin. Ni, Pb, and Cd components were found to be highly concentrated in Locations 1, 3, and 5, suggesting that they originated from anthropogenic sources. Furthermore, PCA was used to demonstrate seasonal variations in PTE concentrations across all locations (Fig. 2a). Cluster analysis and PCA (Fig. 2a and b) were plotted using SPSS version 25 software. PTEs

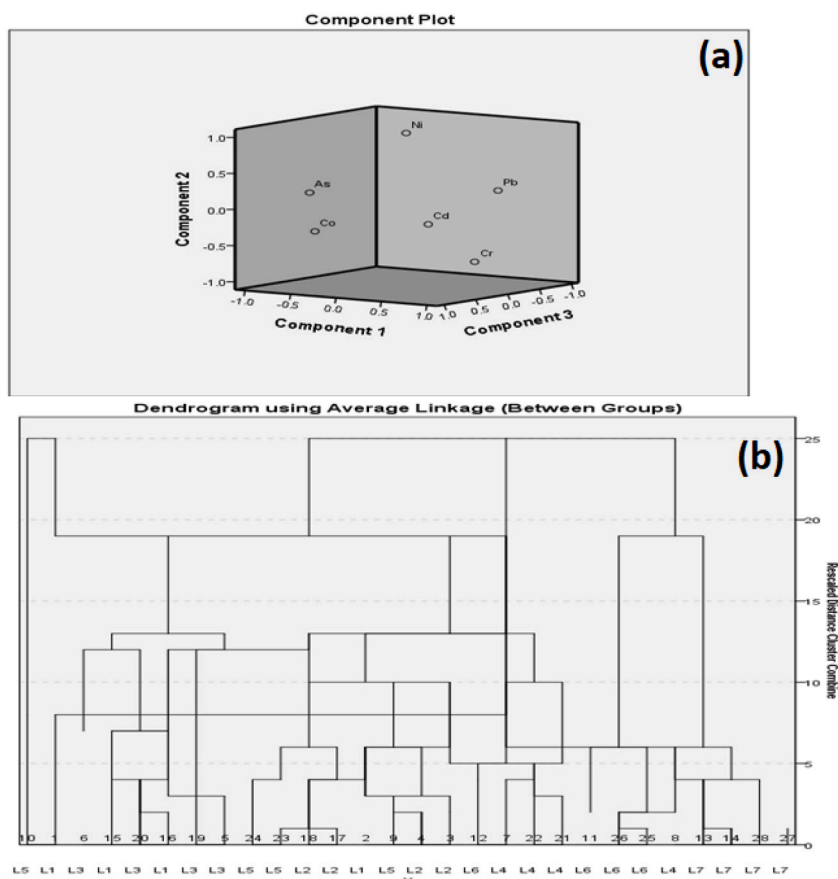


Fig. 2. (A) PCA showing seasonal distributions (b) Cluster analysis graph showing distribution of PTEs across locations in the samples.

grouped together on the same axis indicate that these PTEs have a similar origin in the samples.

### 3.3. Effects of the influence of physicochemical parameters and their seasonal variations

The results of seasonal variation of some physicochemical parameters of sediment samples from Ilorin at seven (7) different locations have been summarized in Table 4. Table 4 shows the seasonal and mean values of pH at seven different locations. The highest mean pH value of  $7.85 \pm 0.21$  was observed in location 6, while the lowest value of  $5.75 \pm 0.35$  was found in location 1. The pH of the sediment was found to be the lowest at the point of discharge, however, it increased as the distance to the industry increased. A significant variation between rainy and dry seasons was observed, with a coefficient of variation (CV) of 99.9%. The highest pH value was recorded during the dry season (Table 4). The pH values ranged from 5.50 to 8.0, with values below 7 being considered acidic and values above 7 being considered basic. A pH value of 7 is neutral, and the acceptable limit set by the WHO ranges from 6.5 to 8.5. Locations 1, 2, and 3 were found to be acidic, while the others were basic, with an increase in acidity observed from the rainy to the dry season. This is likely due to anthropogenic activities such as industrial discharge and farming [40]. Literature suggests that water becomes more corrosive as the pH value decreases. Increased pH levels are caused by decreased photosynthetic activity, as well as the absorption of carbon dioxide and bicarbonates. While pH levels in drinking water do not directly affect human health, they do impact other water quality characteristics such as the solubility of metals and the persistence of microorganisms, which can indirectly impact human health [54]. The order of increasing seasonal values is dry < rainy seasons, as summarized in Table 4. More so, from the two-way analysis of variance computed, significant variations of P ( $\leq 0.05$ ) were found only in location.

Table 4 consists of the seasonal and mean values of electrical conductivity in the seven different locations. The biggest mean value for it is  $272 \pm 18.4$  mS/cm, which is in location 6, and the smallest is  $144 \pm 26.9$  mS/cm, which is in location 5. A very high and significant variation was observed for rainy and dry seasons, with a coefficient of variation (CV) of 99.1%. The highest electrical conductivity value of 297 mS/cm was recorded during the rainy season. Table 4 shows that the seasonal values of electrical conductivity increase from the dry to the rainy season. The two-way analysis of variance without interaction revealed significant variations ( $p \leq 0.05$ ) only in location. The acceptable range for electrical conductivity, as set by WHO, is between 400 and 600 mS/cm, and all values recorded in all locations were within this range [40]. The conductivity of water is influenced by the ionic species present in the water or sediments. The mobility of the ions at a specific temperature affects both anions and cations in water and sediments [55]. In addition, the geology of the region through which the water travels also has a major impact on conductivity in streams and rivers. Streams that pass through granite bedrock tend to have lower conductivity, as granite contains more inert materials that do not ionize when washed into the water. Conversely, streams that pass through clay soil tend to have higher conductivity, due to the presence of materials that ionize when washed into the water [51].

**Table 4**

Seasonal and mean ( $\pm$ SD) values of the physicochemical parameters of the sediment samples.

| Physicochemical properties | Location      | Rainy season (mg/kg) | Dry season (mg/kg) | Mean Location (mg/kg) |
|----------------------------|---------------|----------------------|--------------------|-----------------------|
| pH                         | Location 1    | 6.0                  | 5.5                | $5.75 \pm 0.35$       |
|                            | Location 2    | 6.6                  | 5.8                | $6.20 \pm 0.57$       |
|                            | Location 3    | 6.7                  | 6.3                | $6.50 \pm 0.28$       |
|                            | Location 4    | 7.0                  | 7.3                | $7.15 \pm 0.21$       |
|                            | Location 5    | 7.2                  | 7.5                | $7.35 \pm 0.21$       |
|                            | Location 6    | 7.7                  | 8.0                | $7.85 \pm 0.21$       |
|                            | Location 7    | 7.0                  | 7.2                | $7.10 \pm 0.14$       |
|                            | Mean Season   | $6.89 \pm 0.53$      | $6.80 \pm 0.94$    | -                     |
|                            | CV%           | -                    | <b>99.9</b>        | -                     |
|                            | $p \leq 0.05$ | -                    | <b>NS</b>          | -                     |
| Electrical Conductivity    | Location 1    | 297.0                | 201.0              | $249.0 \pm 67.9$      |
|                            | Location 2    | 205.0                | 225.0              | $215.0 \pm 14.1$      |
|                            | Location 3    | 180.0                | 120.0              | $150.0 \pm 42.4$      |
|                            | Location 4    | 211.0                | 200.0              | $205.5 \pm 7.78$      |
|                            | Location 5    | 163.0                | 125.0              | $144.0 \pm 26.9$      |
|                            | Location 6    | 259.0                | 285.0              | $272.0 \pm 18.4$      |
|                            | Location 7    | 233.0                | 240.0              | $236.5 \pm 4.95$      |
|                            | Mean Season   | $221 \pm 46.1$       | $199 \pm 59.8$     | -                     |
|                            | CV%           | -                    | <b>99.1</b>        | -                     |
|                            | $p \leq 0.05$ | -                    | <b>NS</b>          | -                     |
| TDS                        | Location 1    | 125.0                | 133.0              | $129.0 \pm 5.66$      |
|                            | Location 2    | 99.0                 | 103.0              | $101.0 \pm 2.83$      |
|                            | Location 3    | 109.0                | 112.0              | $110.5 \pm 2.12$      |
|                            | Location 4    | 100.0                | 110.0              | $105.0 \pm 7.07$      |
|                            | Location 5    | 116.0                | 120.0              | $118.0 \pm 2.83$      |
|                            | Location 6    | 151.0                | 166.0              | $158.0 \pm 10.6$      |
|                            | Location 7    | 99.00                | 95.00              | $97.00 \pm 2.83$      |
|                            | Mean Season   | $114 \pm 19.0$       | $120 \pm 23.7$     | -                     |
|                            | CV%           | -                    | <b>99.9</b>        | -                     |
|                            | $p \leq 0.05$ | -                    | -                  | -                     |

\*NS = not significant; CV% = coefficient of variation;  $p \leq 0.05$  = significance level at 5%.

Table 4 presents the seasonal and mean values of total dissolved solids (TDS) in seven different locations. The highest mean value of TDS,  $158.5 \pm 10.6$  mg/L, was observed in location 6, while the lowest value,  $101 \pm 2.83$  mg/L, was found in location 2. A very significant variation was observed between the rainy and dry seasons, with a coefficient of variation (CV) of 99.9 %. The highest TDS value of 166.0 mg/L was recorded during the rainy season (as shown in Table 4). The seasonal values follow the order of increasing magnitude: rainy < dry, as summarized in Table 4. Additionally, the two-way analysis of variance without interaction showed a significant difference ( $P \leq 0.05$ ) in the effects of season and location. There is an inverse correlation between the electrical conductivity and TDS of the samples: the higher the electrical conductivity, the lower the TDS, and vice versa [40]. The existence of rock elements in the area that are resistant to dissolution may be the cause of the elevated TDS values in water and sediments, which show that the water is highly mineralized. Surface run-off components such as bicarbonates, chlorides, nitrate, salt, potassium, calcium, and magnesium may contribute to increased total dissolved solids in water and sediments. Hard water that cannot form lather is unsuitable for bathing and washing and is unsafe for ingestion [56–59].

### 3.4. Health risk assessments

For the average daily intake via the ingestion pathway in the rainy season, the calculated ADIing ranges from maximum values of lead ( $4.79 \times 10^{-8}$  mg/kg-day) to minimum values of arsenic ( $1.07 \times 10^{-9}$  mg/kg-day) at locations 3 and 6, respectively (Table S1). Lead contributes the highest intake through the ingestion pathway. Similarly, for the ADI via the inhalation pathway, the calculated ADIinh ranges from maximum values of lead ( $7.04 \times 10^{-12}$  mg/kg-day) to minimum values of arsenic ( $1.58 \times 10^{-13}$  mg/kg-day) at locations 3 and 6, respectively, with lead still contributing the highest intake through the inhalation pathway. For the ADI via dermal contact, the range is from maximum values of lead ( $1.91 \times 10^{-4}$  mg/kg-day) to minimum values of arsenic ( $4.28 \times 10^{-6}$  mg/kg-day), with lead also contributing the highest from locations 3 and 6, respectively.

In the dry season, the average daily intake via the ingestion pathway was calculated for the adult population from the results in Table S2. The ADIing ranges from maximum values of arsenic ( $1.48 \times 10^{-2}$  mg/kg-day) to minimum values of cadmium ( $1.43 \times 10^{-10}$  mg/kg-day) at location 4. Arsenic contributes the highest intake through the ingestion pathway. Similarly, for the ADI via the inhalation pathway, the calculated ADIinh ranges from maximum values of lead ( $7.85 \times 10^{-12}$  mg/kg-day) to minimum values of cadmium ( $2.10 \times 10^{-14}$  mg/kg-day) from location 4, with lead still contributing the highest intake through the inhalation pathway. For the ADI via dermal contact, the range is from maximum values of chromium ( $1.05 \times 10^{-3}$  mg/kg-day) to minimum values of cadmium ( $5.70 \times 10^{-7}$  mg/kg-day), with chromium contributing the highest from locations 1 and 4, respectively.

In Table S3, the Hazard Index (HI) was calculated for the rainy season, and it was found that all the Hazard Index values were less than one, which is the standard set by USEPA, except for Cr [34]. The HI value for Cr was slightly higher than one, with values of 1.24 in location 6 and 1.09 in location 3. This indicates that there is no probable non-cancerous effect from the other potential toxic elements (PTEs). The incremental lifetime cancer risk (ILCR) was also estimated, and it ranged from As ( $3.99 \times 10^{-8}$ ) maximum to Pb ( $1.82 \times 10^{-10}$ ) minimum, with As contributing the highest cancer risk, all in location 5. The risk grade of all the potential toxic elements under study falls into Group I across all locations, which is completely acceptable. It is important to note that cancer risks greater than  $1.0 \times 10^{-4}$  are considered high as they pose a higher cancer risk, while values below  $1.0 \times 10^{-6}$  are considered not to pose any cancer risk to humans [60–67]. Therefore, the acceptable range falls between  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-6}$ , indicating that the estimated cancer risks from the PTEs in the sediment samples fall within an acceptable range.

For the dry season, the Hazard Index (HI) was estimated for all the potential toxic elements (PTEs) in the sediment samples collected from the study locations, as documented in Table S4. The results show that all the HI values for Pb, Co, Ni, and Cd across all locations were less than one (<1), which is the standard set by the USEPA for non-cancerous effects [34,68,69]. However, for Cr and As, HI values greater than one were observed. Location 1 had the highest HI value for Cr ( $1.76 \times 10^{-1}$ ), followed by As with a HI value of 5.41 in location 4. Therefore, there may be some probable non-cancerous effects due to exposure to these elements. The incremental lifetime cancer risk (ILCR) was estimated for the PTEs in the sediment samples, and it ranges from As ( $2.22 \times 10^{-2}$ ) max. To Cd ( $5.43 \times 10^{-11}$ ) min., all in Location 4, with As contributing the highest cancer risk. The risk grade of Pb, Cr, and Cd falls in Group I across all locations, which is considered acceptable. However, the risk grade of As in locations L1, L4, and L6 falls in Group VII, and in L3, it falls in Group VI. The risk grade of Ni in locations L1, L2, L4, L5, and L6 falls in Group VI, and in L3, it falls in Group VII. Cancer risks greater than  $1.0 \times 10^{-4}$  are considered high as they pose a higher cancer risk, while values below  $1.0 \times 10^{-6}$  are considered to pose no cancer risk to humans. Therefore, the acceptable range falls between  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-6}$ , and appropriate measures should be taken to mitigate the risks associated with exposure to As, Ni, and Cr in some of the study locations.

### 3.5. Ecological risk assessment

The accumulation coefficient ( $C_f^i$ ) of the PTEs in the sediments in the rainy and dry seasons is given in Table S5. Accumulation coefficients of PTEs in sediment samples are important in ecological risk assessment because they provide a measure of the degree to which PTEs are accumulating in the sediment and can be used to estimate the potential risk to the ecosystem. It was observed that the highest accumulation coefficient of PTEs in the samples was observed for arsenic in location 1 for the rainy season (21.7) and chromium in location 6 for the dry season (153). It was also observed that the accumulation coefficients for nickel and cadmium were below the detectable limit for both the rainy and dry seasons. Similar observations were also made for arsenic in the dry season. In the rainy season, the accumulation coefficient of arsenic was the highest in locations 1, 3, and 5, while that of lead was the highest in locations 2, 4, and 6. This shows that lead and arsenic have the highest degree of accumulation in the sediment during the rainy season. In the dry

season, the accumulation coefficient of chromium was the highest in locations 1, 3, and 6, while that of lead was the highest in locations 2, 4, and 5. This shows that lead and chromium have the highest degree of accumulation in the sediment during the dry season.

The ecological risk coefficient is a measure used in ecological risk assessment to evaluate the potential risk of a single element on an ecosystem. It represents the ratio of the concentration of a single element in the environment (such as soil, sediment, or water) to a threshold value, which is typically based on established guidelines or standards. The ecological risk coefficient of a single element  $E_r^i$  provides information on the potential impact of that element on the ecosystem. A high ecological risk coefficient indicates that the concentration of the element is high relative to the threshold value, suggesting a greater potential risk to the ecosystem. The threshold value used to calculate the ecological risk coefficient can vary depending on the element being evaluated, the type of ecosystem being assessed, and the intended use of the site. The potential ecological risk index  $R_i$  is a method used to assess the potential ecological risk of multiple pollutants in soil or sediment. The  $R_i$  was developed as an improvement to the single-element ecological risk assessment method, which only considers one pollutant at a time.

According to the calculated  $E_r^i$  values for the rainy season (Table S6), arsenic is the major PTE polluting all the locations, and its mean value is 118. The potential ecological risk indices were found in the following order: As > Pb > Co > Cr. The potential ecological risk indices were found in the following order As > Pb > Co > Cr. The order of  $R_i$  values is L3>L5>L1>L4>L2>L6. According to Hakanson [37],  $R_i$  values for L3, L5, and L1 indicate a moderate ecological risk, while L4, L2, and L6 have a low ecological risk.

According to the calculated  $E_r^i$  values for the dry season, lead is the major PTE polluting all the locations, and its  $E_r^i$  mean value is 394. The potential ecological risk indices were found in the following order: Pb > Cr > Co. The mean accumulating coefficients of Pb, Co, and Cr were found to be 78.7, 5.63, and 92.7, respectively. The order of  $R_i$  values is L3>L4>L1>L2>L6>L5. According to Hakanson [37],  $R_i$  values for L3, L4, and L1 indicate a very high ecological risk, while L2, L6, and L5 have a considerable ecological risk.

#### 4. Conclusion and recommendations

This study investigated the presence of six potentially toxic elements (PTEs) in sediments surrounding a pharmaceutical industry in Ilorin, Nigeria. Analysis revealed varying concentrations of lead, cobalt, nickel, chromium, cadmium, and arsenic, with lead having the highest mean concentration and notable hotspots of contamination identified through principal component analysis. The physico-chemical properties of sediments showed seasonal variations, with varying pH and total dissolved solids during the dry season. The Hazard Index was mostly less than one across locations, indicating little to no probable non-cancerous effect, but the incremental lifetime cancer risk for arsenic and nickel was high and required attention. Ecological risk assessments highlighted arsenic accumulation during the rainy season and chromium accumulation during the dry season, suggesting potential ecological risks.

While this study offers significant insights into the human and ecological risks posed by potentially toxic elements (PTEs) in sediments near a pharmaceutical industry in Ilorin, Nigeria, there are several targeted areas for future research and action. Firstly, given the seasonal variations observed, future studies should extend monitoring periods to capture longer-term trends and chronic exposure patterns. This will enhance our understanding of the persistence and cumulative effects of PTEs, enabling more effective risk management strategies. Additionally, expanding the investigation beyond sediment samples to include water and biota could provide a more comprehensive assessment of the ecological impact, aligning with the identified hotspots of contamination. Furthermore, considering the dynamic nature of pharmaceutical industrial processes, continuous monitoring and assessment of implemented mitigation measures are imperative to track changes and ensure long-term environmental protection. To facilitate focused remediation efforts, future research should aim to identify and quantify the contributions of various pollution sources, thus enabling more targeted and efficient strategies. By addressing these recommendations, future studies can build upon our findings and contribute to a more thorough understanding of the health and environmental concerns associated with PTEs in pharmaceutical-industrial contexts, ultimately supporting informed decision-making and proactive risk mitigation efforts.

#### Compliance with ethical standards

This article does not contain any studies involving human or animal subjects.

#### CRedit authorship contribution statement

**Hussein K. Okoro:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Project administration, Supervision, Validation, Visualization. **Muyiwa M. Orosun:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation. **Salman A. Umar:** Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Khurshed Muzammil:** Data curation, Formal analysis, Funding acquisition, Investigation, Writing – review & editing. **Clement O. Ogunkunle:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – review & editing. **Kingsley O. Iwuozor:** Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation. **Ebuka Chizitere Emenike:** Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation. **Saiful Islam:** Data curation, Formal analysis, Funding acquisition, Investigation, Resources, Writing – review & editing. **Jane C. Ngila:** Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation. **Caliphs Zvinowanda:** Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation.

## 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.

## Acknowledgment

The authors extend their appreciation to the Deanship of Research and Graduate Studies at King Khalid University for funding this work through a Large Research Project under grant number RGP2/220/45.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e31685>.

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