



# Environmental and human health risk assessments for potentially toxic elements in the soils of a prospective phosphate mining area of Hinda district, Republic of the Congo

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## Abstract

Soils from a prospective phosphate mining area in the Hinda district of the Congo were analyzed using the ICP-MS technique in order to assess the environmental pollution and human health risks presented by potentially toxic elements (PTEs). The results showed that the mean concentrations of PTEs exceeded the global crustal average. Environmental pollution was assessed, showing the study area polluted by PTEs. Human health risk was also assessed, with the results showing the level of cancer risk greater for children than that for adults, indicating that children are more susceptible to the carcinogenic effects of PTEs than their adult counterparts.

**Keywords** Potentially toxic elements · Soil contamination · Prospective phosphate mining area

## Introduction

Economic development due to rapid urbanization and industrialization, as well as agricultural activities, disturbs the geochemical cycle of several elements, particularly trace elements. Some of these elements are essential to human health at acceptable concentrations (oligo-elements) [1], but others are particularly toxic for living organisms, and these are known as potentially toxic elements (PTEs) [2]. These elements can originate from natural processes, such as volcanic eruption and rock weathering, but they can also derive from various human activities, such as mining, agriculture, etc. [3].

Soil serves many functions aside from feeding plants, such as filtering rainwater and storing all kinds of contaminants of natural or artificial origin. It hosts an intense and complex system of life. Soil is now largely accepted as the part of the environment that is most exposed to contamination by trace elements [4, 5], and this matter has attracted increasing attention around the world [6–10]. Many studies related to trace element pollution in soils have focused on assessing the concentrations and the ecological and environmental risks they present [4, 11–13]. Indeed, due to their accumulation and non-biodegradable nature in soils, trace elements can have adverse effects on the ecosystem and human health [4, 9]. For instance, high levels of PTEs in soil have an irreversible influence on plant growth by altering the soil's properties and structure [14], and they can cause substantial harm to the human body through dermal contact and ingestion [15]. This is especially true for children, who are more vulnerable than adults in terms of risk assessment indices [16].

A survey of this kind has never been carried out in this part of the world. Considering the mining history of the Republic of the Congo and the number of mining sites operated by mining companies to meet international requirements [17, 18], as well as abandoned mines [19] in the country, it is prudent to consider the health of those living around mining areas. This issue had attracted increasing attention

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from researchers and public authorities in the Republic of the Congo.

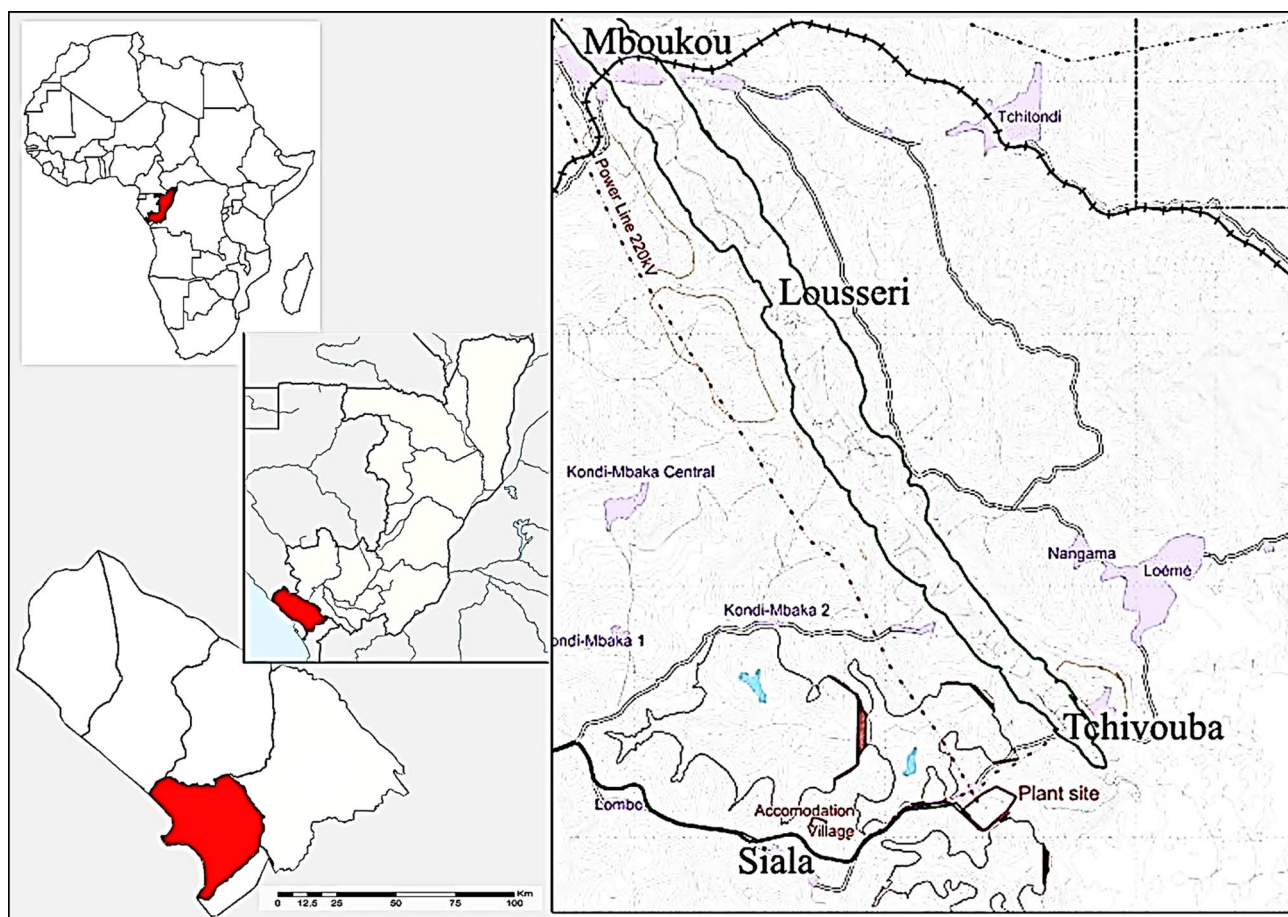
Moreover, no information is available about the effects of potentially toxic elements on the health of people living around a prospective phosphate mining area in the Hinda district of the Republic of Congo. Thus, collecting some baseline data about soil pollution in this prospective phosphate mining area will be vitally important for protecting human health and informing future research. The main aims of this study were therefore as follows: (1) Determine the concentrations of seven (7) selected potentially toxic elements (As, Cu, Cd, Hg, Cr, Pb, and Zn) in soil samples collected from different villages in Hinda district. (2) Assess the current soil contamination in the study area in terms of the contamination factor ( $C_f$ ) and the pollution load index (PLI). Finally, (3) investigate the carcinogenic health risks of potentially toxic elements according to the proposed methods of the United States Environmental Protection Agency [20]. This should help control pollution and enable preventive measures to be taken in the study area prior to exploiting phosphate ore resources.

## Materials and methods

### Study area

The Republic of the Congo is split between twelve (12) departments, and one of these is the Kouilou department, which alternates between dry and wet seasons. The wet seasons typically occur in March–April–May (MAM) and September–October–November (SON), while the dry seasons are usually in June–July–August (JJA) and December–January–February (DJF). The area also has a tropical climate, and it is geologically characterized by white quartzite with schistose intercalation.

Hinda district is within the Kouilou department alongside the Kakamoeka, Madingo-Kayes, Mvouti, Nzambi, and Tchiamba-Nzassi districts (Fig. 1), and it is more affected by anthropogenic activities. It is located at latitude  $4^{\circ}36'48''$  S and longitude  $12^{\circ}02'37''$  E about 34 m above sea level. It has an approximate population of 32,995 people. The average temperature is  $24.5^{\circ}\text{C}$ , while the average annual precipitation is 1746 mm [21].



**Fig. 1** Study area of Hinda district in the Republic of the Congo [21]

This study was conducted around four (4) villages in Hinda district (Mboukou, Siala, Louceri, and Tchivouba), because these villages have been listed as potential sites for phosphate mining by the COMINCO Resources Ltd. mining company. The deposit comprises a large, structurally controlled and confined sedimentary accumulation of primary biogenic and secondary phosphate mineralization. There are two main phosphate-bearing sedimentary layers. The Grey Maastrichtian (Gm) upper cretaceous layer represents the primary source of phosphate rock, with it providing 90% of the ore. The upper layers of the Gm have been subjected to tropical weathering and decarbonation, with the resulting weathered layer being designated the Beige Maastrichtian (Bm) [21].

### Sample collection, preparation, and analysis

Samples were collected at about 10 cm below the surface after removing any vegetal cover. A total of 24 soil samples were collected at each village. They were collected from different locations identified by COMINCO Company Ltd., and these were detected in the study area by the iron bars that had been driven into the earth and surrounded with cement. Each sampling point was associated with coordinates from a Garmin GPS system, and the samples were stored in clean, labelled polyethylene bags. The samples were then transferred to CNESTEN (the Nuclear Center for Energy Sciences and Nuclear Techniques) for conditioning and treatment. Once there, the samples were oven dried at 70 °C until the weight became constant before being ground into powder form with an agate mortar and then sieved for storage in polyethylene containers. Precautionary measures were taken to avoid any contamination.

### Dissolution procedure and analysis

Soil samples were placed in a 50 ml tube with 5 ml of nitric acid (HNO<sub>3</sub>) [22]. Some 3 ml of hydrofluoric acid (Hf) from Merck KGaA, 64,271 Darmstadt were also added to the tube at this point. After one hour, seven (7) drops of oxygenated water (H<sub>2</sub>O<sub>2</sub>) and two (2) spoons of

boric acid (H<sub>3</sub>BO<sub>3</sub>) [23] were added to the solution, which was then left overnight to facilitate the sample's digestion [24–26].

After 24 h, the digested solution was further digested in a microwave (ETHOS EASY, milestone Connect) for 1 h before being transferred to the tube and filled with H<sub>2</sub>O<sub>2</sub> to about 50 ml. Finally, the diluted solution was weighed [23].

Soil from ANALYSIS ISE2012.1 was used as the standard reference material for quality assurance purposes. This standard reference material and the background sample were prepared in the same manner as the samples.

Quality assurance and quality control were carried out using duplicates, method blanks, and a certified reference material (CRM) that was a multi-element solution with seven (7) components, namely 0.001 mg/l each of Ba, Bi, Ce, Co, In, Li, and U (CPA chem, Ref. No: 161D. D001.2.5N05C.L5 of 29/05/2020). Standard solutions provided by Merck (Darmstadt, Germany) were used for calibration curves. In the present study, all the solutions were prepared using ultrapure water. The analytical precision was considered to be ± 10%. The 24 soil samples from each village were digested and analyzed alongside one sample of the CRM. All the analyses were conducted in duplicate, with the mean values being used for data analysis. ICP-MS with an iCAP Q (Thermo Scientific) with a branded sample changer TELEDYNE (ASX-560) was used for sample analysis, while qualitative and quantitative analysis were carried out using the iCAP Q software. The recoveries of rare earth elements in the spiked quality control samples varied from 96.1% to 107.3%.

### Assessment of PTE pollution in the samples

To assess the PTE contamination levels in the samples from the study area, the contamination factor (CF) and pollution load index (PLI) were considered. These metrics are described in Table 1. The background concentration used in this present study relates to the upper continental crust (UCC) [27].

**Table 1** The metrics used to assess PTE contamination levels in the soil samples from the study area

Parameter	Equation	Conditions
Contamination factor (CF) [28, 29]	$C_f^i = \frac{C_i}{B_i}(1)$ Where C <sub>i</sub> is the concentration (mg/kg) of metal i in the samples and B <sub>i</sub> is the background concentration (mg/kg) value for metal i	CF < 1: Low contamination 1 < CF < 3: Moderate contamination 3 < CF < 6: Considerable contamination CF > 6: High concentration [30, 31]
Pollution Load Index (PLI) [30, 32, 33]	$PLI = \left( C_f^1 \times C_f^2 \times C_f^3 \times \dots \times C_f^n \right)^{1/n} \quad (2)$ Where C <sub>f</sub> <sup>n</sup> is the contamination factor of metal i	PLI < 1: Not polluted PLI > 1: Polluted [34]

**Table 2** Parameters used for the present study

Parameters	Symbols	Units	Values		References
			Children	Adults	
Body weight	BW	Kg	10	60	Present study
Exposure duration	ED	Years	5	30	Present study
Exposure frequency	EF	Days/years	350	250	[38]
Skin surface area	SA	cm <sup>2</sup>	2373	6032	[39]
Soil intake ratio	IR	mg/day	200	100	[9]
Skin adherence factor	AF	mg/cm <sup>2</sup>	0.2	0.07	[40]
Lifetime	LT	Years	70	70	Present study
Average time	AT	Days	25,550	25,550	Present study

## Human health risk assessment

The risk to human health was assessed for the adults and children residing in the study area, which as mentioned above is a prospective phosphate mining area. Phosphate rocks are visible on the ground of the study area, such as in agricultural fields and around people's dwellings. It was therefore important to assess the carcinogenic health risks posed by potentially toxic elements due to accidental ingestion, dermal contact, and inhalation by the local population.

However, as the phosphate in the study area was in a rock state, we focused our study on the two pathways of ingestion and dermal contact.

The average daily doses for ingestion ( $ADD_{ing}$ ) and dermal contact ( $ADD_{derm}$ ) were calculated to assess the risks according to the following equations [35, 36]:

$$ADD_{ing} = \frac{C_s \times IR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

$$ADD_{derm} = \frac{C_s \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (4)$$

The carcinogenic risk (CR), meanwhile, was assessed using the following equation [10]:

$$CR = \sum_{i=1}^n ADD_i \times SF_i \quad (5)$$

where  $SF_i$  corresponds to the carcinogenic slope factor of metal  $i$  (mg/kg/day).

Furthermore, the total carcinogenic risk (TCR) is defined as:

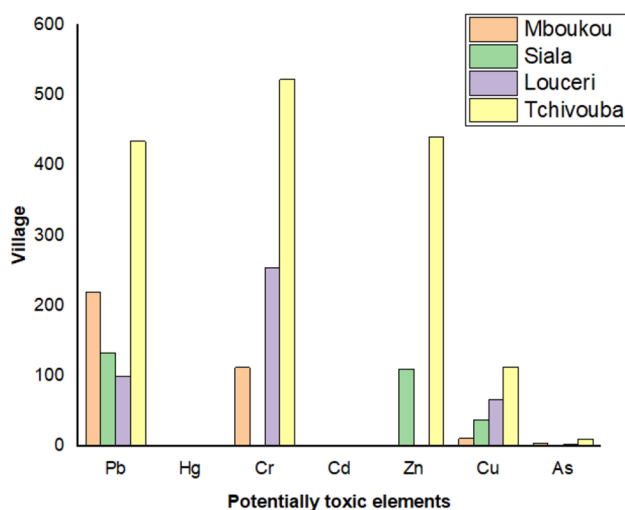
$$TCR = \sum_{i=1}^n CR_i \quad (5)$$

The acceptable range of this is thought to be between  $10^{-6}$  and  $10^{-4}$  [37].

Each factor is defined in Tables 2 and 3.

**Table 3** Factors used for the present study

Elements	ABS	$SF_{ing}$	$SF_{derm}$	Reference
Pb	$10^{-3}$	$8.5 \times 10^{-3}$		[41]
Hg	$10^{-3}$			[41]
Cr	$10^{-3}$	0.5		[41]
Cd	$10^{-3}$	15		[41]
Zn	$10^{-3}$			[41]
Cu	$10^{-3}$			[41]
As	0.03	1.5	3.66	[41]

**Fig. 2** Distribution of PTE concentrations (mg/kg) in the study area

## Results and discussion

The mean concentrations of potentially toxic elements in the soil samples from the four villages of the Hinda district are shown in Fig. 2. The potentially toxic elements' concentrations decreased in the following order: Cr > Pb > Zn > Cu > As > Cd > Hg. The highest concentrations



of all the seven potentially toxic elements were observed in Tchivouba village: Cr (500 mg/kg), Pb (434 mg/kg), Zn (440 mg/kg), Cu (113 mg/kg), As (10.48 mg/kg), Cd (1.05 mg/kg), and Hg (0.18 mg/kg). The median values exceeded global soil average values at Cr (254 mg/kg), Pb (176.5), Zn (275 mg/kg), Cu (52 mg/kg), As (5.12 mg/kg), Cd (0.11 mg/kg), and Hg (0.0265 mg/kg) [27], indicating that these potentially toxic elements have been enriched in the overall study area.

The mean total concentrations of Cr, Pb, Zn, Cu, As, Cd, and Hg were clearly greater than the equivalent average upper continental crust (UCC) values (Table 4). Furthermore, compared to other studies around the world, the concentrations of potentially toxic elements found in the present study are higher than those found in other studies, with the exception that Cd concentration was lower than that reported in one study [42]. We surmise that this high concentration is due to the phosphate galleries in Tchivouba village and the presence of phosphate rocks everywhere, such as in agricultural fields, around people's dwellings, and so on. This assumption is supported by our study of natural and artificial measurement that was carried out in the same study area [43].

### Environmental and ecological risk assessment indices

The results of the soil contamination assessment based on the contamination factor ( $C_f$ ) are illustrated in Fig. 3. The  $C_f$  values varied across the villages. The mean  $C_f$  values for the considered PTEs were as follows: Pb (12.31) > Hg (4.81) > Cd (3.76) > Cr (2.77) > Zn (1.96) > Cu (1.78) > As (1.01). The  $C_f$  values for Pb varied from 5.56 in Louceri to 24.11 in Tchivouba, reflecting the very high contamination levels in the study area. The values for Hg ranged from 0.33 in Mboukou to 14.63 in Tchivouba, so the contamination level was low in Mboukou village, moderate in Siala village, considerable in Louceri village, and very high in Tchivouba village. For Cr, the values ranged from 1.4 in

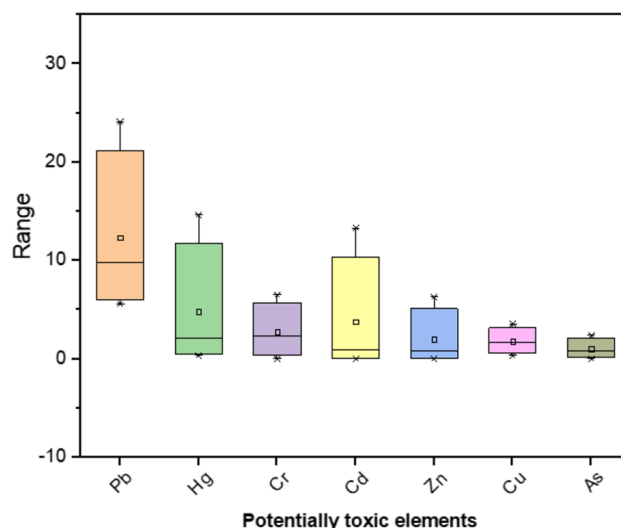


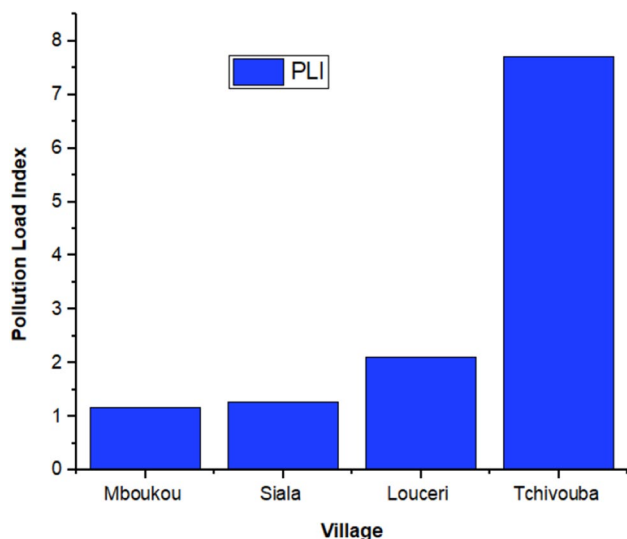
Fig. 3 Contamination factors for the PTEs in the study area

Mboukou to 6.53 in Tchivouba, with there being moderate contamination levels in Mboukou and Louceri villages and a very high level in Tchivouba village. The  $C_f$  values for Cd varied from 0.38 in Siala to 13.29 in Tchivouba, with the contamination level being low in Siala village, moderate in Louceri village, and very high in Tchivouba village. The values for Zn ranged from 1.57 in Siala to 6.29 in Tchivouba, with the contamination level being moderate in Siala village but very high in Tchivouba village. For Cu, the values varied from 0.34 in Mboukou to 3.53 in Tchivouba, with the contamination level being low in Mboukou village, moderate in Siala and Louceri villages, and very high in Tchivouba village. Finally, for As,  $C_f$  values varied between 0.53 (Louceri) and 2.38 (Tchivouba), reflecting a low contamination level in Siala village and moderate contamination levels in Mboukou and Tchivouba villages.

The pollution load indices (PLI) were determined for the present study area, and the results of this are illustrated

**Table 4** Summary of the measured PTE concentrations in the soil samples from a prospective mining area in Hinda district (mg/kg) alongside background values from the UCC and reported concentrations in other studies

Country	Cr	Pb	Zn	Cu	As	Cd	Hg	Reference
European soils	94.8	32	68.1	17.3	11.6	–	–	[44]
Turkish Soil Pollution Control Regulation	100	300	300	140	–	–	–	[45]
Turkey, Bursa city	125	81	477	40	–	–	–	[46]
Turkey, Thrace region	173	33	45	20	8	–	–	[47]
China, Shenyang	67.9	116.76	234.8	92.45	–	1.1	–	[42]
China, Shanghai	107.9	70.69	301.4	59.25	–	0.52	–	[48]
Republic of the Congo, Hinda district	500	434	440	113	10.48	1.05	0.18	Present study
UCC	80	18	70	32	4.4	0.079	0.012	[27]



**Fig. 4** Pollution load indices for the study area

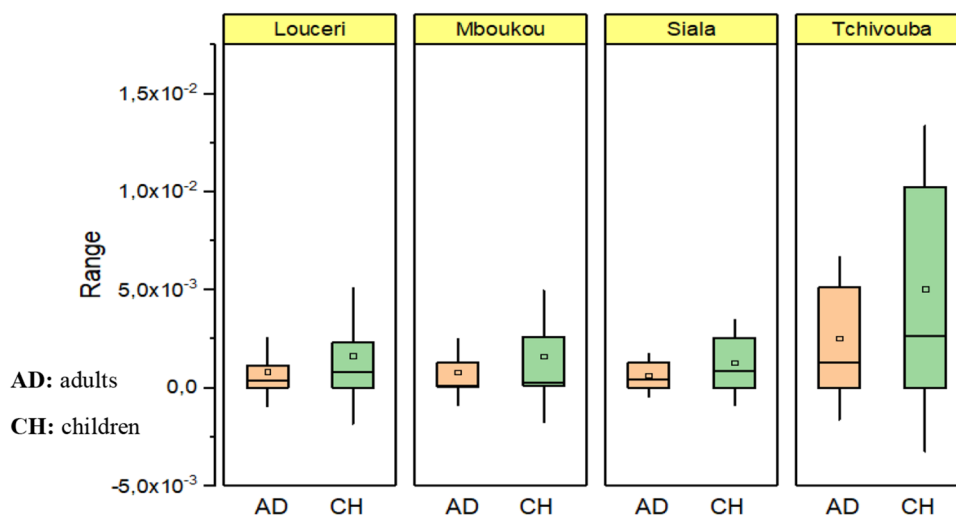
in Fig. 4. These show that the whole study area was polluted to varying degrees.

### Human health risk assessment

A human health risk assessment was carried out for all the potentially toxic elements investigated in the present study, and the results obtained for the four (4) villages are presented in Fig. 5.

The mean carcinogenic risk levels were Cr ( $6.90 \times 10^{-3}$ ) > Zn ( $6.41 \times 10^{-3}$ ) > Pb ( $5.17 \times 10^{-3}$ ) > Cu ( $1.33 \times 10^{-3}$ ) > As ( $1.41 \times 10^{-4}$ ) > Cd ( $9.25 \times 10^{-6}$ ) > Hg ( $1.38 \times 10^{-6}$ ) for children and Cr ( $3.45 \times 10^{-3}$ ) > Zn ( $3.21 \times 10^{-3}$ ) > Pb ( $2.59 \times 10^{-3}$ ) > Cu ( $6.65 \times 10^{-4}$ ) > As ( $7.16 \times 10^{-5}$ ) > Cd ( $4.63 \times 10^{-6}$ ) > Hg ( $6.91 \times 10^{-7}$ ) for adults.

**Fig. 5** Carcinogenic risk levels due to PTEs in soil samples from a prospective phosphate mining area in Hinda district



The carcinogenic risk levels therefore followed the same trend for both children and adults in the study area.

We found the cancer risk levels to be greater than  $1 \times 10^{-4}$  for both children and adults, with Cr, Zn, Pb, Cu, and As contributing greatly to cancer risk in the present study area. Urgent remediation action is therefore required in this area, especially as Fig. 5 clearly shows that children are more exposed to risk than adults [16].

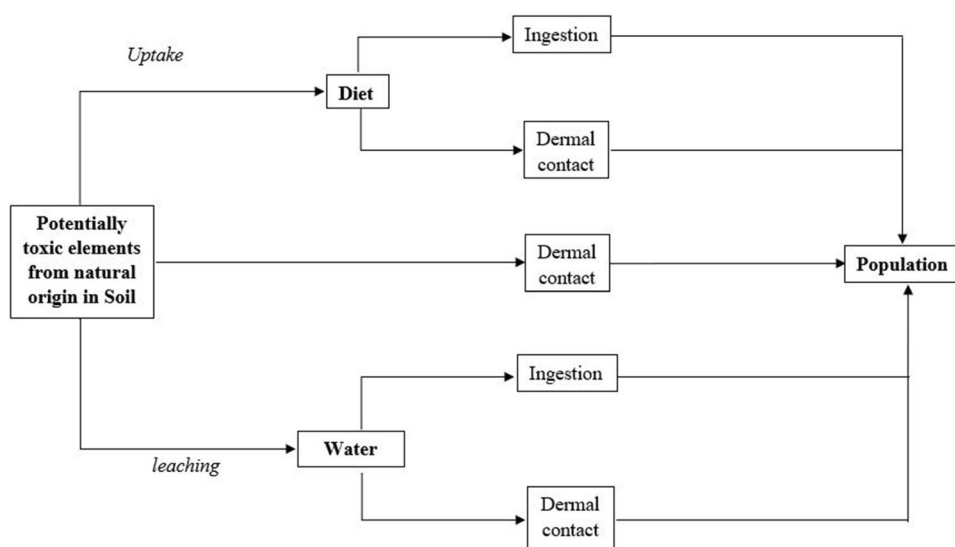
The potential pathways by which the PTEs in the soil of the prospective phosphate mining area of Hinda district contaminate the local population through ingestion and dermal contact are clearly illustrated in Fig. 6.

PTEs can be directly absorbed by ingesting locally grown food. In addition, during rainfall, they can leach away from soils and pollute the water supply, such as rivers.

The population of the study area can be acutely or chronically exposed to high levels of PTEs, and this can result in severe disorders and extreme damage from the oxidative stress due to free radical formation [49]. More specifically, the central nervous and immune systems of children and adults in the study area can be affected by high exposure to lead (Pb) through ingestion or dermal contact. In addition, the high exposure to chromium (Cr) through ingestion or dermal contact can lead to an increased risk of respiratory issues. Arsenic (As) can cause skin and neurological issues, as well as diabetes, while a high exposure to cadmium (Cd) can affect the endocrine system, lungs, and so on [50].

Another potential pathway for contamination relates to how children often like to play on the ground and in agricultural fields, leading to them being directly contaminated through dermal contact with the contaminated soils of the study area. This pathway is all the more important given that children in the area spend most of their time barefoot, whether it be in the house or outside, such as in their parent's agricultural fields. This explains why they are more exposed to PTEs than adults in the present study area (Fig. 5).

**Fig. 6** Environmental pathways by which PTEs in the soil of Hinda district contaminate the local population



## Conclusion

This study determined PTE concentrations through ICP-MS for different soil samples that were collected from a prospective phosphate mining area in Hinda district. The contamination levels were alarmingly high, with these being principally influenced by the phosphate rocks that were present everywhere in the study area. Indeed, the mean concentrations were found to be above those for the upper continental crust (UCC), and compared with other studies around the world, the PTE concentrations determined in the present study were higher than those reported by other studies. Ecological indices were also determined for the study area, with the results showing that the study area was polluted with a pollution load index above one ( $PLI > 1$ ). The carcinogenic risks were also evaluated, and the alarming results were above the recommended level of  $1 \times 10^{-4}$  for both children and adults. In addition, children were found to be more susceptible to the carcinogenic health effects of PTEs, leading to an increased risk of cancer. The environmental pathways for PTEs were also described, with this showing the contamination of children and adults in the study area through ingestion and dermal contact. Overall, this provides evidence that local residents in the considered study area are at an increased risk of cancer due to exposure to potentially toxic elements.

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## Declarations

**Conflict of interest** The authors declare that they have no conflicts of interest.

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