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Exposure assessment of heavy metals in soil near a massive coal-fired cement industry in Nigeria

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ABSTRACT

Industrial and anthropogenic activity-induced mobilisation and dispersion of potentially toxic materials into the atmosphere and human environment have been linked to serious threats to human health. Inductively coupled plasma mass spectrometry was used to determine the concentrations of heavy metals (Cr, Pb, Ni, Cu, Zn, and Mn) in soil samples collected near a coal-fired cement factory in northeast Nigeria. For heavy metal concentrations, except for Cr, mean values were lower than the Canadian soil quality requirements (Cr = 76.44 > 64 mg kg–1, Pb = 19.32 – 70 mg kg – 1, Ni = 29.09 – 50 mg kg–1, Cu = 5.03 - 63 mg kg–1, Zn = 10.15 – 200 mg kg–1). For adults and children, a lifetime exposure risk assessment was made for ingestion, inhalation, and skin contact. The majority of metal pollution in the tested soils was due to human activity, according to statistical analysis. Adults and children are most likely to be exposed through ingestion, according to risk assessments. Children's hand-to-mouth eating practises may be to blame for their increased risk of illness. Non-carcinogenic health impacts were shown to exist in the subpopulations for all of the metals studied, with the exception of Cr, which had the highest potential for non-carcinogenic health effects.

Introduction

Anthropogenic activities have drawn great attention because of the indestructible and non-degradable nature of heavy metals and potentially toxic contaminants, along with their toxicity and effects on human health [1–4]. It has been shown that coal combustion and cement manufacture are major sources of heavy metals in the environment [5–9]. As the principal anthropogenic channels via which humans are exposed to greater levels of metal burdens than the typical background [10,11], they have become indispensable. Soil contamination and environmental pollution have long been related with coal combustion [8,12]. Human health concerns have also been linked to coal combustion [9,10]. Metals linked to coal that may be toxic are mobilised and released into the environment during the combustion process.

Combustion stack and combustion product leaking emissions to the atmosphere [12–17]. Toxic air pollutants in the form of cement dust have long been a problem in cement manufacturing, making it one of the least environmentally friendly processes [18,19]. A huge region is covered by wind and eventually soil deposits these metals after they have been released into the atmosphere. The human population is exposed to soil contaminants by direct ingestion, inhalation, and dermal contact via exposed skin [20–23]. Asthma and lung cancer may be caused by heavy metals that are confined to the tissues and circulatory system of the human body [24–26]. In other cases, they have been linked to organ failures or nervous/endocrine disorders [23,27]. Freedman et al. [28] connected heavy metal pollution to brain injury and nervous system dysfunction, whereas Okedeyi et al. [19] found a relationship between impaired reproduction and child development and heavy metal exposure breakdown. Children's hand-to-mouth eating practises may be a contributing factor to their higher risk of heavy metal exposure [22].

Cement manufacturing giant Ashaka Cement Factory Plc (AshakaCem) in northern Nigeria relies completely on coal to generate electricity. AshakaCem is a major environmental problem because of the combination of dust emissions from cement manufacture and coal burning. Even though the plant has emission control measures in place, the dust filters' collection effectiveness is insufficient to keep gaseous contaminants from seeping into the soil. While the plant employees and the public are constantly exposed to soil contamination, emissions from automobiles and trucks engaged in transportation operations surrounding AshakaCem contributed considerably. Long-term exposure to this substance may have mutagenic, teratogenic, or carcinogenic effects, all of which increase the chance of death [23,29]. Soil samples near AshakaCem have to be tested for the presence of these heavy metals and their potential health effects on humans. Ashaka Cement's metal pollution levels are unknown, despite the fact that several studies have been carried out in other parts of the globe to determine how dangerous these pollutants are to human health. For this purpose, the researchers conducted a pilot study to evaluate soil pollution caused by emissions from the coal-fired AshakaCem and to determine the level of exposure for both children and adults to each of the exposure routes. Results from this study will aid in the development of a quantitative estimate of the likelihood that any of the dangers associated with metal toxins will be realised in diverse populations. The outcomes of this study will aid factory

employees in implementing safe and effective ways to protect themselves against pollution caused by industry. It will also assist the appropriate regulatory agencies in developing policies and devising control mechanisms to improve environmental quality.

Materials and method

Sampling and sample preparation

At 10055′49″N and 11028′34″E, the Ashaka cement plant (AshakaCem) is situated. AshakaCem, which has been operating continuously since 1979, is Nigeria's biggest cement plant. Coal combustion provides the majority of the factory's energy needs. The factory's harmful emissions from coal combustion and cement manufacture were reduced by installing dust bag filters as pollution control equipment. The AshakaCem plant in Gombe state, Nigeria's northeastern region, is the subject of a soil study. In order to record the location of each point, a global positioning system was used (GPS). Polyethylene bags with clearly labelled contents contained the samples, which were then carefully transferred to the lab for testing. It was necessary to sift and fully homogenise the soil samples through a 2mm mesh after they had been dried for 72 hours at room temperature in the laboratory. Following a three-step acid digestion method, heated plates were used to digest each sample. In a 250 ml volumetric flask, 1.00 0.01 g of soil sample was added to 10 ml of 1:1 HNO3. For 15 minutes, the slurry was kept at 95 5 degrees Celsius in a watch glass and allowed to reflux. There were no brown fumes after cooling the sample to room temperature, therefore it was refluxed again with the addition of 5 ml concentrated HNO3 (70 percent) until no brown fumes were noticed. Then, 2 ml deionized water and 3 ml of 30% H2O2 were added carefully without any loss (to a maximum of 10 ml). The mixture was cooked on a hot plate until the effervescence dissipated. When the sample had cooled, the Whatman No. 41 filter was used to remove any impurities. Using a 100 ml volumetric flask, the filtered digestate was transferred and filled up to the mark with deionized water. For analysis, the final solutions were kept at 4 °C.

Instrumentation

The inductively coupled plasma mass spectrometry (ICP-MS) 7500 series from Agilent Technologies, USA, was used at the ICP-MS laboratory at the Chemistry Department of the University of Malaya in Malaysia for the elemental analysis. All sample preparation equipment was properly cleaned with distilled water and 15 percent HNO3 (v/v). As with the samples, the standards and blanks were made using the same exact dilution procedures as the latter. A 10 mg l1 calibration stock solution for each of the tested elements was prepared using diluted multi-element standard solutions (1 g l1) for ICP-MS (Agilent Technologies, USA, part No. 8500-6940). To calibrate instruments prior to analysis, this was utilised Each analyte's minimum detection limit (MEDL) was calculated as the standard deviation of the blank signals multiplied by three. Cr, Pb, Ni, Cu, and Mn each had a MEDL (g g-1) of 0.03, 0.01, 0.03, 0.02, and 0.02, respectively. It was determined whether or not the samples included the following elements: Cr, Pb, Ni, Cu, Zn, and Mn. The ICP-MS sample injection system comprises of a temperature-controlled nebulizer and spray chamber attached to an auto-sampler. The ICP-MS' responsiveness was maintained by maintaining the same operating parameters throughout the measurement period. All samples were produced and analysed in triplicate to ensure reproducibility, and the findings were presented as the mean with a 95% confidence level. Using verified values for various trace elements from the National Research Council of Canada's SLR-4 reference material and ICP reference material, the obtained findings were compared to the originals (Merek). The recoveries ranged from 83% to 103%, which was in excellent accord with the certified values.

Potential health risk assessment model

Health risk evaluations are based on the chance that any of the dangers associated with heavy metal pollution will be realised in any exposed population. Estimates of metal exposure in children and adults from soil samples collected around AshakaCem were made using a health risk assessment model developed by the United States Environmental Protection Agency (USEPA). According to Table 1, the risk assessment parameters used in this study are displayed, whereas RfD and CPF values are given in Table 2. Metals in soils may be ingested, inhaled, or absorbed via the skin by three primary routes: DIing, DIinh, and DIing (DIderm). The toxicity of pollutants and the extent of exposure determine the health concerns associated with metal pollution [34]. The daily intake of each potentially toxic metal is used to determine human exposure. separately, through individual exposure pathway. The daily intake (DI) for each pathway, expressed in mg kg−1 day−1is calculated from the equation [31]:

$$DI_{ing} = C \times \frac{R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (1)$$

$$DI_{inh} = C \times \frac{R_{inh} \times EF \times ED}{BW \times PEF \times AT} \quad (2)$$

$$DI_{derm} = C \times \frac{ABF \times SA \times SAF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

Other parameters, such as Ring and Rinh, are specified in Table 1 in the same way as in Table 1.

Using the formulae [26], the lifetime average daily dose (LADD) in mg kg-1 day-1, used to estimate carcinogenic hazards for the Cr, Pb, and Ni inhalation route for both children and adults, is determined.

Table 1
Risk assessment parameters of heavy metals adopted in this study.

ID	Parameter	Value used			References
		Common	Child	Adult	
AT	Average time for non-carcinogens (days/year)	365	-	-	USEPA [31]
EF	Exposure frequency (days/year)	350	-	-	USEPA [31]
DF	Dilution factor indoor	0.4	-	-	Grzetic and Ghariani [32]
PEF	Particulate emission factor (m^3/kg)	$1.36x10^9$	-	-	USEPA [31]
ABF	Dermal absorption factor for all metals	0.001	-	-	De Miguel et al [33]
IR	Ingestion rate (mg/day)	-	200	100	USEPA [38]; Grzetic and Ghariani [33 31,32]
ED	Exposure duration (years)	-	6	30	Grzetic and Ghariani [32]
IN	Inhalation rate (m^3/day)	-	7.6	20	Zheng et al [22]
SA	Exposed skin surface area (cm^2)	-	2800	5700	USEPA [31]
SAF	Skin adherence factor for soil ($mg/cm^2/h$)	-	0.2	0.07	USEPA [31]
BW	Body weight (kg)	-	15	70	USEPA [31]

Table 2
RfDs (reference dose) and CPFs (cancer potency factor) of heavy metals ($mg\,kg^{-1}\,day^{-1}$) adopted in this study, values adopted from De Miguel et al. [33]; Xu et al. [26].

Metals	Cr	Pb	Ni	Cu	Zn	Mn
RfD_{ing}	3.00×10^{-3}	3.50×10^{-3}	2.00×10^{-2}	4.00×10^{-2}	3.00×10^{-1}	4.60×10^{-2}
RfD_{inh}	2.86×10^{-5}	3.52×10^{-3}	2.06×10^{-2}	4.02×10^{-2}	3.00×10^{-1}	1.43×10^{-5}
RfD_{dermal}	6.00×10^{-5}	5.25×10^{-4}	5.40×10^{-3}	1.20×10^{-2}	6.00×10^{-2}	1.84×10^{-3}
CPFs	$4.20 \times 10^{+1}$	4.20×10^{-1}	8.40×10^{-1}			

$$LADD_{child} = C \times \frac{EF \times R_{inh-child} \times ED_{child}}{BW_{child} \times PEF \times AT} \quad (4a)$$

$$LADD_{adult} = C \times \frac{EF \times R_{inh-adult} \times ED_{adult}}{BW_{adult} \times PEF \times AT} \quad (4b)$$

where C ($mg\,kg^{-1}$) is the metal concentration in the soil sample. Other parameters are as defined in Table 1.

Risk characterization

Non-carcinogenic health risks for each human being who is exposed to a single metal in soils may be expressed in terms of a dimensionless quantity known as the hazard quotient (HQ). To quantify the toxicological risk of metal exposure, the anticipated daily intake of each metal is compared to its associated reference dose (RfD) in a specific exposure route. It is written as follows:

$$HQ = \frac{DI}{RfD} \quad (5)$$

Human health risk due to carcinogenic elements is calculated as "the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen" [32]. It is a dimensionless level of probability expressed as:

$$Risk_{cancer} = DI \times CPF \quad (6)$$

When using Eqs. to determine the daily intake for each metal, we get DI (mg kg1 day1). Reference dosage (mg kg1 day1), cancer potency factor (mg kg–1 day–1), and RfD for each metal are specified as follows: (1)–(3) (Table 2). For a specific toxic metal, the RfD is the daily human exposure level (including sensitive subpopulations) at which any exposure might result in lifelong risk [32,35]. As a result, if the DI value for a particular pollutant is greater than the associated RfD (i.e. HQ > 1), the exposure route has a larger potential of having an adverse impact on health than a carcinogenic one [36,37]. Instead, the cancer potency factor (CPF) measures the likelihood of developing cancer as a result of exposure to a substance [34,38]. Non-carcinogenic and carcinogenic hazards are stacked on top of each other. "HI" stands for "chronic non-carcinogenic hazard index," and it is calculated by adding up the HQ values for various contaminants and/or numerous exposure pathways.

$$HI = \sum_{i=1}^{n} HQ_i = \sum_{i=1}^{n} \frac{DI_i}{RfD_i} \quad (7)$$

Ith metal's HQ value, DI value, and RfD are referred to as HQi, DIi and RfDi correspondingly. Non-carcinogenic health consequences are unlikely to occur if HI 1. There is an increased possibility of non-carcinogenic consequences with rising HI [31] when HI is more than 1.

Cumulative carcinogenic risk, which reflects the likelihood that a person may get cancer as a result of exposure to several carcinogenic contaminants at the same time, is represented in the following way: [32]

$$Total\ \ cancer\ \ risk = \sum_{i=1}^{n} DI_i \times CPF_i \quad (8)$$

The daily intake (DIi) and cancer potency factor (CPFi) for the ith pollutant are given here. For regulatory purposes, the precautionary range for carcinogenic risk is 1E06 – 1E04 [40,41]. This research employed hazard index and cancer risk methodologies to evaluate cumulative human health exposure hazards from heavy metals in soil samples surrounding AshakaCem across the three exposure paths. For the purposes of this investigation, all of the site-base parameters for all metals (Table 1) are taken to be constants. The total lifetime population exposure approximation of 70 years was also used to estimate the risks. In establishing the link between human health and metal toxicity and quantifying carcinogenic and non-carcinogenic health effects through any exposure framework, risk assessment models, despite their uncertainties, have become indispensable tools [23].

Results and discussion

Metal concentrations

Samples of soil from around AshakaCem, Nigeria, show siX heavy metal concentrations in Table 3. Table summarising the smallest and largest values as well as their corresponding kurtosis and standard deviation

Table 3
Descriptive statistics of heavy metal concentrations (mg kg^{-1}) in soil samples around AshakaCem.

	Co-ordinate			Metal concentration (mg/kg)					
Sample ID	Long	Lat	pH	Cr	Pb	Ni	Cu	Zn	Mn
ASS1	10° 56′ 06″	11° 28′ 33″	7.4	101	15.6	36.5	5.8	6.3	814.5
ASS2	10° 55′ 46″	11° 28′ 21″	7.5	104	26.6	44.7	9.6	11.7	570.7
ASS3	10° 55′ 38″	11° 28′ 44″	7.8	97.2	19.7	34.1	15.1	23.5	995.6
ASS4	10° 55′ 35″	11° 28′ 21″	7.7	95.8	29.2	35.6	4.01	20.3	361.6
ASS5	10° 55′ 37″	11° 28′ 59″	7.2	92.7	37.2	32.6	6.5	9.0	322.2
ASS6	10° 55′ 35″	11° 29′ 01″	7.7	85.9	23.9	30.7	4.5	3.2	141.1
ASS7	10° 55′ 28″	11° 28′ 33″	7.0	90.4	39.7	37.7	6.9	23.1	1080
ASS8	10° 55′ 16″	11° 28′ 37″	7.7	82.7	10.5	31.3	2.3	4.1	338.5
ASS9	10° 55′ 34″	11° 28′ 17″	7.2	81.7	15.3	31.8	3.5	4.0	240.0
ASS10	10° 55′ 33″	11° 28′ 15″	8.0	74.5	15.0	28.1	2.8	3.7	284.1
ASS11	10° 55′ 38″	11° 28′ 14″	7.8	80.7	14.4	31.2	4.9	3.4	373.0
ASS12	10° 55′ 40″	11° 28′ 17″	7.6	61.6	20.3	24.1	7. 8	11.6	298.1
ASS13	10° 55′ 42″	11° 28′ 51″	7.5	63.3	24.6	22.4	4.8	35.7	326.9
ASS14	10° 55′ 45″	11° 28′ 48″	7.6	67.4	13.9	22.5	2.9	4.6	266.6
ASS15	10° 56′ 00″	11° 28′ 53″	7.1	55.0	6.1	21.0	3.4	0.4	336.7
ASS16	10° 56′ 03″	11° 28′ 54″	7.3	62.6	20.1	30.1	6.8	15.7	822.0
ASS17	10° 56′ 12″	11° 28′ 47″	8.0	57.7	12.3	22.7	1.5	4.8	744.6
ASS18	10° 56′ 26″	11° 28′ 43″	7.7	60.1	19.1	23.3	2.8	7.8	363.1
ASS19	10° 53′ 39″	11° 28′ 08″	7.1	56.3	10.8	20.2	3.1	8.0	325.6
ASS20	10° 53′ 20″	11° 28′ 11″	7.1	58.3	12.3	21.3	1.6	1.8	304.9
Mean ± SD				76.4 ± 16.6	19.3 ± 8.8	29.1 ± 6.8	5.03 ± 3.2	10.1 ± 9.2	466 ± 271
Skewness				0.20	0.94	0.47	1.78	1.46	1.19
Kurtosis				−1.51	0.56	−0.34	4.17	1.83	0.16

There is also a discussion about skewness. AshakaCem is surrounded by neutral to slightly alkaline soils, as indicated by the pH values of the studied soils, which ranged from 7.0 to 8.0

Mn, Cr, and Ni are the most common metals in the soils studied. Average concentrations of Pb, Zn, and Cu were less than 20 mg kg1. For each of the six metals studied (Cu > Zn > Pb > Ni > Cr > Mn), the mean concentration values (B-values) were all below the baseline (Pb > 19.32 > 70 mg kg-1, Ni > 29.09 > 50 mg kg-1, Cu > 5.03 > 63 mg kg-1).

Except for Cr (Cr = 76.44 > 64 mg kg1), the Canadian soil quality recommendations for agricultural soils (CCME, 2007) include Zn (Zn = 10.15 200 mg kg1) as an acceptable limit for agricultural soil quality. Table 4 shows that these results are in the same range as those reported by other researchers in comparable investigations. In addition, all heavy metals except Cr and Ni had kurtosis values above zero, indicating that the metals were distributed in the soil samples at a steeper angle than is normal. There was also evidence of skewness in the amounts of Cu; Zn; and Mn (Table 3).

When it comes to Cr concentration, the range is 55.03 mg kg1 to 103.90 mg kg1.

An average of 76.44 milligrammes per kilogramme was found. Cement industry rotaries have linings that wear and tear, resulting in a high concentration of Cr in the studied soil samples [42]. A system with a redoX potential of 400 mV and pH values between 7.0 and 8.0 will always be dominated by Cr (VI), according to Greti and Ghariani [32]. The redoX potential of aerated soils may reach 400 mV. Cr (VI) could be assumed to be the dominant chromium species in soils because pH plays a significant role in determining the distribution and mobility of heavy metals soil samples were analysed.

With a mean concentration of 19.32 mg kg1, the Pb levels were found to vary from 6.06–39.67 mg kg1. The presence of lead (Pb) in the soils analysed may be linked to emissions from coal burning for the creation of electricity. It's possible that the nearby cement plant's mining and processing of lime stone contributed significantly to the presence of pb in the soil samples tested. According to Odoh et al. [9], leaded gasoline is still the primary fuel source for the majority of Nigeria's cars and trucks, resulting in 2800 metric tonnes of lead (Pb) being dumped into urban soils per year. As a consequence, high truck and vehicle exhaust emissions, which move raw materials into and completed goods out of the cement mill, may have contributed to the soil Pb deposition [42,43].

Cu content ranged from 1.48 mg kg-1 to 15.11 mg kg-1, with an average of 5.08 mg kg-1 (Table 3). In

the soil samples examined, it's possible that emissions from the cement plant and exhausts from cars engaging in various activities surrounding the cement factory impacted the Cu levels [9]. Additional sources of Cu in soil include the corrosion of metallic wastes from the cement plant that are discharged surrounding the facility and the mechanical aberrations of the automobiles.

Zn concentrations in all soil samples analysed were found to be on the low side.

It is 10.14 milligrammes per kilogramme. Findings from comparable studies showed this value to be lower than previously reported (Table 4). When it comes to vulcanised car tyre wear, Zn in soils has been linked to a variety of adverse effects, including increased emissions, mechanical aberrations, and accelerated decomposition. galvanic acid corrosion of vehicle components,

Table 4
Comparison of heavy metal concentrations (mg kg^{-1}) of the present study and other authors.

Country	Technique(s) used	Cr	Pb	Ni	Cu	Zn	Mn	References
Belgrade, Serbia	AAS	70.23	350.06	123.67	122.29	268.37	641.8	Crčetić and Ghariani [32]
Catalonia, Spain	ICP-MS, AAS	10.3	16.4	11.3	27.6	38.2	213.7	Schuhmacher et al. [34]
Riyadh, Saudi Arabia	ICP-AES	9.5	4.27	-	3.8	15.22	-	Al-Oud et al. [18]
Volta Region, Ghana	EDXRF	961	13.3	245.26	27.97	35.02	544.92	Addo et al. [3]
Sagamu (Nigeria)	AAS	156.6	666.1		613.4	188.5		Ogunkunle and Fatoba [50]
Gombe (Nigeria)	ICP-MS	76.44	19.32	29.09	5.03	10.14	465.49	Present study

Zn and Cu may also accumulate in soils from sources such as lubricants and air depositions from coal-burning activities [47]. Ni concentrations in soil samples ranged from 20.19 mg kg1 to 44.72 mg kg1, with a mean value of 29.09 mg kg1. Ni buildup in the soils analysed might be caused by cement manufacture and other human-made activities in the vicinity of the facility. It has been reported that industrial and agricultural activities contribute to the accumulation of nickel (Ni) in surface soils. Humans who are exposed to high levels of Ni in soils can suffer from lung fibrosis, skin allergies, and even cancer. The presence of nitrates in soil samples near AshakaCem necessitates careful attention.

The average concentration of Mn detected in the soil samples analysed was 465.49 mg kg-1. Mn is often found in soils in quite high concentrations under natural settings [49]. Mn cannot be deemed a pollutant since its presence in the examined soils cannot be attributed to human activities. The distribution of these metals in the vicinity of AshakaCem demonstrates the impact of cement production, coal combustion, and vehicular emissions.

Statistical analysis

Using Pearson's correlation matriX and factor analysis, the heavy metals com-position was analysed using multivariate statistical analysis. By doing so, we hope to uncover any links between the metals found in the soil samples we've examined. These relationships give a wealth of information on the origins and distribution of metals across a system's many subsystems.

Using soil samples collected at AshakaCem, we calculated the Pearson's correlation matrix for heavy metal concentrations. The association between Cr and Ni was considerably positive (r2 = +0.930). For the metals, this strong correlation indicated a common contamination source that could be anthropogenic or coal combustion. To demonstrate their similar genesis from corrosion of metallic wastes, automotive emissions and cement manufacturing pollutants, Pb showed a reasonably significant positive association with Ni (r2 = +0.571) and Zn (r2 = +0.585). A minor connection (r2 = +0.563) was found between Mn and Cu, showing that Mn and Cu were derived from the surrounding soil (a natural source) [8,49], but Cu accumulation may be impacted by human activity.

Factor analysis (FA)

Using FA and Varimax rotation with Khaisar normalisation, data on heavy metal sources and distribution in soils were clarified and made more accurate. FA was used in this study. Using the Varimax rotation, the results of the factor loadings are shown in Table 5, along with their relative percentages of variance and communalities. A total of 75.20 percent of the variance could be explained by just two important factors. Approximately 39% of the overall variation is explained by Factor 1, which relies primarily on the components Cr and Ni. Anthropogenic activities such as coal combustion and lime stone processing near the factory were identified as the primary source of metals by this factor. Also supporting this is the fact that Cr and Ni have a significant positive correlation coefficient (Table 5). in Factor 2, Zn, Mn, Cu and Pb had strong positive loadings.

Table 5
Pearson correlation matrix and Varimax rotated factor loadings of heavy metals in soil samples around AshakaCem.

Pearson correlation matrix							Factor analysis			
	Cr	Pb	Ni	Cu	Zn	Mn		Factor 1	Factor 2	Communality
Cr	1.000							0.96	0.17	0.95
Pb	0.545	1.000						0.50	0.57	0.58
Ni	0.930	0.571	1.000					0.95	0.23	0.95
Cu	0.545	0.424	0.556	1.000				0.47	0.67	0.67
Zn	0.204	0.585	0.222	0.515	1.000			0.00	0.91	0.83
Mn	0.322	0.285	0.441	0.563	0.424	1.000		0.26	0.68	0.53
							Variance (%)	39.28	35.92	
							Cumulative (%)	39.28	75.20	

accounted for 36% of the total variance. This factor suggested that both natural (local soil) and anthropogenic inputs are the principal sources of accumulation of these metals in the studied soil samples.

Table 6
Daily intake of heavy metals from the studied soil samples by children and adults through the three exposure routes.

		Children					Adults				
Element		DI_{ing}	DI_{inh}	DI_{derm}	Total	LADD	DI_{ing}	DI_{inh}	DI_{derm}	Total	LADD
Cr	Min	4.24×10^{-3}	1.18×10^{-7}	1.18×10^{-5}	4.25×10^{-3}	1.18×10^{-7}	2.26×10^{-3}	3.33×10^{-7}	9.02×10^{-6}	2.27×10^{-3}	3.32×10^{-7}
	Max	8.00×10^{-3}	2.23×10^{-7}	2.23×10^{-5}	8.02×10^{-3}	2.22×10^{-7}	4.27×10^{-3}	6.28×10^{-7}	1.70×10^{-5}	4.29×10^{-3}	6.28×10^{-7}
	Mean	5.89×10^{-3}	1.64×10^{-7}	1.64×10^{-5}	5.90×10^{-3}	1.64×10^{-7}	3.14×10^{-3}	4.62×10^{-7}	1.25×10^{-5}	3.15×10^{-3}	4.62×10^{-7}
Pb	Min	4.67×10^{-4}	1.30×10^{-8}	2.25×10^{-6}	4.69×10^{-4}	1.30×10^{-8}	2.49×10^{-4}	3.66×10^{-8}	1.72×10^{-6}	2.51×10^{-4}	3.66×10^{-8}
	Max	3.04×10^{-3}	8.50×10^{-8}	8.52×10^{-6}	3.05×10^{-3}	8.49×10^{-8}	1.63×10^{-3}	2.40×10^{-7}	6.50×10^{-6}	1.64×10^{-3}	2.40×10^{-7}
	Mean	1.49×10^{-3}	4.14×10^{-8}	4.05×10^{-6}	1.49×10^{-3}	4.14×10^{-8}	7.94×10^{-4}	1.17×10^{-7}	3.09×10^{-6}	7.97×10^{-4}	1.17×10^{-7}
Ni	Min	1.55×10^{-3}	4.33×10^{-8}	4.34×10^{-6}	1.55×10^{-3}	4.32×10^{-8}	8.30×10^{-4}	1.22×10^{-7}	3.31×10^{-6}	8.33×10^{-4}	1.22×10^{-7}
	Max	3.44×10^{-3}	9.58×10^{-8}	9.61×10^{-6}	3.45×10^{-3}	9.57×10^{-8}	1.84×10^{-3}	2.70×10^{-7}	7.33×10^{-6}	1.85×10^{-3}	2.70×10^{-7}
	Mean	2.24×10^{-3}	6.23×10^{-8}	6.25×10^{-6}	2.25×10^{-3}	6.23×10^{-8}	1.20×10^{-3}	1.76×10^{-7}	4.77×10^{-6}	1.20×10^{-3}	1.76×10^{-7}
Cu	Min	1.14×10^{-4}	3.17×10^{-9}	3.18×10^{-7}	1.14×10^{-4}		6.08×10^{-5}	8.95×10^{-9}	2.43×10^{-7}	6.11×10^{-5}	
	Max	1.16×10^{-3}	3.24×10^{-8}	3.25×10^{-6}	1.17×10^{-3}		6.21×10^{-4}	9.13×10^{-8}	2.48×10^{-6}	6.24×10^{-4}	
	Mean	3.87×10^{-4}	1.08×10^{-8}	1.08×10^{-6}	3.88×10^{-4}		2.07×10^{-4}	3.04×10^{-8}	8.24×10^{-7}	2.07×10^{-4}	
Zn	Min	2.70×10^{-5}	7.50×10^{-10}	7.52×10^{-8}	2.70×10^{-5}		1.44×10^{-5}	2.12×10^{-9}	5.74×10^{-8}	1.44×10^{-5}	
	Max	2.74×10^{-3}	7.66×10^{-8}	7.68×10^{-6}	2.75×10^{-3}		1.47×10^{-3}	2.16×10^{-7}	5.86×10^{-6}	1.48×10^{-3}	
	Mean	7.80×10^{-4}	2.17×10^{-8}	2.18×10^{-6}	7.83×10^{-4}		4.17×10^{-4}	6.13×10^{-8}	1.66×10^{-6}	4.18×10^{-4}	
Mn	Min	1.08×10^{-2}	3.02×10^{-7}	3.03×10^{-5}	1.09×10^{-2}		5.80×10^{-3}	8.53×10^{-7}	2.31×10^{-5}	5.82×10^{-3}	
	Max	8.28×10^{-2}	2.31×10^{-6}	2.32×10^{-4}	8.31×10^{-2}		4.44×10^{-2}	6.53×10^{-6}	1.77×10^{-4}	4.46×10^{-2}	
	Mean	3.57×10^{-2}	9.98×10^{-7}	1.00×10^{-4}	3.58×10^{-2}		1.91×10^{-2}	2.81×10^{-6}	7.63×10^{-5}	1.92×10^{-2}	

Health risk assessment

Using Eqs. (1)–(4b), we estimated the DI and LADD of heavy metals from soil samples collected near AshakaCem for children and adults, and the findings are shown in Table 6. As a general rule of thumb, the maximum daily intakes of Cr and Pb for children are 8.02 10–3 mg kg–1 per day and for adults are 6.28 10–3 mg kg–1 and 2.40 10–7 mg kg–1 respectively. Ni and Cu have cumulative maximum exposure levels of 3.45 103 and 1.17 103 mg kg1 day1 for children, and 1.85 103 and 6.24 104 mg kg1 day1 for adults, respectively. Children and adults have a Zn maximum DI of 2.75 10-3 and 1.48 10-3 mg kg-1 day-1 respectively.

Compared to inhalation and cutaneous absorption, the DI of all the metals tested is 2–4 orders of magnitude greater when taken orally than ingested. There is also a significant difference in the average daily consumption of Cr, Pb, and Ni compared to the daily intake of Cu and Zn. In humans, the daily intake of the metals is 2–4 orders of magnitude greater by food than through inhalation and skin contact. For adults, Cr and Ni have a total exposure dosage of 103 mg kg-1 day-1, which is greater than Pb, Zn, and Cu (104 mg kg-1 day-1) in the same order of magnitude.

There was a higher mean daily consumption of mn in Mn. For children and adults, these values are 3.58 102 and 1.92 102, respectively. DI values for both subpopulations were lower than their respective RfD values for all the examined metals, except for Cr, when compared to three exposure pathways. Metal exposure did not pose any non-carcinogenic harm to either children or adults, according to the results of this study. Cr., on the other hand, is seeing a different pattern. Children and adults have DIing values for Cr of 1.96 and 1.05 mg kg1 day1, respectively. These values were higher than the USEPA's RfD for Cr of 3.00 103 mg kg1 day1 [40]. The consumption of Cr, which is present in its carcinogenic form (Cr+6) in the examined soil samples, should thus be given serious consideration. For both children and adults, the ingestion route accounted for around 99 percent of the total daily metal consumption. As a result, for both populations, soil ingestion is the primary route of metal exposure. Children were found to be exposed to metal pollution in soil samples at a higher rate than adults, according to an analysis of exposure rates. Due to their daily hand-to-mouth eating habits, this may be the cause.

For carcinogenic metals, the average daily intake (LADD) of Cr was found to be greater than Pb (4.18 108 mg kg–1 day–1) and Ni (6.23 108 mg kg–1 day–1), which were both found to have lower LADD values. For adults, the LADD for Cr, Pb, and Ni were all in the same range of (10–7 mg kg–1 day–1).

Health risk levels

To determine the non-carcinogenic and carcinogenic risks (HI) for children and adults, we used Eqs. (5)–(14) to construct hazard quotients (HQs) for each exposure pathway. Table 7 shows the findings of the study. As Zn, Cu, Ni, Pb, Mn, and Cr decreased, so did the HQ and HI for non-carcinogenic risk for both children and adults.

There was also a rising order of ingestion > dermal contact > inhalation for the three exposure routes,

except for Mn, which had an ingestion > inhalation > dermal contact increasing order for both adults and children alike.

The soil ingestion route (QIing) contributes roughly 89 percent of the entire risk for children and 79 percent of the total risk for adults. This further revealed that metals from the soil samples investigated are the major source of non-carcinogenic danger in both subpopulations. The findings are consistent with previous research [22,26,35]. This study has also shown that the non-carcinogenic hazards to children and adults from the metals discovered in soil samples near AshakaCem were lower than unity (the safety limit) for Pb, Ni, Cu, Zn, and Mn, all of which had HI values below unity (the safety limit). However, in this investigation, children and adults were shown to have a greater toxicological risk of exposure due to Cr. The cumulative hazard indices for children and adults were 2.24 and 1.27, respectively, attributable to Cr consumption across the three exposure pathways (Table 7). Cr is a problem since these values are beyond the safety limit of unity. This is a serious issue since the very toxic Cr (VI) specie of Cr has an absorption rate of 2–8 percent when consumed [50] and is found in analysed soils.

Of the three exposure routes evaluated, the cumulative hazard index attributable to metal exposure was 3.70 for children and 2.23 in adults (Table 7). Of this, Cr ingestion accounted for about 99 percent. According to these findings, children have a greater non-carcinogenic risk from heavy metal exposure than adults. Due to their hand-to-mouth eating practises, contaminated soil may easily be eaten [22, 51].

For Cr, Pb, and Ni, the carcinogenic risk values in the examined soil samples were 6.87 10–6, 1.74 10–9 and 6.87–10–9, respectively, as shown in Table 6.

As a general rule of thumb, the lower the number, the more likely it is that the person is a youngster. In the soil samples tested, the average lifetime cancer risk for children and adults was 2.31 106 and 6.51 106 for exposure to Cr, Pb, and Ni, respectively. This study found that children had a cancer risk that is 0.4 times greater than that of adults when exposed to these three carcinogenic metals. According to the US Environmental Protection Agency (USEPA), the cancer risk threshold for children (6.87 106) and adults (1.94 105) from exposure to Cr is more than 1 10 [40]. One hundred and ninety-nine percent of the cancer risk came from eating foods containing Cr. Because of this, the soils analysed contain a significant amount of Cr. The accumulation of Cr in human tissues after prolonged exposure might have negative consequences on the digestive system. Lung and stomach cancers may be triggered by an overabundance of Cr in the body [23].

Conclusions

The heavy metal contents in 20 randomly selected soil samples from the vicinity of an AshakaCem coal-fired cement plant in northern Nigeria were studied. There was a diminishing order in the findings. concentrations of metals as follows: Mn Cr Ni Pb Zn Cu, nevertheless Their average concentrations fall within the range of values published in the scientific community. for the same kinds of investigations. Coal combustion was detected statistically, cement output and vehicle emissions are the two most important factors. These metals can be found in the soils that were sampled because of the research. Risk assessment for human health exposure pathway to dirt intake was shown to be the most dangerous. children and adults are at risk. Probability of exposure that does not cause cancer Within the three exposure pathways, both children and adults were exposed except for Cr, which has an HI of more than 1. This Cr should be given the utmost care and worry, according to the author. The In general, children's cumulative HI values were found to be greater, suggesting Children are more likely than adults to get contaminated by metals. adults. The carcinogenic metals' cancer risk levels were not unknown. the US Environmental Protection Agency's (USEPA's) range of acceptable risk, demonstrating that Metals in the examined soils have a minor impact on carcinogenesis. Risk assessment models, despite their inherent flaws, have shown to be beneficial in detecting potentially harmful exposures. pathways that may provide a significant risk in assessing Health effects on any population exposed to metal exposure in general. The study's overall findings will be useful to the government in adopting a risk-based strategy for policy design and the prevention of heavy metals' ill effects on both humans and the environment Pollution of metals.

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