

HEAVY METALS EVALUATION AND HUMAN HEALTH RISK ASSESSMENT OF FOUR BRANDS OF NIGERIAN PORTLAND CEMENT SOLD IN ZARIA, NIGERIA

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ABSTRACT

This study investigated the concentration of some select heavy metals (Cd, Cu, Fe, Pb, Zn, Ni, Mn and Co) in four cement samples, Bu, Da, Ak and Sk and assessed their health risks to potential users. Samples were collected from Samaru market, Zaria; and processed using Atomic Absorption Spectrophotometric method, following acid (aqua reggia) digestion. Fe reported highest concentration (542.99 mg/kg) in sample Ak, while Zn gave the lowest concentration value (1.016 mg/kg) as detected in Da). Cd concentration ranked in the order Da > Ak > Sk > Bu; Cu ranked Da > Ak > Sk > Bu; Fe ranked Ak > Da > Sk > Bu; Pb ranked Da > Ak > Sk > Bu; Zn ranked Ak > Sk > Bu > Da; Ni ranked Ak > Sk > Da > Bu; Mn ranked Sk > Ak > Da > Bu and Co ranked Ak > Sk > Da > Bu. Human risk assessment arising from exposure to heavy metals was validated from the result by estimating daily heavy metal intake and then computing the cancer and non-cancer risks (ILCR and THQ). Hazard Quotient HQ) and Health Index (HI) for adult and children exposure pathways was also determined. Metals under consideration were found to be below the threshold limit (10^{-6} - 10^{-4}) and similar result was recorded for the cumulative cancer risk (Σ ILCR) of the studied Portland cement. Metal content in all samples in the immediate does not pose cancer or non-cancer risks.

Key words: Kiln, Exposure, Portland cement

INTRODUCTION

Cement is a binder, a substance used in construction that sets, hardens and adheres to other materials, bringing them permanently together. Cement is a grey powder made by burning calcined lime and clay. It is mixed with water to form mortar or mixed with sand, gravel, and water to make concrete [1]; it has been variously classified either as a hydraulic (lime) cement, natural cement or Portland cement. The major component of cement includes: Lime Stone (Ca_2CO_3), Silicon oxide (SiO_2), Aluminum Oxide (Al_2O_3), Iron Oxide (Fe_2O_3), two main Oxide - Sodium Oxide and Potassium Oxide [2]. Various researchers have implicated metals as threats to human health because they pose both cancer and non-cancer risks to humans. Heavy metals in the environment can impact human health through any, some or all exposure routes by direct ingestion, inhalation or dermal contact, thereby amplifying the risk of cancer [3] [4] [5].

Cement production and application has been established as an important emission source of heavy metals into our environment, which can leach or deposit on or within any or all of plant, animal, human or soil matrices [6].

Metal compounds present in substances are indestructible by combustion process in the kiln. The cement kiln will redistribute any metals in the input materials by releasing them either as Kiln emissions, dust or in the final cement product, clinker. Metal compounds may be oxidized or reduced during the combustion process, it is not destroyed. Therefore, any metal present in the fossil fuel or raw feed, natural or waste, will be present either in the kiln stack emissions, the cement kiln dust (CKD) or the clinker. The metals entering a cement kiln via fuel or raw material feed may be categorized as volatile, semi-volatile and refractory, based on their volatiles. It is safe to assume that concentrations of trace elements in input

materials will be reflected in the trace element concentrations of cement product [1].

[18] Inferred that the release of trace elements from concrete is negligibly small during phase of use. An increased release of trace elements is possible under special assumptions after demolition, but the knowledge available does not suffice to assume a definite assessment.

The effect of cement dust exposure among construction workers involved in a full-scale construction project has been comparatively investigated, where full-shift personal exposure measurements were performed for several job types. Inhalable dust and cement dust exposures (based on analysis of elemental calcium) concentrations were determined. Even though elemental measurements showed highest but very variable cement percentages in the cement plant and very low percentages of cement during reinforcement work and pouring [7].

This research's intent is to investigate the amount of Cd, Cu, Fe, Pb, Zn, Mn, Co and Ni in four different brands of Portland cement and their health effect for two exposure pathways (via inhalation and dermal routes), with the aim of establishing the health hazard the metal component of the cement may pose to their users.

Materials and Methods

Chemicals, reagents and glassware

All chemicals and reagents were of analytical grade and all standards were prepared from reagent grade chemicals (Perkin Elmer Pure – Atomic Spectroscopy Standard). All glassware was rinsed successively with detergent and distilled water three times prior to use.

Sample Collection

Four cement brands were obtained from Samaru market, Sabon Gari LG Area of Kaduna State and labeled Bu, Da, Ak and Sk.

Experimental

Following methods described by [8]; Cement samples were weighed, deposited in polythene bags and labeled, then taken to the laboratory for processing and analysis. A 3 g mass of each sample was weighed out separately and placed into correctly labelled 100 mL beaker, and moistened with few drops of distilled water; 5 mL Aqua-regia (a combination of HNO₃ and HCl in the ratio 1:3) was then added to each beaker. Each beaker was covered with a watch glass and placed on a hot plate in a fume cupboard and allowed to

boil, after which it was allowed to simmer for 45 minutes. The mixtures were removed from the hot plate and placed on a heatproof mat where it was allowed to cool. The watch glass was removed to allow liquid drain into the beaker. The content of the beaker was filtered through a Whatman No. 4 filter paper, into 100 mL volumetric flask. The filtrate was made up to the mark with distilled water. Filtration was done using Whatman No. 4 filter paper. The filtrate was analysed for the heavy metals Cd, Fe, Pb, Zn, Mn, Ni, Cu, Co.

Human Health Risk Assessment

Health risk has been described as a state or likelihood of harmful effects to humans resulting from environmental pollution. Human pollutant intake is the effective amount of pollutants that enters the human body and is transported through the blood system to target tissues and organs. [9]. The potential exposure pathways for heavy metals in cement powder evaluated in this investigation shows that humans could be exposed to heavy metals via inhalation or inhalation of cement powder.

Tables 1 and 2 describes exposure calculation parameters (chronic intake dose in mg/kg/day) of toxic elements [9], while table 3 displays values for reference dose and slope factor for some investigated elements.

Non-cancer risks

This is estimated as numerical quantity of exposure level over an established period of time (usually a lifetime) with a reference dose derived for a similar exposure period [9].

Non-cancer risks were determined after computing the target hazard quotient (THQ) for individual heavy metals, by inputting determined values into the equation 1 [10].

$$THQ = CDI \times RfD \quad (1)$$

CDI is documented as the chronic daily intake of chemical carcinogen in mg/kg BW/day (table 1), used to express the lifetime average daily dose of exposure to the chemical, while RfD is defined as “reference dose” for either inhalation or dermal exposure pathway (mg/kg/day), it is an estimation of the maximum permissible risk on human population through daily exposure to toxic metals. Furthermore, the potential risk to human health via multiple heavy metals were evaluated as the chronic hazard index (HI), which is a summation of all THQ values calculated earlier

for a particular exposure pathway. This was adopted from [22]:

$$HI = THQ_1 + THQ_2 + \dots + THQ_n \quad (2)$$

Where 1, 2, ..., n are individual heavy metal.

The calculated hazard (HI) is compared to established levels: population is assumed to be safe when $HI < 1$ and at a level for concern when $1 < HI < 5$ [11].

Cancer risks

This refers to the incremental probability of an individual developing any kind of cancer in a lifetime resulting from carcinogen exposure [9]. The possibility of cancer risks in the studied Portland cements through intake of carcinogenic heavy metals was calculated by adopting the model described by [11], where it is mentioned as Incremental Lifetime Cancer Risk (ILCR). This is calculated as:

$$ILCR = CDI \times CSF \quad (3)$$

CDI here still remains as earlier mentioned and CSF is the cancer slope factor, it is the risk produced by a lifetime average dose of 1 mg/kg BW/day. Level of acceptable $ILCR$ for regulatory purpose is considered within the ranges of 10^{-6} and 10^{-4} [10]. The range of risks borderline designated by the EPA ranges from 1×10^{-4} to 1×10^{-6} and unacceptable if the recorded risks values are beyond 1×10^{-4} . A carcinogenic risk of 1×10^{-4} poses health hazards; therefore, it is sufficiently large and need immediate attention and reaction [12].

Cumulative cancer risk may result from exposure to multiple carcinogenic heavy metals; this was estimated as the sum of individual heavy metal increment risks using the following equation [5].

$$\sum_1^n = ILCR_1 + ILCR_2 + \dots + ILCR_n \quad (4)$$

Where $n = 1, 2, \dots, n$ for this work is the individual carcinogenic heavy metals present in the various Portland cement samples.

Table 1. Mathematical models for evaluating daily intake dose through dermal and inhalation

Exposure Pathway	Exposure Calculation
Inhalation of cement powder	$CDI_{inhalation} = \frac{CS \times IR_{air} \times EF \times ED}{BW \times AT} \quad (5)$
Dermal absorption of cement powder	$CDI_{dermal} = \frac{CS \times AF \times SA \times ABS \times CF \times EF \times ED}{BW \times AT} \quad (6)$

Table 2. Parameters for computing exposure studies

Parameter	Definition	Value	
		Children	Adult
CS	Heavy metal concentration in cement powder	Recorded value	Recorded value
IR_{air} (m ³ /day)	Inhalation rate	10	20
BW (kg)	Body weight	15 kg	70 kg
EF (days/year)	Exposure frequency	180	180
ED (years)	Exposure duration	6	34
SA (cm ²)	Skin surface area	2800 cm ²	5700 cm ²
AF (mg/cm ²)	Skin adherence factor	0.2	0.07
ABS	Dermal absorption factor	0.001	0.001
FE	Dermal exposure ratio	0.61	0.61
CF (kg/mg)	Conversion factor	10^{-6}	10^{-6}
AT (days)	Average time: Carcinogens	365 x 70	365 x 70
	Non-carcinogens	365 x ED	365 x ED
PEF (m ³ /kg)	Particulate emission factor	1.3×10^9	1.3×10^9

Table 3. Reference doses and cancer slope factors for heavy metals

Element	IARC classification	RfD _{inhal} (mg/kg/d)	RfD _{dermal} (mg/kg/d)	CSF _{inhal}	CSF _{dermal}
Cd	1	2.40 E-06	1.00 E-05	6.30	1.50
Cr	1	2.86 E-05	6.00 E-05	4.20	
As	1	3.01 E-04	1.23 E-04	15.1	3.66
Ni	1	2.06 E-02	5.40 E-03	0.84	
Pb	2B	3.60 E-03	5.25 E-04	1.50	
Mn	-	-	-	-	
Hg	3	8.60 E-04	2.10 E-05		
Zn	-	3.00 E-01	6.00 E-02	-	
Cu	-	4.02 E-02	1.20 E-02	-	
Co	2B	5.70 E-06	1.60 E-02	9.80	
Fe	-	-	-	-	

Notes: IARC; 1= definite human carcinogens, 2B= possible human carcinogens and 3= non-carcinogenic.
Sources: [9; 13].

RESULTS

Table 4. Metal concentrations in different brands of Portland cement

Element	Present Study (mg/kg)			
	Bu	Da	Ak	Sk
Cd	5.20	7.88	6.80	5.49
Cu	5.16	9.00	8.78	5.72
Fe	380.44	451.20	542.99	396.80
Pb	149.40	248.48	162.23	158.09
Zn	1.028	1.016	1.80	1.77
Ni	8.12	16.16	33.62	28.62
Mn	79.32	81.86	224.37	284.13
Co	13.16	17.96	22.77	18.32

Health Risk Assessment

Daily intake of heavy metals

Daily intake of heavy metals for all samples through inhalation and dermal surface exposures

by adults and Children are presented in table 5 (a-d).

Table 5a. Chronic Daily Intake of investigated heavy metals in sample Bu

Pathway	Cd	Cu	Fe	Pb	Zn	Ni	Mn	Co
Inhalation (Children)	10.00 E-09	9.91 E-10	7.31 E-11	2.87 E-11	1.97 E-10	1.56 E-12	1.52 E-11	2.53 E-12
Dermal (Children)	3.35 E-08	3.32 E-08	2.43 E-05	9.56 E-06	6.62 E-09	5.20 E-07	5.08 E-06	8.42 E-07
Inhalation (Adult)	5.64 E-10	5.59 E-10	4.12 E-08	1.62 E-08	1.11 E-10	8.80 E-10	8.60 E-09	1.43 E-09
Dermal (Adult)	1.46 E-07	1.45 E-07	1.07 E-05	4.18 E-06	2.89 E-08	2.27 E-07	2.22 E-06	3.67 E-07

Table 5b. Chronic Daily Intake of investigated heavy metals in sample Da

Pathway	Cd	Cu	Fe	Pb	Zn	Ni	Mn	Co
Inhalation (Children)	1.50 E-09	1.73 E-09	8.67 E-11	4.78 E-11	1.95 E-10	3.11 E-12	1.57 E-11	3.45 E-12
Dermal (Children)	5.08 E-08	5.80 E-08	2.89 E-05	1.59 E-05	6.54 E-09	1.03 E-06	5.24 E-06	1.15 E-06
Inhalation (Adult)	8.50 E-10	9.76 E-10	4.89 E-08	2.69 E-08	1.10 E-10	1.75 E-09	8.87 E-09	1.95 E-09
Dermal (Adult)	2.21 E-07	2.53 E-07	1.26 E-05	6.96 E-06	2.85 E-08	4.52 E-07	2.29 E-06	5.03 E-07

Table 5c. Chronic Daily Intake of investigated heavy metals in sample Ak

Pathway	Cd	Cu	Fe	Pb	Zn	Ni	Mn	Co
Inhalation (Children)	1.31 E-09	1.69 E-09	1.04 E-10	3.12 E-11	3.46 E-10	6.46 E-12	4.31 E-11	4.38 E-12
Dermal (Children)	4.38 E-08	5.65 E-08	3.48 E-05	1.04 E-05	1.16 E-06	2.15 E-06	1.44 E-05	1.46 E-06
Inhalation (Adult)	7.37 E-10	9.60 E-10	5.89 E-08	1.76 E-08	1.95 E-10	3.64 E-09	2.43 E-08	2.47 E-09
Dermal (Adult)	1.91 E-07	2.47 E-07	1.52 E-05	4.54 E-06	5.10 E-08	9.41 E-07	6.28 E-06	6.38 E-07

Table 5d. Chronic Daily Intake of investigated heavy metals in sample Sk

Pathway	Cd	Cu	Fe	Pb	Zn	Ni	Mn	Co
Inhalation (Children)	1.05 E-09	1.10 E-09	7.63 E-11	3.04 E-11	3.40 E-10	5.50 E-12	5.46 E-11	3.52 E-12
Dermal (Children)	3.54 E-08	3.68 E-08	2.54 E-05	1.01 E-05	1.14 E-03	1.83 E-06	1.82 E-05	1.17 E-06
Inhalation (Adult)	5.95 E-10	6.20 E-10	4.30 E-08	1.71 E-08	1.92 E-10	3.10 E-09	3.08 E-08	1.99 E-09
Dermal (Adult)	1.54 E-07	1.61 E-07	1.11 E-05	4.43 E-06	4.97 E-03	8.01 E-07	7.96 E-08	5.13 E-07

Table 6. Hazard Quotient (HQ) and Health Index (HI) for adult and children exposure pathways

Exposure Pathways		Hazard Quotient (HQ)						HI = ΣTHQ
		Cd	Cu	Pb	Zn	Ni	Co	
Bu								
Adult	Inhale	1.35 E-15	2.25 E-11	5.83 E-11	3.33 E-11	1.81 E-11	8.15 E-15	5.83 E-11
	Dermal	1.46 E-12	1.74 E-09	2.19 E-09	1.73 E-09	1.23 E-09	5.87 E-09	1.28 E-08
Children	Inhale	2.40 E-14	3.98 E-11	1.03 E-13	5.91 E-11	3.21 E-14	1.44 E-17	9.91 E-11
	Dermal	3.35 E-13	3.98 E-10	5.02 E-09	3.97 E-10	2.80 E-09	1.35 E-08	2.21 E-08
Da								
Adult	Inhale	2.04 E-15	3.92 E-09	9.68 E-11	3.30 E-11	3.61 E-11	1.11 E-14	4.09 E-09
	Dermal	2.21 E-12	3.04 E-09	3.65 E-09	1.71 E-09	2.44 E-09	8.05 E-09	1.89 E-08
Children	Inhale	3.60 E-15	6.95 E-11	1.72 E-13	5.85 E-11	6.41 E-14	1.97 E-17	1.28 E-10
	Dermal	5.08 E-13	6.96 E-10	8.35 E-09	3.92 E-10	5.56 E-09	1.84 E-08	3.34 E-08
Ak								
Adult	Inhale	1.77 E-15	3.86 E-11	6.34 E-11	5.85 E-11	7.50 E-11	1.41 E-14	2.36 E-10
	Dermal	1.91 E-12	2.96 E-09	2.38 E-09	3.06 E-09	5.08 E-09	1.02 E-12	1.35 E-08
Children	Inhale	3.14 E-15	6.79 E-11	1.12 E-13	1.04 E-10	1.33 E-13	2.50 E-17	1.72 E-10
	Dermal	4.38 E-13	6.78 E-10	5.46 E-09	6.96 E-08	1.16 E-08	2.34 E-08	1.11 E-07
Sk								
Adult	Inhale	1.43 E-15	2.49 E-11	1.59 E-08	5.76 E-11	6.39 E-11	1.13 E-14	1.60 E-08
	Dermal	1.54 E-12	1.93 E-09	2.33 E-09	2.98 E-04	4.33 E-09	8.21 E-09	2.98 E-04
Children	Inhale	2.52 E-15	4.42 E-11	1.09 E-13	1.02 E-10	1.13 E-13	2.01 E-17	1.46 E-10
	Dermal	3.54 E-13	4.42 E-10	5.30 E-09	6.84 E-05	6.84 E-05	1.87 E-08	6.84 E-05

Table 8. Cancer Risk Exposure Pathways for adult and children

Sample and Receptor Pathways		ILCR: (CDI × CSF)				Σ ILCR
		Cd	Pb	Ni	Co	
Bu:						
Adult	Inhale	3.55 E-09	2.43 E-08	7.39 E-10	1.40 E-08	4.26 E-08
	Dermal	2.19 E-07	-	-	-	
Children	Inhale	6.30 E-08	4.31 E-11	1.31 E-12	2.48 E-11	6.31 E-08
	Dermal	5.03 E-08	-	-	-	
Da:						
Adult	Inhale	5.36 E-09	4.04 E-08	1.47 E-09	1.40 E-08	6.12 E-08
	Dermal	3.32 E-07	-	-	-	
Children	Inhale	9.45 E-09	7.17 E-11	2.61 E-12	3.38 E-11	9.56 E-09
	Dermal	7.62 E-08	-	-	-	
Ak:						
Adult	Inhale	4.64 E-09	6.81 E-06	3.06 E-09	2.42 E-08	6.84 E-06
	Dermal	2.87 E-07	-	-	-	
Children	Inhale	8.25 E-09	4.68 E-11	5.43 E-12	4.29 E-11	8.35 E-09
	Dermal	6.57 E-08	-	-	-	
Sk:						
Adult	Inhale	3.75 E-09	6.65 E-06	2.60 E-09	1.95 E-08	6.68 E-06
	Dermal	2.31 E-07	-	-	-	
Children	Inhale	6.62 E-09	4.56 E-11	4.62 E-12	3.45 E-11	6.70 E-09
	Dermal	5.31 E-08	-	-	-	

DISCUSSION***Concentration of heavy metals in cement samples***

The metals, Cadmium (Cd), Copper (Cu), Iron (Fe), Lead (Pb), Zinc (Zn), Nickel (Ni), Manganese (Mn) and Cobalt (Co) were investigated in four Portland cement samples and their results were presented in table 4. The amount of Cd in sample Bu is 5.20 mg/kg, and 7.88 mg/kg in Da, Ak recorded 6.80 mg/kg and Sk 5.49 mg/kg. Concentration of Cu in Bu is 5.16

mg/kg while Da is 9.0 mg/kg, Ak and Sk gave 8.78 mg/kg and 5.72 mg/kg respectively. Sample Bu reported a concentration 380.44 mg/kg for Fe, 451.2 mg/kg for Da, 451.20 mg/kg for Ak and 396.80 mg/kg for Sk. Concentration of Pb in Bu read 149.4mg/kg while Da recorded 248.48 mg/kg, Ak and Sk had concentrations of 162.23 and 158.09 mg/kg respectively. Concentration of Zn in Bu, Da, Ak and Sk is 1,028, 1,016, 1.80 and 1.77 mg/kg. Ni in Bu is 8.12 mg/kg, in Da is 16.16 mg/kg, 33.62 mg/kg in Ak and 28.62 mg/kg

in Sk. Results for Bu revealed the quantity of Mn as 79.32 mg/kg, in Da as 81.86 mg/kg, Ak as 224.37, then 284.13 mg/kg as concentration of Mn in Sk. Varying Co concentrations (13.16 mg/kg, 17.96 mg/kg, 22.77 mg/kg and 18.32 mg/kg) was tabulated for samples Bu, Da, Ak and SK.

Concentration of Cd in all four samples were at the range of 5.20-7.80 mg/kg, [16] reported 4 mg/kg in their research findings. Sample Da recorded the highest value for Cd (7.88 mg/kg) while Bu has the least (5.20 mg/kg).

Cu in the present work read below both regulatory limits (table 4). This result strongly agrees with a study on the analysis of metal contents in Portland type V and MTA-based cements by [4], concentrations of 5.00, 6.00, 5.00 and 5.00 mg/kg for 4 cement types was reported. Concentration of Cu in studied samples followed the order Da > Ak > Sk > Bu.

There is no regulatory limit for quantity of Fe in the environment, notwithstanding. The present work informed higher values (380.44-542.99 mg/kg) over literatures [14] [1].

Pb was validated in sample Da as 248.48 mg/kg, this findings is similar to that of [15]; while a study by [17] revealed higher concentration.

Concentrations of Zn in all samples were low as compared to result by [18], where higher values were recorded in various types of cement as well as their production stages, and all exceeded results for present work.

Mixed concentration values for Ni have been reported by researchers at lower concentrations (0.5, 0.25, 0.3 and 3 mg/kg) [1], [18] and [14], both reported similar and higher values but within the estimated values for present work.

Concentration of Mn in present study was considerably above values presented by [14].

Findings on Co however was far above that reported by [1]. The health risks associated with Co have not been fully established and only Austria has an established permissible limit of 50 mg/kg of Co in soil. This metal, unlike certain other trace metals, has human benefits; it is a part of vitamin B₁₂, an essential to human health. However, uptake of high concentrations of Co induces vomiting, nausea, vision problems, heart ailments and thyroid damage [19].

Non-carcinogenic analysis

In this research work, exposure and risk assessment was achieved following methodology laid down by [24]; Owing to application and significance of cement in building constructions, and also from findings in table 4, human exposure to heavy metals is considerably possible and may occur through pathways of inhaled dust particles and dermal absorption.

It has been established that the degree of toxicity of heavy metals to human health is directly related to their daily intake [20]. The chronic daily intake of heavy metals via inhalation and dermal pathways by local adults and children is listed in tables 5 (a-d); however, this work considered dermal and inhalation exposure pathways because they are the most obvious paths of exposure.

As presented in table 6, HQ for all metals was highest for Zn in sample Sk (dermal exposure in adults), while exposure in same sample (for children) was also determined highest also for dermal exposure in all samples, this is followed by Ni at the dermal exposure pathway. The lowest HQ value was reported for the metal Co, via inhalation in children for all samples; with sample Ak (2.50 E-17) highest followed by Sk (2.01 E-17), then Da (1.97 E-17) and least is Bu (1.44 E-17).

All studied heavy metals had total HQ below 1; this suggests that the health risk associated with exposure to Zn, Co, Cd, Cu, Pb and Ni were within an acceptable level of non-carcinogenic health risk for all Portland cement samples. From the computed HQs, it is safe to infer that the contribution of the six metals to non-carcinogenic health risk follow the order: Co > Cd > Ni, Cu, Zn and Pb recorded similar HQ values.

To estimate the total potential non-carcinogenic impacts induced by several metals, this is carried out from the summation of the HQs for each metal and expressed as a hazard index (HI) (also presented in table 6). Similarly, all HI obtained for all samples were below 1, indicating a neglectable non-carcinogenic risks to users of the cement.

Carcinogenic risk analysis

Result presented is in agreement with [7], there exists no risk of cancer from any of the exposure pathways because values recorded in table 7 for cancer risk exposure pathways for adult and children were below the stipulated level (10^{-6} and

10^{-4}), except for Pb in samples Ak (6.81×10^{-6}) and Sk (6.65×10^{-6}) recording highest values in study samples, above 10^{-6} but below 10^{-4} . Potential carcinogenic risk for Pb from both samples still exists, especially due to possibility of bioaccumulation and concentration of these metals resulting from long term exposure. Furthermore, cumulative cancer risk ($\Sigma ILCR$) for heavy metals was computed for inhalation exposure pathway for children and adults. Results shows none of the samples exceeded the recommended threshold limit ($>10^{-4}$).

The Health and Safety Executive (HSE, UK) in 1994, advanced no convincing evidence for an increased incidence of any site-specific cancer resulting from cement exposure, data available at that time was not consistently and reassuringly negative; the HSE in 2005 reviewed findings in more recently published studies, revealing amplified incidences of cancer manifestations at several body parts (stomach, lungs, colon, head and neck). A causal association between Portland cement exposure and cancer has however not been established and therefore the uncertainty concerning a possible cancer risk abounds. Besides a possible cancer risk, occupational exposure to cement dust has been associated with

reduced respiratory function. Existing evidence is not tangible enough to establish exposure-response relationships for these effects ([7].

Conclusion

The investigation of levels of heavy metals in four Portland cements collected in Samaru market, Zaria has revealed high levels of Cd, Pb, Ni, Mn and Co. Cu and Zn obviously pose no serious environmental concern, while the hazard posed by Fe was not ascertained. It is important to state that bioaccumulation via surface absorption of Cd, Pb, Ni, Co, are of extreme danger to health and wellbeing of plants and individuals interacting with them via direct or indirect exposure. In this study, exposure valuation was carried out by measuring the average daily intake (*ADI*) of heavy metals earlier identified through inhalation and dermal contact by adults and children. Adults and Children are separated because of their behavioural and physiological differences. The cancer slope factor (*CSF*), a carcinogen potency factor and the reference dose (*RfD*), a non-carcinogenic threshold are two important toxicity indices applied. The use of any of the investigated Portland cement does not constitute an immediate cancer and non-cancer risk.

REFERENCES

- [1] A. Cipurkovic, I. Trumic, Z. Hodžic, V. Selimbašić and A. Djozic (2014). Distribution of heavy metals in Portland cement production process. *Advances in Applied Science Research*, 5(6): 252-259
- [2] R. Schmidt (2004). *Introduction to Clinker and Cement Phase Analysis*, Workshop, Karlsruhe, Germany Pp. 64
- [3] T. Amari, T. Ghnaya, C. Abdelly (2017). Nickel, Cadmium and Lead phytotoxicity and potential of halophytic plants in heavy metal extraction. *S. Afri. J. Bio*; 111, 99-110
- [4] WHO (1993). Evaluation of certain food additives and contaminants; 41st report of the joint FAO/WHO expert committee on food additives, No. 837; WHO technical report series; WHO: Geneva, Switzerland.
- [5] X. Liu, Q. Song, Y. Tang, W. Li, J. Xu, J. Wu, F. Wang, and P.C. Brookes (2013). Human health risk assessment of heavy metals I soil-vegetable system: A multi-medium analysis. *Science of the Total Environment*, 463-464, 530-540.
- [6] C. O. Ogunkunle and P. O. Fatoba (2014). Contamination and spatial distribution of heavy metals in top soil surrounding a mega cement factory. *Atmospheric Pollution Research*; 5 (2014), 270-282.
- [7] S. Peters, Y. Thomassen, E. Fechter-Rink and H. Kromhout (2019). Personal Exposure to Inhalable Cement Dust among Construction Workers. *Journal of Physics: Conference Series* 151; 012054.
- [8] A. S. Jauro; B. M. Bashir; Y. Ibrahim (2017). Comparison of Some Heavy Metals Pollution in the Soils of Kayel-Baga and Wuro-Sarki Villages Around Maiganga Coal Mine, Gombe-Nigeria.

International Journal of Social Science and Economic Research; Vol. 02, Issue: 03.

[9] Y. Liang, X. Yi, Z. Dang, Q. Wang, H. Luo and J. Tang (2017). Heavy metal contamination and health risk assessment in the vicinity of a tailing pond in Guangdong, China. *International Journal of Environmental Research and Public Health*; 14, 1557.

[10] B. Michael, O. Patrick and T. Vivian (2015). Cancer and non-cancer risks associated with heavy metal exposures from street foods: Evaluation of roasted meats in an urban setting. *Journal of Environmental Pollution and Human Health*, 3, 24-30.

[11] M. S. Sultana, S. Rana, S. Yamazaki, T. Aono and S. Yoshida (2017). Health risk assessment for carcinogenic and non-carcinogenic heavy metal exposures from vegetables and fruits of Bangladesh. *Cogent Environmental Science*, 3:1291107.

[12] H. Alidadi, S. B. T. Sany, B. Z. G. Oftadeh, T. Mohamad, H. Shamszade and M. Fakhari (2019). Health risk assessments of arsenic and toxic heavy metal exposure in drinking water in northeast Iran. *Environmental Health and Preventive Medicine*, 24:59.

[13] O. Johnbull, B. Abbassi, R. G. Zytner (2019). Risk assessment of heavy metals in soil based on the geographic information system-Kriging technique in Anka, Nigeria. *Environmental Engineering Research*, 24(1), 150-158.

[14] M. C. G. O. Dorileo, M. C. Bandeca, F. L. M. Pedro, L. E. R. Volpato, O. A. Guedes, R. D. Villa, M. R. Tonetto, and A. H. Borges (2014). Analysis of Metal Contents in Portland Type V and MTA-Based Cements. Hindawi Publishing Corporation; The Scientific World Journal, Volume 2014, Article ID 983728, 6 pages.

[15] M. Murat and F. Sorrentino (1996). Effect of large additions of Cd, Pb, Cr, Zn to cement raw meal on the composition and properties of the clinker and cement. *Cement and Concrete Research*. Vol. 26, Iss 3, Pages 377-385.

[16] S. G. and S. Sharma (2013). Effect of heavy metal present in cement dust on soil and plants of Nokha (Bikaner). *Current World Environment*; Vol. 8(2), 299-303.

[17] C. O. Ogunkunle and P. O. Fatoba (2013). Pollution loads and ecological assessment of soil heavy metals around a Maga cement factory in southwest Nigeria. *Polish Journal of Environmental studies*; 22(2).

[18] A. A., K.-R. Brautigam, N. Hartlieb, C. Kupsch, U. Richers, P. Stemmermann (2003). Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to the legitimacy of waste utilization. Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft. Wissenschaftliche Berichte. FZKA 6923.

[19] Lenntech Water Treatment (2009). Chemical Properties, Health and Environmental Effects of Cobalt. Lenntech Water Treatment and Purification Holding B.V. www.lenntech.com/periodic/elements/co.htm.

[20] A. A. Mohammadi, A. Zarei, S. Majidi, A. Ghaderpoury, Y. Hashempour, M. H. Saghi, A. Alinejad, M. Yousefi, N. Hosseingholizadeh, M. Ghaderpoori (2019). Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran. *MethodsX*, 6 (1642-1651).

[21] NFPCSP Nutrition Fact Sheet (2011). Joint report of Food Planning and Nutrition Unit (FMPU) of the ministry of Food of Government of Bangladesh and Food and Agricultural Organization of the United Nation (FAO), September 14, 1-2. National Food Policy Plan of Action and Country Investment Plan, Government of the People's Republic of Bangladesh.

[22] EPA/540/1-89/002 (1989). Risk Assessment Guidance for Superfund; Volume 1: Human Health Evaluation Manual (Part A).