RISK ASSESSMENT OF HEAVY METALS LEVEL IN SOILS AND FOOD CROPS AROUND A CERAMICS COMPANY IN AJAOKUTA, KOGI STATE, NORTH CENTRAL NIGERIA

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ABSTRACT

Some metals associated with ceramics emission were determined in agricultural soil and leaves of maize and cassava around the vicinity of a major ceramic company. These metals are released during production process into the environment. Soil samples were collected at depth of 0-15 cm and 15-30 cm at certain distance (100 m, 200 m, 300 m and 400 m). Leaves of maize and cassava were collected around the soil samples area. Samples were collected to make a composite of 24 for both soil and leaves of crops respectively. Soil and plant digest were analysed by atomic absorption spectrometry. Result showed the range of metal (mg/kg) in topsoil Cd (1.00-8.25), Mn (3.75-62.0), Ni (11.0-46.3) and Pb (5.50-101.2). Corresponding value in subsoil was not significantly different ($p>0.05$). The concentration of Mn in leaves of cassava is of concern especially if it will be used in the formulation of animal feed. The geo-accumulation (Igeo) of metals in soil revealed that the soil is slightly polluted. Uptake of metals into crops was low except Mn in cassava leaves. A health risk index (HRI) value for the food crops was <1 except for Mn were HRI>1 for cassava. Overall food crop consumption of the study area does not pose a potential threat at the moment.

Keywords: Ceramics, Heavy metals, Risk assessment, Crop leaves, Metal uptake

INTRODUCTION

The citation of industry brings about industrial development. However, when an industry begins operation there are always generated wastes that should be treated or partially treated before they are released into the environment. In some cases, especially in developing countries such wastes are partially treated or not treated before they are released into the environment. This brings about pollution of soil, water or air depending on the kind of waste generated. Ceramic industries like many other industries are known to generate waste that can cause environmental pollution [1,2,3, 4, 5]. From the extraction of resources till when the final ceramic products emerge, ceramic wastes are generated. Production process leads to the release of emissions into air, water and land [6].

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The emitted particulates are mostly dust particles, lead and fluorine, in addition to other substances such as oxides of sulphur, nitrogen, and carbon, boron, zinc, calcium compounds and heavy metals. All of these contaminate the environment [7, 8]. Particulates have been reported to act as a driver of heavy metals and carry the burden of heavy toxic metals more than coarse fractions [9, 10].

When soil receives heavy metals, it often leads to contamination of the environment and cause damage to human health due to exposure via direct ingestion, inhalation and dermal contact or through the food chain. The risk of metals in edible parts of crops to humans is a matter of concern [10]. Plants absorb metals from the soils hence the pollution of soils with heavy metals is of great concern worldwide due to the potential risk to the environment and as well as human health [11]. Sanfeliu *et al.*, [12] have reported increase in the concentration of particles in the air from the production processes and the storage, handling and transport of raw materials. Greater impact on the levels of heavy metals as a result of particle emissions from the manufacture of pigments, frits and enamels have also been reported [13]. The deposit of heavy metal on plants growing in rooftop gardens in Seoul is said to be due to Asian dust wind which contains various heavy metal [14]. According to Lee *et al.*,, [15] and Kim *et al.*, [16], Asian dust contains heavy metals originating from the desert soil and from the industrial complexes where they are generated. These heavy metals generated can be absorbed by plants from airborne deposits on the parts of the plants exposed to the air from the polluted environments [17]. Food crop and plants can also be contaminated by heavy metals absorbed on the plant leaf surface sourced from atmospheric dust [14]. Chmielewska *et al.*, [18] have reported that heavy metal emission to atmosphere by anthropogenic activities is up to several times higher than their natural emissions. The uptake and accumulation of heavy metals by food crops and vegetables via root system is well documented [19]. However, like plant roots, the aerial organs of plants such as fruits, flowers and leaves can also absorb heavy metals [20]. Reports of previous studies have indicated that plants and vegetables growing near smelters show high foliar level of heavy metals [21, 22]. Hence the concentration of heavy metals in foliar plant organs is often used to describe environmental risk assessment studies as indices of atmospheric pollution load [23-25]. This study was carried out to determine the level of heavy metals (Cd, Mn, Ni and Pb) in soils and in some common food crops around the vicinity of a major ceramics company in Kogi State, Nigeria. Data generated will be important to highlight the potential health risk

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and also serve as baseline data to compare after a prolong period (years) when multivariate analysis will be carried out.

MATERIALS AND METHODS

Description of study area

The Ceramic Company is in Ajaokuta along the Anyigba- Lokoja highway little distance from river Niger. Ajaokuta is on Latitude 07^0 31′ 40.6″ N Longitude 06^0 40′ 24.8″ E. On either side of the company are farm lands with food crops. Food crops are mainly cassava and maize. The characteristic of the soil is ultisol and sandy loam. It lies within the savannah belt. The topography is underlain by igneous and metamorphic rocks belonging to the basement complex composed of granite, miccshists, gneisses and metal sediment which are igneous and metamorphic.

Collection of soil samples

Soil samples were taken randomly at certain distance (100 m, 200 m, 300 m and 400 m).Following a systematic sampling, ten sub subsamples were collected within an area of 10 m by 10 m. The area was divided into 10 sub plots and two soil samples were collected with a stainless steel hand auger sampler at each of the depths of 0–15 and 15–30 cm in each of the subplots. The 20 soil samples each from each depth from each plot were then pooled to make a representative composite soil sample [26]. Samples were dried at ambient temperature, ground and sieved with a 2 mm mesh and kept in polyethylene packages till analysis. Soil pH was measured in H_20(soil:water = 1:1) suspension electrometrically in duplicate [27]. The mechanical properties analysis was carried out as describedby Gee and Bauder [28]. Organic carbon (OC) of dry soil samples were determined by the Walkley–Black method [29]. The heavy metals in soil were extracted using aqua regia in 3:1 (HCl: HNO_3) and heated until no more brown fumes was observed. Then added 5ml of $HClO_4$and heated until about 2 ml was left. The solution was filteredusing a Whatman filter paper no. 42and made up to mark of 20 ml standard flaskand the digestwere determined for Cd, Mn, Ni and Pb byatomic absorption spectrophotometry.(AAS Buck 210 VGP Model).

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Sampling and sample analysis

The leaf of cassava (*Manihot utilisima* Crantz) and maize (*Zea mays*L) that were available food crop samples were taken simultaneously along with the soil samples [26]. The sampled leaves were washed with distilled water and spread out for drying at ambient temperature. Air-dried samples were ground and sieved with a 2 mm mesh and stored at ambient temperature in polyethylenebags till analysis. Extraction of

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crop samples was carried out using a mixture of HNO_3:$HClO_4$ (3:1) as described [30]. The digest were determined as in soil.

Quality assurance and statistical analysis

Duplicates samples were analysed all through. Porcelain mortar and pestle was used to ground each sample. All glassware used was thoroughly washed with Teepol. This was followed by soaking them in 2 M nitric acid overnight and rinsed with de-ionised water. Analar R grade salts were used to prepare stock standard solutions for each of the studied metals. Working standards as dilute aliquots were made from the stock solutions. Freshly prepared reagents were first standardized to confirm their actual strength. The chemicals used were also of analytical grade and reagent blanks were used in all analyses to check reagent impurities. A sample blank digestion was also prepared after every 10 samples. To ensure accuracy and precision of the experimental procedure recovery study for the heavy metals determined was carried out. Average recoveries obtained were acceptable at 82 ± 17 to 102 ± 19%. Data obtained were subjected to analysis of variance using the general linear models. All statistical calculations were performed with SPSS 17.0 for Windows.

Index of geoaccumulation

The extent of contamination level of each heavy metal in the soil was measured using the index of geo-accumulation (Igeo) of metals in soils.

$$Geoaccumulation = Log_2\left[\frac{C_n}{1.5 \times B_n}\right] \quad [31]$$

here $C_n$is the determined concentrationof the examined metal in the soil and $B_n$is the geochemicalbackground concentration of the same metal. Factor1.5 is the background matrix correction factor. Igeo of metals in soils as an important tool often used to measure the contamination status of the soils depending on the range, from uncontaminated, slightly contaminated or extremely contaminated.

Uptake factor

The Uptake factor (UF) of heavy metals from soils to crops was calculated as follows:

$$UF = \frac{metal\ concentration\ in\ soil\ on\ dry\ weight\ basis}{metal\ concentration\ in\ crop\ extract}$$

The soil-to-plant uptake factor, can also be called accumulation factor, transfer factors or concentration factor, is seen as an index for evaluating the uptake potential of a metal from soil to plant [33].

Daily intake of metals (DIM)

The daily intake of metals from plant sources was calculated as follows:

$$DIM = \frac{C_{metal} \times C_{factors} \times C_{food\ intake}}{BW_{average\ weight}} \quad [34]$$

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Where C_{metal} is the concentration of metal in food crop, C_{factor} is the conversion factor (0.085), $C_{food\ intake}$ is the average daily intake of food crop (0.345 kg/person) and $BW_{weight\ average}$ was taken as 60 kg for adult from. The average daily intake of cassava produce (ojeabacha) was obtained through a survey that include taking body weights of 100 adults (males and females) to arrive at average weight of 60 kg were asked for their daily intake of ojeabacha.

Health risk index (HRI)

Human health risk from consumption food crops around Ceramics Company was estimated by HRI. HRI indicates the ratio of the daily intake of metals (DIM) to the Reference dose (RfD) as described [34].

$$HRI = \frac{DIM}{RfD} \qquad [34]$$

The RfD values for Ni, Mn and Pb were 0.02, 0.033 and 0.004, mg/kg^{-1} day^{-1}, respectively [35-37].

RESULTS AND DISCUSSION

Soils physicochemical properties

The characteristics of the soil physicochemical properties are given in Table 1. The soil pH indicates that the soil is mainly acidic. Soil acidity increased slightly as you move further from the ceramic complex. The increase in acidity may be due to the effect of the settling down of dust particulates from the company particularly at a distance of 300 m with average pH value of 2.88±0.18. The pH range of 2.88 to 4.99 recorded in this study area is lower compared to values 5.59 to 6.90 reported for farmland soil in Kogi State [38]. Solubility of heavy metals in soils increases when the pH of the soil is low and this enhances the plant uptake and accumulation potential and eventually it becomes a threat to human health [39, 33]. Other factor responsible for increase in soil acidity has also been attributed to intensive farming practices [40, 41]. Overall averages of clay and silt fraction of the soil are 9.8±1.5% and 13.5±1.5% respectively. The soil in this area was sandy-silt in classification. The differences in the result for the topsoil (0-15cm) and subsoil (15-30cm) is not significant ($p>0.05$).

Heavy metal level in agricultural soil

The concentration of Cd, Mn, Ni and Pb determined in soil of the area studied at various distance (100 m, 200 m, 300 m, 400 m) from the company site is shown in Fig 1. Result shows that the concentration of metals within 100m from the company was higher. The concentrations of the metals are in the following order: Pb > Mn > Ni > Cd at 100m. The concentration of lead decreases as the distance

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Table 1: Physicochemical properties of soil

Properties	Depth (cm)	Distance (m)				Overall	
		100	200	300	400		
		Mean±SD	Mean±SD	Mean±SD	Mean	Mean(SD)	Range
pH	0-15	4.06±0.07	4.99±1.39	2.88±0.16	3.26±0.84	3.80±0.93	2.60- 6.20
	15-30	4.38±0.69	5.46±1.2	2.59±0.26	3,28±1.8	3.9±1.5	
OC (%)	0-15	1.71±0.58	1.70±0.42	1.02±0.17	0.95±0.10	1.35±0.42	1.00-2.40
	15-30	2.39±1.9	1.54±0.28	1.46±0.56	0.89±0.01	1.57±0.59	
Sand (%)	0-15	76.8±0.14	76.4±0.76	76.9±0.08	76.9±1.30	76.7±0.39	76.2-76.9
	15-30	76.9	76.8±0.14	76.6±0.44	76.5±±0.51	76.7±0.31	
Silt (%)	0-15	15.5±0.85	13.7±5.0	12.9±4.3	11.9±1.3	13.5±1.5	5.92-16.1
	15-30	10.4±6.4	13.1±4.2	9.22±3.8	6.28±.31	9.8±4.2	
Clay (%)	0-15	7.70±0.71	10.2±4.2	12.2±1.4	11.2	9.8±1.5	7.20-17.2
	15-30	7.700.70	10.2±4.2	14.2±4.2	17.2	12.2±4.5	

from the company increases. This trend was observed also for the other metals. The pattern of metal concentration at 200 m is Ni > Mn >Pb > Cd, at 300 m is Ni >Pb > Mn >Cd while at 400 m the pattern is the same as in 200m. The recorded concentration of Pb was the highest among the metals determined while the metal with lowest concentration was Cd. The level of Pb varies widely as concentration ranged from 1.00 to 107.6

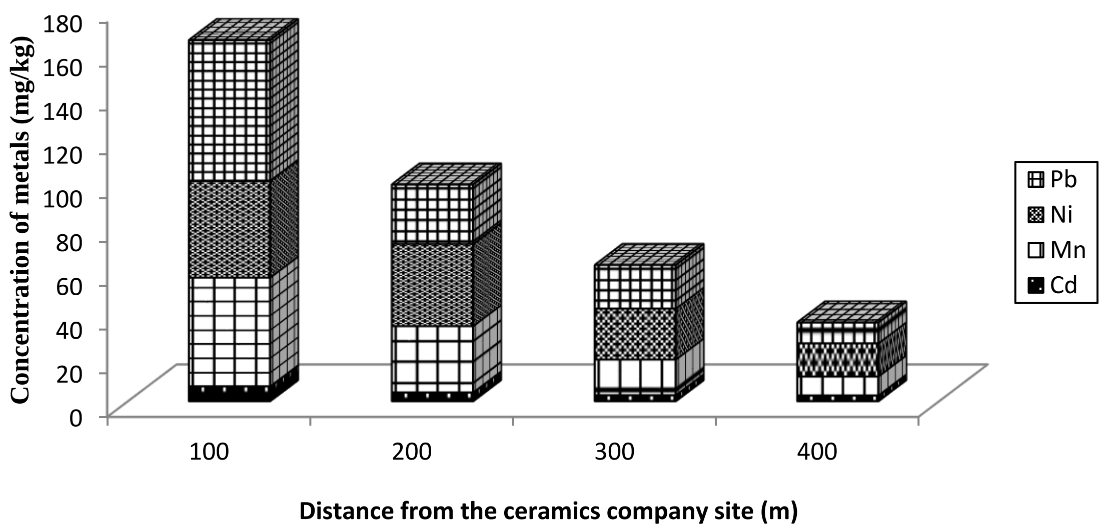

Fig 1: Average concentration of metals in top soil at each sampled distance

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mg/kg with average value of 62.1 mg/kg (Table 2). Although overall average concentration of Pb was the highest, however, the average value obtained was within Canadian regulated limits of 70 mg/kg [42] and

European Union regulated limits of 300 mg/kg [43] for agricultural soils (Table 2). The range of result obtained shows that the area of 100 m from the site of the company (Fig 1) had highest value of 107.6 mg/kg and was above the permissible limits of 70 mg/kg as given by the Canadian regulated limits. This may suggest that 100 m distance is the closest point source of possible pollution. The range of values of this study (1.00 to 107.6 mg/kg) is significantly higher compared to range of 7.7 to 22 mg/kg of Pb levels of agricultural soil in the vicinity of the ceramic industrial site, Niger State Nigeria as reported [44].

Although Cd level was the lowest among the heavy metals determined, however, all values obtained were above the 1.4 mg/kg as

heavy metals resulting from ceramics industry has been reported [45].

recommended by Canadian regulated limits. Increased in soil Cd value in a southeastern China town of Taihu as result a background concentration of 0.11 mg/kg for Cd has been recorded [46]. They inferred that the soil cadmium pollution in the Chinese town may be due to the region's prosperous ceramic industry. In ceramics industrial areas in Spain, various degree of Cd soil pollution has been reported ranging from light pollution in Onda to medium pollution in Alcora, and extreme pollution in Castellón [47]. Cadmium level obtained in this study ranged from 1.00 to 8.25 mg/kg (Table 2). Cadmium level in soils in this study could be attributed to anthropogenic activity resulting from the ceramics industry prosperity. Earlier work by [38] in farmland soil in Kogi State has reported a lower mean value of 0.60 mg/kg for Cd compared to 4.00 mg/kg of this study. This finding is in line with the report of Liao *et al.*, [46] of increase Cd concentration in soil attributed to ceramic industry.

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Table 2: Overall heavy metal content in soil (mg/kg)

Properties	Depth (cm)	Range	Median	Mean	SD	Regulated limits (mg/kg) CCME [42]	EU [43]
Cd	0-15	1.00-8.25	4.38	4.00	2.40	1.4	130
	15-30	0.01-8.00	4.13	3.90	2.90		
Mn	0-15	3.75-62.00	23.9	26.2	18.1	-	-
	15-30	1.25-48.50	31.0	28.2	16.5		
Ni	0-15	11.0-46.30	30.9	30.0	12.6	50	75
	15-30	5.25-58.00	33.0	35.4	19.2		
Pb	0-15	5.50-101.20	22.9	30.2	29.7	70	300
	15-30	1.00-107.60	48.6	62.1	53.0		

Although increased Cd level can also be attributed to widespread intensive use of organic and especially mineral fertilizers [48], however, the increase in Cd level of this study may not be attributed to increase use of fertilizer as most of the farmers in this area attested to non use of fertilizer as they have no money to get fertilizers and government has not given them the opportunity to acquire them since they are very expensive. Pb and Cd have been reported as major pollutants from ceramics industry [49] and Liao,*et al.*,[46] in their investigation of the production of ceramic products reported soil contamination by cadmium in area where ceramic factory operates. The level of Cd therefore should be of concern because if the form in which it is present is in the exchangeable, it will become easily available to food crops. The average concentration (30.0 mg/kg) of Ni was within Canadian Regulated Limits of 50 mg/kg [42] and European Union regulated limits of 75 mg/kg [43]. The obtained Ni mean value of 30.9 mg/kg is higher than the value of 2.1 mg/kg reported [44] in similar work carried out in Niger State Nigeria and the difference is significant ($p<0.05$.) The size and production output of this company may have been a major contributing factor. A large number of ceramic manufactures has been held responsible for the high levels of atmospheric Zn, Pb and As in Chancheng District in Chinahence the suggestion that a control policy should be in place for heavy metals such as Cd, Pb, Zn, and Cu [50]. Because of the essential nature of Mn in the food chain, there has not been any regulated limit for Mn. Nickel (Ni) is also considered as essential element. The observed result as given in Fig 3 shows a decrease in heavy metal concentration as distance from point source

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increases. Similar observation has been reported [51].

Heavy metals level in leaves of food crops

The average content of metals determined Cd, Mn, Ni and Pb in leaves of maize and cassava are given in Fig 2 and Fig 3. The concentration of metals decreases with increase in distance from the pollution point source. The order of metal concentration was Mn> Pb> Ni in the leaves of maize while in cassava the order was Mn >Ni >Pb. Cadmium was below detection limit in both food crops. The non detection of Cd in the leaves of maize and cassava could be as a result of the form in which it is available in the soil and this may have possibly influence its availability to crops. It could also be as result of the response by different crops to heavy metal accumulation as [52] reported in a study that plants respond differently to heavy metal accumulation. Mn ranged from 10.5 mg/kg to 20.5 mg/kg. The value (20.5 mg/kg) at 100 m the closest point of sampling to the ceramics complex was twice the value (10.5 mg/kg) at 400 m away. This trend was

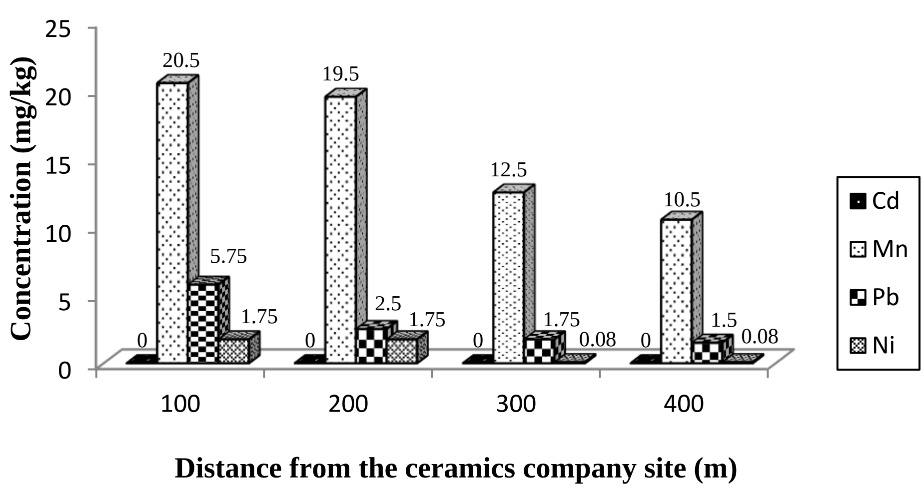

Fig 2: Level of metals in leaves of maize

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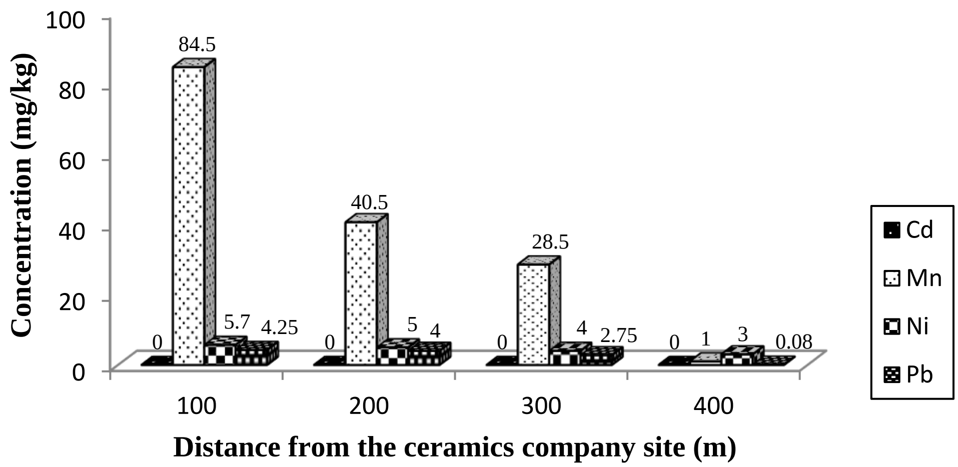

Fig 3: Level of metals in leaves of cassava

observed for the other metals except Cd that was below detection limit. The most dominant metal was Mn. The level of Mn at 100 m and 200m in cassava leaves is significantly higher than the level in maize. The Mn average level of 84.5 mg/kg recorded at 100 m is considered to be high in food crops. The 84.5 mg/kg Mn concentration is in excess of the threshold micronutrient level required in animal feeds of 70 mg/kg [53, 54]. Clemente *et al.,* [54] have earlier observed that concentrations of Mn higher than 60 mg/kg in grape and pepper can be considered high in plants.The level of Ni ranged from 0.08 mg/kg to 1.75 mg/kg in the leaves of maize. Corresponding level in cassava leaves ranged from 3.00 mg/kg to 5.70 mg/kg. The observed level of Pb ranged from 1.50 mg/kg to 5.75 mg/kg and 0.08 mg/kg to 4.25 mg /kg for maize and cassava leaves respectively. The acceptable permissible limits of Ni (10 mg /kg) and Pb (9mg /kg)for food were stipulated by SEPA and FAO/WHO [55, 56] in their capacity as regulatory bodies. The national environmental quality standard range of Ni has also been given as 1-5 mg/kg [57]. The average concentration of Ni and Pb therefore is within permissible limit. However, effort should be in place for continuous monitoring since it has been reported that heavy metal pollution changes with time, especially with metals like Cu and Pb [58, 59].

Geo-accumulation (Igeo) of metals in soils

The result of the Igeo of metals in soils as calculated according to Muller [31] is given in Table 3. Employing the Igeo classification,

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the sequence of heavy metal contamination in soil is Cd> Pb > Ni. Result indicated that the soil is slightly polluted. The contamination level at distance of 100 m is dominant for the three metals. That metal concentration varies with age, the concentration of Cd and Pb in this study should be monitored frequently and a control measure put in place such that their level will not pose health risk with time.

Uptake factor of metals into crops

Soil–crop uptake factors revealed that accumulation of metals determined into maize and cassava leaves investigated were low except for Mn in cassava leaves (Table 4). The order of UF for these metals is Mn> Pb> Ni. This gave an indication that Mn was the most bio-available. Giving the fact that in formulation of feed for animals there is permissible limit for the level of Mn therefore makes the leaves of cassava and maize in this area under study unsafe for such purpose.

Human exposure through consumption of food crops with metals

The daily intake of metal value for adult through the food crop consumption ranged from 4.9 x 10^{-5} to 0.04, 0.001 to 0.003, and 3.9 x10^{-5} to 0.002 mg/kg $person^{-1}$ for Mn, Ni and Pb respectively as given in Fig 4. DIM was not calculated for Cd since it was below detection limit in food crops in this study. Heavy metal DIM pattern were Mn>Ni>Pb. The uptake of heavy metals by food crops has a direct bearing with potential toxicity in human. The toxicity is dependent on the daily intake [60, 61].

Table 3: Geo-accumulation(Igeo) of metals in soils

Sample Distance (m)	Cd	Mn	Ni	Pb
100	0.85	-	0.49	0.85
200	0.62	-	0.42	0.47
300	0.46	-	0.21	0.34
400	0.44	-	0.02	0.02

I_{geo} classification: $I_{geo} \leq 0$, class 0, unpolluted,

$0 \leq I_{geo} \leq 1$, class 1, from unpolluted to slightly polluted,

$1 < I_{geo} \leq 2$, class 2, moderately polluted,

$2 < I_{geo} \leq 3$, class 3, from moderately polluted to strongly polluted,

$3 < I_{geo} \leq 4$, strongly polluted,

$4 < I_{geo} \leq 5$, class 5, from strongly to extremely

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Table 4 Uptake factor of metals into crops

Food crop leaves	Cd	Mn	Ni	Pb
Maize (n=24)	-	0.64	0.02	0.13
Cassava (n=24)	-	1.42	0.09	0.23

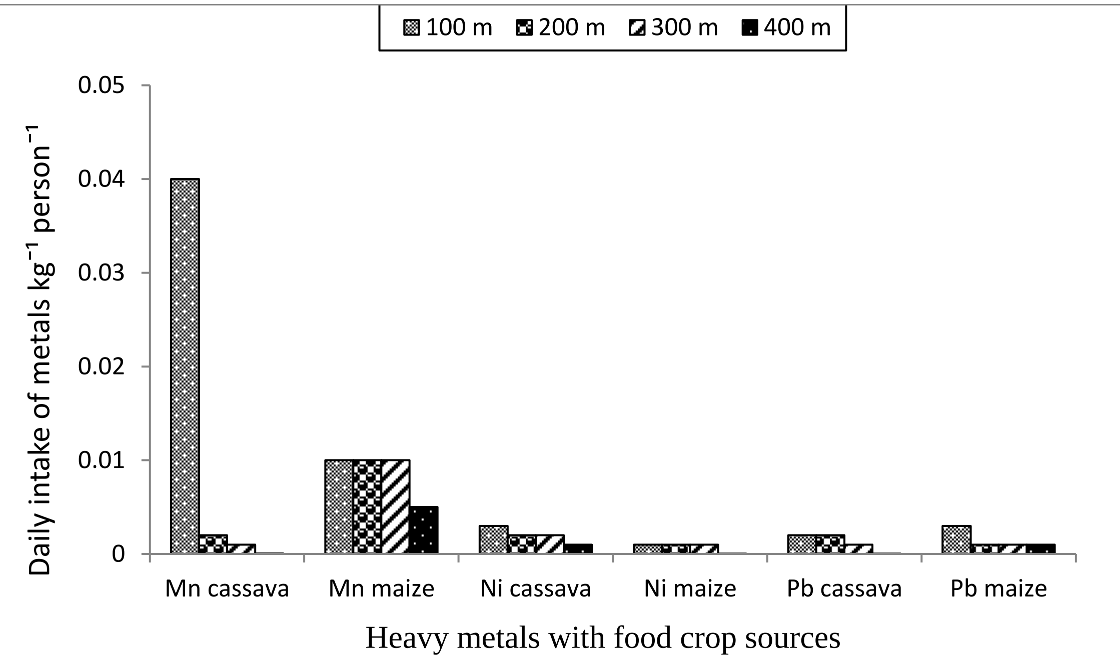

Fig 4: Daily intake of metal through consumption of food crops by adults in area of study

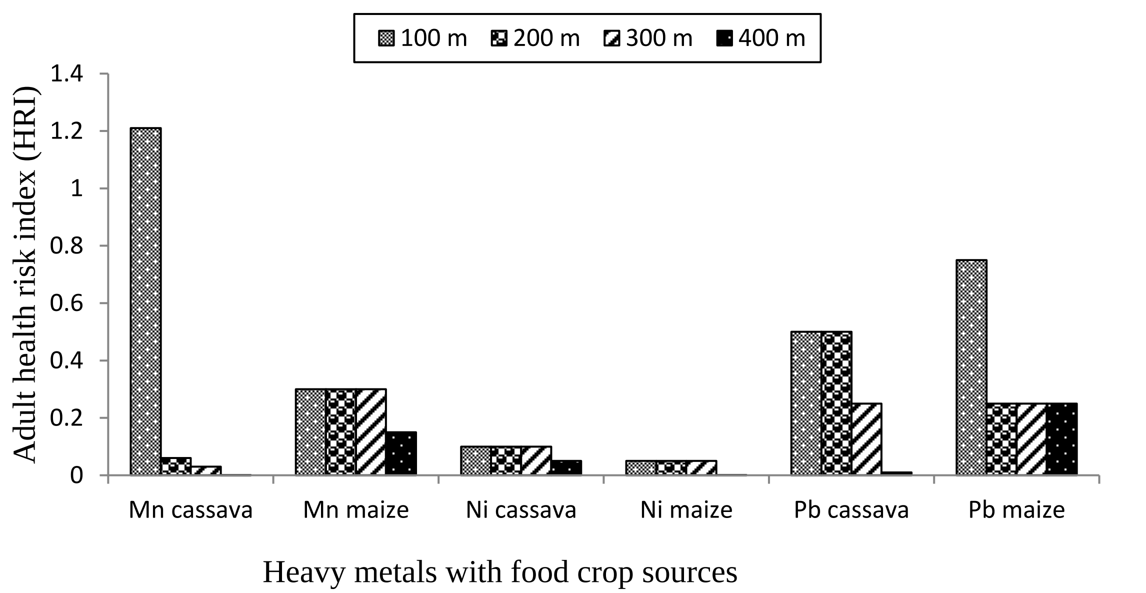

Fig 5 : Each food crop health risk index to adulth through food crops consumption

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The accumulation of heavy metals in human therefore increases as the rate of food crop intake increases and vice versa [62]. In the assessment, the HRI >1 for any heavy metals in food crops pose health risk but if HRI<1 it is safe [63]. In this study daily intake of metals as well as the health risk values indicates that the food crop studied are safe from the heavy metals as HRI < 1 except Mn with HRI > 1 for cassava obtained within 100 m distance from the ceramic company (Fig.5). That at the moment there is no potential health risk of the food crops in the area of study especially with regard to toxic metal like Cd, it should not make the relevant authority concern to relax. Data of this study will serve as baseline for future reference.

CONCLUSION

The study has revealed that the level of Cd in the soil was high and above regulatory standard needed for agricultural soil. All the other metals were within the standard limit. However, the concentration of Pb at 100 m from the pollution point source is worrisome and should be of concern. The level of Mn in leaves at this distance should also be of concern. The non detection of Cd in the leaves of maize and cassava is good considering the toxicity of Cd. Therefore further work especially the speciation of Cd in the soil to see if it is available in the residual phase since it was below detection limit in the leaves of the food crops. The average amounts of the analyzed metals increase in both soils and plant tissues at decreasing distance from the ceramic factory, suggesting that the factory represents a source of metals. The concentrations found are not yet of major concern, however this potential source of contamination deserves attention.

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