Environmental Risk Assessment and Spatial Distribution of the Heavy Metal Contamination in Surface Soils around the Effurun Market

Ogunkeyede, A.O.*, Adebayo, A. A., Raji, S. A. and Amuchi, D.

Department of Environmental Toxicology and Management, College of Science, Federal University of Petroleum Resources, Effurun Delta State, Nigeria

**Corresponding Author*

Abstracts: - **Anthropogenic activities such as vehicular emission, industrial activities and constructions have resulted in an elevated concentration of heavy metals in the surface soils. The metal particles can be free from the surface soil when they are disturbed and re-entrained in the air, which necessitated the need to investigate surface soil at the market environment where adults and children are present on daily basis. This study assesses the concentration of heavy metal pollution, ecological and health risk factors in surface soil at the Effurun market. Samples were collected from eight (8) sampling points such as household material (EMH), fish (EMFs), fish and commodities (EMF-C), Abattoir (EMA 1 & 2), fruit sections (EMF 1 & 2) and lastly, main road (EMMR). The samples were digested and analyzed in triplicate for contents of Lead (Pb), Nickel (Ni), Cadmium (Cd) and Copper (Cu) in the surface soil. The average concentration of the heavy metals in all the sampling points varies from 3.48±2.39 (Cd) to 47.92±28.2 mg/kg (Pb). The highest concentration of Pb and Cu was observed at EMA1 and lowest at EMF. The EMA 1 has the highest concentration of heavy metals, which necessitate the performance of ecological risk and possible health risk on the soil at this sampling point. The EMA 1 gives moderate ecological risk and shows that inhalation was the potential exposure pathway for adults and ingestion pathway for possible health risks to children by the available the heavy metals. The potential non-carcinogenic and carcinogenic analysis showed that both children and adults will be affected. However, adults will be most affected by the non-carcinogenic and carcinogenic metals in the soil. Therefore, people around the Abattoir are susceptible to both non-carcinogenic and carcinogenic diseases unless the policymakers at the Effurun market did something to regulate the activities of the meat sellers at the Abattoir.**

Keywords: **Ecological risk, GIS, Spatial distribution, Heavy metal and Health risk**

I. INTRODUCTION

Soil contamination with heavy metal is a worldwide problem. Although traces of metal present are low in the soil results from weathering processes from the parent rock, while the other sources of heavy metals in the soil are pedogenic and anthropogenic input [1, 2]. Wet and dry atmospheric deposits and hydraulic deposits were means through which heavy metals enter the soil, which in turn influence the society health through food chain and cause a substantial hazard to the environment [3]. It has been reported that metals tend to be present in the parent rock in non-phytoavailable form due to poor solubility properties, thus having very little impact on biota. However, surface soil particle within urban area commonly have elevated concentration of heavy metal and other pollutant due to the effects of human activities, such as vehicular emission, industrial activities and road construction [4]. Urbanization and uncontrolled migration movement to urban cities have resulted in anthropogenic activities that led to the percentage increase of heavy metal in surface soil, which serve as a threat to human health via inhalation, ingestion and dermal contact absorption [5, 6]. Xu *et al.* [6] has shown that metals in the soil particles can enter the human body through inhalation, ingestion and dermal contact, which results in accumulation in adipose tissue, deposit in the circulatory system, causing respiratory and even mortality. It was further stated that the grain size of a particle determines the number of dust particles inhaled, ingested and through dermal contact by humans [7]. Unfortunately, children are exposed to metals at markets, playground and residential area in Nigeria, which might result in ingestion of significant amount of soil between 39 and 270mg/kg as reported by Mugoša and Đurovi [8] due to the typical hand-to-mouth behaviour of age six and below.

Many metals are required in varying quantities in organisms for mineral formation but some are damaging to body organs in man at a certain concentration [9]. Therefore, contamination and environmental risk of metals in surface soil, street dust particles should be investigated in detail because active person typically inhales 10000L to 20000L of air daily [10]. Surface soils that contain heavy metals are the vital source of exposure of children and vulnerable people. There is three main pathway of exposure such as inhalation, ingestion and dermal contact for heavy metals to enter the human body [11]. It was reported that roadside specks of dust with its heavy metals have a high possibility of causing cough/breathing in children and adults during inhalation [12]. The literature reviewed on the Effurun market about heavy metal contamination using ecological and health risk model for surface soil have not been seen in any published work. The aims of this study are to quantify the concentration of heavy metals in the surface soil from Effurun Market, investigate the degree of pollution and daily intake amount of toxic element through surface soil and to present health risk assessment method for heavy metals through exposure pathways for people around the Effurun market.

II. EXPERIMENTAL

Study area background

Uvwie is one of the twenty-five local government area in Delta state and one of the areas under the Urhobo Kingdom. Uvwie is located approximately between 5°31'2.52"N and 5°45'0.22"E. The area shared boundary with Okpe Kingdom in the North, Udu and Ughievwen in the North-West, Agbarho Kingdom in the North-East, Agbarho-Ame in the East, Okere kingdom in the South and Itsekiri in the South-West it is the gateway town for the city of Warri, border town to Osubi Airport and centre of civilization for Urhobo people.

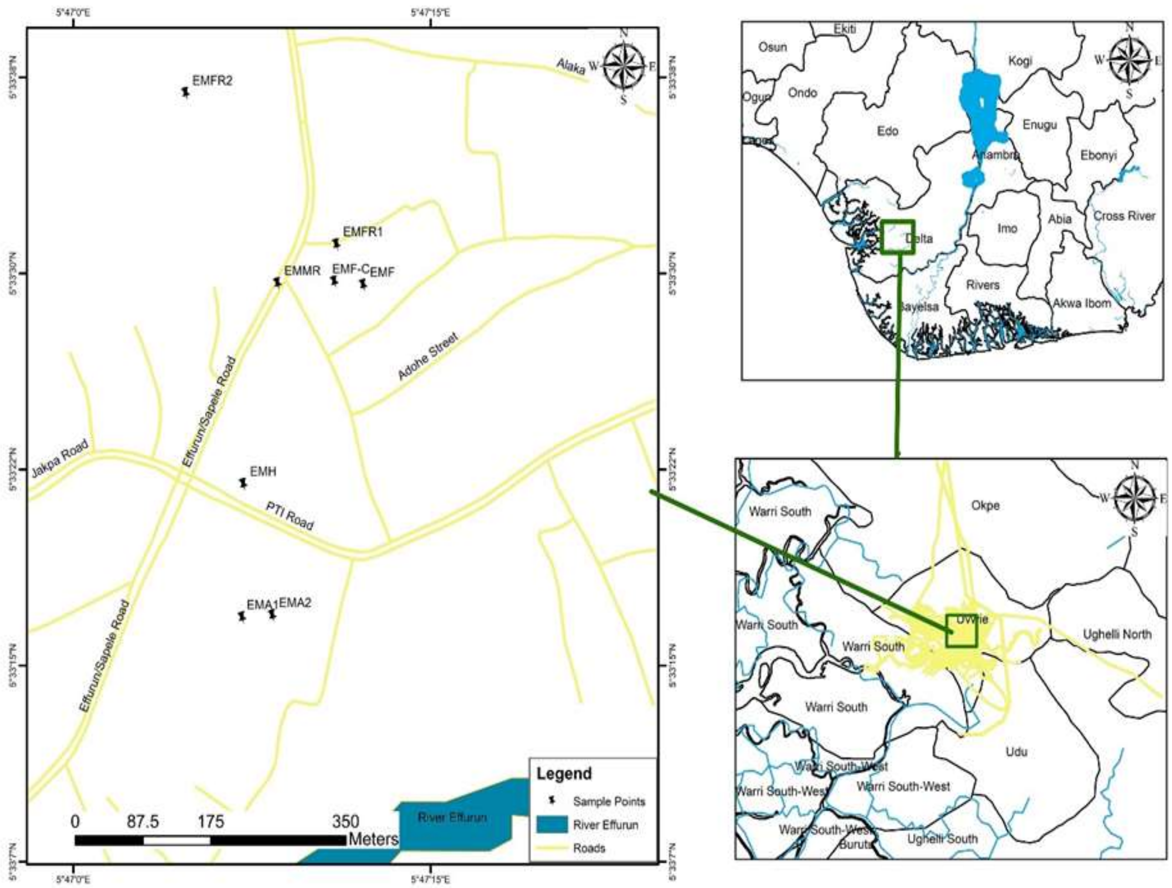

Figure 1: Location and land use type of the study area and sampling point

Uvwie LGA headquarters is Effurun, where the market for this study is located. It is the main market for Urhobo people and it has grown over the years due to urbanization and the population increase to spread from petroleum training institute (PTI) road to Jakpa section and along Warri-Sapele road. The market is systematically grouped in sessions as follows; fruits A & B, fish and commodity, fish, household material, Abattoirs A & B, and the main road (Table 1). Sampling points were obtained with the aid of a global positioning system (GPS) to identify each location (see Table 1).

Table 1: description of the sampling points within the Effurun market

Sampling Point	Code Name	Latitude	Longitude
Household material section	EMH	5°33'13"N	5°47'10"E
Fish section	EMF	5°33'19"N	5°47'14"E
Fish and commodities	EMF-C	5°33'19"N	5°47'13"E
Abattoir A	EMA1	5°33'09"N	5°47'10"E
Abattoir B	EMA2	5°33'09"N	5°47'11"E
Fruit section A	EMFR1	5°33'20"N	5°47'13"E
Fruit section B	EMFR2	5°33'25"N	5°47'08"E
Main road	EMMR	5°33'19"N	5°47'11"E
Control soil	Control	5°34'01"N	5°50'26"E

Sampling and analytical method

A total of 8 surface soils were collected from the market. At each sampling points, samples were collected by sweeping with a broom and clean tray on the roadsides and some sections of the market, while surface soils were collected at other points. The three replicates were analyzed to obtain the mean values and standard deviation of the concentration of selected heavy metals in the soil. The actual latitude and longitude coordinates of each sampling site were recorded by a global positioning system (GPS). Soil samples were air-dried, homogenized and sieved through 2mm mesh and stored in a polyethene bags before analysis at ambient temperature. The soil extractable form of Pb, Cd, Ni and Cu forms was determined after extraction with 20 ml aqua regia mixture (HCl and HNO_3 in ratio 3:1) and 10 ml of 30 % hydrogen peroxide (H_2O_2) for 2 hours on the gentle heating to avoid loss of analytes. After cooling of acid-extractable metal solution, samples were filtered through Whatman No. 45 filter paper into a 100 ml standard flask. The filtrate was diluted to 100 ml with distilled water [13]. The metal concentrations were determined with Atomic Absorption Spectrometry in three replicates to minimize error and cross contamination was avoided. The mean value and standard deviation of the results were obtained from three replicate of each sampling points. The soil organic carbon was measured by the wet oxidation method of Walkley and black and the soil pH was determined in 1:1 water-to-soil. The Electrical conductivity was measured in saturation extract of soils using an EC meter.

Statistical analysis

Descriptive statistical parameters were calculated using XLSTAT 2018.6 excel add-in. Correlations between heavy metals were assessed by using Pearson correlation coefficient. Other exploratory analysis of datas were performed with cluster and the biplot to understand the relationship between variables via multivariate techniques used to analyze data tables and extract important information for later representation as a set of new orthogonal variables. The source contributions of the pollutant metals were further established by using quantification of anthropogenic concentration (QAC) formula, which employs the concentration of the control sample as background concentration that represents the lithogenic metal [14]. The QAC is calculated as shown below.

QAC = ((x – xc)/x) X 100 Equation 1.

Where x = mean concentration of metal in each sampling point, xc = mean concentration of the control soil sample.

Geostatistical analysis

The best approach for spatially mapping and analyzing distributed phenomenon such as heavy metals within a small area is the spatial numerical analysis method known as IDW (Inverse Distance Weighted). IDW is a spatial interpolation technique that perfectly relates and implements the first law of geography which states that closer phenomenon is more related than those farther apart. Based on this hypothesis, IDW substantially assumed that the degree of correlations and similarities between neighbours is proportional to the spatial between them that can be defined as a distance reverse function of every point from neighbouring points. It is very germane to consider expression of the radius of known quantities to be mapped with respect to the power of the distance reverse function to be used as weights for the numeral interpolation. A key consideration herein is the sufficiency of the number of sampling points. However, this accuracy is determined to a large extent by the power of the inverse distance interpolator parameter *P* (15& 16).

Succinctly, IDW is expressed as:

$$Z_0 = \frac{\sum_{i=1}^{N} z_i . d_i^{-n}}{\sum_{i=1}^{N} d_i^{-n}} \quad \text{Equation 2}$$

where:

Z_0 = the estimation value of variable *z* in point *I*.

z_i = the sample value in point *I*.

d_i = the distance of sample point to estimated point.

N = the coefficient that determines weigh based on a distance.

n = the total number of predictions for each validation case.

This procedure was implemented across the surface of the study area using ArcGIS 10.5 software package. Based on the result from the IDW, kriging was chosen as the best evaluator of interpolation of the contamination factor and the degree of contamination factor of the present study.

Assessment of soil ecological risk

The evaluation of the metals in the surface soil gives the magnitude of pollution/contamination of the surface soil and possible ecological and health risk associated with their presence in the soil. The soil contamination was assessed based on the following parameters: contamination factor (CF), ecological risk (Er), potential ecological risk index (RI), index of geo-accumulation (Igeo) and health risk assessment model (8). The AAS results show the concentration of the metals analytes in the soil, while these assessment models described the soil quality and potential ecological risk of metals in the soil. The assessment method used in this study was proposed by Hakanson to assess the potential ecological and environmental effects with the toxicological behaviour of heavy metal contaminants (17). This assessment process quantitatively isolates the extent of potential hazards and reveals the comprehensive influence of multiple contaminants in a particular environment. It has been reported as the most recent scientific and comprehensive approach to assessing heavy metal contamination in soils (17, 18 &19). The status of quality or contamination of a contaminated site can be defined by comparing the result with the categories specified for each index as shown in Tables 2.

Table 2 Classification of ecological tools to assess the properties of contamination soil (Mugoša and Đurovi., 2016)

CF	Extent of contamination	Er	Category	RI	Category	I-geo	Class	Soil quality
CF< 1	Low contamination	< 40	Low	< 150	Low risk	I-geo ≤ 0	0	Unpolluted
1< CF ≤ 3	Moderate contamination	40 << 80	Moderate	150 ≤ < 300	Moderate risk	0 < I-geo ≤ 1	1	Unpolluted to moderately polluted
3 < CF≤ 6	Considerable contamination	80 << 160	Considerable	300 ≤ < 600	Considerable risk	1< I-geo ≤ 2	2	Moderately polluted
CF>6	Very high contamination	160 << 320	High	≥ 600	Very high risk	2 < I-geo ≤ 3	3	Moderately to strong polluted
		≥ 320	Very high			3 < I-geo ≤ 4	4	Strongly polluted
						4 < I-geo ≤ 5	5	Strongly to extremely polluted
						I-geo > 5	6	Extremely polluted

Contamination factor and degree of contamination factor

The contamination factor is used to evaluate the quality of the soil at the Effurun market. The quality is affected by the impact of anthropogenic activities on the concentration of heavy metals in the soil (20). The degree of contamination factor reveals the comprehensive influence of multiple contaminants in the soil at the Effurun market. The contamination factor is the ratio between the total metal content in the soil (C_s) and normal background concentration levels (C_n). It gives the soil quality or metal enrichment in the soil.

$$CF = \frac{C_s}{C_n} \quad \text{Equation 2}$$

While the degree of contamination of heavy metal in soil is

$$C_d = = \sum CF$$

The ecological risk index and degree of the potential ecological risk index

The ecological risk assesses the heavy metal toxicity and the response of environment in the soil, while the potential ecological risk index (RI) sums the risk factor of all the heavy metals in the soil and explain the underline risk associated with the contaminated site (21). The toxic response factor (Trf) of metals represents the toxicity of particular metal and the sensitivity of environment to contamination; though it could be determined according to the "elements abundance principle" and the "elements release principle" (17). There are varied toxic response factor used in many works of literature but the Trf used for the metals in this study are Cu – 5, Pb – 5, Cd – 30 and Ni – 5 (1, 22 & 23).

$$E_r = T_{rf} \quad \text{Equation 3}$$

$$RI = \Sigma E_r \quad \text{Equation 4}$$

Where, E_r = ecological risk index, T_{rf} = toxic response factor, C_n = concentration of the heavy metal, RI = potential ecological risk index

Geo—accumulation index (I-geo)

This is an index used to measure the accumulation of contaminant in the soil (24, 25). It is possible to compare the level of accumulation elsewhere with the current study due to the use of background concentration and the I-geo can be expressed mathematically as:

$$I\text{-}geo_n = \log (C_n/1.5B_n) \quad \text{Equation 5}$$

where C_n is the measured concentration of analytes and B_n is the background concentration of a sample. The 1.5 factor was used to account for the variation of heavy metals depending on anthropogenic influences on the metal background (26).

Exposure pathway of toxic heavy metals into the body

Surface soil at market area can serve as a sink for heavy metals from anthropogenic activities and long with organics (9). The release of the heavy metal in the surface soil may pose a serious health risk to the human within the market area. According to Gawade *et al*. (11), people can be exposed to toxic heavy metals through a common pathway such as inhalation, ingestion and dermal. It further stated that occupational and ambient air exposure of people by ingestion and inhalation of Cd and Pb were possible, which could result in brain damage (low IQ in children), bone disease (osteomalacia), loss of appetite, fatigue, renal dysfunction, abdominal pain, birth effects, weight loss, hyperactivity, itai itai disease, kidney damage and death at chronic exposure (9 & 10). Therefore, it is of an essence to characterize the possible pathway the Pb and Cd in the surface soil can enter into human within the market. This characterisation requires the use of a risk characterisation tool that models the possible pathway for them to enter the body. There was three pathway established by USEPA (27, 28) to evaluate the most prominent pathway of the toxic heavy metals can enter the human body. Chronic daily intake (mg/kg/day) (Equation 6, 7 & 8) can be used for estimating each route of exposure pathway can be applied because it considered the health risk to children and adult in the market (27; 29). The exposure pathway for adults in the market will be mostly inhalation resulting from wind-blown surface soil dust and dermal contact from products, garbage and other anthropogenic activities while children below the age of 6 will mostly have ingestion as their pathway because of the repetitive hand-to-mouth behaviour and mouthing nonfood item (11).

$$D_{inh} = \frac{Csoil\ x\ InhR \times EF \times ED}{PEF \times BW \times AT} \quad \text{Equation 6}$$

$$D_{ing} = \frac{Csoil\ x\ IngR \times EF \times EDXCF}{BW \times AT} X10^{-6} \quad \text{Equation 7}$$

$$D_{derm} = \frac{Csoil\ x\ SA \times SL \times ABS \times EF \times EDXCF}{BW \times AT} X10^{-6} \quad \text{Equation 8}$$

The pathways formula was used to calculate the non-carcinogenic risk and carcinogenic risk associated with the metals. The non-carcinogenic risk is referred to as Hazard quotient, which is calculated by dividing each equation (Equation 6, 7 & 8) by reference dose (RfD) values (20). The results were compared with risk acceptability for non-carcinogenic health effect; the acceptable values are HQ <1 and it can be assumed that no non-carcinogenic risk is observed and when it is HQ >1, a possible non-carcinogenic risk to human (30). Ni, Pb and Cd carcinogenic properties have been reported many studies and it will be of importance to calculate the cancer risk they pose to both children and adult within the market using the equation below (20).

$$R_{Total} = \sum_{i=1}^{m} \sum_{j=1}^{n} (LADDXSF)_{ij} \quad \text{Equation 9}$$

If the $R_{Total} > 1E-04$ as unacceptable, R_{Total}<1E-06 are not considered to pose a significant health risk and when is no cancer risk R_{Total} is lying between 1E-04 and 1E-06 are generally considered acceptable, depending on the situation and circumstances of exposure (42).

III. RESULTS AND DISCUSSION

The average concentration of heavy metals

The mean soil pH and soil organic carbon (SOC) ranges from 7.40 – 8.90 and 1.40 – 5.03 respectively. The soil samples from the market revealed varying mean concentrations of the four analysed metals (Pb, Cu, Ni and Cd) obtained after triplicate analysis as shown in Table 3. Metal concentration in the range of 17.83 – 112.27 mg/kg Pb; 9.57 – 18.43 mg/kg Ni; 0.13 - 7.69 mg/kg and 3.52 – 156.14 mg/kg Cu in dry soil was observed in the sampling point within the market area. The concentration of all the studied metals at the market was higher compared to the uncontaminated control soil. The concentrations of metals studied in the soil at EMA1 were higher compared to other sampling points except the Cd concentration. The concentration of Pb and Cu in the soil from the road side might be attributed to motor vehicles, which corroborate the QAC and the cluster analysis that they are from similar source and they have anthropogenic source. The EMA 1 metal values were very high because of tyres and other materials the workers at the abattoir used for burning the cows and goats to prepare them for their customer. The results from this current study corroborate with the work of Khan and Kathi (31) report on roadside surface-soil.

Table 3: Heavy metals concentration, soil pH and SOC

location	The concentration of heavy metals (mg/kg)				Soil pH	SOC (%)
	Pb	Ni	Cd	Cu		
EMMR	17.8±0.63	BDL	0.98±0.10	10.7±0.25	7.4	3.8
EMH	60.1±1.49	9.57±0.95	3.79±0.06	4.53±0.18	7.7	3.03
EMFR 1	39.4±0.59	BDL	2.49±0.04	5.53±0.05	6.8	2.03
EMFR 2	31.9±0.66	BDL	7.69±0.19	9.18±0.07	7.7	4.11
EMA 1	112±1.12	18.4±0.84	6.53±0.24	156±1.10	6.4	5.03
EMA 2	52.0±0.75	6.80±0.20	3.48±0.05	60.5±0.05	6.8	4.79
EMF	19.6±0.65	BDL	0.13±0.03	3.52±0.85	8.7	3.67
EMF-C	50.3±1.44	BDL	2.78±0.06	4.26±0.04	8.9	1.4

The percentage of Pb released by vehicles that gets deposited on road side is 25 %, while the remaining fraction of are airborne contaminating areas more remote from the point of its emission. The Pb deposited in the road dust and vehicle traffic at the market surface soil has lesser mobility and they remain in the surface soil. Therefore, it is a risk for children due to two reasons: their typical hand-to-mouth behaviour of ages less than or equal six and past work that revealed that soil ingestion of children while playing might be around 39 - 270 mg/kg (8).

Descriptive Statistical analysis of the heavy metals in the soil samples

The descriptive statistical parameters were used to evaluate the raw data of the heavy metals extracted from the surface soil at the Effurun market. The mean concentration of the samples ranges from 3.48 to 47.92 mg/kg as shown in Table 4. The coefficient of variation (CV) values of the metals ranged from 62.86 to 169.10 %, indicating moderate variations of these metals within the study area. Cu showed the highest CV value of 169.10 %, suggesting that it has the greatest variation among the soil samples with highest probability of being influenced by the anthropogenic factor including burning of tyre at the abattoir section of the market. The CV of all the metals is very high and it can be logically explained that these elements are affected by anthropogenic factors (32).

Table 4. Descriptive statistic parameters of extractable heavy metals at Effurun Market (mg/Kg)

Variable	Sample Mean	Minimum	Maximum	Standard Deviation	CV%	Kurtosis	Skewness
Pb	47.92	17.82	112.27	30.13	62.86	2.89	1.49
Ni	4.35	0.00	18.42	6.82	156.90	1.71	1.52
Cd	3.48	0.12	7.69	2.56	73.62	-0.41	0.54
Cu	31.80	3.52	156.14	53.77	169.10	5.05	2.26
pH	7.550	6.400	8.900	0.899	11.910	-0.991	0.424
SOC (%)	3.483	1.400	5.030	1.270	36.460	-0.662	-0.555
EC	861.250	391.000	1893.000	618.066	71.764	-0.201	1.271

Correlation values among the heavy metals

The correlation analysis is widely used for environmental analysis to check the possible relationships among the metals and other variables such as soil organic carbon (SOC), using Pearson's correlation coefficients as shown in Table 5.

Table 5 Pearson correlation coefficient analysis between metals, soil pH and % SOC in surface soil at Effurun market area

Variables	Pb(mg/kg)	Ni(mg/kg)	Cd(mg/kg)	Cu(mg/kg)	pH	SOC (%)
Pb(mg/kg)	**1**	**0.924**	0.572	**0.859**	-0.507	0.305
Ni(mg/kg)		**1**	0.481	**0.867**	-0.579	0.545
Cd(mg/kg)			**1**	0.484	-0.403	0.381
Cu(mg/kg)				**1**	-0.647	0.652
pH					**1**	-0.537
SOC (%)						**1**

Values in bold are different from 0 with a significance level alpha=0.05

The correlation analysis showed significant ($p<0.05$) correlations with positive correlations between metals from each sampling points as follows: Pb vs. Ni, r = 0.924; Pb vs Cd, r = 0.572; Pb vs Cu, r = 0.859. The Pb correlate with all the metals ($p<0.05$); however, correlation with Ni was the highest. Cu showed remarkable correlation with Pb (0.86) and Ni (0.87), followed by Cd (0.484). The high correlations among the metals reflect that the accumulation of the pollutant may have resulted from anthropogenic activities in the market. Furthermore, SOC correlate with all metals but strong with Pb and Cu as an influencing factor on their concentration in the soil because of the formation of complex stable compounds with metals. The SOC concentration resulted mostly from market organic wastes and aerial particles. It suggested that SOC and the metals are likely to have similar sources (33 & 34). The cluster analysis was used in this current study to identify contamination sources as formally use by (35 & 36). The analysis was performed on metals concentration in the soils by the furthest neighbour linkage method based on the correlation coefficients (Pearson coefficient). The result of the analysis is shown in the dendrogram (Figure 1). The dendrogram is the most important result of cluster analysis. It indicates all the observations and at what level of similarity any two clusters were joined. It is commonly displayed as a tree diagram (Figure 2). The cluster analysis displayed in this current work by dendrogram grouped the observations into three classes. This classification shows similarity in the sources of the observations as shown in Table 6. The Dendrogram confirmed that Pb, Ni, Cu and SOC have similar sources different from Cd and pH. It means that Pb, Ni, Cu and SOC resulted from market wastes or anthropogenic activities.

Table 6: Observations grouping according to class generated from cluster analysis

Observation	Class
Pb(mg/kg)	1
Ni(mg/kg)	1
Cd(mg/kg)	2
Cu(mg/kg)	1
pH	3
SOC (%)	1

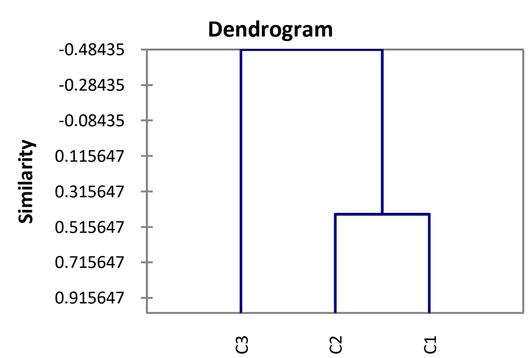

Figure 2. Dendrogram for the heavy metals obtained by furthest neighbour method

Principal component analysis (PCA)

The PCA was used in this current work to indicate the sources of the metals whether they are mixed, lithogenic or anthropogenic sources. Table 5 shows that four factors had an effect on the variables which suggested multiple sources for the metals. However, the scree plot (Figure 2) was able to show that only two factors accounts (Table 6) for most of the total variability in the data.

The Bioplot graph in Figure 3 shows that the Cd observations in all the sampling locations differ from the other metals, which further confirm the dendrogram of the heavy metals that Cd source in the soil is different from other metals due to contribution from lithogenic and anthropogenic sources.

The Pb, Ni, and Cu show that they are strong influence by F1, while Cd was strongly influenced by F2. This suggested that Pb, Ni, Cu had their major source as anthropogenic activities within the Effurun market while Cd might be mixed source (lithogenic and anthropogenic activities). The bioplot in Figure 3 shows that the data appear normal and no extreme outliers are apparent. The data of Pb, Ni, Cu have large positive loadings on factor 1, so this factor describes anthropogenic source has the major activities that led to the concentration of the metals in the surface soil, while Cd has large positive loading on factor 2, which suggested mixed sources that could not be interpreted clearly enough. The PCA analysis has confirmed the result of class shown in the cluster analysis that most metal concentration in the surface soil originated from anthropogenic activities within the Effurun market. Therefore, the ecological risk of metals that are majorly influenced by the anthropogenic activities will be examined.

Table 4 Observations grouping according to class generated from cluster analysis

Observation	Class (c)
Pb	1
Ni	1
Cd	2
Cu	1
pH	3
SOC (%)	1

Table 5. Eigenvalues table for variables

	F1	F2	F3	F4
Eigenvalues	3.781	0.698	0.069	0.035
Variability (%)	63.011	11.641	1.149	0.579
Cumulative %	63.011	74.652	75.801	76.380

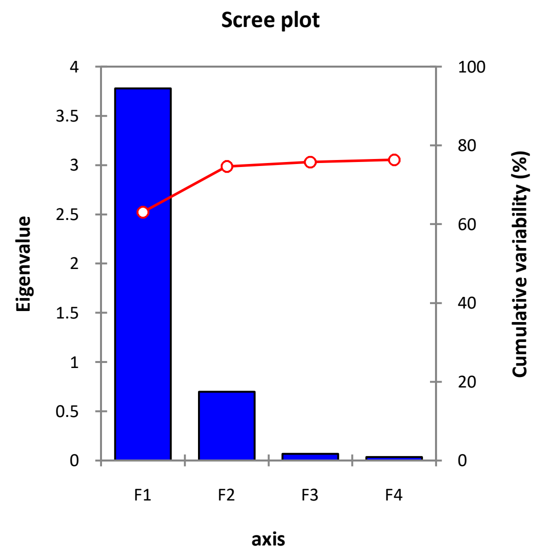

Figure 2: Scree plot showing the number of the factor versus corresponding eigenvalues

Table 6: correlation between variables and factors

	F1	F2
Pb	0.963	-0.102
Ni	0.945	-0.223
Cd	0.680	0.732
Cu	0.925	-0.205

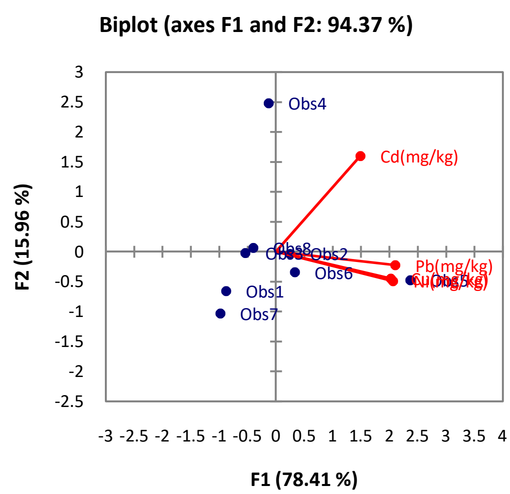

Figure 3. Biplot graph of variables showing data structure

The result of the dendrogram analysis and the Bipolt graph shows that the Cd source contribution is probably differs from other metals and the pH. Therefore, QAC was necessary to confirm percentage contribution from anthropogenic activities on the metal concentration of the surface soil of the market. The QAC result gave 97.4 % anthropogenic contribution See below, which means activities within the market and cars passing the road contribute to the Cd concentration.

QAC = ((3.48 - 0.09)/3.48)*100

= 0.974* 100

= 97.4 %

The metals analysis has shown that their main source in the surface soil of the market is anthropogenic sources. According to Wuana and Okieimen (9), the concentration of metals in the soil has been grouped into target and intervention values as shown in Table 7. Cu has the lowest target value, Ni had the highest value. In this current study, Pb and Cu were the metals above the target values but lower than the intervention level.

Table 7: Metal grouping into target and intervention level (mg/kg)

Variables	Target	Intervention
Pb	35	210
Ni	140	720
Cd	100	380
Cu	0.30	10

However, it is essential to determine the possible ecological and health risk it may pose if the concentrations of these metals are not controlled.

Geoaccumulation index (Igeo)

I-geo values of the heavy metals at each sampling points were displayed in Table 8. The pollution of the sampling points ranged from unpolluted to extremely pollution. The Cd showed significant or extreme pollution in most of the sampling point at EMFs (unpolluted) and EMMR (strong pollution). Pb had values ranging from unpolluted to moderate pollution except EMA 1 that shows extreme pollution. Cu and Ni values can be categorized into same group of unpolluted parameters except EMA1 that is moderately polluted with Cu. Considering all the values of the metals together per each sampling point, EMA 1 can be classified as the most polluted soil sample location within the market.

Table 8: Igeo for surface soil at Effurun market

Location	Pb	Ni	Cd	Cu
EMMR	0.85	0.00	3.28	0.13
EMH	2.86	0.09	12.64	0.05
EMF 1	1.88	0.00	8.31	0.07
EMF 2	1.52	0.00	25.64	0.11
EMA 1	5.35	0.16	21.75	1.89
EMA 2	2.48	0.06	11.61	0.73
EMFs	0.93	0.00	0.42	0.04
EMF-C	2.40	0.00	9.28	0.05

Spatial structure of the extractable heavy metals

The experimental semivariogram of soil heavy metal concentrations could be fitted with an exponential model for Cu and Ni, pentaspherical for Cd and Pb for Gaussian model (Table 9). The spatial dependency degree is calculated by dividing nugget effect by sill (C0+C). The ratios are very low and it means weak spatial dependency of variable (37,38 & 39). The weak spatial dependency can be due to significant influence of external factors at the market (34). The major external influences are traffic and other anthropogenic activities. Based on Table 8, it is clearly seen that Cu had the highest nugget/still ratio, which verified that Cu has been affected by anthropogenic activities. The result of mean concentration of Pb, positive marked correlation ($p< 0.05$) with Cu and the cluster analysis of the two metals infer that they have similar source. The nugget/sill of all the metals was approximately similar to each other, revealing a weak spatial dependency.

Table 9. Variogram analysis for the parameters studied

Parameters	Model	Nugget C0	Sill (C0+C)	DSD [C0/(C0+C)]*100	Range (m)	RMS	R2
Pb	Gaussian	466.901	3697.644	12.627	1520.101	27.719	0.006
Ni	Exponential	8.983	88.313	10.171	1520.101	5.243	0.060
Cd	Pentaspherical	1.187	8.915	13.318	580.624	2.723	0.255
Cu	Exponential	786.147	5437.664	14.457	1520.101	48.893	0.148

Ecological risk assessment of heavy metals in the surface soils

Surface soils at the Effurun market are important exposure sources of heavy metal to people, especially the children, vulnerable adults, cleaners and other members of society represent the customers and sellers. The risks associated with the heavy metals will be examined using GIS map for contamination factor and ecological risk to interpret the possible potential ecological impact because the QAC and descriptive analysis of the metals confirmed that anthropogenic sources is the major pollution source i.e. possibly from fine aerial particle and garbage generated within the Effurun market.

Contamination factors (CF) using spatial analysis of GIS

GIS has been used for environmental studies in past researches performed because of its potential to understand spatial distribution of heavy metals (40). The spatial distribution and variability of metal concentrations were interpolated with ordinary Kriging method because it is a better tool to assess the possible sources of enrichment or contamination factor and Ecological risk at hot sport (41). The contamination factors of various metals in the soils from sampling points were presented in the geochemical map in Figure 4. Based on the contamination factor categories, all sampling points vary from considerable to very high contamination for Pb, low to moderate for both Ni & Cd and low to high contamination for Cu. From the map, it shows that EMA 1 and EMA 2 were very high contaminated with Pb and Cu, although the other sampling points were considerably contaminated with Pb but low contamination for Cu. In addition, EMA 1 and EMA 2 were moderately contaminated with Ni and Cd.

Ecological risk (Er) and potential ecological risk

The ecological risk in this study evaluates the impact of the result of exposure metals in the surface soil as presented in Figure 5. The pollution of the soil with heavy metals in all the sampling point shows that it varied from low to moderate risk. The Pb and Ni had similar pollution range of low risk, which agrees with the strong correlation value of 0.924, which further confirmed that they are probably from similar source of anthropogenic activities. The Cd and Cu concentration in the soil reaches moderate risk. The result highlighted possible pollution concern associated with Cd due to fossil fuel burning within the market and vehicles passing the road through the market. The potential ecological risk index of the sampling points were generally low except EMA 1 (RI = 198.18), which has the highest value representing the moderate ecological risk to the environment (see Table 10).

Table 10: Potential ecological risk of metals

Sampling points	RI
EMMR	23.24
EMH	73.15
EMF 1	46.31
EMF 2	95.44
EMA 1	198.18
EMA 2	90.19
EMFs	12.40
EMF-C	53.97

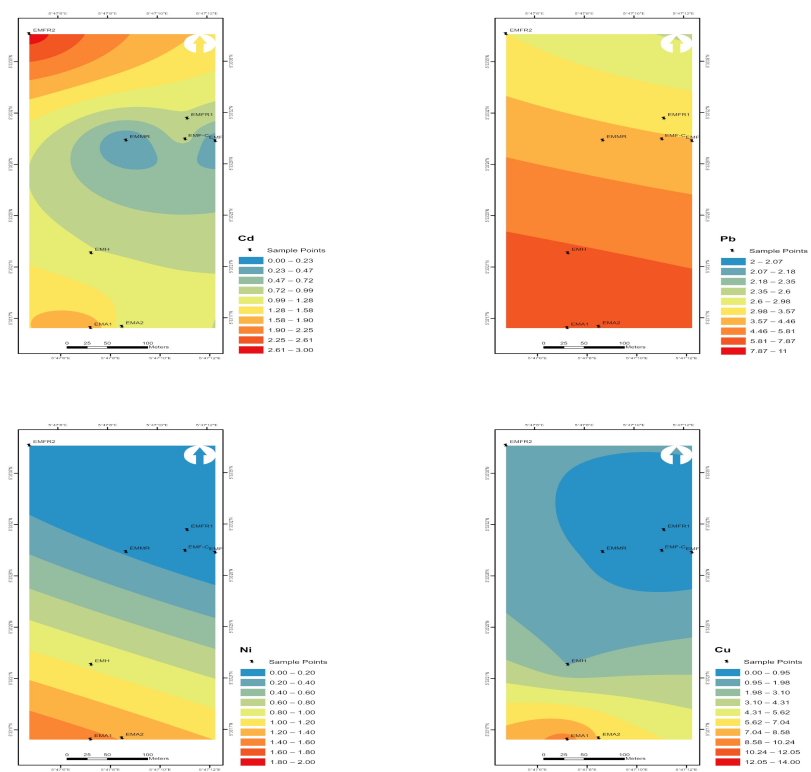

Figure 4. Spatial variability of contamination factors of extractable heavy metals in all the sampling point within the Effurun market.

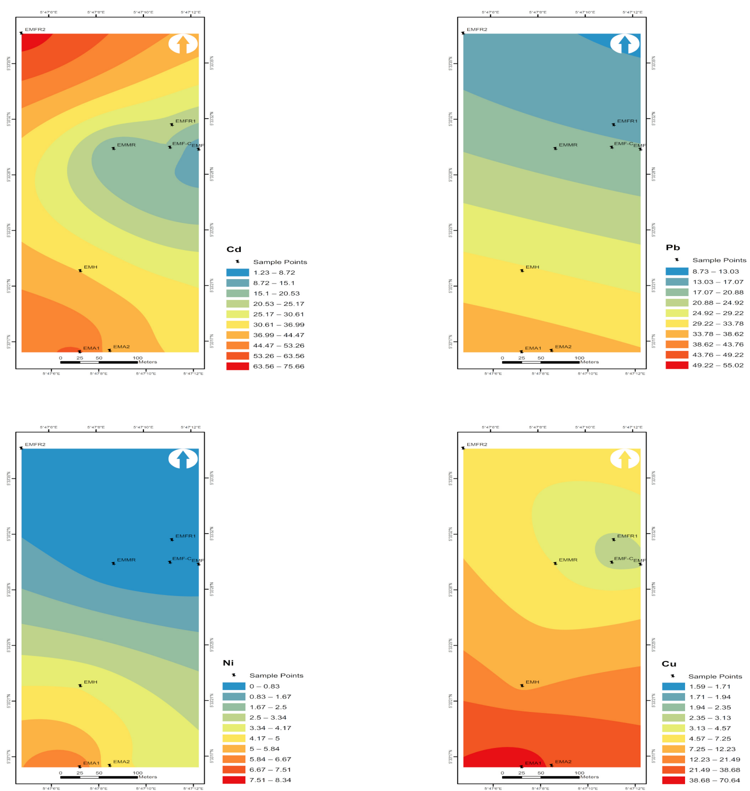

Figure 5: Spatial variability of the ecological risk of extractable heavy metals in all the sampling point within the Effurun market

Health risk assessment of the surface soil at Effurun market

The EMA 1 is the surface soil from abattoir that is a major supplier of meat to many people in Effurun environs. Therefore, the surface soil sample was used to examine the possible health risk pose to human. The risk assessment tool was used to examine heavy metals pathways of entering the body and those metals that could cause non-carcinogenic and carcinogenic risk to human.

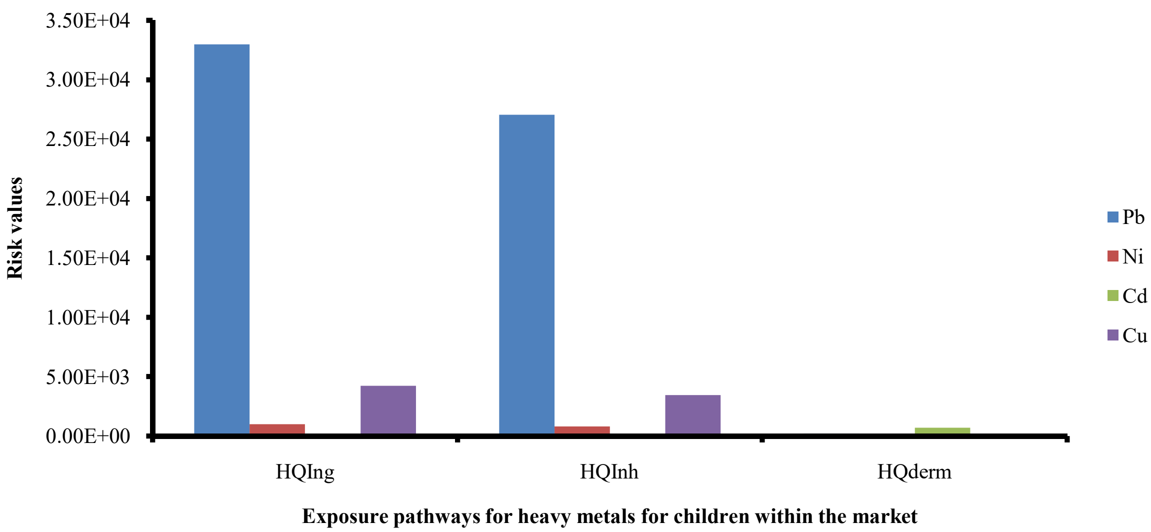

Figure 7: The three exposure pathways for heavy metals to enter children bodies within the market.

Exposure pathway

The three pathways earlier stated Ingestion, inhalation and dermal contact were examined for each metal using equation 6.7 & 8. The results obtained were presented in Figure 7 & 8 for children and adult around the EMA 1 sampling point at the Effurun market. Figure 5 shows the major potential risk to children is via soil ingestion because HQ values for ingestion are the highest result and above 1. The major contribution to the HQ value came from Pb, which means that the children are likely to suffer from low IQ, hyperactivities, renal malfunction and other central nervous related disease (9). However, heavy metal contamination of surface soil of Effurun market poses a serious non-carcinogenic risk to adults in the market through soil inhalation from wind-blown dust. The major contributing element for adults risk is the same for children (Pb). Therefore, the major health challenge faced by children and adults in the market will be Pb related illnesses. The ingestion observed for adults might have resulted from wind-blown dust deposit on food eaten or hand are not regularly washed before using it to eat around the EMA 1 sampling point. The hazard index (HI) is a sum of hazard quotients for all exposure pathways of toxic metals to the people group (children and adults) in the market vicinity. It was used to measure the non-carcinogenic metals that might affect the human group in the market. If the HI<1, unlikely to result in adverse health effects over a lifetime of exposure, while HI>1 there is the potential of risk to health effect over a lifetime exposure. The HI for all the pathways were far higher than 1 but the health risk will impact the adult more than the children according to Figure 9 around the vicinity of the EMA 1 sampling point in the market. Figure 10 revealed the cancer risk effect of Ni, Cd and Pb on the body of children and adults around the EMA 1 location over a lifetime of exposure. The results showed the CR values for both children and the adults were more than 1.0E-04. This indicates that the people in the vicinity around the EMA1 were susceptible but adults are more susceptible than children that adults will be much affected than children. The results of this study have limitations in measuring the health risk of people at the market because it doesn't give detail specific mechanisms and processes of heavy metals in the human body for diagnosis of possible diseases, although it suggested the health risk the people might suffer. The results could help the government to consider regulation on the use of tyre for burning of the cow at the abattoir.

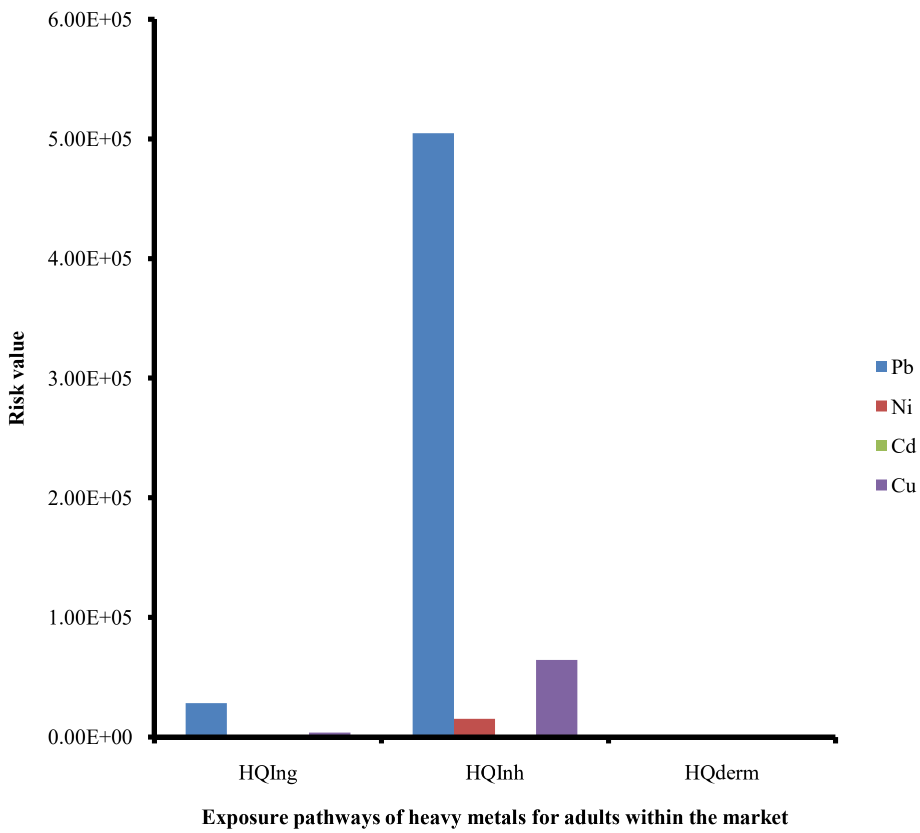

Figure 8: The three exposure pathways for heavy metals to enter adults' body within the market

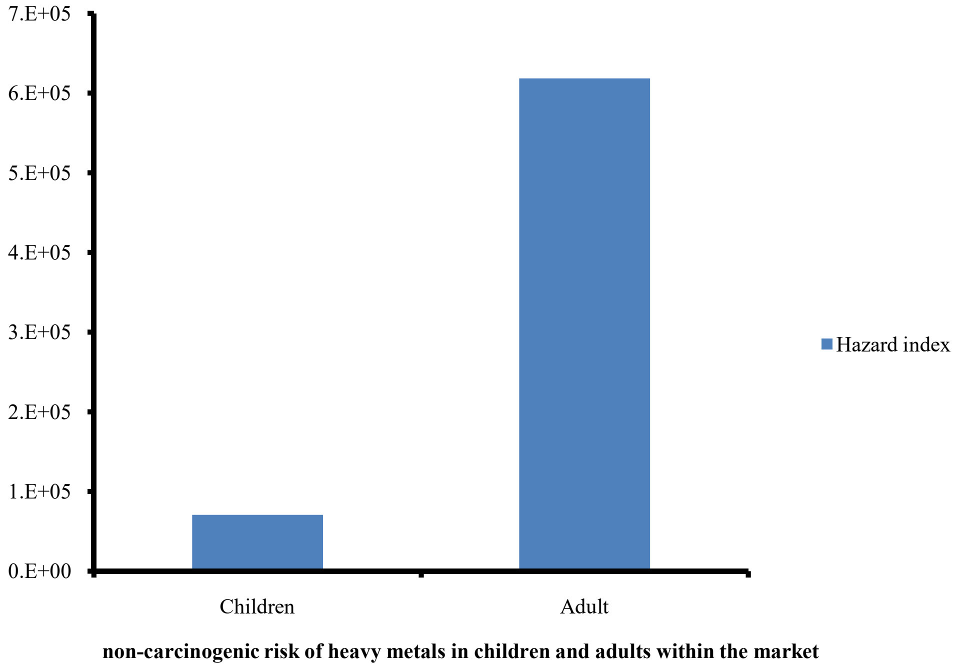

Figure 9: Hazard index for people within the Effurun market

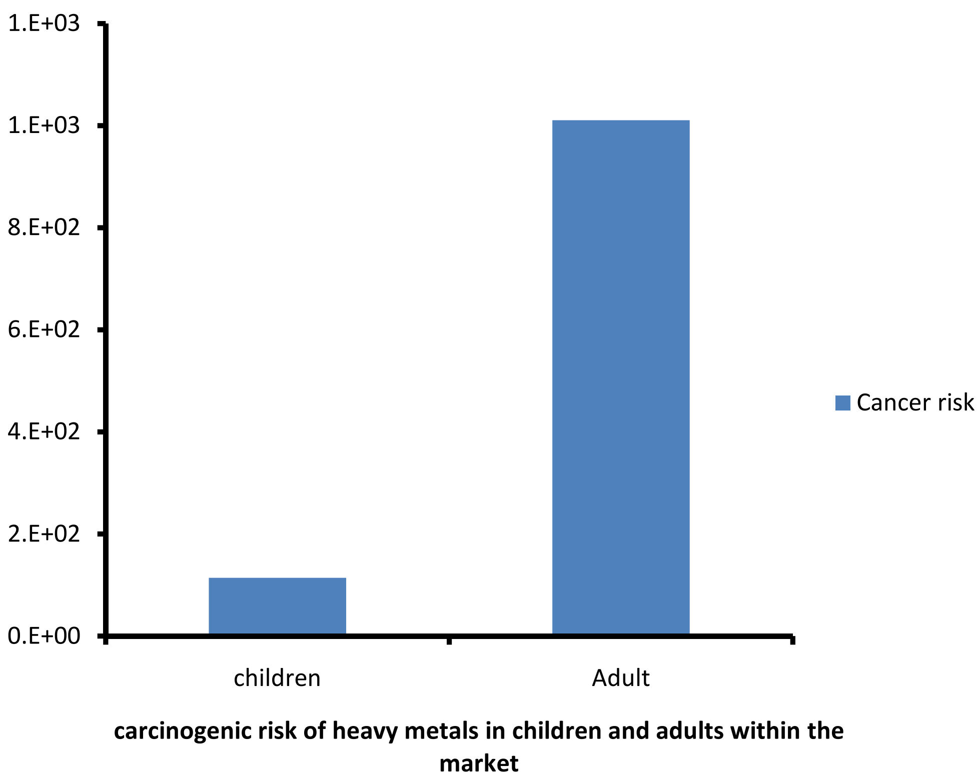

Figure 10: Cancer risk for people within the Effurun market

V. CONCLUSION

The present study focuses on the concentration, evaluation of environmental risk with the aid of spatial distribution of heavy metals in the surface soil of Effurun market. The analysis of the surface soil at the Effurun market shows EMA 1 soil contained the highest concentrations of Pb and Cu while EMF has the least concentration for Ni, Cd and Cu. Cluster and QAC analysis was able to show that Pb, Ni, Cd, and Cu have similar sources. Since % SOC sources are fine aerial particles and organic waste within the market and the Pearson correlation coefficient of the % SOC with the Pb, Ni and Cu show similar sources (which are anthropogenic sources). It explains that the heavy metals sources were anthropogenic activities. The heavy metals in the surface soil show no significant impact on the soil at most of the sampling point considers for ecological risk. The moderate ecological risk and significant health risk observed at sampling point EMA 1 poses a potential threat to the local environmental quality and public health. Therefore, there is a need for Effurun market policymakers and regulator to address the method of meat preparation for consumers at Effurun environs.

REFERENCES

[1]. Jiao X, Teng Y, Zhan Y, Wu J, Lin X., 2015. Soil Heavy Metal Pollution and Risk Assessment in Shenyang Industrial District, Northeast China. PLoS ONE 10(5): e0127736. doi:10.1371/journal.pone.0127736

[2]. Ngole-Jeme and Veronica, M., 2016 ‘Heavy metals in soils along unpaved roads in south west +90u{)}=10.1007/s13280-015-0726-9.

[3]. Li, J., Pu, L., Liao, Q., Zhu, M., Dai, X., Xu, Y., Zhang, L., Hua, M. and Jin, Y. 2014 ‘How anthropogenic activities affect soil heavy metal concentration on a broad scale: a geochemistry survey in Yangtze River Delta, Eastern China’, Environmental Earth Sciences, 73(4), pp. 1823–1835. doi: 10.1007/s12665-014-3536-7.

[4]. Orlowska, Kalina; Mazurek, Ryszard; Kowalska, Joanna; Gasiorek, Michal; Zadrozny, Pawel; Jozefowska, Agnieszka; Zaleski, Tomasz; Kepka, Wojciech; Tymczuk, M. 2017. Chemosphere Assessment of heavy metals contamination in surface layers of Roztocze National Park forest soils (SE Poland) by indices of pollution’, Chemosphere, 168, pp. 839–850. doi: 10.1016/j.chemosphere.2016.10.126.

[5]. Akan, J.C., Audu, S.I., Mohammed, Z., Ogugbuaja, V.O., 2013. Assessment of heavy metals, pH, organic matter and organic carbon in roadside soils in Makurdi metropolis, Benue State, Nigeria. J. Environ. Prot. 4, 618e628.

[6]. Xu, Xue, Lu, Xinwei, Han, Xiufeng and Zhao, Ni., 2015 Ecological and health risk assessment of metal in resuspended particles of urban street dust from an industrial city in China’, 108(1), pp. 72–79.

[7]. Li, H., Shi, A. and Zhang, X., 2015 ‘Particle size distribution and characteristics of heavy metals in road-deposited sediments from Beijing Olympic Park’, Journal of Environmental Sciences (China), 32, pp. 228–237. doi: 10.1016/j.jes.2014.11.014.

[8]. Mugoša, B. and Đurovi, D. 2016 ‘Assessment of Ecological Risk of Heavy Metal Contamination in Coastal Municipalities of Montenegro’, 13(4), pp. 393–408. doi: 10.3390/ijerph13040393.

[9]. Wuana, R. A. and Okieimen, F. E. 2011. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation, ISRN Ecology, 2011, pp. 1–20. doi: 10.5402/2011/402647.

[10]. Gbadebo, A. M. and Bankole, O. D. 2007. Analysis of potentially toxic metals in airborne cement dust around Sagamu, Southwestern Nigeria. Journal of Applied Sciences, 7 (1), 35-40.

[11]. Gawade, A., Deshmukh, P., Shivankar, V. and Gavali, L. (2016) ‘Analysis of Roadside Dust for Heavy Metal Pollutants in Navi Mumbai’, International Journal of Engineering Technology, Management and Applied Sciences, 4(7), pp. 80–88.

[12]. Yousif, K. M. (2016) ‘Preliminary Assessment of Heavy Metal in Selected Sites within Duhok City, Iraq’, American scientific Research Journal for Engineering, Technology, and Sciences, 26(2), pp. 316–325.R6i.ip

[13]. Ishak, I., Rosli, F. D., Mohamed, J. Mohd Ismail, M. F. 2015. ‘Comparison of digestion methods for the determination of trace elements and heavy metals in human hair and nails’, Malaysian Journal of Medical Sciences, 22(6), pp. 11–20. doi: 10.1021/bc050081u.

[14]. Adebayo, A.J., Jayoye, J.T., Adejoro F., Ilemobayo I.O. and Labunmi, L. 2017. Heavy metal pollution of automechanic worshop soils within Okitipupa, ondo state, Nigeria. Academic Jpournal of Environmental Science. 5(12): 215 - 223

[15]. Burrough, P.A., & McDonnell, R.A., 1998. Creating continuous surfaces from point data. In: Burrough, P.A., Goodchild, M.F., McDonnell, R.A., Switzer, P.,Worboys, M. (Eds.), Principles of Geographic Information Systems. Oxford University Press, Oxford, UK.

[16]. Setiano, A. & Triandini, T. 2013. Comparison of kriging and inverse distance weighted (IDW) interpolation methods in lineament extraction and analysis. J. SE Asian Appl. Geol., Vol. 5(1): 21–29.

[17]. Wang, J., Liu, W.,Yang, R., Zhang, L. and Ma, J. et al. (2013) ‘Assessment of the potential ecological risk of heavy metals in reclaimed soils at an opencast coal mine’, Disaster advances, 6(S3), pp. 366–377.

[18]. Mathur, R., Balaram, V. and Satyanarayanan, M. (2016) ‘Assessment of heavy metal contamination of road dusts from industrial areas of Hyderabad , India’, Environmental Monitoring and Assessment. Environmental Monitoring and Assessment, 188(514), pp. 1–15. doi: 10.1007/s10661-016-5496-8.

[19]. Zhang, G. Bai, J., Zhao, Q., Jia, J. and Wen, X. 2017. Heavy metals pollution in soil pro fi les from seasonal- fl ooding riparian wetlands in a Chinese delta : Levels , distributions and toxic risks, Physics and Chemistry of the Earth. Elsevier Ltd, 97, pp. 54–61. doi: 10.1016/j.pce.2016.11.004.

[20]. Gu, Y., Gao, Y. and Lin, Q. 2016 ‘Applied Geochemistry Contamination , bioaccessibility and human health risk of heavy metals in exposed-lawn soils from 28 urban parks in southern China â€TM s largest city , Guangzhou’, Applied Geochemistry. Elsevier Ltd, 67, pp. 52–58. doi: 10.1016/j.apgeochem.2016.02.004.

[21]. Hakanson, L., (1980) Ecological risk index for aquatic pollution control. A sedimentological approach. Water Res 14(5):975–1001

[22]. Sun, Y., Zhou, Q., Xie, X., Liu, R., (2010) Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J Hazard Mater 174: 455–462

[23]. Kowalska, J., Mazurek, R., Ga̧siorek, M., Setlak, M., Zaleski, T., Waroszewski, J., 2016. Soil pollution indices conditioned by medieval metallurgical activity e a case study from Krakow (Poland). Environ. Pollut. 218, 1023-1036.

[24]. Ljung, K.; Selinus, O.; Otabbong, E. 2006. Metals in soils of children’s urban environments in the small northern European city of Uppsala. Sci. Total Environ., 366, 749–759.

[25]. Shi, P.; Xiao, J.; Wang, Y.; Chen, L. 2014. Assessment of ecological and human health risks of heavy metal contamination in agriculture soils disturbed by pipeline construction. Int. J. Environ. Res. Public Health, 11, 2504–2520.

[26]. Kabir, M.I.; Lee, H.; Kim, G.; Jun, T. 2011. Correlation assessment and monitoring of the potential pollutants in the

surface sediments of Pyeongchang River, Korea. Int. J. Sediment Res., 26, 152–162.

[27]. USEPA. 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, U.S. Environmental Protection Agency, 4–24.

[28]. USEPA. 2011. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency, Washington, DC.

[29]. (Nurul Syazani Yuswir, Sarva Mangala Praveena, Ahmad Zaharin Aris, Sharifah Norkhadijah Syed Ismail, Claire de Burbure and Zailina Hashim (2015) 'Heavy Metal Contamination in Urban Surface Soil of Klang District (Malaysia)', Soil and Sediment Contamination, 24(8), pp. 865–881. doi: 10.1080/15320383.2015.1064090

[30]. Man, Y.B., Sun, X.L., Zhao, Y.G., Lopez, B.N., Chung, S.S., Wu, S.C., Cheung, K.C., Wong, M.H., 2010. Health risk assessment of abandoned agricultural soils based on heavy metal contents in Hong Kong, the world's most populated city. Environ. Int. 36, 570-576.

[31]. Kathi, S. and Khan, A. B. 2014. 'Evaluation of heavy metal and total petroleum hydrocarbon contamination of roadside surface soil', pp. 2259–2270. doi: 10.1007/s13762-014-0626-8.

[32]. Luo, W., Lu, Y., Giesy, J.P., et al (2007) Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China. Environ Geochem Health 29:459–471. doi:10.1007/s10653-007-9115-z

[33]. Sabir, M. and Zia-ur-rehman, M. (2015) 'Phytoremediation of Metal- Contaminated Soils Using Organic Amendments : Prospects and Challenges', Soil Remediation and Plants, (December), pp. 503–523. doi: 10.1016/B978-0-12-799937-1.00017-6.

[34]. Sarmadian, F., Mahmoudabadi, E and Moghaddam, R. N. (2015) 'Spatial distribution of soil heavy metals in different land uses of an industrial area of Tehran (Iran)', International Journal of Environmental Science and Technology. Springer Berlin Heidelberg, pp. 3283–3298. doi: 10.1007/s13762-015-0808-z.

[35]. Lee, C.S.L., Li, X., Shi, W., et al (2006) Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci Total Environ 356:45–61. doi:10.1016/j.scitotenv.2005.03.024

[36]. Zheng, Y-M, Chen, T-B, He, J-Z (2008) Multivariate geostatistical analysis of heavy metals in topsoils from Beijing, China. J Soils Sediments 8:51–58. doi:10.1065/jss2007.08.245

[37]. Zhao, K, Liu, X, Xu, J, Selim, H.M., (2010) Heavy metal contaminations in a soil-rice system: identification of spatial dependence in relation to soil properties of paddy fields. J Hazard Mater 181:778–787. doi:10.1016/j.jhazmat.2010.05.081

[38]. Li, X, Liu, L, Wang, Y et al (2013) Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. Geoderma 192:50–58. doi:10.1016/j.geoderma.2012.08.011

[39]. Dragovic´ R, Gajic´ B, Dragovic´ S et al (2014) Assessment of theimpact of geographical factors on the spatial distribution of heavy metals in soils around the steel production facility in Smederevo (Serbia). J Clean Prod. doi:10.1016/j.jclepro.2014. 03.060

[40]. Monitha, M, Jayakumar, C, Nagendra Gandhi, N (2012) Environmental toxicology assessment and remediation of toxic metals in soil. Int J Environ Biol 2(2):59–66.

[41]. Viguri, J.R., Irabien, M.J., Yusta, I, Soto, J., Gomez, J., Rodriguez, P, Martinez-Madrid, M, Irabien, J.A., Coz, A. (2007) Physico-chemical and toxicological characterization of the historic estuarine sediments.Amultidisciplinary approach. Environ Int 33:436–444

[42]. Nurul Syazani Yuswir, Sarva Mangala Praveena, Ahmad Zaharin Aris, Sharifah Norkhadijah Syed Ismail, Claire de Burbure and Zailina Hashim (2015) Heavy Metal Contamination in Urban Surface Soil of Klang District (Malaysia), Soil and Sediment Contamination: An International Journal, 24:8, 865-881, DOI: 10.1080/15320383.2015.1064090