



Assessment of Heavy Metals Concentration in Soil of Champion Breweries Plc, Aka Offot, Uyo, Southern Nigeria Using X-Ray Fluorescence Technique

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Abstract

The contamination of heavy metals present in soil of Champion Breweries Plc, Aka Offot, Uyo, in Southern Nigeria was assessed. In application of XRF techniques, seventeen (17) heavy metals, namely potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), arsenic (As), bromine (Br), rubidium (Rb), strontium (Sr), yttrium(Y), and zirconium (Zr), were determined from each of the soil samples obtained at four (4) sampling sites. Fe had the highest concentration in all the sampling sites in the range of 17320.0 - 29380.0 ppm and Ga had the lowest concentration in all the foursampling site, ranging from 8.16 - 62.713 ppm. Co was only detected in one sampling site. The Enrichment factor (EF), geo-accumulation index (Igeo) and contamination factor (CF)

were used as pollution indices to assess the toxicity threat posed on that part of the ecosystem by the investigated heavy metals. The results of the three pollutions indices were similar, indicating that the part of the industry was highly polluted with Cr, Rb, Zr, Zn, and Mn, Pb at some point. These high inputs of the heavy metals might be due to pronounced anthropogenic influences around the studied area. Analysis of multivariate statistics such as Pearson's Correlation coefficient and cluster analysis were also applied to ascertain the relationship and sources of investigated heavy metals. Both positive and negative correlations were observed among some heavy metals. Rb was observed to have a strong positive correlation with As, Ga, Zn. Ti has a strong negative correlation with Cr, Br, Rb and a strong positive value with Fe and Zr which suggest that these elements are from the same origin. Low correlation between Ca -As, Ga -Zr, Mn - Rb, etc suggest that they come from different sources. Cluster analysis revealed two main clusters, this shows that elements in each of the cluster can specifically be said to come from the same source.



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Keywords: X-Ray Fluorescence (XRF) technique; heavy metals; soil pollution; enrichment factor (EF), geo-accumulation index (Igeo); contamination factor (CF)

Introduction

Contamination by metals in the soil has become widespread in a global context. Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust and industrial activities have been the major sources of soil contamination with heavy metals. Increasing metal pollution has severely disturbed the natural ecosystem and harmed human health through food chain (Cai *et al*, 2009, Liu *et al*, 2016).

Champion Breweries Plc is currently producing total of 1,000,000 hectoliters yearly (Annual report, 2021). Champion Breweries Plc is located on the boundary of Uyo and Ibesikpo Asutan LGA in Akwa Ibom State. The most important sources of heavy metals in the environment are the anthropogenic activities such as mining, smelting procedures, steel and chemical industry, iron industry, traffic, agriculture as well as domestic activities (Ene et al., 2009). Chemical and metallurgical industries are the most important sources of heavy metals in soils (Pantelica et al, 2008; Suciu et al, 2008). The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity, plant growth etc (Vries et al, 2007; Popescu et al, 2009; Stihi, 2008; Ene et al, 2009).

The attractiveness of non-destructive methods and the ability to perform simultaneous multielemental determinations has led to an extensive application in industrial and research laboratories of accurate, precise and sensitive atomic and nuclear analytical techniques for the investigation of different types of materials (industrial, geological, archaeological, biological, environmental etc), such as neutron activation analysis (NAA) (Popescu et al, 1996; Ene et al, 2009; Suciu et al, 2008), X-ray fluorescence (XRF) and particle-induced X-ray emission (PIXE) (Stihi et al, 2006). For the analysis of environmental samples, XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation. Quantitative and qualitative analyses are performed without acid digestion processes and a great number of elements can be determined simultaneously in a short time. The main objective of this paper is to determine the level of soil pollution with heavy metals, in Champion Breweries Plc, Aka Offot, Uyo, whose activity lasted from 1976, being one of the most active brewery companies in the Southern region of Nigeria and representing a great potential of environmental contamination.

2.0 Material and Methods

2.1 Study Area and Soil Samples Analysis

Champion Brewery Plc is one of long-standing industries in Akwa Ibom State, Southern Nigeria. Four (4) sites were sampled CHB1 -CHB4 (Fig. 1) within the coordinates of 7°55'8" and 7°55'19" N and 5°0'13" and 5°0'16" E with an estimated area of 23,154 km². Over the course of the year, the temperature typically varies from 21°C and 32°C. Composite soil samples were collected at four sampling sites of Champion Breweries Plc, Aka Offot, Uvo, with the coordinates of the sampling site and labeled as CHB1, CHB2, CHB3, and CHB4 respectively as shown in table 1. In this study, the samples were collected during the dry season between the period of 4th January 2020 to 10th January 2020.





Fig 1: Location of Champion Breweries Plc and sampling points

Table 1: Sampling Point

S/N	Sample Point	Longitude	Latitude
1	CHB01	7°55'8.67900"	5°0'11.57472"
2	CHB02	7°55'19.11612"	5°0'14.27148"
3	CHB03	7°55'18.12756"	5°0'16.22700"
4	CHB04	7°55'16.12756"	5°0'13.22700"

All the samples were collected in the most active site of the industry. Global Positioning System (GPS) was used in taking the point or location where each sample was collected. Rubber containers were used in collecting the samples and masking tape in labeling each sample. The soil was first dried, ground to a fine powder with the aid of mortar and pestle. 2g of each of the samples were weighed and then poured into a sample holder and covered with cotton wool to prevent it from spraying. The bottom of the sample's holder is made of polypropylene which is a thermoplastic. The sample holders containing the sample were run in a vacuum or air for 10 minutes and they were inserted into the XRF Spectrometer for the Elemental analysis.

Enrichment factor (EF), index of geoaccumulation (Igeo), and contamination factor (CF) were employed to assess heavy metal distribution and contamination in the sample of the study area. According to (Ackerman, 1980, Loring *et al.*, 1995), enrichment factor (EF) is given as

$$EF = \frac{\left[\frac{C_{m}}{C_{n}(Fe)}\right] \text{sample}}{\left[\frac{C_{m}}{C_{n}(Fe)}\right] \text{Shale}} \qquad 1$$

where C_n is the value of the metal, adopted as a reference element, C_m is the measured concentration of an element. The numerical results indicate different pollution levels. Values of $0.5 \le EF \le 1.5$ suggest that the trace metal concentration may come entirely from natural weathering processes (Zhang, and Liu, 2002). However, an EF>1.5 indicates that a significant portion of the trace metals was delivered from non-crustal materials so, these trace metals were delivered by other sources, like point and non-point pollution and biota (Klerks and Levinton 1989) with EF index, soil quality state can be indicated by different



classes. EF values were interpreted as suggested by Ho et al., (2010), and Birch (2003), where EF<1 indicates no enrichment; $1 \le EF \le 3$: minor enrichment; $3 \le EF \le 5$ moderate enrichment; $5 \le EF \le 10$ moderately severe enrichment; $10 < EF \le 25$: severe enrichment; 25<EF \leq 50: very severe enrichment; EF>50 is extremely severe enrichment. The background value (reference) is that of average shale (Ho et al., 2010).

According to Muller (1969), Index of geoaccumulation is used for measuring the degree of metal pollution (Praveena *et al.*, 2007; Praveena *et al.*, 2008; Chakravarty and Patgiri, 2009). This index is expressed as follows:

Igeo =
$$\log_2(\frac{Cn}{1.5Bn})$$
 2

 C_n is the measured concentration of an element in soil dust, B_n is the geochemical background value, and the constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and detect a minimal anthropogenic influence. Müller (1981) has defined seven classes of Geo-Accumulation Index. Based on the Igeo value, the degree of heavy metal contamination is classified as follows: 1) Igeo < 0: unpolluted; 2) $0 \le Igeo < 1$: unpolluted to moderately polluted; 3) $1 \le Igeo < 2$: moderately polluted; 4) $2 \le Igeo < 3$: moderately to strong polluted; 5) $3 \le Igeo < 4$: strongly polluted; 6) $4 \le Igeo < 5$: strongly to very strongly polluted; 7) Igeo ≥ 5 : very strongly polluted. ($1 \le Igeo < 2$ (Aksu *et al.*, 1997).

To access the elemental concentration in Soil, numerical Soil Quality Guidelines (SQGs) were applied. Soil Quality Guideline includes a threshold effect concentration (TEC) obtained from the analysis of the Control materials and a probable effect concentration (PEC) obtained from the reference material and their respective concentration of elements in samples soil investigated (Table 2).

Table 2: Comparison of measured concentration of elements in Soil samples with the certified data in the
 Standard reference materials (CERD, OAU)

Element	Mean Conc. (ppm)	Certified Values (PEC) (ppm)	Experimental Values (TEC) (ppm)
K	993.521	12100.00	12130.00
Ca	1286.223	163000.00	162328.00
Ti	4505.731	3000.00	3527.00
V	399.096	66.00	75.00
Cr	145.015	60.00	59.00
Mn	633.250	631.00	647.00
Fe	24680.000	25700.00	25670.00
Ni	205.105	26.00	26.50
Cu	301.636	11.00	12.60
As	102.058	13.40	14.10
Br	178.668	7.00	8.10
Sr	32.502	108.00	107.00
Y	43.112	21.00	24.50
Zr	65.775	185.00	187.00

Table 3 shows the concentration of heavy metal form Champion brewery Plc. If the mean

concentration of elements in the samples soil is below the TEC values, harmful effects are not



likely to be observed. On the other hand, if the mean concentration of elements in the soil is above the PEC values, harmful effects are likely to be observed. According to (MacDonald *et al.*,2000) most of the TEC

values provide an accurate basis for predicting the absence of soil toxicity, and most of the PECs provide an accurate basis for predicting soil toxicity.

Table 3:	Results of XRF a	analysis of Soil	from Champ	ion Brewery	y Plc, Ak	a Offot in	Uyo	Local			
Government											

Elements	CHB 1	CHB 2	CHB 3	CHB 4
K	<884.785	529.055±166.814	<1486.522	1073.721 ± 280.999
Ca	2432.083 ± 420.586	527.814 ± 66.575	1244.502 ± 253.815	940.492 ± 141.078
Ti	3896.492 ± 647.595	5021.188 ± 852.972	5596.388 ± 918.154	3508.857 ± 282.707
V	<396.477	<360.37	<496.287	<343.249
Cr	180.086 ± 39.506	<69.507	<136.558	193.910 ± 57.092
Mn	522.394 ± 122.322	605.274 ± 96.517	774.383 ± 152.335	630.947 ± 107.912
Fe	22960.000 ± 0.267	29060.000 ± 0.313	29380.000 ± 0.336	17320.000 ± 0.029
Co	0	0	820.418 ± 101.681	0
Ni	207.226 ± 41.516	192.774 ± 39.622	268.303 ± 50.197	538.241 ± 51.555
Cu	83.246± 17.228	105.391 ± 18.237	80.928 ± 14.509	138.667 ± 23.526
Zn	136.547 ± 28.387	136.755 ± 24.996	137.066 ± 25.209	304.303 ± 26.097
Ga	<23.519	<8.146	<35.63	<62.713
As	<36.930	<8.623	<43.265	<83.629
Br	65.207 ± 8.312	41.687 ± 4.802	36.821	119.384 ± 19.183
Rb	<54.683	45.012± 7.159	<53.163	77.618 ± 24.959
Sr	<79.119	65.624 ± 15.456	<84.637	<101.196
Y	<164.215	<62.597	<157.143	<200.319
Zr	$1281.817{\pm}138.440$	1375.8 ± 83.346	1816.995 ± 173.699	1305.313 ± 187.242

3.0 Results and Discussion

Enrichment factor, Geo-accumulation index and Contaminator factor of Champion Brewery Plc, Aka Offot, Uyo Local Government Area is represented in table 4 - 6 respectively. Enrichment factor serves as the means of quantifying and identifying anthropogenic activities with global elemental cycle (Veerasingam et al., 2010). According to Ekaete et al., 2015 if 0.5<EF<1.5 the concentration is entirely due to natural weathering origin. The higher the EF values the more severe is the anthropogenic contributions.

The enrichment factor (EF) values of heavy metals in soil of Champion Brewery Plc are shown in Table 4. EF at CHB1 (Fig. 2) follows the sequential trend as Br > Ni > Zr > Y > Cu >V > Cr > Zn > As > Ga > Ti > Rb > Fe > Mn > Sr>K > Ca > Co. Appling the above interpretation, this part of the industry is moderate severely enriched with V, Ni, Cu, Br, Y, Zr, moderately enriched with Cr and Zn. Elements K, Ca, Ti, Fe, Ga, Mn, Sr, As, Rb are minorly enriched with other heavy metals. The EF values at site 2 (CHB2) follows the sequential trend as Co < Ca < K < As < Sr < Ga < Rb < Mn < Fe < Cr < Ti < Y < Zn < V < Br < Ni < Zr < Cu. (Fig. 3). Appling the above interpretation this part of the Champion Brewery Plc is moderate severely enriched with Ni, Cu, Zr, moderately enriched with V and Br and Ti, Cr, Fe, Zn, and Y are minorly enriched.

The EF values at site 3 (CHB3) follows the sequential trend as; Ca < K < Sr < Rb < Fe < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Ga < Br < Y < Cu < Mn < Ti < Cr < Zn < As < Cu < Mn < Ti < Cr < Zn < As < Cu < Mn < Ti < Cr < Zn < As < Cu < Mn < Ti < Cr < Zn < As < Cu < Mn < Ti < Cu < Mn <



V < Zr < Ni < Co (Fig 4). Appling the above interpretation this part of the Champion Brewery Plc is extremely enriched with Co, moderate severely enriched with V, Ni, Cu, Y and Zr, moderately enriched with Br and K, Ca, Ti, Cr, Mn, Fe, Ga, Zn, Rb, Sr Y, and As are minorly enriched. The EF values at site 4 (CHB4) follows the sequential trend as; Co < Ca < K < Fe < Sr < Mn < Ti < Rb < Cr < V < Ga < As < Zn < Zr < Y < Cu < Br < Ni (Fig 5).Appling the above interpretation, this part of the industry is extremely enriched with Ni with value of 30, severely enriched with Cu, Br, Y and Zr, moderately Severe enriched with V, Zn, Ga, As, and K, Ca, Ti, Mn, Fe, Rb and Sr are minorly enriched.

Elements	CHB1	CHB2	CHB3	CHB4
K	0.08	0.04	0.11	0.13
Ca	0.02	0.00	0.01	0.01
Ti	1.24	1.26	1.39	1.47
V	5.91	4.24	5.78	6.78
Cr	3.41	1.04	2.02	4.87
Mn	0.90	0.83	1.05	1.45
Fe	1.00	1.00	1.00	1.00
Со	0.00	0.00	80.54	0.00
Ni	8.74	6.43	8.85	30.10
Cu	7.39	7.39	5.61	16.31
Zn	3.12	2.47	2.45	9.22
Ga	2.39	0.65	2.83	8.45
As	2.93	0.54	2.68	8.79
Br	9.00	4.55	3.97	21.84
Rb	1.20	0.78	0.91	2.26
Sr	0.83	0.54	0.69	1.40
Y	7.49	2.26	5.60	12.12
Zr	7.66	6.5	8.49	10.35

Table 4: Enrichment Factors of Heavy metals from Champion Brewery Plc.









Fig 3: Spatial variation values of EF, Igeo and CF of CHB1



Fig. 4: Spatial variation values of EF, Igeo and CF of CHB3



Fig. 5: Spatial variation values of EF, Igeo and CF of CHB4





The values of geo-accumulation index (Igeo) of elements in soil samples of CHB1 - CHB4 are shown in Table 5. From the Table it is evident that K, Ti, Cr, Mn, Fe, Zn, Ga, As, Rb, Sr fall in class '1' which exhibit from uncontaminated to moderately contaminated status while the Igeo of V, Ni, Cu, Br, Y, Zr fall into class '2' which exhibit moderately contaminated status in the sample. Elements in soil samples of CHB2 show K, Ti, Cr, Mn, Fe, Zn, Ga, As, Rb, Sr, Y into fall in class '1' exhibiting uncontaminated to moderately contaminated status while the Igeo of Ni, Cu, Br, Zr fall into class **'**2' which moderately exhibit contaminated status in the sample. CHB3 has K, Ti, Cr, Mn, Fe, Zn, Ga, As, Br, Rb, Sr fall in

Table 5: Geo-accumulation Index of Heavymetals from Champion Brewery Plc

Elements	CHB1	CHB2	CHB3	CHB4
K	0.01	0.01	0.02	0.02
Ca	0	0	0	0
Ti	0.22	0.29	0.32	0.2
\mathbf{V}	1.06	0.96	1.33	0.92
Cr	0.61	0.24	0.46	0.66
Mn	0.16	0.19	0.24	0.2
Fe	0.18	0.23	0.23	0.14
Со	0	0	18.5	0
Ni	1.57	1.46	2.03	4.08
Cu	1.33	1.68	1.29	2.21
Zn	0.56	0.56	0.56	1.25
Ga	0.43	0.15	0.65	1.14
As	0.53	0.12	0.62	1.19
Br	1.62	1.03	0.91	2.96
Rb	0.22	0.18	0.21	0.31
Sr	0.15	0.12	0.16	0.19
Y	1.35	0.51	1.29	1.64
Zr	1.38	1.48	1.95	1.4

Contamination factor is calculated as the ratio between the soil metal content at a given station and the background concentration levels (Ekaete *et al* 2015). Hakanson in 1980 modified Contamination Factor stating that

class '1' which exhibit uncontaminated to moderately contaminated. V, Cu, Y, Zr are in class '2' which means they exhibit moderately contaminated status. Ni fall into class '3' which exhibit moderately polluted to polluted and Co fall into class '6' which exhibit very strongly polluted. It could be seen that Igeo values in CHB4 has K, Ca, Ti, V, Cr, Mn, Fe, Rb, Sr within the range 0<Igeo<1 which fall in class '1' and these elements exhibit uncontaminated to moderately contaminated status while the Igeo of Zn, Ga, As, Y, Zr fall into class '2' which exhibit moderately contaminated status in the sample. Ni exhibit heavily contamination and Cu and Br exhibit moderately to heavily contamination.

contamination factor follows these classes; if CF<1, low contaminations, 1 < CF < 3, moderate contamination, 3 < CF < 6, considerable contamination and CF > 6, very high contamination is employed in this study.

shows values Table 6 the of mean contamination factor (CF) of elements in soil samples of CHB1 are K (0.07), Ca (0.02), Ti (1.10), V (5.29), Cr (3.05), Mn (0.81), Fe (0.89), Ni (7.82), Cu (6.61), Zn (2.79), Ga (2.14), As (2.62), Br (8.05), Rb (1.07), Sr (0.74), Y (6.70) and Zr (6.85). Considering the contamination level classification described above, K, Ca, Fe, Mn and Sr exhibit low contamination status, Ti, Zn, Ga, As, Rb exhibit moderate contamination status. Cr and V exhibit considerable contamination and Ni, Cu, Y, and Zn exhibit very high contamination status in soil of Champion Brewery Plc.

The values of mean contamination factor (CF) of elements in soil samples of CHB2 as shown in Table 6 are K (0.04) Ca (0.00), Ti (1.42), V (4.80), Cr (1.18), Mn (0.94), Fe (1.13), Ni (7.27), Cu (8.36), Zn (2.80), Ga (0.74), As (0.61), Br (5.15), Rb (0.88), Sr (0.61), Y (2.55) and Zr (7.36). From the contamination level described above, it's evident that K, Ca, Mn, Ga, As, Rb, and Sr exhibit low contamination



status, Ti, Cr, Fe, Zn, Y exhibit moderate contamination status, V and Br exhibit considerable contamination and Ni, Cu, and Zr exhibit very high contamination status in soil of CHB2 Champion Brewery Plc. Table 6 shows the values of mean contamination factor (CF) of elements in soil samples of CHB3 are K (0.12) Ca (0.01), Ti (1.59), V (6.62), Cr (2.31), Mn (1.20), Fe (1.14), Co (92.18), Ni (10.12), Cu (6.42), Zn (2.80), Ga (3.24), As (3.07), Br (4.55), Rb (1.04), Sr (0.79), Y (6.41) and Zr (9.72). K, Ca, and Sr exhibit low contamination status, Ti, Cr, Mn, Fe, Zn, Rb exhibit moderate contamination status, Ga, As and Br exhibit considerable contamination and V, Co, Ni, Cu, Y and Zr exhibit very high contamination status in soil of CHB3 Champion Brewery Plc.

The values of mean contamination factor (CF) of elements in sediment samples of CHB4 are K (0.09) Ca (0.01), Ti (0.99), V (4.58), Cr (3.29), Mn (0.98), Fe (0.67), Ni (20.31), Cu (11.01), Zn (6.22), Ga (5.70), As (5.93), Br (14.74), Rb (1.52), Sr (0.95), Y (8.18) and Zr (6.98). K, Ca, Ti, Mn, Fe and Sr exhibit low contamination status, V, Cr, Ga, As exhibit considerable contamination and Ni, Cu, Zn, Br, Y and Zr exhibit very high contamination status in soil of CHB4 Champion Brewery Plc.

To determine the common source of elements and to establish the relations among elements Pearson's correlation matrix was calculated for elements in the soil samples. Table 7 shows both the negative and positive significant correlation between elements in soil of Champion Brewery Plc. K - Br, Ga - Zr, Ca -As, Br, Sr has a week positive correlation. Mn has a positive moderate correlation with Sr and Fe. Cr - Cu, Ca - V, K - Ni and Cu - Y also have moderate correlation. Rb has a strong positive correlation with As, Ga, Zn and moderate positive correlation with K, weak correlation with Mn. It is evident that K has a weak negative correlation with Fe and Cu. Ca has a negative weak correlation with Ti, Fe, Ni,

Zn, Zr and moderate negative Correlation with Mn, Cu. Ti has a strong negative correlation with Cr, Br, Rb and moderate negative correlation between Ni, Cu, Zn, As, Y and Sr. Vanadium V has a moderate negative correlation with Br and Zn. Cr has strong correlation with Fe. Fe has a strong negative correlation with Br. Zr has weak negative correlation with Cu, Cr and Zn. Generally, low correlation between elements such as Ca -As, Ga -Zr, Co -As, Mn – Rb, etc suggest that they come from different sources.

Hierarchical clustering results from elements concentration in soil samples of Champion Brewery Plc (Fig. 6) revealed 2 main clusters. Cluster 1 contains Ga, As, Br, Rb, Sr, Cu, Cr, Y, Zn, V, Na, Co and K. Cluster 2 is divided into 2 sub clusters. Sub cluster 1 contains Mn, Zr, Ca, Ti and sub cluster 2 contains Mn and Fe, this might be due to mineralogy of the study area, reflecting the predominant mineral rock type; magnetic and alkali feldspar. From the result of the cluster analysis elements in each of the cluster can specifically be said to come from the same source.

3 Conclusion

Heavy metals from industrial areas generally come from iron, steel, power and chemical manufacturing plants that irresponsibly use the soil as a dumping ground for their refuse (Fusion, 1999). Elemental analysis of soil apart from revealing the contribution of soil sources, it also indicates the accumulation of metals (elements) in deposit from anthropogenic sources. Three pollution indices namely, enrichment factor, geo-accumulation index and contamination factor were applied to assess the pollution status of the elements The three pollution indices agreed with one another on the contamination status of those elements in all soil samples studied. Thus, the pollution indices revealed similar sequential trend of heavy metals. The three pollution indices agreed



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Stations	K	Ca	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr
CHB 1	0.07	0.02	1.1	5.29	3.05	0.81	0.89	0	7.82	6.61	2.79	2.14	2.62	8.05	1.07	0.74	6.7	6.85
CHB 2	0.04	0	1.42	4.8	1.18	0.94	1.13	0	7.27	8.36	2.8	0.74	0.61	5.15	0.88	0.61	2.55	7.36
CHB 3	0.12	0.01	1.59	6.62	2.31	1.2	1.14	92.18	10.12	6.42	2.8	3.24	3.07	4.55	1.04	0.79	6.41	9.72
CHB 4	0.09	0.01	0.99	4.58	3.29	0.98	0.67	0	20.31	11.01	6.22	5.7	5.93	14.74	1.52	0.95	8.18	6.98

Table 6: Contamination Factor of Heavy metals from Champion Brewery Plc

Table 7: Correlation (Pearson) coefficient matrix between elements in soil samples of Champion Brewery Plc

	Κ	C a	Τi	V	C r	M n	F e	Сo	N i	C u	Z n	G a	A s	B r	R b	S r	Y	Zr
Κ	1																	
Ca	0.183	1																
Τi	0.245	-0.332	1															
V	0.753	0.248	0.719	1														
Cr	0.463	0.589	-0.727	-0.063	1													
Mn	0.753	-0.431	0.686	0.706	-0.175	1												
Fe	-0.018	-0.209	0.947	0.597	-0.822	0.415	1											
Co	0.824	-0.034	0.75	0.946	-0.101	0.897	0.547	1										
Ni	0.329	-0.268	-0.578	-0.362	0.62	0.163	-0.799	-0.138	1									
Cu	-0.218	-0.545	-0.595	-0.759	0.235	-0.13	-0.699	-0.526	0.833	1								
Zn	0.136	-0.283	-0.684	-0.542	0.582	-0.01	-0.856	-0.331	$.980^{*}$	0.911	1							
Ga	0.589	-0.042	-0.503	-0.088	0.768	0.282	-0.754	0.09	0.946	0.609	0.874	1						
As	0.541	0.067	-0.603	-0.141	0.841	0.162	-0.824	0.003	0.931	0.596	0.874	.991**	1					
Br	0.028	0.003	-0.882	-0.627	0.735	-0.29	977*	-0.51	0.893	0.824	0.944	0.81	0.855	1				
Rb	0.333	-0.015	-0.725	-0.367	0.794	0.001	-0.908	-0.212	.966*	0.747	.953*	.954*	.973*	0.949	1			
Sr	0.611	0.066	-0.536	-0.058	0.83	0.239	-0.773	0.09	0.915	0.547	0.841	.994**	.996**	0.807	0.95	1		
Y	0.663	0.45	-0.562	0.102	.963*	0.095	-0.737	0.126	0.699	0.24	0.615	0.871	0.911	0.688	0.825	0.919	1	
Zr	0.739	-0.165	0.833	0.912	-0.248	0.922	0.638	$.987^{*}$	-0.185	-0.502	-0.368	0.006	-0.095	-0.579	-0.294	-0.009	-0.015	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).





Fig. 6: Hierarchical Clustering results (dendrogram) of elements concentrations in soil samples of Champion Brewery Plc

with one another on the contamination status of those elements in all soil samples studied. Thus, the pollution indices revealed similar sequential trend of heavy metals. From the result of the analysis, the concentration of some of the elements was quite high namely: K, Ca, T, Zr, and Fe, the concentrations of As, Ga, Br, and Rb, on the average were below 100 ppm. As and Ga with the concentration of 8.623ppm and 8.146 respectively were detected in soil from CHB2 only.

Iron (Fe) was observed to be the element with the highest concentration on the average followed by Ti. It was also found that the concentration of elements varies with soil particulate size. Taking iron as the normalizing element, element - iron ratio records Ti/Fe ratio as the highest. The element - iron ratio is important as it offers data for calculating the enrichment factor of each element detected in the soil, thereby suggesting the contamination level of the soil by the individual element. Metal such as Ti as well V, Cr, Mn, Zn, Cu and Fe are toxic to the environment and may have a wide range of health issues associated with their contamination, considering that their concentration is higher than the threshold limit as shown in Table 2.

References

- Ackerman F (1980) A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. Environ. Technol Lett 1: 518-527.
- Aksu, A. E., Yasar, D and Uslu, O. (1997).
 Assessment of Marine pollution in Izmar Bay: Heavy Metal and Organic Compound Concentration in Surficial Sediments.
 Department of Earth Sciences, Center of Earth Resources Research Memorial University of Newfoundland, St. John's Newfoundland, Canada A1B3X5
- Birch, G., (2003). A scheme for assessing human impacts on coastal aquatic environments using sediment source.

- Cai D., Zhang, H., Shen, D., Zhao, X., Li, C. (2009). Environmental changes record derived from sediment cores in Huixian Karst wetlands, Guilin, China. J. Guangxi Norm. Univ. Nat. Sci. Ed, 27, 94–100.
- Chakravarty, M., and Patgiri, A.D., (2009). Metal pollution assessment in sediments of the Dikrong River, NE India. J. Hum. Ecol., 27(1): 63-67.

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- Ekaete, A. J., Ibironke, O., K., Olatunde, P. S.
 & Olaoye, O. P. (2015) HeavyMetals pollutions and its associated Ecological Risks in Lagos Lagoon Sediments, Southwestern Nigeria. ACSJ, 9 (3), 20334
- Ene A., Popescu I. V., & Stihi C, (2009). Applications of proton-induced X-ray emission technique in materials and environmental science, Ovidius Univ. Ann. Chem. 20 (1), 35.
- Fusion, J. (1999). What Is Soil Pollution? Available at http://www.ehow.com/about 5107995 soilpollution html, accessed February 2, 2009.
- Hakanson I., (1980): Ecological risk index for aquatic pollution control, a sedimentological Approach. Water resources,14; 975- 1001.
- Ho, H. H., Swennen, R., Damme, A.V., (2010).
 Distribution and contamination status of heavy metals in estuarine sediments near Cua Ong Harbour, Ha long Bay, Vietnam. Geol. Belgicia. 13/1-2: 37-47.
- Klerks P. L, and Levinton J. S, (1989) Rapid evolution of metal resistance in a benthic oligochaete inhabiting a metal-polluted site. Biol Bull 176: 135-141
- Loring D. H, Naes K, Dahle S, Matishow G. G, & Illin G (1995) Arsenic, trace metals, and

organic micro contaminants in sediments from the Pechora Sea, Russia. Mar Geol 128: 153-167

- Liu D., Li Y., Ma J., Li C., Chen X., (2016). Heavy metal pollution in urban soil from 1994 to 2012 in Kaifeng City, China. Water Air Soil Pollut, 227, 154. [CrossRef]
- MacDonald, D. D., Ingersoll, C. G. and Berger, T. A. (2000). Development and Evolution of Consensus -Based Sediment Quality Guidelines for Freshwater Ecosystem Archives of Environment and Contamination Toxicology, 39: 20-31
- Muller, G. (1969). Index of Geo-Accumulation in Sediments of the aaaaarhine River Geo. J., 2(3): 108-118.
- Müller G (1981). Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chem Ztg 105: 157-164
- Pantelica A., Cercasov V., E. Steinnes, P. Bode, & B. Wolterbeek, (2008) Investigation by INAA, XRF, ICPMS and PIXE of Air Pollution Levels at Galati (Siderurgical Site), Book of abstracts, 4th Nat. Conf. of Applied Physics (NCAP4), Galati, Romania, September 2008 (A. Ene – Editor). Galati University Press, Galati, Romania.
- Popescu I.V., Stihi C., Cimpoca Gh.V., Dima G., Vlaicu Gh., Gheboianu, Bancuta I., Ghisa V., & State G. (2009):Analysis Environmental Samples by Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-AES), Rom. Journ. Phys. 54 (7-8), 741.
- Praveena, S. M., Radojevie, M., Abdullah, M. H., Aris, A. Z., (2007). Factor –cluster analysis and enrichment study of



mangrove sediments- An example from Mengkabong Sabali. The Malaysian J. Analytical Science 2(2): 421-430

- Praveena, S. M., Ahmed, A., Radojevic, M., Abdullah, M. H., Aris, A. Z., (2008). Heavy metals in mangrove surface sediment of Mengkabong Lagoon, Sabah: Multivariate and geo-accumulation index approaches. Int. J. Environ. Res., 2(2): 139-148.
- Stihi C, A. Bancuta, I.V. Popescu, M. Virgolici,V. Cimpoca, M. Gugiu and Gh. Vlaicu,(2006) Air pollution studies using PIXEand ICP Methods, Journal of Physics:Conference Series 41, 565.
- Stihi C, Popescu I.V., Gheboianu A., Frontasyeva M., Ene A., G. Dima, O. Bute, V. Cimpoca, V. Stihi, C. Oros, S. Dinu, M. Voicu (2008). Mineral Content of Native Vegetables Obtained by Energy Dispersive X-ray Fluorescence Spectrometry, Journal of Science and Arts, 9 (2), 332.
- Suciu I, C. Cosma C., Todica M., Bolboaca S. D., & Jantschi L., (2008). Analysis of soil

heavy metal pollution and pattern in Central Transylvania, Int. J. Mol. Sci. 9, 434

- Veerasingam, S. Venkatachalapathy, R. & Mohan, R. (2010). Assessment of Trace in Petroleum Hydrocarbons Metals Contamination in Marine Sediments off Chennai, Bay of Bengal, India International conference Recent on Frontiers in Applied Spectroscopy, Department Annamalai of **Physics** University, India.
- Vries W. de, Romkens P.F., & Schutze G. (2007). Critical soil concentrations of cadmium, lead, and mercury in view of health effects on humans and animals. Reviews of Environmental Contamination and Toxicology 191, 91.
- Zhang J, Liu CL (2002). Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemical fluxes Estuar Coast Shelf Sci 54: 1051-1070.

