

EFFECT OF MINING OPERATION ON THE LEVEL OF HEAVY METALS IN SOILS FROM AREAS AROUND TANTALITE MINES IN OGAPA OTTO, NASARAWA STATE, NIGERIA



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Abstract: The effect of mining on the concentration of heavy metals in soils from areas around tantalite mines was studied. Forty topsoil samples and fifteen control samples were collected with hand auger at 0 - 20 cm depth from the study area. The samples were prepared and analysed for heavy metals such as Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn using atomic absorption spectrophotometer, AAS. The results of the metal analyses in soils obtained for the samples have the mean concentrations of 4.71±0.36, 12.60±4.74, 21.89±24.44, 18.65±12.40, 2533.01±996.26, 79.08±42.83, 445.91±360.97, 0.00, 839.04±199.33 mg/kg for Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn, respectively. For the control samples, the mean concentrations were 3.73±0.96, 22.64±6.45, 0.00, 32.05±7.23, 396.27±90.04, 33.03±7.89, 228.44±127.01, 0.00 and 984.91±275.63 mg/kg for Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn, respectively. The study revealed that the mean concentrations of heavy metals in the soil samples are higher than mean concentrations of heavy metals in the control samples due to mining activities except Co, Cu and Zn which are lower than their mean concentrations in control samples. All the mean concentrations of metals are lower than the tolerable maximum permissible limits recommended by FAO/WHO except for Zn that is higher and it is an indication of contamination. Although, there is no serious concern in terms of metal pollution for now it is necessary that there is periodic monitoring because with time there could be bioaccumulation that could lead to elevated levels of these metals and eventual translocation into the food chain with the potential health risks. Remediation measures should also be put in place to take care of the elevated levels of zinc. Keywords: Mining, heavy metals, soil, contamination, environment, pollution

Introduction

Developments in different areas of human endeavour such as industry, agriculture and other technological advancements have contributed to contamination of the environment (Ali et al., 2017). The environmental contaminants that have been of serious concern are heavy metals and mining is an important source of heavy metal contamination of the soils. Mining is a process of digging open the earth to remove the crude ore, crushing and in some cases concentration of the crude ore to remove the mineral of interest. In the third world countries or developing countries, Nigeria inclusive the excavations are done in very crude manner and therefore, heaps of wastes and open pits that eventually becomes ponds are left behind without any form of reclamation or protection (Akubugwo et al., 2010). The mining industries discharge relatively high level of heavy metals that are associated with the ore being mined as contaminants into the soils.

Heavy metals could be said to be any metallic or chemical elements that have high density and are potentially hazardous even at low concentration (Laghlimi *et al.*, 2015). Heavy metals are generally present everywhere in the environment due to natural phenomenon as well as anthropogenic activities and humans are faced with problems of exposure to the metals through various pathways such as ingestion, inhalation and contact with the skin (Laghlimi *et al.*, 2015). Heavy metals from anthropogenic sources in the soil are known to be of higher mobility than those from the lithogeneous or pedegeneous origin.

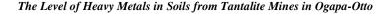
The heavy metals are non biodegradable and they accumulate in the soils. Crop plants grown on such soils contaminated with heavy metals are likely to take up the metals from the soil, bio-accumulate them in the tissues and when animals feeds on the plants, bio-accumulation also takes place and eventually the bulk of it is transferred into the food chain. It is through the food chain that it gets to humans with the associated health risks. In some cases it could lead to phytotoxicity in plants where, it affects the quality of the crops or it results in stunted growth of crops (Akubugwo *et al.*, 2010).

The aim of this research work is to evaluate the level of heavy metals in the soils from around the tantalite (tantalum pent– oxide ore) mines in Ogapa Otto in Nasarawa Local Government Area, Nasarawa State, Nigeria. This would help to ascertain the contributions from the mining activity with regards to the heavy metal concentrations in soils from around the mining location when compared to those of the control soil samples.

Materials and Methods

Topsoil samples from the depth of 0 - 20 cm (Alfred *et al.*, 2015) were collected from the areas around tantalite mines located in Ogapa Otto, Nasarawa Local Government Area, Nasarawa State. The samples were collected using hand auger. Sample points were located and recorded using GPS. Sampling was done randomly but evenly distributed around four major mine pits in the mining location. A total of forty (40) samples were collected and control samples collected were fifteen (15) from a location in the community at a distance of about 5 km away from the mines, where there is no mining activity (Fig. 1).

Soil samples were air dried for seven days. They were then ground into fine particles with laboratory mortar and pestle, screened using 2.00 mm mesh size sieve, packed in sample bags, labelled and kept pending analysis (Barkouch and Pineau, 2015). 1.00 g of the air dried soil sample was weighed into a 100.00 cm³ conical flask and 20.00 cm³ of freshly prepared aqua regia (1:3 HNO₃: HCl) was added, digested on a hot plate for 3 h, then evaporated and allowed to air cool, filtered and diluted or made up to 50.00 cm³ with de-ionized water. It was kept awaiting analysis for heavy metals using Atomic Absorption Spectrophotometer (Alfred *et al.*, 2013).



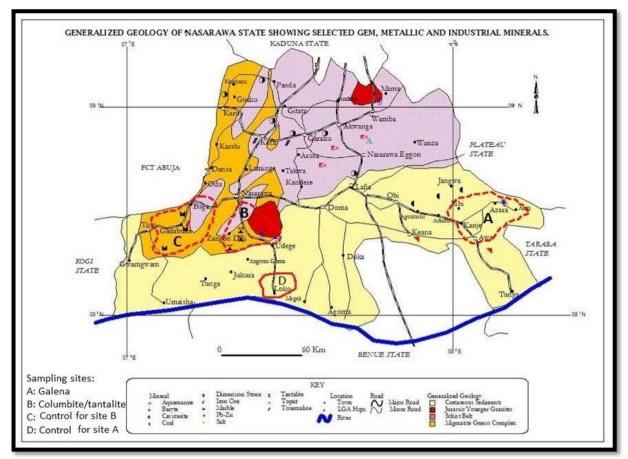


FIG 1: Map of Nasarawa State – the generalised geology showing selected gem, metallic and industrial minerals and the sampling location marked 'B'

The concentrations of Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn in the soil samples were determined with an Atomic Absorption Spectrophotometer, AAS (Model No. AA280FS) manufactured by Agilent Technologies, USA. All chemicals used were of reagent grade from BDH (British Drug House) and pure deionized water was used throughout the experiment. All plastic ware used were soaked in 5% HNO₃, properly washed and rinsed very well. (Barkouch and Pineau, 2015; Abeh *et al.*, 2007).

Data analysis

The results obtained would be subjected to statistical evaluation. Parameters evaluated were grand mean, standard deviation, coefficient of variation and correlation using R statistical software.

Results and Discussion

The Tables 1, 2, 3 and 4 show results of the concentrations of heavy metals in the soils from around the four major mine pits in the tantalite mining location at Ogapa Otto, Nasarawa Local Government Area, Nasarawa State. Table 5 shows the results obtained for heavy metal concentrations in the soil samples from the control location where there was no mining activity taking place. Table 6 shows the mean concentrations for heavy metals in soils from around the tantalite mining location as well as the mean concentrations of metals in control samples and the maximum tolerable recommended limits for the metals by regulatory bodies (FAO/WHO, 2014). Table 7 shows the correlation between analysed metals in soils from the tantalite mining location.

Table 1: Metal concentrations (mg/kg) in soil from tantalite mining area, Pit 1

Location Point	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
1	4.40	16.00	54.00	4.50	3809.85	108.10	305.90	0.00	584.00
2	4.50	17.50	66.10	11.00	4242.44	120.20	374.50	0.00	279.40
3	4.20	20.10	88.00	16.00	4298.32	111.40	476.80	0.00	835.40
4	4.00	25.20	65.80	14.30	3971.93	119.6	400.80	0.00	912.40
5	3.80	14.30	58.60	0.00	4705.90	126.10	2186.00	0.00	864.90
6	4.10	15.20	65.00	0.00	4027.27	122.00	1403.10	0.00	769.30
7	5.20	17.30	43.80	0.00	3231.45	106.50	61.50	0.00	798.80
8	4.60	7.30	49.40	0.00	2953.13	107.80	151.50	0.00	837.20
9	4.80	8.80	44.30	0.00	2650.11	98.80	281.00	0.00	773.40
10	5.20	6.30	41.90	0.00	2519.02	100.10	274.70	0.00	791.20

Table 2: Metal concentrations	(mg/kg) in soil from tantalite mining area,	Pit 2

Location Point	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
1	4.90	12.30	25.70	0.00	1584.20	100.90	270.10	0.00	673.00
2	4.50	10.40	32.90	0.00	1283.67	100.60	268.70	0.00	281.10
3	4.70	14.50	18.80	24.40	1581.77	104.50	607.70	0.00	143.50
4	4.80	17.40	29.80	22.90	1597.21	102.30	550.60	0.00	963.70
5	4.70	6.60	24.20	1.30	1330.61	96.70	266.30	0.00	845.50
6	5.10	14.00	11.30	18.40	1307.63	112.00	243.50	0.00	832.60
7	4.70	8.30	26.80	35.60	3039.69	106.90	560.80	0.00	902.50
8	4.80	15.50	42.50	35.90	2994.65	106.80	573.60	0.00	871.50
9	5.00	2.80	0.00	20.00	1149.32	106.30	14.10	0.00	858.40
10	5.00	9.20	8.70	20.10	1119.39	103.10	159.70	0.00	812.10

Table 3: Metal concentrations (mg/kg) in soil from tantalite mining area, Pit 3

Location Point	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
1	4.60	8.50	10.00	25.50	2229.77	114.60	589.60	0.00	857.60
2	4.90	5.70	20.30	24.30	2330.69	105.00	539.60	0.00	891.00
3	5.40	16.80	14.80	20.00	1807.81	103.00	424.10	0.00	902.10
4	5.10	8.40	14.60	21.00	1768.79	106.00	431.90	0.00	953.50
5	5.20	10.40	5.00	26.30	2240.55	13.10	394.50	0.00	922.80
6	4.70	15.00	0.00	22.40	2320.77	18.60	432.90	0.00	932.90
7	4.40	15.60	0.00	22.20	1824.57	23.50	641.30	0.00	884.40
8	4.80	6.90	8.90	24.60	1958.97	9.20	650.40	0.00	916.20
9	5.00	13.00	0.00	17.20	1655.14	105.00	415.50	0.00	864.30
10	5.20	15.10	0.00	20.10	1582.94	105.00	342.70	0.00	836.30

Table 4: Metal concentrations (mg/kg) in soil from tantalite mining area, Pit 4

Location Point	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
1	4.60	13.60	0.00	32.20	2669.15	19.20	295.00	0.00	1009.80
2	4.40	9.70	4.40	31.60	2648.82	11.90	273.70	0.00	908.50
3	4.70	10.90	0.00	41.20	3975.65	25.00	506.40	0.00	969.30
4	4.50	15.70	0.00	38.70	3970.35	13.40	521.70	0.00	994.60
5	4.10	11.70	0.00	34.10	3151.57	19.60	141.60	0.00	996.20
6	4.60	22.20	0.00	34.00	3274.01	29.80	203.60	0.00	992.90
7	4.70	8.50	0.00	21.80	2360.42	21.00	369.00	0.00	1037.20
8	4.80	11.20	0.00	21.30	2232.59	25.60	404.90	0.00	1050.80
9	4.80	10.10	0.00	23.00	1991.24	16.50	436.80	0.00	1006.30
10	4.90	15.90	0.00	20.10	1928.94	117.60	390.40	0.00	1004.80

 Table 5: Metal concentrations (mg/kg) in soil samples from control location

Location Point	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
1	4.00	25.60	0.00	44.80	527.84	44.70	321.90	0.00	1050.10
2	4.40	31.80	0.00	44.90	570.31	44.30	452.20	0.00	1093.40
3	2.40	32.10	0.00	30.70	417.16	35.70	221.00	0.00	1092.10
4	4.10	21.30	0.00	31.90	430.16	36.90	273.30	0.00	1064.90
5	4.50	22.90	0.00	25.20	329.02	26.50	112.30	0.00	1116.80
6	4.20	20.00	0.00	27.30	364.07	34.90	370.80	0.00	1068.40
7	1.40	14.30	0.00	28.00	328.47	26.20	291.60	0.00	1030.10
8	4.10	21.60	0.00	28.20	318.98	21.00	288.70	0.00	1128.10
9	4.00	34.40	0.00	44.40	547.49	45.00	392.70	0.00	1112.80
10	4.40	21.50	0.00	31.60	381.84	38.20	167.40	0.00	981.50
11	2.20	25.70	0.00	35.50	433.80	31.60	226.70	0.00	1104.50
12	3.40	18.30	0.00	30.70	358.06	26.50	101.70	0.00	984.40
13	4.20	21.00	0.00	24.00	325.96	28.80	83.80	0.00	1110.10
14	4.60	17.70	0.00	24.00	285.40	22.30	60.40	0.00	801.80
15	4.10	11.40	0.00	29.50	325.50	32.90	62.10	0.00	34.70
Min.	1.40	11.40	0.00	24.00	285.40	21.00	60.40	0.00	34.70
Max.	4.60	34.40	0.00	44.90	570.31	45.00	452.20	0.00	1128.10
Mean	3.73	22.64	0.00	32.05	396.27	33.03	228.44	0.00	984.91
M. Dev.	0.74	4.89	0.00	5.52	73.22	6.46	105.62	0.00	151.63
SD	0.96	6.45	0.00	7.23	90.04	7.89	127.01	0.00	275.63

Cadmium was detected in all the soil samples from the tantalite mining location. The mean concentration of cadmium in soils from tantalite mining location was 4.71±0.36 mg/kg (Table 6). This value is higher than the concentration of cadmium in one soil sample from a study area around a gold mine which was 0.20 mg/kg and was not detectable in all the other samples (Ali et al., 2017) and it is also higher than mean concentration of cadmium of 0.99 mg/kg in soils from around Pb-mine as reported by Laghlimi et al. (2015). The mean value of cadmium content in soils from the study area is lower than the cadmium contents in soils that were collected from points of 0, 5, 10 and 30 m from a randomly selected excavated site in Ishiagu mines which were 48.57, 40.44, 39.34 and 11.60 mg/kg respectively as reported by Akubugwo et al. (2010). The mean value of cadmium contents in the soils from the study is slightly higher than the mean concentration of cadmium from the control samples which is 3.73±0.96 mg/kg and this could be largely attributed to the mining activity. The value is also higher than the maximum permissible recommended limits of 3.00 mg/kg for cadmium in soils by WHO/FAO (2014) and it is an indication of contamination.

The mean concentration of cobalt in soils from tantalite mining location is 12.60±4.74 mg/kg (Table 6). The cobalt concentration is higher than the mean values of cobalt (0.62±0.16 mg/kg and 0.22±012 mg/kg) in soils from the windward and leeward of copper-nickel mine reported by Alfred et al. (2013). The cobalt concentrations in soils from the study location is higher than the mean cobalt concentrations in soils in mining areas with values of 5.42 mg/kg and a range of 0.00 - 16.50 mg/kg reported by Laghlimi et al. (2015) and Ali et al. (2017) respectively. The concentration of cobalt in soils from the tantalite mining location is lower than that of the control site. This could be due to difference in the compositional and mineralogical characteristics of the parent/source geological materials between the mining location and the control site. The mean value of cobalt in soils from the study location is lower than the value of 50.00 mg/kg recommended as the maximum permissible limits by WHO/FAO, (2014).

The mean chromium concentration in soils from the mining location was 21.89±24.44 mg/kg. This value is within the range values of 5.00 - 120.00 mg/kg reported by Ogbonna et al. (2013) and is lower than the mean value of chromium 5,750 mg/kg in soils from lowland paddy fied around a chromite mine in Vietnam (Kien et al., 2010). The value is higher than the mean concentration of cobalt in soils from around an iron ore mining field which ranged from 4.18 -17.57 mg/kg (Olatunji and Osibanjo, 2012). The mean chromium concentration in soils of 73.38 mg/kg from a copper mining location (Xianfeng et al., 2018) is higher than the value from the tantalite mining location. The mean chromium concentration from the study location is higher than its mean concentration from the control site which was recorded to be 0.00 mg/kg. This difference in the concentrations of chromium in soils from the study area and the control location could be attributed to the mining activity on the study location. The value is however; lower than the recommended maximum permissible limit of 100.00 mg/kg by the regulatory bodies (Table 6).

The copper mean concentration in soil samples is 18.65 ± 12.40 mg/kg. This value is higher than the values of copper in soils from around a gold mining location, 3.02 ± 3.23 mg/kg for active mine site and 2.22 ± 3.09 mg/kg for abandoned mine site (Adebayo *et al.*, 2017). The value is within the range values for the concentration of copper 8.80 - 145.00 mg/kg in soils from around active tantalum-niobium mines (Oyebamiji *et al.*, 2018). The values are higher than the mean values of copper in soils from different sampling points in a site, 1.13, 5.13,

1.38 and 0.64 mg/kg reported by Mofor *et al.*, (2017). The mean concentration of copper in soils from the tantalite location is lower than the value of 32.05 ± 7.23 mg/kg recorded for the control site and could be due to the difference in the compositional and mineralogical characteristics of the parent/source geological materials. WHO/FAO, 2014 tolerable recommended maximum permissible limit of 100.00 mg/kg is higher than mean concentration of copper in soils from the study location (Table 6).

The mean concentration of iron in the soils from tantalite mining location is 2533.01±996.26 mg/kg (Table 6). The value is higher than the range values for the mean concentrations of iron 7.00 - 222.00 mg/kg in soils collected from active tantalum-niobium mines (Oyebamiji et al., 2018). The value is lower than the mean concentrations of iron in soils from around iron mining area which was 60,924.50 mg/kg (Ameh, 2014). The concentration of iron in soils from areas around a gold miming location ranged from 3,566.00 -14,635.00 mg/kg (Ali et al., 2017) and this is higher than the concentration of iron recorded in the present study. The values obtained from the present study are also all higher than the mean concentration of iron in soils from around coppernickel mine which was 189±77 mg/kg in the leeward direction and 264±119 mg/kg in the windward direction (Alfred et al., 2013). The mean concentrations of iron from the studied mining location is higher the mean concentration of iron in soils from the control site which was 396.27±90.04 mg/kg. This could be attributed to mining activity. The values are all lower than the concentration of 50000.00 mg/kg which is the recommended maximum permissible limits by WHO/FAO, 2014 for iron in soils.

The mean concentration of 79.08±42.83 mg/kg was obtained for lead in soils from the tantalite mining location. This value is lower than the mean concentration of 127±8.28 mg/kg for lead in agricultural soils from the surrounding of a mining site in Marrakech, Morocco (El-fadeli et al., 2015). The value from the current study is also lower than all the concentrations recorded for lead in soils from around molybdenum mine with different land use from barren land (998±6 mg/kg), wheat field (736±21 mg/kg), rape field (664±19 mg/kg) to apple seedling field (1126±26 mg/kg) as reported by Han et al. (2019). The concentrations of lead in soils from a lead zinc mine at different distances from the mine pit 0, 5, 10 and 30 m are 34,311, 24,943, 17,351 and 6,246 mg/kg respectively ((Akubugwo et al., 2010) and these values are all higher than the mean concentration of lead in soils from the present study. The mean concentration of lead in soils from the present study is higher than the mean concentration of lead in soil samples from the control site which is 33.03±7.89 mg/kg and that could be due to mining activity. The recommended tolerable maximum permissible limit of 100.00 mg/kg by WHO/FAO (2014) for lead in soils is higher than the value of 78.08 mg/kg recorded for this work (Table 6).

The mean concentration of manganese in soils from the tantalite mining locations is 445.91±360.97 mg/kg. The value is higher than the concentration of manganese in soils from areas around iron ore mining field which ranges from 2.80 -3.90 mg/kg (Olatunji and Osibanjo, 2012). The value is within the range of 0.00 - 655.00 mg/kg for manganese in soils around a gold mine (Ali et al., 2017) but the value is lower than total concentration of manganese in soils from areas near a coal mining field which ranged from 549.6±49.4 -1411.7±144.2 mg/kg (Kiran et al., 2012). The mean concentration of manganese in soils from the study area is higher than the mean concentration of manganese in the soil samples from the control site which was 228.44±127.01 mg/kg due mining activity. The recommended maximum permissible limit of 2000.00 mg/kg for manganese in soils by

WHO/FAO, 2014 is higher than 445.91 mg/kg for manganese in soils recorded for the present research (Table 6).

Nickel was not detectable in soils from tantalite mining location as well as in the soils from the control site. This could be attributed to the fact that nickel might not be one of heavy metals that are associated with tantalum pent–oxide ore. Therefore, for the soils from this location, it is far from being compared with 50.00 mg/kg of nickel in soils that FAO/WHO, 2014 recommends as the maximum tolerable limits.

The mean zinc concentration in soils from the tantalite mining location is 839.04 ± 199.33 mg/kg. This value is higher than the range concentrations of 1.50 - 296.00 mg/kg for zinc in soils around a coal mining field (Sahoo *et al.*, 2016). The value is also higher than the range of mean zinc concentrations in soils from different locations of a gold

mining basin in South Africa which is 21.82 - 82.50 mg/kg (Caspah *et al.*, 2016). The mean zinc concentration in soils from this study is higher than the mean concentration of zinc in soils (16.09 mg/kg) from Pb – Zn mines (Paulinus, 2015). The value is also higher than the mean concentration of zinc 689.66 mg/kg reported by Huang *et al.*, (2017). The mean zinc concentration from the study area is higher than 300.00 mg/kg which is the recommended maximum permissible limits by WHO/FAO, 2014 (Table 6) which is an indication of contamination. The value of mean concentration of zinc in soils from the tantalite location is lower than that of the control mean value of 984.91±275.63 mg/kg which could be attributed to the difference in the compositional and mineralogical characteristics of the parent/source geological materials between the mining location and the control site.

Heavy metal	Study area mean value	SD	CV%	Control mean value	FAO/WHO (2014)
Cd	4.71	0.36	7.64	3.73	3.00
Co	12.60	4.74	37.62	22.64	50.00
Cr	21.89	24.44	111.65	ND	100.00
Cu	18.65	12.40	66.49	32.05	100.00
Fe	2533.01	996.26	39.33	396.27	50,000.00
Pb	79.08	42.83	54.16	33.03	100.00
Mn	445.91	360.97	80.95	228.44	2000.00
Ni	ND	NA	NA	ND	50.00
Zn	839.04	199.33	23.76	984.91	200.00

ND- Not detectable, NA- Not available, SD- standard deviation, CV- Coefficient of variation

Heavy Metal	Cd	Со	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Cd	1.00								
Со	- ^w 0.33	1.00							
Cr	- ^w 0.42	^w 0.33	1.00						
Cu	0.05	0.05	- ^m 0.60	1.00					
Fe	- ^m 0.65	^w 0.45	^m 0.57	0.00	1.00				
Pb	0.05	0.11	^m 0.62	- ^m 0.56	0.00	1.00			
Mn	-0.05	0.14	^w 0.30	-0.13	- ^w 0.42	0.16	1.00		
Ni	NA	NA	NA	NA	NA	NA	NA	1.00	
Zn	0.08	-0.07	- ^w 0.42	^w 0.43	0.03	- ^w 0.45	0.00	NA	1.00

w= weak correlation, m= moderate correlation, s= strong correlation

Tantalite mining location has moderate correlations for Cr - Fe and Cr - Pb and a weak one for Co - Cr, Co - Fe, Cr - Mn and Cu - Zn (Table 7). Strong correlation implies that the metals have the same source and have greater dependence on each other. Moderate correlation is an indication of the metals coming from the same source and having moderate dependence on one another. Weak correlation implies weak relationship and weak dependence of one metal on the other. There is also a negative correlation in the following order; moderate correlation for Cd - Fe, Cr - Cu and weak correlation for Cd - Cr, Cr - Zn, Cu - Pb, Fe - Mn, Pb - Zn. The negative correlation is an indication that as the concentration of one is increasing the other one will be decreasing. The degree or extent of the relationship is shown by whether it is strong, moderate or weak.

Conclusion

The mean metal concentrations for all metals analysed are higher than the values from the control site as a result of mining activity except for Co, Cu and Zn that have their mean concentrations in soils from control site higher due to compositional and mineralogical characteristics of parents /source geological materials that are different for the two sites. The mean metal concentrations are also lower than the WHO/FAO (2014) recommended maximum permissible limits except for Zn which is higher than the permissible limit and this is an indication of high level of pollution by the metal. It is evident therefore, the soils is not under the risk of metal pollution except for zinc. The coefficient of variation for the mean concentrations of metals ranged from 7.67% in Cd to 111.65% in Cr which implies that Cd is the least varied in the soils while Cr is the most varied in the soils from the study location. The correlation study showed both negative and positive moderate to weak correlation between some of the metals.

Conflict of Interest

Authors declare that there is no conflict of interest related to this study.

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