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Research paper

Determination of heavy metals and essential minerals in water, soil and edible plant samples from the vicinity of ankpa coal mine, kogi state

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Abstract

This research work determined the physicochemical properties (pH, temperature, electrical conductivity, total dissolved solids and total suspended solids) of water, heavy metals (Cr, Cd, Cu, Pb and Zn) and essential minerals (P, Ca, K, Mg and Na) in water, plant and soil samples collected from the vicinity of Ankpa Coal mine, Kogi State. The heavy metals were analyzed using a Flame Atomic Absorption Spectrophotometer machine and the essential minerals analyzed using Microwave Plasma Atomic Emission Spectrophotometer machine. Results obtained for physical parameters of water are within the ranges; pH (4.51-6.91), temperature (19.8-26.5˚C), electrical conductivity (110-210 µs/cm), TDS (7.0-13 mg/l) and TSS (0-1.5 mg/l). The heavy metals concentration in water are as follows; Cd (ND), Pb (0.001-0.077 mg/l), Cr (0.028-3.459 mg/l), Cu (0.09-0.057 mg/l) and Zn (0.050-0.161 mg/l). In plants, Cd (ND), Pb (0.043-0.096 mg/kg), Cr (0.138-0.325 mg/kg), Cu (0.139-0.153 mg/kg) and Zn (0.150-0.510 mg/kg). In soils, Cd (ND), Pb (0.127-0.664 mg/kg), Cr (1.206-4.718 mg/kg), Cu (0.155-0.934 mg/kg) and Zn (0.00-0.400 mg/kg). Results obtained for essential minerals ranged as follows; In water, P (0.19-43.31 mg/l), Ca (5.75-158.63 mg/l), K (5.04-32.28 mg/l), Mg (1.98-11.34 mg/l) and Na (10.70-28.29 mg/l). In plants, P (15.12-23.90 mg/kg), Ca (30.13-144.44 mg/kg), K (64.10-119.06 mg/kg), Mg (10.38-25.69 mg/kg) and Na (0.94-3.55 mg/kg). In soil, P (180.01-1879.51 mg/kg), Ca (11.61-85.18 mg/kg), K (3.02-114.98 mg/kg), Mg (2.59-14.05 mg/kg) and Na (8.24-15.03 mg/kg). The results were compared with the maximum permissible limit (MPL) set by World Health Organization (WHO), Food and Agricultural Organization (FAO) and recommended dietary intake set by Food and Nutrition Board (FNB). The physicochemical parameters were all within WHO maximum permissible limit for drinking water. Lead and Cr exceeded the MPL set for drinking water, all heavy metals were within set limit for plants. Lead, Cu and Chromium exceeded the MPL set for soil. The essential minerals in all samples were compared to recommended dietary intake (RDI). Correlation analysis was done using Pearson's correlation coefficient. In plants Zn correlated positively with Ca (0.9298), K (0.7860) and Mg (0.9967) and in soil samples Cu correlated positively with P (0.8212), K (0.8191) and Na (0.8658), Cr correlated positively with P (0.9911), K (0.9915) and Na (0.8363) and Lead correlated positively with P (0.9734), K (0.9905) and Na (0.7948). It can be inferred from this result that Ankpa coal mine has negatively impacted its vicinity.

Keywords: *Heavy Metals; Essential Minerals; Total Dissolved Solids (TDS); Total Suspended Solids (TSS); Maximum Permissible Limits (MPL); Macro and Micro Elements; Microwave Plasma Atomic Emission Spectroscopy (MP-AES); and Pearson's Correlation Analysis.*

1. Introduction

Mining can be a significant source of metal contamination of the environment owing to activities such as mineral excavation, ore transportation, smelting and refining, disposal of the tailings and wastewater around mines (Adriano 2001; Chopin and Alloway 2007 Jung 2001; Razo et al., 2004). The problem of water quality is more severe in the areas where mining and mineral processes' industries are located. In mining, several classes of wastes are produced which may cause various types of pollution and ultimately contamination occurs (Farhaduzzaman et al., 2012). So, it is of great importance to evaluate the surface and ground water in every state of Nigeria where mining is on-going or had earlier taken place.

Heavy metals are natural constituents of the Earth's crust and since they cannot be degraded or destroyed, they are considered persistent environmental pollutants. Heavy metal pollution originates from anthropogenic sources, such as untreated domestic and industrial wastewater discharges, accidental chemical spills, direct soil waste dumping, and residues from some agricultural inputs (Tchounwou et al., 2012) and are present in air, sediments, and water. These elements have been associated with environmental degradation, poor water quality, stunted plant growth (Wongsasuluk et al., 2014), and different human diseases (Mico et al., 2006) due to their toxicity at very low doses.

Essential mineral elements are nutrients required by living organisms for the proper functioning of their systems. Minerals are elements that originate in soil and cannot be created by living organisms such as plants and animals (Khan et al., 2015). Plants absorb minerals from soils and animals get their minerals from the plants.

2. Materials and methods

2.1. Reagents and solutions

All reagents used were of analytical grade. Distilled water was used for the preparation of all solutions. All glassware used were properly cleaned by first washing with detergent and water, and then rinsed severally with distilled water and dried.

2.2. Sampling

Sampling locations were divided into six (6) namely: Awo-akpali, Onupi-village, Awo- etiuku, Awo-Ojuwo and Onupi-Yardi and Ekale-le (control Location). From each sampling location, two (2) surface water samples, one (1) ground water sample, one (1) plant sample and one (1) soil sample were collected. From the control location, one (1) surface water, one (1) ground water, one (1) plant and one (1) soil sample were collected. A total of seventeen (17) water samples, six (6) soil samples, and Five (5) edible plants were collected.

2.3. Preparation of samples

Water Sample Solutions for MPAES and AAS Analysis.
Water samples (250ml) from each sampling points within the sampling locations were mixed together in a one liter (1 L) sterile plastic bottle and exactly 2 ml concentrated nitric acid was added to prevent microbial activities. A composite water sample was made from each of the sampling points by mixing exactly 100ml of the pre-treated water sample in 500ml sterile sampling bottles to make 300ml composite water samples. This was done for all the samples collected in each sampling location. The samples were stored in a dry place and labelled accordingly.

2.4.1. Preparation of soil samples

Soil Sample Solution for MPAES and AAS Analysis.
Soil samples (400 g) from each sampling points were dried and properly mixed together with the aid of a mortar and pestle. A 2 mm sieve was used to sift the soil samples in order to separate the debris, stone and other unwanted materials from the collected soil samples. A composite soil sample was made by mixing exactly 100 g of the soil sample was from each sampling points (3 points) to make 300 g of composite soil sample. This was done for each soil sample collected in the different sampling location. It was stored in a plastic container and labelled accordingly.

2.3.2. Preparation of plant samples

Plant Sample Solution for MPAES and AAS Analysis.
Plant samples (leaves and stem) were rinsed with water to remove sand, stone and debris. It was dried in an oven at 75 ˚C and weighed till a constant weight was achieved. It was grounded to powdered form with the aid of a mortar and pestle. Exactly 10 g of the pre-weighed plant sample from each sampling point (3 points) was mixed together to make a 30 g composite plant sample for each location. The samples were stored in a cleaned, dried plastic container and labelled appropriately (Abdul et al., 2012).

3. Results and discussions

The results of the physicochemical parameters of water samples, the concentration of heavy metals in plants, soil and water samples and the concentration of essential minerals in plant, soil and water samples are presented below.

Table 1: Average Values of Physicochemical Parameters of Ground Water Samples

Sample	Temp(˚C)	pH	E.C(µS/cm)	TDS(mg/l)	TSS(mg/l)
Ground Water 1	26.4±0.10	4.5±0.00	165±0.00	11.1	1.00
Ground Water 2	19.8±0.10	6.50±0.01	200±2.00	10.5	0.93
Ground Water 3	25.8±0.11	6.31±0.10	110±1.40	11.3	0.70
Ground Water 4	21.3±1.00	6.36±0.00	180±2.00	9.60	1.40
Ground Water 5	25.7±1.00	5.55±0.22	130±4.00	12.4	0.91
Ground Water 6	25.7±0.00	6.81±0.00	100±3.00	9.80	0.50
Ground Water 7	26.5±0.02	6.65±0.00	170±1.00	10.60	1.50
Control Sample	24.2±0.21	6.51±0.00	190±0.00	10.30	1.20

Key: TDS = Total Dissolved Solid; TSS = Total Suspended Solid; EC = Electrical Conductivity
The physicochemical parameters of the ground water samples analyzed from the study areas are presented in Table 1. There were no variations in the physicochemical properties of the ground water samples. Water temperature values in the study area ranged from 19.8-26.5 ˚C. The groundwater temperature ranged from 21.23-26.5 ˚C. This suggests that the water temperature is generally ambient and good for consumers who prefer cool water to warm water and for the specific reason of water quality; since, high temperature negatively impact water quality by enhancing the growth of micro-organisms which may alter taste, colour, odour and cause corrosion problems (UNICEF, 2008). Therefore it is important that the groundwater temperature is not too high in order not to have microbial proliferation (Yilmaz and Koc, 2014)

Table 2: Mean Concentration (mg/l) of Heavy Metals (Cu, Cr, Pb, Zn and Cd) and Standard Deviation in Ground Water Samples

Sample	Cu	Cr	Pb	Zn	Cd
Ground water 1	0.047 ± 0.0009	3.459 ± 0.0294	0.001 ± 0.0134	0.090 ± 0.010	ND
Ground water 2	0.050 ± 0.0013	1.982 ± 0.0203	0.049 ± 0.0195	0.161 ± 0.001	ND
Ground water 3	0.028 ± 0.0048	0.474 ± 0.0240	0.002 ± 0.0091	0.061 ± 0.000	ND
Ground water 4	0.033 ± 0.0045	1.643 ± 0.0060	0.041 ± 0.0185	0.090 ± 0.000	ND
Ground water 5	0.028 ± 0.0043	0.028 ± 0.0091	0.000 ± 0.0118	0.070 ± 0.010	ND

Ground water 6	0.045 ± 0.0018	4.927 ± 0.0401	0.002 ± 0.0135	0.080 ± 0.010	ND
Ground water 7	0.035 ± 0.0047	0.108 ± 0.0126	0.004 ± 0.0137	0.140 ± 0.001	ND
Control sample	0.002 ± 0.0017	0.011 ± 0.0140	0.001 ± 0.0010	0.031 ± 0.001	ND
WHO (2011) STD	1.30	0.1	0.015	5.0	

Key: ND- Not detected, STD- standard; WHO = World Health Organization.

Results presented in table 2 showed that heavy metals investigated did not exhibit significant elevated levels in ground water samples after comparison with the maximum permissible limits (Cu-1.30, Cr-0.1, Zn-5.0, Pb-0.015 mg/l) set by WHO 2008. All the metals analyzed were present except Cd that wasn't detected in the samples. Chromium presented the highest in ground water samples. Zn and Cu were well within the set standards. The order of increase in concentration of the heavy metals in ground water samples: Cr>Pb>Zn>Cu. The activities of the coal mine may have resulted in the steady accumulation of heavy metals in its vicinity.

Table 3: Mean Concentration (Mg/L) of Essential Minerals (P, Ca, Mg, K And Na) and Standard Deviation in the Ground Water Samples

Sample	P	Ca	K	Mg	Na
Ground water 1	43.31±0.75	13.85±0.17	7.58±0.09	3.87±0.20	17.81±0.18
Ground water 2	24.30±0.37	158.63±1.10	14.74±0.15	6.79±0.37	21.43±0.25
Ground water 3	7.13±0.21	6.69±0.07	5.04±0.05	4.28±0.18	15.58±0.020
Ground water 4	21.49±0.31	9.15±0.08	9.10±0.05	4.41±0.02	17.30±0.07
Ground water 5	0.13±0.04	12.12±0.13	8.67±0.09	5.15±0.03	16.63±0.018
Ground water 6	03.36±0.81	13.43±0.22	7.78±0.07	4.35±0.03	19.06±0.06
Ground water 7	1.31±0.08	5.75±0.03	7.52±0.12	4.19±0.05	13.60±0.12
Ground water C	15.20±0.20	11.10±0.09	9.29±0.32	2.15±0.01	15.93±0.13
WHO (2011) STD	-	100-300	-	30	200

Key: WHO – World Health Organization.

Results obtained in table 3 for essential minerals (P, K, Mg, Na, Ca) in water are compared with the maximum permissible limit set by WHO 1998 and recommended dietary intake by FNB 1989. All essential minerals analyzed were present in varying concentrations with average mean concentration (AMC): 24.73, 18.26, 9.52, 9.33 and 4.94 mg/l for Ca, Na, P, K and Mg respectively. As seen in the chart below, the concentration of essential minerals in groundwater samples followed the trend Ca>Na>P>K>Mg.

Table 4: Mean Concentration (mg/kg) of Heavy Metals and Standard Deviation in the Plant Samples

Plant Sample	Cu	Cr	Pb	Zn	Cd
Pumpkin leaves	0.153±0.0028	0.138±0.0249	0.093±0.0048	0.150±0.000	ND
Bitter leaves	0.139±0.0023	0.209±0.0130	0.057±0.0121	0.510±0.010	ND
Spinach	0.142±0.0113	0.139±0.0125	0.096±0.0359	0.150±0.020	ND
Bushbuck	0.153±0.0020	0.225±0.0280	0.073±0.0327	0.210±0.010	ND
Scent leaves	0.142±0.0039	0.325±0.0193	0.043±0.0138	0.290±0.010	ND
$Spinach_{control}$	0.124±0.0010	0.126±0.0140	0.029±0.0010	0.044±0.021	-
WHO/FAO 2011	10	1.3	2.0	50	1

Key: ND- Not detected; WHO = World Health Organization; Food and Agricultural Organization.

The concentration of heavy metals in plant samples are presented in Table 4. Results obtained were well within WHO maximum permissible limit (Cu-10, Cr-1.3, Zn-50, Pb-2.0). All metals analyzed were present (Cu-0.139-0.153, Cr-0.138-0.325, Zn-0.150-0.510, Pb-0.043-0.096 mg/kg) in amounts below the compared maximum permissible limits which indicates no heavy metal contamination in the plant samples. Zinc presented the highest concentration across the plant samples (0.51 mg/kg-Pumpkin and 0.29 mg/kg-Scent leaves) and lowest in Bitter leaves-0.15 mg/kg and Spinach-0.15 mg/kg, followed by chromium (Scent leaves-0.325 mg/kg and bushbuck-0.225 mg/kg) then copper (Pumpkin leaves-0.15 3 mg/kg and Bushbuck-0.142 mg/kg) and lead (Pumpkin leaves-0.098 and Spinach-0.043 mg/kg), Zn>Cr>Cu>Pb. Cadmium was not detected in any of the plant samples. As seen in the chart, the increasing level of heavy metals in the plant samples followed the trend: Zn>Cr>Cu>Pb. There was no heavy metal contamination in plant samples hence no basis for comparison.

Table 5: Mean Concentration (mg/kg) of Essentials Minerals and Standard Deviation in the Plant Samples

Plant Sample	P	Ca	K	Mg	Na
Pumpkin leaves	18.79±0.20	30.13±0.29	80.51±0.45	10.75±0.19	0.94±0.09
Bitter leaves	21.73±0.020	144.44±0.33	124.34±0.61	25.69±0.27	2.04±0.10
Spinach	18.00±0.15	64.63±0.42	49.93±0.38	10.38±0.12	2.29±0.08
Bush buck	23.90±0.21	46.53±0.27	100.0±0.78	12.87±0.12	3.55±0.02
Scent leaves	17.74±0.037	63.66±0.40	119.06±0.68	17.50±0.20	2.03±0.06
$Spinach_{Control}$	15.12±0.10	51.24±0.21	64.10±0.39	19.31±0.01	1.50±0.70

The concentration of essential minerals in plant samples are presented in Table 5. The essential minerals in plants were found in varying concentrations in the plant samples. The concentration of the essential minerals in the plant samples. There was no basis for comparison as these are minerals required in the body in large amounts and only conforms to a stipulated recommended dietary intake. Potassium (AMC-89.15 mg/kg) presented the highest concentration across the plant samples, then Ca (AMC-66.77 mg/kg), P (AMC-19.21 mg/kg), Mg (AMC-16.08 mg/kg) and Na (AMC-2.05 mg/kg).

Table 6: Mean Concentration (mg/kg) of Heavy Metals and Standard Deviation in the Soil Samples

Soil Sample Location	Cu	Cr	Pb	Zn	Cd
Awo-Akpali	0.155±0.0008	1.206±0.0150	0.127±0.0043	0.050±0.010	ND
Onupi	0.934±0.0059	4.718±0.0129	0.572±0.0161	0.000±0.010	ND
Awo-Etiuku	0.937±0.0036	4.673±0.0151	0.664±0.0049	0.000±0.010	ND
Awo-Ojuwo	0.357±0.0033	4.086±0.0090	0.522±0.0155	0.400±0.030	ND
Onupi-Yardi	0.239±0.0007	1.950±0.0045	0.142±0.0183	0.200±0.010	ND
$Ekalele_{control}$	0.153±0.0006	1.401±0.0010	0.128±0.0044	0.002±0.001	-
WHO/FAO 2011	0.40	1.30	0.125	1.50	

Key: ND = Not detected; WHO = World Health Organization; Food and Agricultural Organization.

The concentration of heavy metals in soil samples are presented in Table 4.9. The results obtained were compared with WHO maximum permissible limits (Cu-0.40, Cr-1.30, Pb-0.125 and Zn-1.50) and only Zinc was within set standards. Chromium, Copper and Lead were all above the maximum permissible limit in the soil samples (Cr-1.206-4.718 mg/kg, Cu-0.239-0.937 mg/kg and Pb-0-0.40 mg/kg). The concentration of the metals across all soil samples are presented in appendix 4. Again, Cr showed the highest concentration (Onupi-4.718 mg/kg), followed by Copper (Awo-Etiuku- 0.937 mg/kg) and then Lead (Awo-Etiuku-0.664 mg/kg). Cadmium was not also detected in the soil samples. As observed in the chart, the increasing level of heavy metals in the soil samples followed the trend: Cr>Cu>Pb>Zn. Comparing the most contaminated location to the least, this trend was observed: Awo- Etiuku>Onupi>Awo-Ojuwo>Onupi-Yardi>Awo-Akpali. This may be due to the proximity of the sampling location to the coal mine.

4. Correlation analysis

Pearson's correlation coefficient was used to compare heavy metals in soil and essential minerals in plant samples.

Table 7: Pearson's Correlation Results for Heavy Metals in Soil and Essential Minerals in Plant Samples

Plant/soil sample	Soil Cu	Soil Cr	Soil Zn	Soil Pb	Soil P	Soil Ca	Soil K	Soil Mg	Na
Plant Cu	1								
Plant Cr	-0.2621	1							
Plant Pb	0.4695	-0.9299	1						
Plant Zn	-0.6348	0.3983	-0.2431	1					
Plant P	0.9317[a]	0.0362	-0.1531	0.3245	1				
Plant Ca	-0.7795	0.9410[a]	-0.9038	0.9298[a]	0.2341	1			
Plant K	0.9309[a]	0.9954[a]	-0.8979	0.7860[a]	0.3785	0.5101	1		
Plant Mg	0.8466[a]	0.4532	-0.7481	0.9967[a]	0.2748	0.9000	0.2637	1	
Plant Na	0.0819	0.3062	-0.2651	0.8293[a]	0.6729	0.0440	0.1070	-0.0122	1

Key: [a]Correlation is significant at 0.01 confidence level.

In the correlation analysis, Cu correlated positively with P (0.9317), K (0.9309) and Mg (0.8466), Cr correlated positively with Ca (0.9410) and K (0.9954), while Lead correlated positively with Ca (0.9298), K (0.7860), Mg (0.9967) and Na (0.8293). All correlations are significant at 0.01 confidence level. Zinc correlated negatively with the entire essential mineral.

The growth and development of plants are affected by the conditions of the growing environment (Soil). Accumulation of heavy metals in soil can result in various deficiencies such as reduction in cell activities and inhibition of growth in plants as reported by Osuocha et al., 2015. They also result in chlorosis, reduced water and nutrient intake and damaged roots, Irum et al., 2013. The results of this study indicated a decrease in plant nutrients when compared to the control. This reduction may be due to the effect of heavy metals present in the soil as reported by Osuocha et al., 2016. Low nutrient uptake and distribution within the plant may be attributed to unavailability of essential minerals due to increased level of heavy metals in the soil caused by mining activities around the area. Similar decrease in plant nutrients in heavy metals contaminated soil have been reported in Cucuma sativus, Abu Muriefah, 2008 on Lemma polyrrhiza John et al., (2008), on Glycyrrhiza Uralensis Zheng et al., (2010). Heavy metals such as Cd and Cr and Pb have been reported to significantly decrease plant nutrients, Abdulsalam et al., (2015). According to Sandalio et al., 2005, reduction in plant nutrients by heavy metal induced toxicity could be the direct consequences of decreased uptake of nutrients

5. Conclusion

At the end of this research work, the physicochemical parameters (Temperature, electrical conductivity, total suspended solids and total dissolved solids) of water samples at Ankpa coal mine were all within WHO (2008) permissible limit for portable water except P^H that was above the set limit. Heavy metals contamination (Cr, Cu and Pb) was observed in the water and soil samples. Cadmium was not detected in any of the samples. Essential minerals concentration (P, Ca, K, Mg and Na) were low across all samples when compared with the recommended dietary intake (FNB, 1989). The correlation analysis showed positive correlation between some heavy metals and essential minerals in the plant samples which mean the accumulation of heavy metals in the soil can affect the absorption of essential nutrients by the plants.

Generally, Ankpa coal mine activities has affected the water and soil in its vicinity considering the fact that some heavy metals (Cr, Cu and Pb) were found above its maximum permissible limit which indicates a contamination and this may have resulted in the low levels of essential minerals observed in the plant samples and the correlation analysis showed a positive correlation between heavy metals and essential minerals which may indicate that the presence of the heavy metals in the soil samples has affected the absorption of essential minerals by the plant samples.

6. Conflicts of interest

The authors declare no conflicts of interest.

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