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THE ASSESSMENT OF SOILS, ROADSIDE SEDIMENTS, STREAM SEDIMENTS, AND GROUNDWATER SOURCES WITH REFERENCE TO HEAVY METALS CONCENTRATIONS IN OTUKPO, BENUE STATE, NIGERIA

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Abstract

The quality of soil for agricultural practices and groundwater for drinking in the study area (Otukpo) is of concern considering its vulnerability to contamination by heavy metals. Our urban geochemical knowledge of the industrial activities in Otukpo area right up to the present day remains very scanty. Literature reviews show that past and current studies are rare: Hence, the need for research to fully quantify and compare the presence of potentially harmful elements (PHE) in urban soils, road-deposited sediments, and stream sediments of the study area by exploring the spatial and geochemical linkages. Thus, metal contamination of the urban environment can have long-term environmental and health implications. This research therefore, seeks to investigate the heavy metals concentrations in urban soil, road and stream sediments, and surface and groundwater in Otukpo area with a view to establishing the occurrence and distribution patterns of the selected heavy metals (Cu, Pb, As, Cd, Zn, Ag, Fe, V, Co, Hg and Ni) as well as the implications of variations in local geology. The application of a database is used to develop a framework for sustainable management of heavy metals in the soil, surface, and groundwater of the study area. Safe and unsafe areas were delineated for proper domestic, agricultural, and industrial uses. The data provided by this study depicts the potential trend of heavy metals in the study area and will be used to develop appropriate management/mitigation measures.

Keywords: Roadside Sediments; Stream Sediments; Groundwater Sources; Heavy Metals Concentrations.

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1.0 Introduction

1.1 Background to the Study

The World Urbanization Prospects: 2001 Revision prepared by the United Nations speculates that the world's population is expected to grow from 6.1 billion in 2000 to 8.3 billion in 2030. As of 2000, an estimated 47% of the world's population already lived in urban areas, and the urban population will likely exceed 50% by 2007. The statistics also indicate that nearly all of the expected growth in population in the next three decades (2000-2030) will take place in urban areas, with almost no growth in the rural population (United Nations, 2001). The statistics undeniably suggest that the urban environment will soon become the most dominant human habitat for the first time in history. From an environmental and health perspective, this profound geographical development will have a critical influence on our immediate environment and its quality for human health. On a daily basis, numerous human activities, including municipal, industrial, commercial, and agricultural operations; release a variety of potentially toxic pollutants into the environment (Nriagu and Pacyna, 1988). Within the urban environment, where these activities are especially intense, emissions of both metal and organic pollutants are often vastly accelerated, inevitably rendering the urban environment particularly susceptible to environmental degradation and contamination (Nriagu, 1988; Kreimer, 1992; Thornton, 1993). The prolonged presence of the contaminants in the urban environment, particularly in urban soils, and their close proximity to the human population can significantly amplify the exposure of the urban population to metals via inhalation, ingestion, and dermal contact (Mielke and Reagan, 1998; Boyd *et al*., 1999; Mielke *et al*., 1999). These metals may include non-essential ones, such as Cd and Pb that can be toxic even at trace levels, and biologically essential elements, such as Cu and Zn, which might cause toxic effects at elevated concentrations (Callender, E. and Rice, K.C., 2000). Other indirect consequences of trace metal contamination of the urban environment include the subsequent migration of the pollutants to receiving bodies of water via urban runoff, resulting in the trace metal enrichment of sediments (Sutherland and Tolosa, 2000; Ip *et al*., 2004). The research seeks to investigate the concentration of heavy metals in urban soil, road and stream sediments, and groundwater in the Otukpo area.

A significant proportion of the increasing populace in the study area does not have access to potable water supply. This can be attributed to the inability of the Government to supply potable water and the lack of maintenance of existing facilities. This has made the exploitation of groundwater to become a common practice as many residential and commercial premises use hand-dug wells and boreholes for domestic and industrial water supplies. Considering the proximity of the water table to the ground surface and the depth of hand-dug wells, the quality of groundwater for drinking in the study area is of concern considering its vulnerability to contamination by heavy metals. Nowadays, a number of mining and quarrying companies (generating waste dumps) exist in Otukpo of which only about 20% are already naturally or artificially re-cultivated. The remaining amount of material in these waste dumps is left littered in the environment.

The research therefore, investigates the heavy metals concentrations in urban soil, road and stream sediments, surface and groundwater in Otukpo area with a view to establishing the occurrence and distribution patterns of the selected heavy metals (Cu, Pb, As, Cd, Zn, Ag, Fe, V, Co, Hg and Ni) as well as the implications of variations in local geology.

2.0 Methodology

2.1 Materials
Apparatus/ Instruments, Reagents and Chemicals

The instruments and materials that were used during the analysis are as follows;

2.1.1 Laboratory materials:

Beakers, measuring cylinder, stirrer, spatula, tongs sample bottles (made of Teflon or plastic), digestion vessels, porcelain crucibles, graduated pipette, volumetric flasks, conical flasks, stop watch, 2-mm plastic sieve, porcelain mortar and pestle, What-man No 1 filter paper, hot plate, Hot Oven box for drying glassware, weigh balance, metal spade, pH meter, Muffle Furnace, Fume Cupboard, desiccator and atomic absorption spectrometer (AAS Bulk Scientific Model 6800).

2.1.2 Reagents and Chemicals: Aqua-regia [mixture of Trioxonitrate (V) acid (HNO_3) and Hydrochloric Acid (HCl) in the ratio of1:3], distilled water, Potassium Dichromate, 0.4N Ferrous Sulphate, Ferroin Sulphuric Acid (98 % w/w), Sodium Fluoride, Potassium Chloride, 1N Ammonium Acetate, Sodium Ethylene diamine tetra acetic Acid (EDTA) (99.5 % w/w), Citric Acid(99.5 % w/w).

2.1.3 Safety kits: gas mask, goggles, laboratory coat, surgical gloves.

a) Soil and Roadside Sediments

Geochemical mapping of the entire urban area involvesthe collection of samples (soils and drainage sediments) from predetermined positions on a topographical map (1:50 000) generally at a sampling density of two samples/km^2. The predetermined sample sites are chosen and plotted on the map. Typically, 30 to 60 urban subsamples would be composited into 10 to 20 samples for geochemical analysis. Alternatively, sampling spots of about 20-30m apart from each other will be mapped out for soil sample collection within each sampling site. For both targeted and general surveys, surface soil is collected using a stainless steel hand trowel from 0 - 20 cm depth.

b) Stream Sediments

Drainage sediments collected along the course, in the active channel of the stream or river, using a stainless steel hand trowel. Along 500 m of the stream channel, 5 - 10 subsamples is collected from upstream and downstream of the selected site; and the locations were recorded and presented (Fig. 1).



Fig. 1: Refuse Dump Along stream Channels around Amonda Area

The enrichment factors for soils are calculated using the following equation:

EFc = (Cx/CFe) soil/(Cx/CFe) Earth's crust

Where (Cx/CFe) soil is the ratio of concentration of the element being determined (Cx) to that of Fe (CFe) in the soil sample and (Cx/CFe) earth's crust is the ratio in the reference Earth's crust.

c) Water Sampling.

Water sampling conducted during the fieldwork exercise involved many areas. Sample locations are located on a 1:50,000 scale topographic map (enlarged from 1:100,000 Otukpo Sheet). Water samples for analyses collected from ground sources include: ponds, pits, boreholes, and streams found in and around the area (Fig. 3). The release of deleterious materials into the water with short-term or long-term has environmental effects (s) on the earth's ecological balance and reduces the quality of life (Coker 2007). Water quality assessment plays a crucial role in understanding the health of aquatic ecosystems and their impact on biota. In the contents of rice mill industrial waters, a comprehensive analysis of water parameters is essential to ascertain the amount of heavy metals concentration. Many studies reveal the adverse effects of poor water quality on the environment (smith et al., 2018; Johnson et al., 2020). Contaminants in the area of study around the rice mill industry such as heavy metals and organic pollutants can significantly affect the growth and reproduction of biota, causing biodiversity loss (Jones et al., 2019; Liu et al., 2021)



Fig. 2: Stream Flowing in the Amonda Area

2.1.4 Water Quality Parameters

- **P^H**

One of the basic parameters that influence the quality of water and affects the physiology of aquatic organism is the P^H value. Excessive P^H values can lead to high mortality or decrease in reproductive success and the high levels can disrupt the metabolic processes of biota (Williams et al., 2017).

- **Total suspended solids (TSS)**

Recent studies have shown that high TSS concentrations can lead to decrease in biodiversity and change environmental structure (Nguyen et al., 2020). TSS is important for assessing the quantity of particulate matter present in the water. High increase in TSS levels can negatively affect biota by decreasing/reducing light penetration, distorting photosynthetic processes, and clogging the respiratory systems of aquatic organism (Chen et al., 2019).

- **Total Dissolved Solids (TDS) and Total Solids (TS)**

The dynamics of TDS and TS with respect to biota is important for assessing the water quality and its effect on aquatic life. The measurements of these two parameters (TDS & TS) give an insight into the dissolved and suspended solids content in the water. Excessive quality of TDS & TS levels can affect the osmoregulation of aquatic organism, resulting to physiological stress and distorted growth (Kasangaki et al., 2018).

- **Chloride**

Chloride in water can originate in water from both natural and anthropogenic sources. Chloride is an important parameter in water quality assessment. Excessive amounts of chloride in water can be an indication of industrial discharges, road salts, or agricultural runoff (Elliott et al., 2019). The increased concentration of chloride in water can harm aquatic biota, particularly amphibians and invertebrates (Frances et al., 2021).

- **Sulphate**

Sulphate ($SO4^{2-}$) may occur naturally in groundwater and can also be present as a result of human activities, such as industrial processes, mining, and agricultural practices. Sulphate is

a common ion commonly found in water. Sulphate is formed when sulphur compounds, such as sulphides and sulphur dioxide, react with Oxygen in the presence of water.

3.2 Method of Data Analyses

The acidity and alkalinity is determined following the procedures of the American Society for Testing and Materials (1982). Heavy metals concentrations in all the samples are determined using the atomic absorption spectrophotometer (AAS). Other methods include:

i. Statistical methods
ii Hydrological method

Statistical Analyses.

Basic statistical analysis is performed in order to present the data obtained during the laboratory analysis, in a more appropriate form suitable for interpretation of the data set. These include descriptive statistics such as minimum, maximum, mean and standard deviation using Microsoft Excel Spreadsheet.

Pollution indices for soil, sediment, and water.

a. Enrichment Factor (EF)

Gomes *et al.,* (2009) described EF as an index that serves as a means for evaluating the degree of metal pollution and defined it to be a double normalized ratio to a reference element Upper Crustal Concentration (UCC) and it is given by the following equation:

$$EF = \frac{Me/_{RE_{sl}}}{Me/_{RE_{ref}}}$$

Where; Me = the concentration of the metal in the soil sample given in mg/kg
RE = the concentration of iron in the soil samples given in mg/kg
Me = the reference concentration of the metal of interest given in mg/kg
RE = the reference concentration of iron given in mg/kg

b. Geo-accumulation Index (I_{geo})

The index is applicable to the contamination of soils by heavy metals. I_{geo} calculated according to the equation below:

$$I_{geo} = log_2 \frac{C_n}{1.5B_n}$$

Where *Cn* represents the concentration of the metal of interest in sediments (soils) *Bn* represents the geochemical background value of element n and 1.5 is the background matrix correlation resulting from terrigenous effects.

c. Pollution Load Index (PLI)

The PLI values of the study area is determined by taking the n^{th} root of the product of the CF of n number of heavy metals assessed, the formulas used in the calculation of the pollution load index as follows:

$$CF = \frac{C_{metal}}{C_{backgroundvalue}}$$

$$PLI = \sqrt[n]{CF1\ xCF2\ xCF3\ x\ \dots xCFn}$$

Where, CF represents the contamination factor, n represents the number of metals considered, C_{metal} is the concentration of a metal in the contaminated site, and $C_{background\ value}$ is the background value of the metal.

d. Degree of Contamination (DC)

The determination of *DC* employ cadmium, copper, iron, lead, nickel and zinc using the formula:

$$DC = \sum_{n=1}^{n} C_f^i = \sum_{n=1}^{n} \frac{C_{0-1}^i}{C_n^i}$$

Where; *n* represents the number of contaminants; C^i_f represents the contamination factor; C^i_{0-1} represents the mean concentrations of metals from the various samples from Otukpo and its environs (six samples) and C^i_n is the concentration of each element within the Earth's crust as a reference value. The degree of contamination, DC is categorized into four classes.

e. Contamination Index (Pi) and Integrated Contamination Index (Pc)

The contamination index (Pi) and the integrated contamination index (Pc) is used in the examination of contamination of Otukpo Area and its environs.

$$P_i = \frac{C_n}{S_i}$$

Where; *Cn* represents the concentration of heavy metals present in ***n*** sample and *Si* stands for the applicable standard value for that metal.

f. Metal Enrichn $Pc = \sum_{i=1}^{n}(Pi-1)\, Pc = \sum_{i=1}^{n}(Pi-1)$

The calculation of the metal enrichment index (MEI) for heavy metals present within soil samples follows the formula:

$$MEI = \frac{C_i - C_o}{C_o} MEI = \frac{C_i - C_o}{C_o}$$

Where; C_i represents the total concentration of each metal *i* obtained in the media studied; C_o is the background value for heavy metals for the samples assessed. Average earth crust will be employed as the background value for this present investigation. The aggregation of all the contaminants into a single value is not done.

3.0 Result and Discussions

The assessment of Soils, Roadside Sediments, Stream Sediments and Water Sources in the Otukpo area with reference to heavy metals concentrations are indicated as summarised:

3.1 Soil contamination

The leakages of spill or underground sources from the industrial zone of Otukpo rice mill results from the discharged chemical, leading to soil contamination. Among the most significant soil contaminants are agricultural products (hydrocarbons, heavy metals, herbicides, pesticides, and chlorinated hydrocarbons). The results are summarised as shown in Table 1 with the results presented as shown in Table 2.

Table 1. Properties of metals analysed around Otukpo rice mill industry soils

Sites	pH	O.C	Sand (%)	Silt (%)	Clay (%)	C.E.C (meq/100 g)
1	6.900	3.970	70.100	16.700	13.200	15.500
2	7.300	3.080	72.100	14.700	14.200	14.700
3	7.400	3.880	72.100	15.700	12.200	16.800
4	6.700	3.870	72.100	17.700	10.200	17.200
5	7.200	3.020	73.100	15.700	11.200	15.800
6	6.800	2.950	71.700	14.900	13.400	13.800
7	7.000	3.910	72.700	14.700	12.600	15.090
8	7.200	2.890	73.700	12.700	13.600	14.200
9	6.600	3.050	70.900	13.500	15.600	15.500
10	7.400	3.110	70.700	14.700	14.600	16.200
11	6.900	3.030	72.700	13.900	13.400	16.080
12	7.100	3.210	70.700	15.900	13.400	16.600
13	7.300	3.980	72.700	10.700	16.600	18.200
14	7.200	3.050	70.700	14.700	14.600	17.500
15	7.500	2.860	72.700	12.700	13.600	19.800
16	7.200	2.890	72.100	15.700	12.200	13.900
17	6.600	3.050	73.700	12.700	13.600	13.800
18	7.400	3.110	70.900	13.500	15.600	15.600
19	6.900	3.030	70.700	14.700	14.600	14.300
20	7.100	3.210	72.700	13.900	13.400	15.600
Mean	7.085	3.258	71.940	14.470	13.590	15.809
STD	0.274	0.405	1.083	1.599	1.503	1.571
MIN	6.600	2.860	70.100	10.700	10.200	13.800

MAX	7.500	3.980	73.700	17.700	16.600	19.800

The pH values ranged from 6.600-7.500, for Otukpo rice mill industrial soil samples. All the soils studied from the rice mill industry were either weakly acid or neutral. The soil organic carbon concentrations ranged from 2.860-3.980. The soils from the study areas were generally moderate to high in organic carbon contents. Most of the soil samples studied from Otukpo rice mill industrial have organic carbon values of more than 2.00%. The clay contents ranged from 10.200- 16.600%. The cation exchange capacities ranged from 13.800-19.800meq/100 g, for Otukpo rice mill industrial soil samples.

Table 2. The summary of soil properties of Otukpo rice mill industry

	pH	**O.C**	**Sand (%)**	**Silt (%)**	**Clay (%)**	**C.E.C (meq/100 g)**
Mean	7.085	3.258	71.940	14.470	13.590	15.809
Std	0.274	0.405	1.083	1.599	1.503	1.571
Range	6.600	2.860	70.100	10.700	10.200	13.800
	7.500	3.980	73.700	17.700	16.600	19.800
Control						
Mean	6.833	1.643	73.333	11.667	16.000	15.167
Std	0.351	0.153	2.466	0.289	0.866	2.082
Range	6.500	1.550	70.500	11.500	15.000	13.500
	7.200	1.820	75.000	12.000	16.500	17.500

The results of heavy metal concentrations in the Otukpo rice mill industrial soil samples are presented in Table 3, and the summary of the results are presented in Table 4. The soil samples from Otukpo rice mill industry revealed a clear elevated level of these heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn). The mean concentrations of heavy metals obtained from the control sites were much lower than those obtained from the soils of the industry under consideration. This reflects a general and diffuse contamination of soils of this rice mill industry by heavy metals investigated. Out of the heavy metals considered, lead (Pb) shows the highest pollution in the site studied. The overall results ranged from 7.250-9.850, 2.200-5.550, 42.560-95.540, 86.980-125.550, 245.650-323.540, 39.650-55.650, 280.890- 389.760 and 133.350-187.780 mg/Kg for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, respectively.

The concentrations of the heavy metals in the area studied (Otukpo rice mill) were generally high especially Pb, Zn, Cd, Cr, Cu and Co. This indicates that these heavy metals in the soil of the rice mill industry are the primary contaminants which were also reflected in the low level of these heavy metals obtained from the control sites in comparison with those obtained from the study sites. Also, the degrees of heavy metals pollution in rice mill industrial soils which were determined by its enrichment factors were also high.

The trace heavy metal concentrations of the top soil samples show that the soils contain sufficient amounts of Pb, Zn, Cd, Cr, Cu and Co as shown in Table 4. These metals that originate from industrial activities are distributed in soils by certain factors; the rain, atmosphere within a distance that depends on the size of particles. The mean concentrations of Pb, Zn, Cd, Cr, Cu and Co inthe soil samples are 315.291±28.763, 161.219±16.695, 8.290±0.854, 67.509±17.032, and 108.349±11.186 and 4.066±1.103 mg/kg, respectively.

Table 3 Total metal contents (mg/kg) of soil from Otukpo rice mill industry

Metals	Cd	Co	Cr	CU	Mn	Ni	Pb	Zn
1	7.890	2.200	55.480	112.340	320.870	50.540	350.450	152.890
2	9.750	2.850	78.580	103.550	250.980	49.780	389.760	165.780
3	8.250	2.550	95.540	124.670	275.250	39.650	354.880	134.350
4	8.520	2.540	45.670	99.560	290.550	45.670	312.230	155.680
5	7.540	3.270	67.970	115.860	267.560	55.650	355.450	166.560
6	9.720	5.550	86.750	86.980	312.550	48.880	311.540	145.550
7	8.510	4.540	89.650	95.890	255.060	54.550	324.650	177.560
8	7.550	3.350	55.650	125.550	310550	48.880	287.560	187.780
9	7.250	5.550	42.560	97.540	260.650	53.440	295.880	167.780
10	8.250	4.650	77.870	110.780	312.770	54.550	315.450	155.650
11	7.750	4.330	67.550	113.880	278.570	51.550	289.470	166.890
12	9.770	5.120	82.880	120.980	321.550	43.660	321.670	145.550
13	7.740	3.560	70.530	98.550	255.670	45.530	288.670	134.790
14	8.150	5.510	54.550	105.650	323.540	53.250	314.250	133.350
15	9.850	3.330	45.670	111.550	245.650	43.560	280.890	178.560
16	8.510	4.540	89.650	95.890	255.060	54.550	324.650	177.560
17	7.550	3.350	55.650	125.550	310.550	48.880	287.560	187.780
18	7.250	5.550	42.560	97.540	260.650	53.440	295.880	167.780
19	8.250	4.650	77.870	110.780	312.770	54.550	315.450	155.650
20	7.750	4.330	67.550	113.880	278.570	51.550	289.470	166.890
Mean	8.290	4.066	67.509	108.349	284.969	50.106	315.291	161.219
STD	0.854	1.103	17.032	11.186	27.883	4.502	28.763	16.695
MIN	7.250	2.200	42.560	86.980	245.650	39.650	280.890	133.350

MAX	9.850	5.550	95.540	125.550	323.540	55.650	389.760	187.780

Table 4. Summary of total metal contents (mg/kg) in the soils of the study area (Otukpo rice mill industry)

Metals	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	**NI**	**Pb**	**Zn**
Mean	8.290	4.066	67.509	108.349	284.989	50.106	315.291	161.219
S.D	0.854	1.103	17.032	11.186	27.883	4.502	28.763	16.695
Range	7.250	2.200	42.560	86.980	245.650	39.650	280.890	133.350
	9.850	5.550	95.540	125.550	323.540	55.650	389.760	187.780
Control								
Mean	0.953	0.693	7.783	17.560	125.400	10.250	4.680	11.560
Std	0.085	0.045	0.516	0.894	4.472	0.894	0.511	0.894
Range	0.860	0.640	7.450	16.560	120.400	9.250	4.350	10.560
	1.050	0.740	8.450	18.560	130.400	11.250	5.340	12.560
E.F	8.699	5.867	8.674	6.170	2.272	4.888	67.370	13.946

Pb and Zn in soils could be derived from industrial sources as well as from abrasion from tyres of motor vehicles. The concentrations of Pb and Zn were found to be high in all the samples from rice mill industry soils while the concentrations of Pb and Zn were found to be low in the soils from control area. The Pb and Zn contents of rice mill industrial soils have been found to enrich by a factor of 67.370 and 13.946. This could be attributed to the rice mill industry in which the process and production of rice require a substantial amount of energy supplied by burning of coal and fossil fuel and traffic activity in the industrial area. The high levels of Zn in the top soils of the study area could be attributed to emission sources from the factory as well as traffic emissions in the area of investigation. Cadmium (Cd), Chromium (Cr) and Copper (Cu) also show a similar distribution pattern in the soils studied with relatively higher concentrations in the site i.e. 7.250-9.850, 42.560-95.540 and 86.980-125.550 mg/Kg as opposed to soils sampled from control areas. Cd may be derived from the mechanical abrasion of vehicles and also associated with tyre wear. The concentration of chromium in the rice mill industrial soil varies from 42.560-95.540 mg/kg with a mean value of 67.509±17.032. The highest concentrations of chromium are recorded in the samples near the plants in the rice mill industry, which could be attributed to wear, friction and emission source of chromium from the plants.

Mutual correlations between the elements done at 95% significance level show positive correlation between Pb and Zn (r = 0.624) suggesting a possible common origin for them (Table 4). Cd and Cr show a very high positive correlation (0.892) between as compared to the other heavy metals.

Hence it can be accounted for their similar source, probably coal as coal contains Cd and Cr in its trace element composition. Coal combustion releases these trace elements which can get

incorporated in the dust along with the other particulates and gets deposited on the top soil of the surrounding area. Cr also shows good positive correlation with Zn (r =0.588) confirming further their common source (Table 5).

The present study shows that the metal concentrations of top soils can be used as a powerful geochemical tool for monitoring the impact of anthropogenic activity. Soil samples show higher concentrations of the heavy metal determined as compared to the heavy metals from control areas indicating the presence of contaminants particles in the area. These heavy metals in the soils from the industry were excess as opposed to the average levels of heavy metals in control soils account for incorporation of industrial activities in the studied areas. Mutual correlation of the heavy metals in the soils suggests a common origin for Pb, Zn, Cd and Cr. The distribution of the metal concentration of the soil in the study area indicated that this area has been affected by anthropogenic activity, in particular the vicinity of the industry, leading to a high accumulation of heavy metals in the soils located within near the factory as compared with the soils from control areas.

Table 5. Metal with good positive correlation confirming common source.

Metals	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	**NI**	**Pb**	**Zn**
		-0.015	0.395	0.892	-0.005	-O.410	0.302	-0.169
			0.045	-0.432	0.112	0.452	-0.377	-0.089
				-0.027	0.001	-0.058	0.467	0.588
					0.357	-0.328	0.003	0.147
						-0.005	-0.055	-0.297
							0.028	0.323
								0.624

3.2 Water Quality

The assessment of Water parameters resources in the Otukpo area with reference to heavy metals concentrations are indicated as summarised:-

Table 6: pH concentrations

Water Samples	pH	Temperature
A	6.76	30.2^0C
B	6.45	30.3^0C
C	6.56	30.4^0C
D	5.91	30.7^0C

Table 7: Total Dissolved Solid (TDS)

Water Samples	TDS	Temperature
A	374ppm	30.2^0C
B	125ppm	30.2^0C
C	107ppm	30.6^0C
D	47ppm	30.7^0C

Chloride (CL^-) concentration

Thus, chloride concentration = number of moles of chloride/ volume of water sample.

Sample A water

	First	Second	Third
Final volume	1.00	2.20	2.80
Initial volume	0.00	1.00	2.20
Volume used	1.00	1.20	0.6

Chloride concentration = 0.0465mol/L

Sample B water

	First	Second	Third
Final volume	0.40	0.90	1.50
Initial volume	0.00	0.40	0.90
Volume used	0.40	0.5	0.6

Chloride concentration = 0.025mol/L

Sample C water

	First	Second	Third
Final volume	3.20	4.00	5.00
Initial volume	2.40	3.20	4.00
Volume used	0.8	0.8	1.00

Chloride concentration = 0.043mol/L

Sample D water

	First	Second	Third
Final volume	2.00	2.40	3.10
Initial volume	1.50	2.00	2.40
Volume used	0.5	0.4	0.7

Chloride concentration = 0.0265mol/L

TOTAL SUSPENDED SOLID (TSS)

TSS (Mg/L) = mass of filter with dired suspended solids (g) – mass of empty filter (g)
ML of sample x 1,000,000

Sample A water
TSS = 8.55 x 10^{-10} mg/L
Sample B water
TSS = 6.85 x 10^{-10} mg/L
Sample C water
TSS = 1.4 x 10^{-10} mg/L
Sample D water
TSS = 8.7 x 10^{-10} mg/L

TOTAL SOLID (TS)

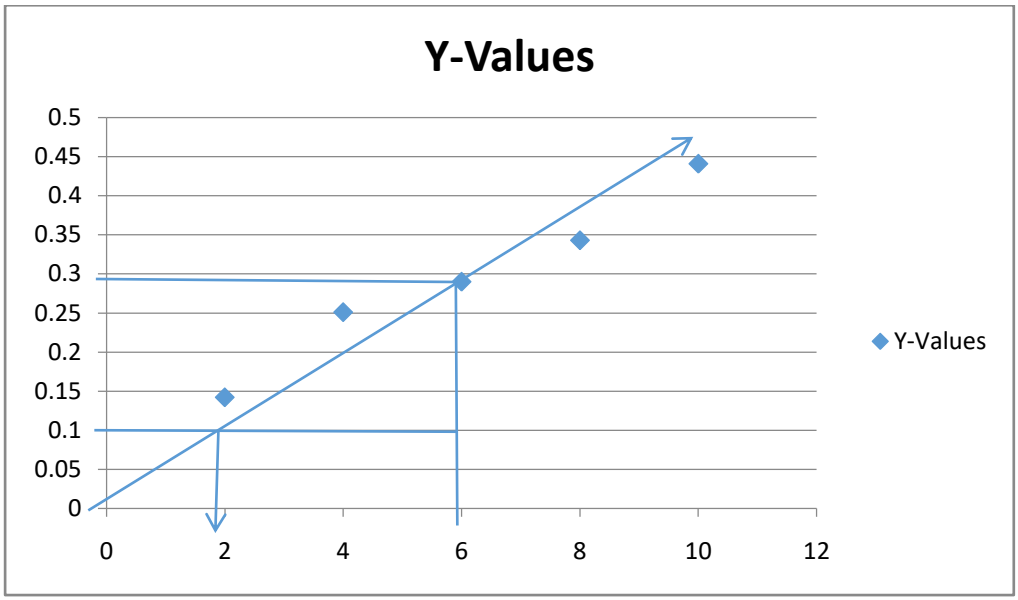
TS (mg/L) mass of residue (mg)**X** 1000
volume of sulphate
Sample A water
TS = 4.450 mg/L
Sample B water
TS = 35, 145mg/L
Sample C water
TS = 8,950mg/L
Sample D water
TS = 170mg/L

PHOSPHATE DETERMINATION

500 0.255
Wavelength Standard Absorbance

Concentration	Absorbance
2ppm	0.142
4ppm	0.251
6ppm	0.290
8ppm	0.343
10ppm	0.441

Figure 4: Graph of Absorbance VS Concentration



The graph of Absorbance against Concentration

y- intercept = 0.06

Slope = 0.04

Thus, finding the concentration of each of the water samples

Concentration = absorbance –y- intercept / Slope

Sample A water

Phosphate Concentration = 0.25mg/L

Sample B water

Phosphate Concentration = 11.28mg/L

Sample C water

Phosphate Concentration = 3.8mg/L

Sample D water

Phosphate Concentration = 6mg/L

PHOSPHATE DETERMINATION

240 0.278

Wavelength standard absorbance

Concentration	Absorbance
2ppm	0.134
4ppm	0.230
6ppm	0.333
8ppm	0.372
10ppm	0.391

y- Intercept = 0.03

Slope = 0.05

Thus, finding the concentration of each of the water samples

$$\text{Concentration} = \frac{\text{absorbance} - \text{y- intercept}}{\text{Slope}}$$

Sample A water
Sulphate Concentration = 33.9mg/L
Sample B water
Sulphate Concentration = 30.4mg/L
Sample C water
Sulphate Concentration = 24.86mg/L
Sample D water
Sulphate Concentration = 26.62mg/L

Water samples

Water quality parameters	A	B	C	D
pH	6.76(30.2^0C)	6.45(30.3^0C)	6.56(30.4^0C)	5.9(30.7^0C)
Total dissolved solid (TDS)	374pp(30.2^0C)	125ppm(30.2^0C)	107ppm(30.6^0C)	47ppm(30.2^0C)
Water quality parameters	A	B	C	D
pH	6.76(30.2^0C)	6.45(30.3^0C)	6.56(30.4^0C)	5.9(30.7^0C)
Total dissolved solid (TDS)	374pp(30.2^0C)	125ppm(30.2^0C)	107ppm(30.6^0C)	47ppm(30.2^0C)
Chloride (Cl^-)	0.0465mol/L	0.025mol/L	0.043mol/L	0.0265mol/L
Total suspended solid (TS)	$9.55x10^{-10}$mg/L	$6.85x10^{-10}$ mg/L	$1.4x10^{-10}$mg/L	$8.7\ x10^{-10}$ mg/L
Total solid (TS)	4.450 mg/L	35,145mg/L	8.950mg/L	170mg/L
Phosphate	0.25mg/L	11.28mg/L	3.8mg/L	6mg/L
Sulphate	33.9 mg/L	30.4 mg/L	24.86 mg/L	26.62 mg/L

Key: Sample A = rice mill water
Sample B = Ijami road water
Sample C = GRA TKP water
Sample D = Enugu Exp. Road water

3.3 Discussion

World health Organization standard (WHO) for the various parameters

pH**(6.5-8.5)**

The pH values of all the samples are within the WHO standard and acceptable range for drinking water in the study area. The values of the pH obtained from the water samples range from 5.9 to 7.6. The pH results fell within the acceptable standard guideline indicating the Normal level. These indicate that the water acidity/alkalinity in the studied area fell within the suitable range of environmental application.

Total suspended solids (TSS) = 5mg/L below

The TSS normal standard concentration values range from $1.4x10^{-10}$mg/L to $9.55x10^{-10}$mg/L. All the sample results fell within the acceptable standard guideline of WHO indicating the Normal level for drinking water. The presence of higher TSS levels in certain locations of study is an indication of suspended solid. This excessive concentration of TSS can be responsible for reduced light penetration thereby affecting photosynthetic activities and reduction of overall water quality.

Total Dissolved Solids (TDS) = 500ppm below

The average level of TDS ranged from 47ppm – 374ppm. Samples from this source meet the WHO standard and are considered safe for drinking. Excessive concentrations of TDS at varying levels can influence water taste. Higher TDS levels might be attributed to natural sources or human activities such as agricultural runoff or industrial activities (chemical discharges).

Total solids (TS) = 600mg/L below

Sample A

Total Solids (TS): has a total solid concentration of 4450 mg/L which exceeds the WHO regulated guideline for drinking water; these clearly suggest a higher concentration of dissolved solids, which can affect the taste and quality of the water.

Sample B

The total solid concentration of 35145mg/L significantly exceeds the regulated WHO guideline for drinking water. The high anomalous concentration of TS is an indication of a potential contamination issue and renders the water unsuitable for human consumption (drinking).

Sample C

The total solid concentration of 8950mg/L is equally above regulated guideline for drinking water; despite the lower concentration compared to sample B; it still indicates a considerable amount of dissolved solids.

Sample D

Sample D, with a total solid concentration of 170 mg/L, is within the WHO guideline for drinking water. The concentration of the dissolved solid in the sample is relatively low compared to the other samples.

From the analyses of the samples A, B, and C, it infers that the samples do not meet the regulated guideline of WHO quality for drinking water in terms of the concentration of total dissolved solids.

These issues of high concentrations of dissolved solids can be addressed by further investigation; and potential water treatment methods to ensure the suitability for consumption.

Chloride Concentration = 250mg/L below

The chloride concentrations ranged from 0.025mg/L-0.0465mg/L. The elevated chloride concentrations may be attributed to natural sources, anthropogenic inputs, or geological characteristics of the area.

Phosphate = 1mg/L below

The concentrations of phosphate level in the sample vary from 0.25mg/L-11.28mg/L.
The excessive phosphate levels can result in eutrophication, promoting algal blooms and disrupting the balance of the aquatic ecosystem.

Sulphate = 1mg/L below

The sulphate concentrations in the samples ranges from 24.86mg/L-33.9mg/L. the level of sulphate concentrations observed indicates implications for biota. High sulphate concentrations can be linked to natural phenomenon or human influences such as mining or industrial waste water discharged into reservoir.

In summary, the highlight of water quality of Otukpo Local Government Area of Benue State is based on the variations observed in the measured parameters which indicate pollution attributed to natural sources, anthropogenic inputs, or geological characteristics of the area. This can have serious adverse effects on both surfaces and ground waters. Water pollution can also be attributed to cases of oil spillages, constant discharges of industrial wastes into water bodies.

To properly address issues of challenges, appropriate measures such as water quality measures, promoting agricultural and regulating industrial discharges into the environment. Similarly, monitoring and periodic assessment of water quality parameters are essential to monitor alterations over time and ensure the sustainability of ecosystem. Industrial effluents, leachates that are produced through the mining process infiltrate and become part of the ground water, and become unsafe for human consumption and for aquatic lives. Mining operations can as well lead to hardening of water as well as changes in physico-chemical parameters such as total dissolved solids, and calcium content.

4.0 Conclusions

The results obtained from the analysis of topsoils collected from various locations in Otukpo rice mill industry of Benue state in Nigeria indicated that the concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were higher than those of control soils. The degree of contamination of Pb and Zn were the highest. Cd, Cr, Cu, and Co also showed high degree of contamination in rice mill industrial soil samples. From this reason, it could be predicted that the contaminations of Pb, Zn, Cd, Cr, Cu, and Co are probably from anthropogenic sources, while those of Ni and Mn may be from parent material in the soil. The observed contaminants were Pb, Zn, Cd, Cr, Cu, and Co and their concentrations and enrichment factors were high in all the soils studied.

The evaluation and determination of water quality provided valuable insights within the Otukpo Local Government Area of Benue State into the current state of water quality. This is achieved the assessment of various parameters such as: - Ph, Total Suspended Solids (TSS),

Total Dissolved Solids (TDS), Total Solids (TS), as well as Chloride concentration. Phosphate, and sulphate. Summarily, the results indicate that the water in rice mill industrial soil samples falls within an acceptable pH range, indicating a favourable acidity/alkalinity level for supporting the biota. However, elevated TSS and TDS concentrations were observed in certain sampling locations, indicating the presence of particulate matter and dissolved solids.

The results do not provide information about changes in the levels of inorganic soil contaminants over time, but they do provide baseline data for comparisons in the future. The distribution of the heavy metal concentration of the soil in study area indicated that the rice mill industry together with the traffic emissions were mainly responsible for heavy metal pollution in this area. Hence, overall levels of Pb, Zn, Cd, Cr, Cu, and Co contaminations are those which call for closer monitoring in sites under considerations. Further study is needed not only to assess the distribution of metals in soil but also to examine variation on small scale. More intensive work is necessary to show any change or increase of metals in the investigated area over time.

5.0 Recommendation

Soil and water are essential to life, both for environmental health and economic growth. Heavy metals are components of the natural environment. However, contaminated soil and groundwater have several adverse effects on plants, humans and the entire environment. Heavy metals are widely known to contaminate soils and groundwater, particularly in industrial areas.

Consequently, the distribution of the heavy metal concentration of the soil in study area indicated that the rice mill industry together with the traffic emissions were mainly responsible for heavy metal pollution in this area. Hence, overall levels of Pb, Zn, Cd, Cr, Cu, and Co contaminations are those which call for closer monitoring in sites under considerations. Further study is needed not only to assess the distribution of metals in soil but also to examine variation on small scale. More intensive work is necessary to show any change or increase of metals in the investigated area over time.

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