Physicochemical and Ecotoxicity Studies of Soil and Water Around an Abandoned Uranium Mine Site in Taraba State, Nigeria.

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Abstract

Soil and water samples from an abandoned uranium mine site were investigated for contamination/pollution to ascertain their quality status. The levels of heavy metals in the soil samples were analyzed by x- ray fluorescence analyzer while other water and soil parameters were determined by standard methods. Ecotoxicity studies indicate pollution for the water samples in the study area in terms of the organic pollution index (1.82) and chemical pollution index for heavy metals (1.18). The physical pollution index (0.42) and the salinity pollution index (0.09) have values < 1suggesting no pollution in terms of these parameters. The heavy metal and organic pollutions coupled with the high presence of coliform count $(56.9 - 83.2 \text{ c} \text{fu}/100 \text{ mL})$, Escherichia coli (45.9–60.3 cfu/100 mL) make the water sources unfit for human consumption. Based on several descriptive statistics, the findings of the study [geo-accumulation index (0.62-5.45); single pollution index (0-150.53); pollution load index (6.92-12.41); enrichment factor index (0-20.32); ecological risk factor (0-6021); risk factor (0-625)] depict varying degrees of pollution for the soil samples. The soil samples from the three study stations are grossly polluted particularly with titanium and uranium. Analysis of variance result for soil indicates significant differences in the metal concentration at $p \leq 0.05$. The observed differences may be due to contribution from anthropogenic activities and not background concentration only. The soil and water bodies in this area should be monitored periodically by the relevant authorities. Phytoremediation that involves growing certain plants for the absorption of heavy metals is highly recommended.

Keywords: Physicochemical, bacteriological, pollution indices, phytoremediation

Introduction

Taraba State is well blessed with enormous solid mineral deposit. Informal and traditional miners in the area have become interested and involved in indiscriminate mining activities. Given the existence of vast areas with untapped mineral potential, it presents the state and the nation an enormous investment opportunity (Merem *et al*, 2017). However, since the country's crude oil was discovered, these potentials have been overlooked for a very long time. In many areas of the state and nation, artisanal and small-scale miners are the ones who are making mineral occurrences, new discoveries known through guesses.

Uranium prospecting and exploitation has been carried out in Mika village, Yorro Local Government Area of Taraba State before Nigeria independence. Large quantities of uranium materials were collected from the sites for several years intermittently before it was abandoned as a result of Government directives under the Central Nigerian Uranium Project. The abandoned uranium sites contain some overburden dug out of the pits which were not reclaimed. The process of exploration and mining of uranium poses high risk to the people of the local community.

It is against this backdrop that this study investigates the pollution status of soil and water samples obtained from the abandoned uranium site in Yorro Local Government Area of Taraba State,

Nigeria and to ascertain the potential health hazard associated with water sources and farmlands in the study area. The aim of the study will be achieved by the following objectives:

- i. To determine the levels of some selected metals in soil and water samples collected from the study area.
- ii. To determine the concentration of coliform count and E. coli in the water samples
- iii. To deploy appropriate descriptive statistics indices such as geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI), enrichment factor (EF), potential ecological risk factor index (PERI), risk factor for the soil samples and ecotoxicity test for water samples to ascertain pollution status.
- iv. To suggest mitigation procedures.

Methodology

Description of Study Area

The research area is situated in Mika ward of Yorro Local Government Area. The Local Government Area is situated between longitude $11^{\circ}20'E$ and $11^{\circ}45'E$ and latitude $8^{\circ}42'N$ to $9^{\circ}12'N$. The study area is shown in Figure 1 below.

Figure 1: Map of the study area in Yorro of Northern Taraba State

Samples collection

Integrated sampling technique was deployed in collecting seven representative number of topsoil samples (up to the depth of 10 cm) from the top surface of the mine spoil. The same collection

procedures were repeated to collect soil samples from a farmland 50 m from the abandoned mine pit, and another farmland 500 m away from the mine site. Water samples were collected from different points of flowing surface water 400 m from the mine site and groundwater 100 m from the surface water. The collected soil samples were mainly dark brown in colouration and were immediately sent to the Spectral Analytical Laboratory, Kaduna, Nigeria for preparation and analysis. The water samples were analyzed in Taraba State Water and Sewage Corporation Central Laboratory, Jalingo, Taraba State, Nigeria and Nicetime Research Laboratory, Taraba State University, Jalingo, Taraba State, Nigeria.

Samples Preparation

The samples were cleaned by removing foreign matters such as stones, leaves, debris, etc. The soil samples were air-dried and fully crushed to the possible finest fraction using acid-washed portal and pestle and finally cleared with a 2 mm sieve, kept in clear zip bags separately and stored in desiccators awaiting digestion.

Experimentation

Total digestion of soil samples for the determination of physicochemical parameters

All soil samples were digested using tri-acid digestion (HF: HNO₃: HClO₄) to completely dissolve the metals. Crystalline matrixes of the samples were destroyed and occluded minerals in the matrix exposed and dissolved by the acids. An aliquot of the sample was digested to dryness in Teflon tube within a hot bock digestion system using a mixture of concentrated HF: $HNO₃$: $HClO₄$. The residue was then dissolved in dilute HNO₃ and used for analysis following procedures adopted by SRC Geoanalytical Laboratories [\(geolab@src.ca.](mailto:geolab@src.ca)).

Determination of physicochemical properties of environmental samples

Total organic carbon and soil colour for soil samples after digestion and parameters of water were determined following standard method protocol as presented by Alpha (1996) and Maiti (2003). Total organic level was determined by ferroin titration as adopted by Walkley and Black (1934). Soil colour was obtained using Munsell Soil Colour Chart. Heavy metals in the soil samples were estimated using ED-XRF analysis but the level of lead was determined employing atomic absorption spectrophotometer (AAS). Bacteriological parameters (total coliform and E. coli) were determined by Colilert 18 method. Other water parameters were analyzed following standard methods using UV/Visible spectrophotometer 6000.

Data analysis

Data were analyzed employing inferential and descriptive statistics. Pollution factor indicators such the geo-accumulation index (Muller, 1969); contamination factor (CF) enrichment factor (Pandey *et al*, 2016), Pollution load index (PLI), (Singh, 1999); Enrichment factor (Cai *et al*, 2019); Ecological risk factor (E_r^i) , Hakanson (1980) were also deployed to ascertain the pollution status of the soil. The status of pollution of the water samples used in the study was investigated using ectoxicity test as adopted by Boluda (2001) and cited by Medjor *et al* (2015). All data analyses were carried out using Microsoft Office Excel 2007 Software.

Statistical analyses and Quality assurance

Standard deviations for all measurements were calculated to checkmate determinant errors and improve precision. Physicochemical properties for soil and water samples were subjected to

analysis of variance (ANOVA) to establish any significant differences between their means for the different sampling sites. SPSS 16.0 statistical package was used to execute the analysis.

Result of the Findings

The results of the physicochemical properties analysis of soil samples used in the study is displayed in Table 1. The pH of the soil samples has a range of 5.80 – 7.80. These values are found to be within the permissible limit of $5.5 - 6.5$ set by DPR (2002) and W.H.O. (2017). pH in the range of $6.5 - 7.5$ is considered neutral and enhances maximum availability of nutrients. pH below this range is acidic and above alkaline. pH values generally indicate soil reactions. The colour of the soils used in the study was dark brown. Nitrate and chloride had a range of 18.2 – 22.24 and 24.75 – 49 in that order and were within the allowable limits set by DPR (2002) and W.H.O. (2017).

Fertile soils contain combined nitrogen in the form of nitrate, nitrite, ammonium salts, nitrates or a urea CO(NH2)2. Nitrogen is essential for plant growth particularly for leaves and also being an important constituent of amino acids and proteins. It plays a vital role in the formation of new cells. The nitrate in the sample from the mined spoils has a highest level and this is as a result of complexation reactions with higher concentration of heavy metals in the sample while the nitrate levels in samples Q and R are readily utilized. Complexes with titanium (II) are the most promising. A complete cycle of atmospheric dinitrogen to ammonia has been reported (Lee, 1996).

 $[Ti(OR)_2N_2] \rightarrow [Ti(OR_2)N_2]^{4-} + 4H^+ \rightarrow N_2H_4 + Ti(OR)_2$

It is also possible since the water sample in the abandoned mined pit indicates high presence of coliform count and E. coli that the station P has a high level of bacteria (nitrosomonas and nitrobacter) in the soil which readily convert other nitrogenous compounds into nitrates. $NH_4^+ \rightarrow NO_2 \rightarrow NO_3^-$

Phosphate in the abandoned mine pit (**P**) had a high value of 225 mg/L in comparison of values obtained for stations **Q** (0 mg/L) and **R** (0 mg/L). Phosphate from the mine spoil sample (P) is likely in the form of phosphate rocks such as fluoroapatite $[3Ca_3(PO_4)_2.CaF_2]$ are very soluble, and thus are of no use to plants, a more probable reason why it is suspiciously present in such high quantity in sampling station P. Sulphate in stations **P** and **Q** had values of 365 and 421 respectively and are exceedingly higher than the standard limits of $30 - 40$ mg/L (DPR, 2002; W.H.O. 2017) and station **R** with a value of 0 mg/L. There is high level of calcium in the soil samples $(4770 -$ 17480) therefore the formation of $CaSO₄$ is inevitable but it is an insoluble waste product and of no value to plants. Its formation is more favourable under acidic conditions as the case of sample P and Q.

The moisture content for the three stations employed in the study had a range of $6.1 - 6.7$ % that is within the permissible limit of $13 - 26$ % set by W.H.O. (2017). Particle distributions of the three sampling stations (**P**, **Q** and **R**) with a range of $1 - 6.7$ n% (silts) and $14 - 26.6$ % (sand) were found to be within the standard limits of $10-20\%$ (silts) and $50-70\%$ (sand) set by W.H.O. (2017) for agricultural soil. The clay had a range of 66.7 - 85% for all the sampling stations but above the allowable limit of $20 - 30\%$ (W.H.O., 2017).

Oil and grease had a range of $30.9 - 33.6$ mg/L above the recommended limit of 30 mg/L set by W.H.O. (2017) for soils. The total organic carbon concentration in all the stations was 0.21 % and within the standard limit of $0.5 - 0.75$ % set by W.H.O. (2017) for agricultural soils. Analysis of variance for the aforementioned parameters shows significant difference at $p \le 0.05$. This implies that the observed difference for these parameters could also be as a result of anthropogenic

activities such as quarry, mining, farming and other human activities and not only contributions from the natural background except for pH. Heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Ti and U levels) Table 1 were found to be extremely higher than the permissible limits set by W.H.O. (2017) for agricultural soils except for Pb that had a value of 0 mg/kg for all the soil samples in the three stations. The normal range of chromium in soil is 100 mg/kg (Wedepohl, 1995). Copper accumulation in the surface horizons is due to its readiness of bioaccumulation and anthropogenic activities (Kabata, 2004). Agricultural chemicals have been associated with sources of pollution of soils with heavy metals (Ferguson & Kasamas, 1999). The mobile forms of these heavy metals have been reported by Alloway (1995) to pose a threat as they may leach in the groundwater aquifers which are drinking water sources for human and animals (Nogawa *et al*, 1987). One of the main sources of zinc pollution in soils is the application of liquid manure, composted material and other agrochemicals such as fertilizers and pesticides in agriculture (Romi & Romic, 2003) as cited by Ogunmodede *et al* (2015). In Nigeria about 47 % of the soils are deficient in zinc. The high concentration of zinc obtained in the soil sample from the mine spoils is an indication that its source as anthropogenic rather than natural background (Aswathanarayana, 1995). Pollutants entering soil interact with its active phase (clay minerals, oxides and hydroxides of iron and manganese, and organic substance) and change their own activity either increasing or decreasing their hazard (Vodyanitskii, 2012). Pb forms stable complex compounds with organic ligands, which become less hazardous for living organisms than metal ions are (Linnik & Nabivanets, 1987) as cited by Vodyanitskii (2012). In this study Pb has a 0 mg/kg in all the stations and therefore poses no health threats.

Key: $P =$ Mine spoils from abandoned mine pit; $Q =$ Soil from farmland 50 meters away from P **R** = Soil from farmland 500 meters away from **P**; *No standard is available; the natural background level for uranium in soil is 2 - 10 mg/kg.

The value of I_{geo} index indicates the presence and also the intensity of anthropogenic contaminants deposits in the soil. The geo-accumulation index from stations (**P**), **Q** and **R** had values in the range of $0 - 7.81$, $0 - 2.97$ and $0 - 5.45$ in that order. The mean I_{geo} values for all the metals were in the range of 0.62 – 5.45, which suggest a class index of 2, uncontaminated to slightly contaminated and class index of 4, highly contaminated soils (Müller, 1969).

Table 2: Geo-accumulation index of the soil close to the abandoned uranium mine site

Parameter	P: Distance 0 Depth $0 - 10$ cm	$Q: Distance\ 50 m$ Depth $0 - 10$ cm	\mathbf{R} : Distance 500 m Depth $0 - 10$ cm	Mean
T _i	5.84	2.54	6.06	4.82
Cr	0.68	-0.56	5.46	1.86
Mn	1.08	0.11	0.66	0.62
Fe	3.59	1.84	1.25	2.23
Co	2.46	1.30	-0.45	1.10
Ni	1.61	0.69	Ω	0.76
Cu	2.47	1.31	1.74	1.84
Pb	θ		θ	
Zn	1.89	Ω	Ω	0.63
U	7.81	2.97	5.56	5.45

Uranium had the highest geo-accumulation indices depicting extreme contamination followed by titanium and least for lead in all the stations (Table 2). The spatial distribution of the heavy metal contaminants in the study stations was demonstrated by the pollution load index as shown in Table 3. The pollution load index (PLI) for the heavy metals studied is highest for spoils from the abandoned mine pit (12.41) with the greatest contributions coming from uranium with a single contamination factor (CF) value of 337. The sampling station (**Q**) 50 m away from the mine pit had PLI value of 6.92 and single contamination factor of 44 for uranium while the station (**R**) 500 m from the mine pit had a PLI of 7.94 and CF of 70.6 for uranium. These values indicate that all the stations are grossly contaminated with uranium as $PLI > 1$ indicates pollution (Tomilson, 1980). Other heavy metals exhibited varying degrees of contamination as shown in Table 3.

Cu 8.33 19.72 5.00 11.02 Pb 0.00 0.00 0.00 0.00 0.00 Zn 5.57 0.00 0.73 2.1 U 337.00 44.00 70.60 150.53

 $PLI = 12.41$ 6.92 7.94 -

Table 3: Contamination factor/single pollution index of the soil close to the abandoned uranium

The contamination profile from Table 3 also supported our earlier assertion that titanium is the second cause of extreme contamination in the three sampling stations deployed in the study. The result of the enrichment factors is displayed in Table 4 shows a homogeneous distribution of the studied metals in all the sampling stations. It was observed that the soils in these stations were depleted as a result of mineral enrichment with the metals as also reported by earlier study <https://doi.org/10.21203/rs.3.rs.320812/v1>. In all the stations of the study the enrichment factors were > 1 for Mn, Co, Ni, Pb, and Zn that depicts background concentration. The enrichment factor for Cr in station **P** was \langle 1(background concentration), in station Q is 1 (depletion to mineral enrichment) and station $\mathbb{R} > 20$ (very high enrichment). The enrichment factor for copper in station **Q** is > 5 (significant enrichment) and in station **R**>1 (depletion to mineral enrichment). Similarly, the enrichment factor in station for Ti in station **P** is > 5 (significant enrichment) and in stations **Q** and **R**> 20 (very high enrichment) while the enrichment factors for uranium in the three stations were > 40 depicting extremely high enrichment.

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The ecological risk assessment results of the heavy metals are displayed in Table 4. Based on the assessment, the potential ecological risk of the heavy metals had the given trend: $U > Ti > Cu >$ $Ni > Fe > Co > Zn > Cr > Mn > Pb$ for the spoil of the abandoned mine site; $U > Ni > Ti > Cr >$ $Co > Fe > Mn > Cu$, Pb, and Zn for station (Q) 50 m away from the mine site and U $> Cr > Ti >$ $Cu > Fe > Mn > Co > Zn > Ni$, Pb for sampling station(\bf{R}), 500 m away from the mine pit. It was found that the values obtained for Co, Fe, Mn, Pb, and Zn were below 40 in all the studied sampling stations thus depicting low potential ecological risk. The ecological risk values for uranium and titanium were far above 320 for all the studied stations and therefore pose very high potential risk to the ecosystem. Similarly, a moderate threat is observed for Cu with a value slightly above 40 for the spoils from the abandoned mine pit (**P**). High ecological risk values of 132 and 98.61 for Chromium and nickel in that order were observed for sampling stations in **Q** and **R** These values are less than $160 < Ei < 320$ and hence regarded as high potential risk to the ecosystem in sampling stations of **Q** and **R**. The risk factor (R1) characterizes sensitivity of the local ecosystem to toxic metals and represents the ecological risk obtained from the entire contamination (Yisa et al., 2012).

The calculated risk factors of the heavy metals were found to be 13,679, 1,972 and 3,090 for stations **P**, **Q** and **R** in that order (Table 5). These values are extremely very high with uranium as the primary contributor in all stations because of its high toxic response factor of 40. Other metals have their toxic response factor in the range of $1 - 5$. The high concentrations of some of these heavy metals notably Ti, Cu and U are toxic to human and animal health via food chain (Perković *et al*, 2017). The United State Environmental Protection Agency (2000) report suggests that ingestion, inhalation and dermal contact are the main route for metal exposures to dwelling populace. Some studies have suggested that exposure to nickel and cadmium is linked to one of the major causes of cancer (Alfaro *et al*, 2015). Nickel is the twenty-second most abundant element in the earth crust by weight. The mine spoils from stations P and Q are slightly acidic ($pH = 5.80$) and 6.20 in that order). Ni dissolves rapidly in dilute acids to form hydrated $[Ni(H_2O)_6]^{2+}$ ions and H2 and also easily oxidized by air forming NiO and is pyrophoric. These are possible reasons why Ni has lowest concentration (0 - 160 ppm) compared with other metals in the same soil samples (240 - 90200 ppm) (Table 1). Another plausible reason for its low concentration could be because under high temperature Ni reacts with chloride to produce NiCl₃ thereby reducing its concentration. Ni has no reaction with H_2O , NO_3 ⁻, PO_4 ³⁻ and SO_4 ²⁻ in the soils (Lee, 1996). The presence of heavy metals in high concentration in the organic layer or topsoil for a long period of time has been reported to poison the soil organisms, reducing their sustainability and productivity in the terrestrial ecosystems (Chrzan *et al*, 2013).

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Analysis of variance on the data obtained for soils in the sampling stations indicates that there are significant differences in the metal concentrations at $p \le 0.05$ in the different stations. This suggests that the observed difference may be due to anthropogenic activities and not only due to background concentration. The anthropogenic inputs of the metals in the soils of the study area are given in descending order as: U (99.70%) > Ti (98.84%) > Fe (94.46%) > Cu (88.00%) > Co $(87.87%)$ > Zn $(82.05%)$ > Ni $(78.13%)$ > Mn $(68.77%)$ > Cr $(58.33%)$ as presented in Table 5. Similar results have been reported by Ogunmodede *et al* (2015).

All parameters for the water samples were found to be within the permissible limit allowed by DPR (2002) and W.H.O. (2017) except for turbidity, chromium, and chemical oxygen demand for water sample from the abandoned mine pit; phosphate, dissolved oxygen, chromium, nickel and chemical oxygen demand for surface water 400 m away from the mine pit; turbidity, phosphate, nickel, chemical oxygen demand for groundwater that is 500 m away from the mine pit. The result of ecotoxicity test used in the study is displayed in Table 6.

Index	K : Distance 0 at foot of L: Distance 400 M: Distance 500 Mean			
	Mine pit	m	m	
PPI	0.33	0.45	0.48	0.42
SI	0.03	0.21	0.04	0.09
OPI	0.78	1.33	3.34	1.82
CPIHM	0.46	2.53	0.55	1.18
GP1	0.40	1.13	1.10	0.52

Table 6: Ecotoxicity and water quality indices of water samples used in the study

Key: PPI = Physical pollution index; **SI** = Salinity index; **OPI** = Organic pollution index

CPIHM = Chemical pollution index for heavy metals; $WOI = Water$ quality index

 $K = W$ ater sample collected from abandoned mine pit;

 $L =$ Surface water sample;

M = Groundwater sample

The result of ecotoxicity studies in Table 6 shows that the physical pollution and salinity for water samples from all the stations $(K, L$ and $M)$ were found to be $\lt 1$ suggesting no pollution. The organic pollution index in station L was slightly >1 and in station M the value was high (3.34)

depicting extreme pollution in terms of this index (Boluda, 2001) but the value obtained for water sample from station K was < 1 (no pollution). The chemical pollution index for heavy metals in station L was > 1 , an indication of pollution while values for stations K and M were less than 1, an indication of no pollution. The general pollution index for water sample from station K is 0.40, a value that is > 1 and indicates no pollution status while water samples from stations L and M had values slightly >1 depicting slight pollution (Boluda, 2001). The ecotoxicity status of the water source from station M depicts pollution of chromium and nickel. This may not be unconnected with these metals being carried along from smaller streams that have their origins in the various mountains flowing into the surface water in the study area. This assertion is corroborated by the fact that the water samples from the abandoned mine pit and groundwater in the study area were only slightly contaminated in terms of chemical pollution index for heavy metals $(0.46 - 0.55)$ < 1 (Boluda, 2001; Medjor et al. 2015). Chromium toxicity has been reported to be associated with health challenges (Reyes-Gutiérrez et al., 2007). These values obtained from the ecotoxicity studies indicate that water sources in the study area are grossly polluted, coupled with the high presence of coliform count and Escherichia coli makes them unfit as drinking water for humans and capable of causing several illnesses (W.H.O, 2017).

Conclusion

The results of the study demonstrated the impact of anthropogenic activities such as quarrying, indiscriminate mining, and farming activities on the abundances of metals in the study area. The soils in all the sampling stations were grossly polluted particularly with uranium and titanium. Water sources are not safe for human and animal consumption being heavily laden with chromium and nickel.

To ensure sustainable, safer, and healthy ecosystem of the study area, government at all levels must take practicable mitigation guidelines such as educating the rural populace of the health implications of engaging these extremely polluted soils in agricultural activities as well as the danger associated with the use of the water sources for drinking and domestic use. The soil and water bodies in this area should be monitored periodically by the relevant authorities and also checkmate the activities of illegal artisan mining activities in the area. Bioremediation and other green remediation technologies such as phytoremediation that involves growing certain plants for the absorption of heavy metals are highly recommended for the study area in order to mitigate and minimize the adverse effects of heavy metal pollution.

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