JASEM ISSN 1119-8362


Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://ww.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 22 (9) 1449 –1456 September 2018

# Seasonal Variation of Soil Chemical Characteristics at Akwuke Long Wall Underground Mined Site, Nigeria

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**ABSTRACT:** The on-going action and plan to revive old coal mines in Nigeria necessitated a study on the soil chemical characteristics at abandoned coal mine in Akwuke, Enugu State, Nigeria. A single factor experiment was conducted in a randomized complete block design (RCBD) with three replications to obtain information on soil status of Akwuke mined site. Soil samples were collected randomly from ten different sampling points at 0-10, 10-20, and 20-30 cm soil depth in four cardinal points at north (N), south (S), east (E), west (W), and at the center (c) of crest, middle slope, and valley of Akwuke mined site. The samples were analyzed for heavy metals, macronutrient, soil pH, and organic matter content. Soil pH (4.29-6.14) in wet season is higher than 4.14-5.58 in dry season at Akwuke mine site. The values of N, P, K, Ca, and Mg in soil at Akwuke mine were higher in dry season than in wet season. The highest soil organic matter content (0.96±0.04%) at Akwuke mine is obtained in dry season at 0-10 cm valley. The concentrations of Ni, Pb, and Cd in soil at mined site ranged from 4.15±0.07 to 19.81±1.29, 6.11±0.13 to 21.10±0.85, and 0.01±0.00 to 3.06±0.08 mg/kg. Mg (89.60±1.41 to 251.9±1.41 cmol/kg). Cd and Ni in soil at the mined site was higher than their allowable limits in Austria, Germany, France, Netherlands, Sweden, and United Kingdom. The high concentrations of these metals (Cd and Ni) in soils could expose both animals and local inhabitants to high levels of Cd and Ni, thus, posing a serious health risks to the local people.

**DOI: https://dx.doi.org/10.4314/jasem.v22i9.15**



**Dates**: Received: 28 June 2018; Revised: 30 July: 2018; Accepted: 27 August 2018

**Key words:** Seasonal variation, Akwuke mine, coal, chemical characteristics

Coal is a hard black mineral found in coalface where it is cut out of the rock. It is the world's most abundant, most accessible and versatile source of fossil energy which was brought to the fore-front of the global energy scene by the industrial revolution of the 10th century (Akinbami *et al*., 2001). The use of coal energy especially for cooking in Nigeria will increase beyond the present level as a result of (a) high poverty rate and increasing decimation of secondary and artificial forest plantations for timber production and construction of household furniture such as upholstery seats, tables, doors among others, (b) the use of coal as source of energy for production of cement in cement industries, and (c) the high rate of pipeline vandalization and oil spillage resulting to extensive burning of vegetation and destruction of soil seed banks cum serious decline in soil fertility, thus, leading to poor regeneration of plant community.

Coal contain heavy metals, hence mining processes such as blasting, excavation, processing and transportation of coal releases metals into the environment and plants growing on such metal contaminated sites will absorb these metals. Herbivorous animals largely depends on plants for food and as cover from predators, and most animals in the wild scratch their bodies against plants as a way of soothing their itching skin. Animal exposure to metals will constitute serious health risk. Since man also relied heavily on plants for food, medicine and shelter, studies on soil metal-contaminated sites and their peripheries are essential for accurate assessment of metal toxicity of soils in relation to possible toxic impacts on human health (Ogbonna *et al*., 2012).

Since 1916 when coal mining commenced in Nigeria, it has become a major land-use particularly in south eastern Nigeria where many natives are employed in the activity. Although coal mining in this area has recently slowed down because of the shift to crude oil as energy source, the spoils and waste still exist and might have enhanced the leaching of metals into the soil. Therefore, there is need to track the level of concentrations of metals in soil at the abandoned mine

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site. This will help to create awareness on the potential danger associated with the on-going action to revitalize coal mining in Nigeria as well as the risk of farming on lands close to the abandoned mine since there is presently, the challenges of land hunger in south east Nigeria. Although several studies have been carried out on mine sites, but most of the research were conducted at surface and mountaintop quarry sites. Furthermore, the research were not carried along crest, middle slope and valley. This study, therefore, is aimed to investigate soil chemical characteristics in different soil depths at crest, middle slope and valley in wet and dry season at a long wall underground mined site.

## MATERIALS AND METHODS

*Study area:* The study on soil chemical characteristics in wet and dry season was carried out at Akwuke long wall underground mined site in Enugu State, Nigeria. Enugu with large deposits of sub-bituminous coal lies within latitude N 6°26' and longitude E 7° 27' with an altitude of 251 m. The climate of Enugu is made up of wet and dry seasons. The wet season is characterized by clouds driven by light winds, relatively constant temperatures, frequent rains and high humidity while the dry season is notably dry with little or no rainfall, hotter days, cooler nights, and lower humidity.

*Sample collections and analysis of soil chemical characteristics:* Soil samples were collected in February and June for dry and wet season at Akwuke mine and control site, respectively. Soil samples were randomly collected from ten different sampling points at the depth of 0-10, 10-20, and 20-30 cm with Dutch soil auger in four cardinal points (i.e. two sampling points each at north (N), south (S), east (E), west (W), and at the center (C) of crest, middle slope and valley of mined site. The control sample was collected in a 5 year upland bush fallow about 2 km from the mined site where there was no visible source of contamination. Samples from each particular soil depth (e.g., 0-10 cm at N, S, E, W, and C) were placed in cellophane bags (about 25 g), labeled well, placed in a wooden box and covered to avoid contamination from external sources and transferred to the laboratory for pre-treatment and analysis. Samples from the same soil depth were bulked together to give a composite sample which were homogenized and air-dried in a circulating air in the oven at 30°C to a constant weight and passed through a 2 mm sieve. Sub-samples from the composite samples were digested according to the method of Sharidah (1999).

The concentrations of Ni, Pb, Cd, As, and Fe in the digested samples were determined using flame Atomic Absorption Spectrophotometer (UNICAM 919 model) after calibrating the equipment with different standard concentrations as follows: Cd: 0.5, 1, and 2 ppm, Pb:1, 5, 10 ppm , Ni: 2, 5, 10 ppm, Fe: 1, 2, 5 ppm, and As:1, 4, 8 ppm. Triplicate digestion of each sample was carried out together with blank digest without the plant sample. Ca and Mg in the digest were determined by EDTA titration method, K and P was determined by flame photometry while total N was extracted by sulfur digestion and determined by the micro-Kjeldahl method (Nelson and Sommers, 1972). Organic matter levels in the air dried soils were estimated indirectly from organic C. Organic C was determined by oxidation of organic matter with a hot mixture of $K_2Cr_2O_7$ and $H_2SO_4$ using the Walkley and Black procedure (Walkley and Black, 1934). The amount of organic carbon was then determined by titration with 0.05N FeSO4 following the procedure outlined by Nelson and Sommers (1982). The organic matter content was obtained by multiplying the organic C content with the factor 1.729 (Nelson and Sommers, 1982) while soil pH was measured using pH meter DEMO 13702.93 manufactured by PHYWE of Germany.

*Experimental design and data analysis:* A single factor experiment was conducted in a randomized complete block design (RCBD) with 3 replications. Data collected on soil chemical characteristics were subjected to a 2-way analysis of variance (ANOVA) using special package for social sciences (SPSS) v. 15 and means were separated at $P < 0.05$ using Duncan New Multiple Range Test (DNMRT).

## RESULTS AND DISCUSSION

*Soil pH, organic matter and macronutrient content in soil:* The results on soil pH, macronutrient (Ca, Mg, K, N, and P), and soil organic matter content in soil at Akwuke mined site in wet and dry seasons is summarized in Table 1. The highest and the lowest values of soil pH were obtained at control site and mine site, respectively. Since there was no mining activity at the control site, the higher soil pH values at the control site may be attributed to the buffering effects of soil organic matter against pH change, in addition to the release of higher basic cations during organic matter decomposition (Oyedele *et al.*, 2008). The pH (5.90±-6.55±0.14) of the control site is higher than 4.14-6.14 obtained from Akwuke mined site. The high acidic nature of the mined site is attributed to flushes of acid mine drainage at Akwuke mine site. Soil pH ranged from 4.29-6.14 in wet season and 4.14-5.58 in dry season at Akwuke mine site. Soil acidity is higher in dry season than in wet season, which is as a result of dilution effect of rainfall. Within Akwuke mine site, soil pH was strongly acidic at the middle slope (4.14) than crest (4.22) and valley (5.39). Most metals do not exist in free form in the pH range of 6.0 to 9.0 (Adie and Etim, 2012). The pH for all middle slope samples analyzed in this study fell below this range (Table 1). It therefore, implies there would be high leaching of metals from the topsoil of the middle slope towards sub soils. Lower pH increase the solubility of metals (Gabriella and Anton, 2005) and this may have contributed to the higher concentration of heavy metals in middle slope of the mined site (Table 2).

**Table 1**: Macronutrient (cmol/kg), soil pH and organic matter (%) content in soil at Akwuke mine site in wet and dry season

| Location | Depth | Season | Ca | Mg | K | N | P | pH ($H_2O$) | OM (%) |
|---|---|---|---|---|---|---|---|---|---|
| Crest | 0-10cm | Wet | $4.22^{efg}$ ± 0.06 | $147.00^{l}$ ± 1.41 | $179.10^{h}$ ± 0.71 | $0.10^{e}$ ± 0.01 | $0.20^{l}$ ± 0.03 | $4.60^{fgh}$ ± 0.02 | $0.86^{c}$ ± 0.05 |
| | | Dry | $6.02^{cde}$ ± 0.14 | $251.90^{e}$ ± 1.41 | $119.55^{n}$ ± 0.64 | $0.22^{de}$ ± 0.04 | $0.34^{ghi}$ ± 0.13 | $4.34^{ij}$ ± 0.04 | $0.96^{c}$ ± 0.04 |
| | 10-20cm | Wet | $4.29^{efg}$ ± 0.20 | $137.00^{jk}$ ± 2.12 | $183.90^{h}$ ± 1.56 | $0.13^{e}$ ± 0.03 | $0.34^{ghi}$ ± 0.03 | $4.53^{h}$ ± 0.03 | $0.20^{b}$ ± 0.01 |
| | | Dry | $8.12^{bc}$ ± 0.14 | $183.20^{g}$ ± 0.42 | $87.10^{o}$ ± 0.57 | $0.29^{de}$ ± 0.06 | $0.43^{gh}$ ± 0.06 | $4.39^{i}$ ± 0.06 | $0.22^{e}$ ± 0.00 |
| | 20-30cm | Wet | $4.25^{efg}$ ± 0.13 | $142.00^{ij}$ ± 1.41 | $180.60^{h}$ ± 1.56 | $0.16^{e}$ ± 0.03 | $0.27^{hi}$ ± 0.03 | $4.58^{gh}$ ± 0.05 | $0.03^{g}$ ± 0.01 |
| | | Dry | $4.11^{efg}$ ± 0.14 | $168.00^{h}$ ± 0.28 | $158.00^{ij}$ ± 12.73 | $0.20^{de}$ ± 0.03 | $0.31^{hi}$ ± 0.04 | $4.22^{jkl}$ ± 0.08 | $0.13^{f}$ ± 0.04 |
| Middle slope | 0-10cm | Wet | $2.81^{fgh}$ ± 0.11 | 133.70k ± 1.27 | $182.50^{h}$ ± 0.85 | $0.12^{e}$ ± 0.01 | $0.35^{ghi}$ ± 0.03 | $4.68^{fg}$ ± 0.02 | $0.64^{d}$ ± 0.05 |
| | | Dry | $4.16^{efg}$ ± 0.06 | $169.00^{h}$ ± 1.13 | $95.60^{o}$ ± 0.99 | $0.28^{de}$ ± 0.06 | $0.38^{ghi}$ ± 0.04 | $4.31^{ijk}$ ± 0.08 | $0.75^{cd}$ ± 0.01 |
| | 10-20cm | Wet | $1.65^{gh}$ ± 0.03 | $115.10^{m}$ ± 0.71 | $156.10^{jk}$ ± 0.42 | $0.14^{e}$ ± 0.03 | $0.42^{gh}$ ± 0.01 | $4.72^{f}$ ± 0.02 | $0.11^{f}$ ± 0.01 |
| | | Dry | $4.09^{efg}$ ± 0.04 | $121.80^{l}$ ± 1.27 | $151.80^{jk}$ ± 0.57 | $0.36^{de}$ ± 0.03 | $0.46^{gh}$ ± 0.04 | $4.19^{kl}$ ± 0.05 | $0.12^{f}$ ± 0.00 |
| | 20-30cm | Wet | $2.20^{gh}$ ± 0.06 | $123.00^{l}$ ± 0.85 | $168.00^{i}$ ± 14.14 | $0.17^{de}$ ± 0.03 | $0.39^{ghi}$ ± 0.04 | $4.29^{jk}$ ± 0.03 | $0.02^{g}$ ± 0.01 |
| | | Dry | $2.00^{gh}$ ± 0.20 | $108.00^{n}$ ± 0.85 | $122.10^{n}$ ± 0.71 | $0.24^{de}$ ± 0.06 | $0.52^{g}$ ± 0.06 | $4.14^{l}$ ± 0.03 | $0.06^{g}$ ± 0.03 |
| Valley | 0-10cm | Wet | $1.21^{h}$ ± 0.04 | $86.25^{o}$ ± 0.21 | $145.95^{kl}$ ± 0.64 | $0.11^{e}$ ± 0.01 | $0.28^{hi}$ ± 0.06 | $6.10^{b}$ ± 0.13 | $0.15^{f}$ ± 0.04 |
| | | Dry | $4.02^{efg}$ ± 0.13 | $193.50^{f}$ ± 0.85 | $126.80^{mn}$ ± 1.27 | $0.19^{de}$ ± 0.04 | $0.33^{ghi}$ ± 0.06 | $5.39^{e}$ ± 0.07 | $0.28^{e}$ ± 0.02 |
| | 10-20cm | Wet | $2.05^{gh}$ ± 0.07 | $68.30^{q}$ ± 0.71 | $124.70^{n}$ ± 1.70 | $0.14^{e}$ ± 0.03 | $0.36^{ghi}$ ± 0.03 | $6.14^{b}$ ± 0.04 | $0.05^{g}$ ± 0.01 |
| | | Dry | $1.05^{h}$ ± 0.07 | $120.20^{lm}$ ± 0.85 | $212.00^{f}$ ± 0.57 | $0.23^{de}$ ± 0.14 | $0.41^{gh}$ ± 0.04 | $5.39^{e}$ ± 0.21 | $0.03^{g}$ ± 0.01 |
| | 20-30cm | Wet | $1.70^{gh}$ ± 0.08 | $78.00^{p}$ ± 0.57 | $136.40^{lm}$ ± 0.28 | $0.13^{e}$ ± 0.01 | $0.30^{hi}$ ± 0.06 | $5.83^{c}$ ± 0.05 | $0.01^{gh}$ ± 0.00 |
| | | Dry | $1.16^{h}$ ± 0.16 | $89.60^{o}$ ± 1.41 | $158.20^{ij}$ ± 0.57 | $0.19^{de}$ ± 0.14 | $0.42^{gh}$ ± 0.04 | $5.58^{d}$ ± 0.02 | $0.01^{gh}$ ± 0.00 |
| Control | 0-10cm | Wet | $9.60^{b}$ ± 0.08 | $301.10^{d}$ ± 0.85 | $422.00^{b}$ ± 0.57 | $0.81^{c}$ ± 0.08 | $2.94^{f}$ ± 0.11 | $6.52^{a}$ ± 0.06 | $20.66^{a}$ ± 0.08 |
| | | Dry | $12.04^{a}$ ± 0.08 | $380.00^{a}$ ± 1.13 | $471.00^{a}$ ± 4.24 | $1.46^{a}$ ± 0.10 | $3.21^{e}$ ± 0.27 | $6.55^{a}$ ± 0.14 | $26.21^{a}$ ± 0.34 |
| | 10-20cm | Wet | $7.14^{bcd}$ ± 0.23 | $310.00^{c}$ ± 12.73 | $280.10^{d}$ ± 0.85 | $0.92^{c}$ ± 0.08 | $4.01^{d}$ ± 0.16 | $6.48^{a}$ ± 0.08 | $1.06^{c}$ ± 0.07 |
| | | Dry | $9.20^{b}$ ± 0.07 | $367.10^{b}$ ± 4.10 | $316.00^{c}$ ± 13.86 | $1.20^{b}$ ± 0.16 | $4.40^{c}$ ± 0.03 | $6.19^{b}$ ± 0.03 | $1.15^{b}$ ± 0.09 |
| | 20-30cm | Wet | $4.03^{efg}$ ± 0.13 | $198.10^{f}$ ± 0.85 | $200.00^{g}$ ± 2.83 | $0.44^{d}$ ± 0.45 | $5.82^{b}$ ± 0.01 | $6.24^{b}$ ± 0.04 | $0.00^{gh}$ ± 0.00 |
| | | Dry | $5.16^{def}$ ± 0.14 | $248.00^{e}$ ± 1.56 | $224.00^{e}$ ± 1.70 | $1.01^{bc}$ ± 0.01 | $6.28^{a}$ ± 0.14 | $5.90^{c}$ ± 0.10 | $0.00^{gh}$ ± 0.00 |

*a,b,c,d,e,f,g,h,i,j,k,l,m,n,o,p,q means in a column with different superscript are significantly different ($P<0.05$)*
*Values are mean ± standard deviation of 3 replications*; OM = organic matter

The highest and the lowest organic matter content in soil is recorded at control site and mine site. The high organic matter content in soil at the control site is associated with the release of more organic matter materials (litterfall) by plants growing on the control plot and possible droppings as well as remains of animals that inhabited the area. Low organic matter are characteristics feature of mine degraded soils (Pokethitiyook, 2008) which tend to inhibit soil forming processes (Weis and Weis, 2004). The highest content of organic matter in soil at Akwuke mined site is recorded in dry season at 0-10 cm valley (0.96±0.04%). The organic matter content in soil in wet and dry season was higher at 0-10 cm than 10-20 and 20-30 cm at the mined site. The result is in conformity with the findings that organic matter content decreases with soil depth (Orimoloye, 2011). The magnitude of decline in organic matter content with depth varied amongst sampling locations (crest, middle slope, and valley) but the rate of decline were highest in valley, followed by middle slope, and lastly crest. The macronutrient content in soils at Akwuke mine and the control site in wet and dry seasons indicate that the highest and the lowest macro-nutrient content in soils were observed at the control site and mine site, respectively (Table 1). The higher content of macronutrient observed at the control site may be attributed to the quality and quantity of litterfall released by the different plant species standing on the control site unlike the Akwuke mine site.

**Table 2:** Heavy metal concentration (mg/kg) in soil at Akwuke mine site in wet and dry season

| Location | Depth (cm) | Season | Ni | Pb | As | Fe | Cd |
|---|---|---|---|---|---|---|---|
| Crest | 0-10 | Rainy | $9.71^{efg} \pm 0.16$ | $15.45^{bc} \pm 0.18$ | $0.00 \pm 0.00$ | $417.00^{f} \pm 1.98$ | $1.73^{c} \pm 0.06$ |
| | | Dry | $4.15^{k} \pm 0.07$ | $12.65^{cd} \pm 0.13$ | $0.00 \pm 0.00$ | $296.10^{k} \pm 8.63$ | $0.68^{de} \pm 0.07$ |
| | 10-20 | Rainy | $11.72^{d} \pm 0.07$ | $15.80^{bc} \pm 0.28$ | $0.00 \pm 0.00$ | $480.70^{c} \pm 2.40$ | $0.72^{d} \pm 0.17$ |
| | | Dry | $10.04^{ef} \pm 0.20$ | $10.45^{de} \pm 0.07$ | $0.00 \pm 0.00$ | $290.00^{k} \pm 4.95$ | $0.07^{gh} \pm 0.03$ |
| | 20-30 | Rainy | $14.30^{c} \pm 0.71$ | $17.62^{b} \pm 0.08$ | $0.00 \pm 0.00$ | $522.00^{a} \pm 1.98$ | $0.61^{de} \pm 0.13$ |
| | | Dry | $8.24^{hi} \pm 0.20$ | $13.60^{cd} \pm 0.28$ | $0.00 \pm 0.00$ | $216.40^{n} \pm 1.27$ | $0.38^{f} \pm 0.03$ |
| Middle slope | 0-10 | Rainy | $10.45^{e} \pm 0.27$ | $15.10^{bc} \pm 0.28$ | $0.00 \pm 0.00$ | $428.10^{e} \pm 0.85$ | $2.92^{b} \pm 0.03$ |
| | | Dry | $6.04^{j} \pm 0.06$ | $10.41^{de} \pm 0.11$ | $0.00 \pm 0.00$ | $362.20^{i} \pm 4.53$ | $0.10^{gh} \pm 0.04$ |
| | 10-20 | Rainy | $11.65^{d} \pm 0.11$ | $12.60^{cd} \pm 0.35$ | $0.00 \pm 0.00$ | $458.00^{d} \pm 2.12$ | $0.17^{g} \pm 0.06$ |
| | | Dry | $8.04^{i} \pm 0.20$ | $8.21^{ef} \pm 0.44$ | $0.00 \pm 0.00$ | $267.60^{l} \pm 1.56$ | $0.01^{h} \pm 0.01$ |
| | 20-30 | Rainy | $12.02^{d} \pm 0.48$ | $10.30^{de} \pm 0.57$ | $0.00 \pm 0.00$ | $506.70^{b} \pm 0.42$ | $0.08^{gh} \pm 0.01$ |
| | | Dry | $9.20^{fgh} \pm 0.42$ | $6.11^{f} \pm 0.13$ | $0.00 \pm 0.00$ | $314.00^{j} \pm 1.56$ | $0.02^{h} \pm 0.01$ |
| Valley | 0-10 | Rainy | $8.85^{ghi} \pm 0.35$ | $15.26^{bc} \pm 6.87$ | $0.00 \pm 0.00$ | $397.80^{g} \pm 11.03$ | $3.06^{a} \pm 0.08$ |
| | | Dry | $6.07^{j} \pm 0.10$ | $17.50^{b} \pm 0.42$ | $0.00 \pm 0.00$ | $389.80^{h} \pm 0.28$ | $0.08^{gh} \pm 0.03$ |
| | 10-20 | Rainy | $16.03^{b} \pm 0.21$ | $21.10^{a} \pm 0.85$ | $0.00 \pm 0.00$ | $258.70^{m} \pm 0.42$ | $0.57^{e} \pm 0.10$ |
| | | Dry | $10.04^{ef} \pm 1.47$ | $15.65^{bc} \pm 0.35$ | $0.00 \pm 0.00$ | $207.80^{o} \pm 3.11$ | $0.05^{gh} \pm 0.03$ |
| | 20-30 | Rainy | $19.81^{a} \pm 1.29$ | $21.72^{a} \pm 0.69$ | $0.00 \pm 0.00$ | $203.00^{o} \pm 4.24$ | $0.29^{f} \pm 0.01$ |
| | | Dry | $12.01^{d} \pm 0.16$ | $13.28^{cd} \pm 0.11$ | $0.00 \pm 0.00$ | $186.00^{p} \pm 2.83$ | $0.11^{gh} \pm 0.03$ |
| Control | 0-10 | Rainy | $0.02^{l} \pm 0.00$ | $1.46^{g} \pm 0.23$ | $0.00 \pm 0.00$ | $70.60^{s} \pm 1.98$ | $0.01^{h} \pm 0.00$ |
| | | Dry | $0.02^{l} \pm 0.00$ | $0.72^{g} \pm 0.04$ | $0.00 \pm 0.00$ | $43.00^{u} \pm 0.99$ | $0.00^{h} \pm 0.00$ |
| | 10-20 | Rainy | $0.01^{1} \pm 0.00$ | $1.01^{g} \pm 0.16$ | $0.00 \pm 0.00$ | $82.00^{r} \pm 2.83$ | $0.00^{h} \pm 0.00$ |
| | | Dry | $0.00^{l} \pm 0.00$ | $0.40^{g} \pm 0.04$ | $0.00 \pm 0.00$ | $38.50^{u} \pm 0.99$ | $0.00^{h} \pm 0.00$ |
| | 20-30 | Rainy | $0.01^{1} \pm 0.01$ | $0.26^{g} \pm 0.04$ | $0.00 \pm 0.00$ | $101.00^{q} \pm 4.24$ | $0.00^{h} \pm 0.00$ |
| | | Dry | $0.00^{l} \pm 0.00$ | $0.22^{g} \pm 0.14$ | $0.00 \pm 0.00$ | $62.20^{t} \pm 1.41$ | $0.00^{h} \pm 0.00$ |

*a,b,c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r,s,t,u means in a column with different superscript are significantly different (P<0.05); Values are mean ± standard deviation of 3 replications*

The highest content of Ca (12.04±0.08 cmol/kg), Mg (380±1.13 cmol/kg), K (471±4.24 cmol/kg), N (1.46±0.10 cmol/kg), and P (6.53±0.49 cmol/kg) in soil were obtained in 0-10 cm at control site in dry season and these values are significantly (P<0.05) higher than the corresponding values of Ca (8.12±0.14 cmol/kg), Mg (251.9±1.41 cmol/kg), K (212±0.57 cmol/kg), N (0.36±0.03 col/kg), and P (0.52±0.06 cmol/kg) observed at Akwuke mined site. The low values of Ca, Mg, K, N, and P at Akwuke mined site is attributed to coal mining activities that involved removal of vegetation to access coal resources from the soil. The removal of vegetation at the Akwuke mine site disrupted the transfer of macronutrients in soil-plant system which altered the cycling of aboveground forest organic materials and their incorporation into the soil at the mine site. The values of these macronutrients (Ca, Mg, K, N, and P) at the control site was 14.52, 13.40, 25.25, 41.99, and 70.96% higher than the highest values recorded at Akwuke mined site. The high organic matter content in soil at the control site (Table 1) is implicated for the higher percentage of macronutrients at the control site. These results corroborate the finding that macronutrient content in unpolluted soil is higher than the levels observed in metal contaminated soil (Ogbonna and Okezie, 2011). Among all the macronutrient investigated in soils at Akwuke mined site, Mg (251.9±1.41 cmol/kg) recorded the highest content in soils, which was obtained at 0-10 cm crest in dry season (Table 1). The value of Mg (251.9±1.41 cmol/kg) in soil at the mined site in dry season is significantly ($P<0.05$) higher than 147.0±1.41 cmol/kg observed in wet season. The higher content of organic matter in soil in dry season (0.96±0.04%) is implicated for the higher content of Mg in dry season at the mined site (Table 1). The value of Mg (89.60±1.41 to 251.9±1.41 cmol/kg) in soil in dry season is higher than 68.30±0.71 to 147.0±1.41 cmol/kg in wet season and this may be attributed to the high level of organic matter in soil in dry season at Akwuke mine site. The level of Mg in soil at Akwuke coal mine site is substantially below 7,000 to 197,000 mg/kg observed in soil at Magnesite mining area in Jelšava and Lubeník in Slovakia (Fazekašová *et al*., 2018) and 4,590 ± 1,029 µg $g^{-1}$ reported at a coal mine site in southern part of Santa Catarina State, Brazil (Zocche *et al*., 2017). The highest content of N (0.36±0.03 cmol/kg) and P (0.52±0.06 cmol/kg) in soil obtained in dry season at 10-20 cm and 20-30 cm middle slope of Akwuke mine is higher than 0.17±0.0 and 0.42±0.01 cmol/kg recorded in wet season at 20-30 cm and 10-20 cm middle slope of the mine site. Since south eastern agro ecological zone of Nigeria is known for high rainfall, the high content of N and P at 10-20 and 20-30 cm at Akwuke mine site is associated with the leaching of these macronutrients (N and P) into lower depths by rainfall. The value of N in soil range from 0.19±0.14 to 0.36±0.03 cmol/kg in dry season, which is higher than 0.10±0.01 to 0.17±0.03 cmol/kg in wet season, and the value of P in soil range from 0.31±0.04 to 0.52±0.06 cmol/kg in dry season, which is higher than 0.20±0.03 to 0.42±0.01 cmol/kg in wet season. The low content of N and P in wet season may be attributed to leaching and diluting effect of rainfall during the wet season. Similarly, metal toxicity may lead to inhibition of enzymes such as phosphates (an enzyme splitting off phosphates from organic molecules) present in soil, hence, affecting the availability of P in the mined site (Ogbonna *et al*., 2011). The value of N (0.10±0.01 to 0.36±0.03 cmol/kg) in soil is relatively higher than 0.11±0.00 to 0.34±0.00 cmol/kg obtained in a roadside soil in Umuahia, Nigeria (Ogbonna and Okeke, 2011).

Calcium in soil range from 1.05±0.07 to 8.12±0.14 cmol/kg in dry season, which is higher than 1.21±0.04 to 4.29±0.20 cmol/kg in wet season. The high level of organic matter in soil during the dry season at Akwuke mine site is implicated for the high content of Ca in soil in dry season The values of Ca (1.05±0.07 to 8.12±0.14 cmol/kg) in soil at Akwuke coal mine site is higher than 1.86 to 2.10 mg/kg reported by Derome and Nieminen (1998) in their study on metal and macronutrient fluxes in heavy metal polluted scots pine ecosystems in SW Finland. The highest value of K (212.00±0.57) in soil was observed in dry season at 10-20 cm valley of Akwuke mine site. The high content of organic matter in dry season is implicated for the high content of K at Akwuke mine. It is observed that the level of K in soil (87.10±0.57 to 212.00±0.57 mg/kg) in dry season is higher than the level (126.80±1.27 to 183.90±1.56 mg/kg) in wet season. The high content of organic matter in soil during the dry season is implicated for the high K in soil in dry season at Akwuke mine site. The values of K in this study (87.10±0.57 to 212.00±0.57 mg/kg) is relatively higher than 8.70±0.40 to 14.06±0.00 mg/kg reported for K in soil at Udege tin/columbite mine site in Nasarawa State, Nigeria (Aremu *et al*., 2010). The values of N, P, K, Ca, and Mg in soil at Akwuke mine were higher in dry season than in wet season and this may be attributed to the fact that macro elements are easily leached, transported or washed away by runoff in wet season, thus, reducing the quantity of these elements available for plant uptake in wet season. Indeed, the pattern of result is in the increasing order: N<P<Ca<K<Mg.

*Heavy metal concentration in soil:* The concentration of heavy metal in soils of mined and unmined (control) sites is summarized in Table 2. The comparison in this study is on the concentrations of the control soils (background soils) and concentrations in mined sites obtained in a number of research works in other cities globally. The results indicate that the highest and the lowest metal concentrations in soil were observed at the mined site and control site, respectively. Since there were no other sources of contamination in the area, the high concentrations of metals in soils of the mined site (unlike the control site) may be attributed to mine spoil from the abandoned mine. Spoil heaps and tailings from excavations constitute the overburdens deposited as mine wastes on surface soil (Mahboob, 2001) and these wastes contain heavy metals that are leached, transported and deposited on soil. Soil concentrations of all metals except arsenic (As) were raised to different degrees in wet and dry season at Akwuke mined site. The concentrations of heavy metal at Akwuke mined site were significantly raised compared to those at the control site, and significant differences was evidenced amongst the three sampling position (crest, middle slope, and valley). The tailings dumped indiscriminately at mines can influence the natural concentrations of heavy metals in soil (Giachetti and Sebastiani, 2006).

The highest concentration of Fe (522.00±1.98 mg/kg) in soil at Akwuke mine is observed at 20-30 cm crest in wet season and it is significantly ($P<0.05$) higher than values obtained at middle slope (428.10±0.85 and 362.20±4.53; 458.00±2.12 and 267.60±1.56; 506.70±0.42 mg/kg), valley (397.80±11.03 and 389.80±0.28; 258.70±0.42 and 207.80±3.11;

203.00±4.24 and 186.00±2.83), and the control site (70.60±1.98 and 43.00±0.99; 82.00±2.83 and 38.50±0.99; 101.00±4.24 and 62.20±1.41 mg/kg) at 0-10, 10-20, and 20-30 cm (Table 2). The high content of Fe at the 20-30 cm depth may be attributed to low content of organic matter in surface soil that enhanced the leaching of this metallic element to 20-30 cm over time. The result is similar to the findings of Fagbote and Olanipekun (2010) that reported higher concentration of Fe in sediment during the wet season than dry season at Agabu bitumen deposit, Ondo State, Nigeria. The values of Fe in soil range from (186.00±2.83 to 522.00±1.98 mg/kg) at Akwuke mine, which is higher than 102.17 to 181.08 mg/kg (Mahboob, 2001) at a mined site in Osun State, Nigeria (Table 3). The highest concentrations of Pb (21.72 ± 0.69 mg/kg) in soil was obtained in wet season at 20-30 cm valley of Akwuke mine and it is significantly (P<0.05) higher than values at crest (15.45 ± 0.18 and 12.65 ± 0.13; 15.80 ± 0.28 and 10.45 ± 0.07; 17.62 ± 0.08 and 13.60 ± 0.28 mg/kg), middle slope (15.10 ± 0.28 and 10.41 ± 0.11; 12.60 ± 0.35 and 8.21 ± 0.44; 10.30 ± 0.57 and 6.11 ± 0.13 mg/kg) and control site (1.46 ± 0.23 and 0.72 ± 0.04; 1.01 ± 0.16 and 0.40 ± 0.04; 0.26 ± 0.04 and 0.22 ± 0.14 mg/kg) at 0-10, 10-20 and 20-30 cm (Table 2). The high concentrations of soil Pb in wet season may be attributed to mine wastes (overburden) that contain metals that are leached, transported and deposited in soils in wet season. The concentration of Pb (6.11 ± 0.13-21.10 ± 0.85 mg/kg) in soil at Akwuke mine is lower than 21-484 mg/kg in soils at the Daduk Au-Ag-Pb-Zn mine, Korea (Chon *et al*., 2001), 2.5-36.3 mg/kg in soils at Zacatecas mine, Mexico (Gonzalez and Gonzalez-Chavez, 2006) and the background values of 11.50-38.20 mg/kg in Beijing, China (Chen *et al*., 2004).

**Table 3:** Comparison of values obtained in this study with previous work at mine sites in Nigeria

| Heavy metals | Levels obtained in this study (mg/kg) | Ranges of values (mg/kg) | Locations in Nigeria | Authors |
|---|---|---|---|---|
| Cd | 0.01-3.06 | 28.8-126.0 | Enyigba, Ebonyi | Oti and Nwabue (2013) |
| | | 0.42-0.70 | State | Ekwue *et al*., 2012 |
| | | 26-210 | Odo Illesa, Osun | Adamu *et al*. (2011); |
| | | 0.8-6.0 | State | Nganje and Adamu (2010) |
| | | | Arufu, Benue State | |
| | | | Benue State | |
| Ni | 4.15-79.00 | 2.0-39.5 | Ishiagu, Ebonyi | Eze and Chukwu (2011) |
| | | 6.34-17.4 | State | Adie and Etim (2012) |
| | | | Osun State | |
| Fe | 186.0-522.0 | 102.17-181.08 | Osun State | **Mahboob (2001)** |
| | | 2.12-4.8 | Enyigba, Ebonyi | Oti and Nwabue (2013) |
| As | 0.001-0.003 | 8.0-18.0 | State | Nganje and Adamu (2010) |
| | | 1.72-2.00 | Benue State | Ekwue *et al*., 2012 |
| | | | Odo Illesa, Osun | |
| | | | State | |
| | | 91.7-1,116.8 | Enyigba, Ebonyi | Oti and Nwabue (2013); |
| Pb | 6.11-81.60 | 11.5-27.7 | State | Adie and Etim (2012) |
| | | 8.00-15.00 | Osun State | Ekwue *et al*., 2012 |
| | | | Odo Illesa, Osun | |
| | | | State | |

The highest concentration of Ni (19.81 ± 1.29 mg/kg) in soil in wet season is observed at 20-30 cm valley of Akwuke mine and the values are significantly (P<0.05) higher than values at crest (9.71 ± 0.16 and 4.15 ± 0.07; 11.72 ± 0.07 and 10.04 ± 0.20; 14.30 ± 0.71 and 8.24 ± 0.20 mg/kg), middle slope (10.45 ± 0.27 and 6.04 ± 0.06;11.65 ± 0.11 and 8.04 ± 0.20; 12.02 ± 0.48 and 9.20 ± 0.42 mg/kg) and control site (0.02 ± 0.00 mg/kg), at 0-10, 10-20 and 20-30 cm (Table 2). The high moisture level in wet season that carried large volume of acid mine drainage may be responsible for the increase concentration of Ni in soil in wet season. The concentration of Ni (4.15 ± 0.07 to 19.81 ± 1.29 mg/kg) in soil at Akwuke mine site is higher than 0.5-13.7 mg/kg in soils at Zacatecas mine, Mexico (Gonzalez and Gonzalez-Chavez, 2006). Since there were no other sources of contamination around the study area, the source of Ni in soil may be attributed to mine spoil from the abandoned mine.

The highest concentration of Cd (3.06 ± 0.08 mg/kg) in soil at Akwuke mine site is obtained in 0-10 cm valley in wet season and the value is significantly (P<0.05) higher than values obtained from crest (1.73 ± 0.06 and 0.68 ± 0.07; 0.72 ± 0.17 and 0.07 ± 0.03 ; 0.13 ± 0.61 and 0.38 ± 0.03 mg/kg), middle slope (2.92± 0.03 and 0.10 ±0.04; 0.17 ± 0.06 and 0.01 ± 0.01; 0.08 ± 0.01 and 0.02 ± 0.01 mg/kg) and valley (3.06 ± 0.08 and 0.08 ± 0.03; 0.57 ± 0.10 and 0.05 ± 0.03; 0.29 ± 0.01 and 0.11 ± 0.03 mg/kg) at soil depth of 0-10, 10-20 and 20-30 cm (Table 2). The high concentration of Cd at valley may be attributed to the high mobility rate of this metal specie (Ogbonna and Okeke, 2011) in soil. The concentration of Cd (0.01 ± 0.00 to 3.06 ± 0.08 mg/kg) in soil at Akwuke mine is higher than 0.34-2.12 mg/kg in China (Bai *et al*., 2008) but relatively lower than 0.4-4.76 mg/kg at the Daduk Au-Ag-Pb-Zn mine, Korea (Chon *et al*., 2001) and

0.3-3.3 mg/kg at Zacatecas mine, Mexico (Gonzalez and Gonzalez-Chavez, 2006). In this study, there was no significance difference (P>0.05) in the values for As both at the coal mine site and control site. This simply infer that coal substances in Akwuke coal mine has very low content of As.

**Table 4:** Allowable limits of heavy metal concentrations in soil (mg/kg) by various countries

| Heavy metals | Levels obtained in this study | Austria | Germany | France | Netherlands | Sweden | UK |
|---|---|---|---|---|---|---|---|
| Cd | 0.01-3.06 | 1-2 | 1 | 2 | 0.5 | 0.4 | 3 |
| Ni | 4.15-79.00 | 50-70 | 50 | 50 | 15 | 30 | 75 |
| Pb | 6.11-81.60 | 100 | 70 | 100 | 40 | 40 | 300 |
| Fe | 186.0-522.0 | NA | NA | NA | NA | NA | NA |
| As | 0.001-0.003 | NA | NA | NA | NA | NA | NA |

*Source: ECDGE (2001); NA= not available*

Soil is said to be contaminated if the concentrations of an element in soils were two-to-three times greater than the average background level (Logan and Miller, 1983). Consequently, soils at the mined site is considered to be contaminated based on the observation that Fe, Pb, Ni and Cd concentrations in all the background (control) soil samples are significantly lower compared to their corresponding values in Akwuke mined site. Similarly, the concentrations of Cd and Ni obtained in this study is higher than the allowable limits of these metals (Cd and Ni) in Austria, Germany, France, Netherlands, Sweden, and United Kingdom (Table 4). At mined site, higher concentrations of metals in soil occurred mostly at 20-30 cm (Tables 2) and this may be attributed to the leaching process and low content of organic matter on surface soil. Heavy metals are complexed by organic matter; but the low content of organic matter on surface soils vis-à-vis low soil pH might have enhanced the leaching of these metals into the sub-soil in wet season. Similarly, the concentrations of heavy metals in soil were generally higher at valley than crest and middle slope and this may be due to the topography of the site coupled with the leaching effect of rainfall as a result of low organic matter in soil.

*Conclusion:* The study indicate that coal mining activities affected the chemical characteristics of soils collected from the immediate environment of Akwuke coal mine. The flushes of acid mine drainage from the coal mine made the soil more acidic. It also increased the level of heavy metals in soil at the mine site but decimated the level of macronutrient in soil. The level of heavy metals in soils is high, thus, there is need to carry out remediation to decontaminate metals in soil.

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