EVALUATION OF HEAVY METALS CONTAMINATION OF SOIL AROUND THE ABANDONED COAL ASH DUMPSITE IN OJI, ENUGU STATE, NIGERIA

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Abstract: The assessment of heavy metals levels in the soil from the Oji coal ash dump was evaluated. Concentration levels of the thirteen metals Fe, Mn, Ni, Pb, Cd, Cu, Cr, Co, Zn, As, Mo, Se and Hg in the soil samples were determined using Atomic Absorption Spectrometer (AAS) Varian 240 AA. The soil samples were subjected to Speciation analysis using the modified Tessier Sequential Extraction Protocol (SEP).The trend for percentage bio-available metals in the soil of the study area was As > Pb > Cd > Fe > Co > Cu > Mn > Mo > Ni > Zn > Cr > Se. The speciation results showed that most of the metals are distributed more in the residual fractions. Hence, metals like Fe, Mn and Se with concentration levels of 572.58±243.75, 220.87±90.53, and 59.45±11.85 mg/kg, respectively did not constitute danger to the environment, since their bio-available fractions did not exceed their standard limits. However, the bio-available fractions of 161.75 mg/kg (44.15%), 8.38 mg/kg (35.39%) and 128.13 mg/kg (37.44%) for As, Cd and Pb, respectively were more prominent and toxic than other metals, as their concentrations were above the values recommended for agricultural soils by USEPA and EU. The results also showed that the heavy metal concentrations were higher in the study area than the background. Consequently, water sources from the study area should undergo proper treatment before use. Also, further studies which will involve analysis of plant samples and water sources of the environment are recommended.

Keywords: Bio-available fractions; heavy metals; Tessier sequential extraction protocol

Introduction

Coal ash is one of the major sources of pollution affecting the general aesthetics of our environment in terms of air, soil and water pollution (Ghosh *et al.*, 2015). The hundreds of tons of coal ash generated in about 40years of the contemporarily non- operative coal fired power plant at Oji were dumped on exposed surface ground adjacent the Oji River and close to residential staff quarters of the Power Holdings Company of Nigeria (PHCN). The use of dry landfills and disposal units without composite liners to prevent leaking and leaching, such like, the coal ash dump at Oji increases the risk from disposal units (PSR, 2010). Fine particles or dusts of coal ash toxins are conveyed through the environment by erosion and run off or by wind (Duszak, 2011). Living next to a coal ash disposal site can increase ones risk of cancer and other diseases, especially if one lives near an un-lined wet ash pond that contains coal ash mingled with other coal wastes (USEPA, 2010).

Ghosh *et al.* (2015), in their review of the impact of coal ash from thermal power plant (TPP) on physicochemical properties of soil reported that coal ash contains significant amounts of fine powdered ferro-alumino-silicate material with Al, Ca, Mg, Fe, Na and Si as the predominant elements and toxic metals such as As, Ba, Hg, Cr, Ni, V, Pb, Zn and Se (Mishra *et al.,* 2013; Ghosh *et al.*, 2015; USEPA, 1999).

These toxic metals can cause several types of diseases like cancer, heart damage, lung disease, respiratory distress, kidney disease, reproductive problems, gastrointestinal illness, birth defect,impaired bone growth in children, nervous system impacts, cognitive deficiency, developmental delays and behavioral problems (USEPA, 2007).

Heavy metal pollution of the soil is caused by various metals, especially Cu, Ni, Cd, Zn, Cr and Pb (Karaca *et al*., 2010). The presence of heavy metals may change the physical, chemical and biological properties of soil. The uptake of heavy metals by plants from the soil can reduce crop productivity by inhibiting physiological metabolism. Also, the metal plant uptake from soils at high concentrations may result in a great health risk considering food-chain implications (Jordao *et al.,* 2006). Consumption of heavy metal contaminated plants or animals as food can seriously deplete some essential nutrients in the food for the body and

that can further be responsible for decreasing immunological defenses (Singh and Ajay, 2011). Some heavy metals (like Fe, Zn, Ca and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended. However, some others (like As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bio-importance in human biochemistry and physiology (Duruibe *et al*., 2007). Heavy metals exert toxic effects on soil microorganism hence results in the change of the diversity, population size and overall activity of the soil microbial communities (Ashraf and Ali, 2007)

Some of the heavy metals i.e. As, Cd, Hg, Pb or Se are not essential for plants growth, since they do not perform any known physiological function in plants. Others i.e. Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements required for normal growth and metabolism of plants, but these elements can easily lead to poisoning when their concentration are greater than optimal values (Garrido *et al*., 2002, Rascio and Izzo, 2011). Heavy metals are dangerous because they are not easily metabolized. So, they tend to bio-accumulate (Ayodele and Bulus, 2007). They are highly persistent, toxic in trace amounts, and can potentially induce severe oxidative stress in aquatic organisms (Arup *et al*., 2018).

Studies have shown that the environmental and health problems associated with coal ash are numerous and worrisome (Ghosh *et al.*, 2015; Carlson and Adriano, 1993). The ranges of toxicants in coal ashcan leach, leak or spill out of coal ash disposal sites and adversely affect human and environmental health(USEPA, 2007). Various surveys show that our environment (water, soil and air) are polluted with heavy metals. The US environmental protection agency's peer-review on human and ecological risk assessment for coal combustion wastes reported that people under such circumstanceshave as much as a 1 in 50 chance of getting cancer from drinking watercontaminated by arsenic,one of the most common and dangerous pollutants in coal ash (USEPA, 2010). Agbozu *et al.,* (2001) reported that heavy metal pollution at Trans-Amadi Industrial Layout in Port Harcourt metropolis was as a result of effluent discharges from some industries in the area. Egborge (1991) related the heavy metal pollution of Warri River to industrialization. Ajiwe *et al.,* (2002) reported that heavy metal concentration in the liver,

FUW Trends in Science & Technology Journal, www.ftstjournal.com
e-ISSN: 24085162; p-ISSN: 20485170; August, 2019: Vol. 4 No. 2 pp. 329 – 336

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kidney and brain of *Citharinus specie* and *Notopterus afer* from River Niger was as a result of industrial wastes discharged into the river.

In 2007, a United States Envionmental Protection Agency(EPA) report identified 63 sites in 26 states where the water was contaminated by heavy metals from coal ash dumps.One of the most common threats that coal ash poses to public health comes from a less dramatic scenario: the slow leakage of pollution from disposal sites such as ponds and landfills(USEPA, 2009).In Wisconsin, fly ash and bottom ash dumped into an old sand and gravel unlined pit contaminated private wells with sulfate, boron, manganese, chloride and iron at levels above the state's enforcement standards and arsenic above the state's preventive action level (PSR, 2010).In Newyork, a leaking dump containing fly ash,bottom ash and other materials generated by Dunkirk steam station on lake erie, contaminated drinking water wells with lead (USEPA, 2007).

Since the advent of industrial revolution till now, there have been several cases of heavy metal poisoning/pollution in different parts of the world,and the end to this ugly trend may not be feasible, as long as Nations(developing and developed) are pursuing technological advancement without adequate mitigation to protect the environment.

Though the thermal power plant at Oji has remained moribund for more than twenty years, some staff of PHCN are still residing in the vicinity. More so, the inhabitants of the neighboring communities have converted the coal ash dumpsite and its surroundings to farming and grazing land; obviously, this may threaten the food chain with heavy metals pollution.

Reports from earlier studies like Ogbuagu (2006), Adaikpoh *et al.,* (2005) and Ohimain *et al*. (2014) dwell more on chemistry, geology and economic importance of the coal, but little or no work was done on the coal ash where most of the non-volatile constituents of coal including heavy metals accumulate when coal is burnt for power generation. Also, little or nothing was known about either the heavy metal concentration or their chemical forms in the area of our study.

It is against this background that this study focuses on the evaluation of the heavy metals contamination of soil around the abandoned coal ash dumpsite in Oji, Enugu State**,** Nigeria. The findings of this study will be of immense benefit to the Federal Government of Nigeria and by extension, the Federal Ministry of Mines and Solid Mineral Development, considering the Federal Government's plan to resuscitate the coal industry.

Materials and methods
The study area
The area under study is in Oji town, Oji River Local Government Area of Enugu State (Fig. 1). It was originally owned by Umubo village in Agbalaenyi Ward Nachi in Udi Local Government Area of Enugu State, before it was declared urban, following the commissioning of the power plant in 1956. The coal ash dump site and the power generating plant are separated by a distance of about 800 m.The location of the study area measured with GPS (etrex 30) model, shows that the coal ash dump (Plate 1), lies on the elevation of 89m, at latitude 6° 15' 21.996" N and longitude 7° 16' 40.08" E.
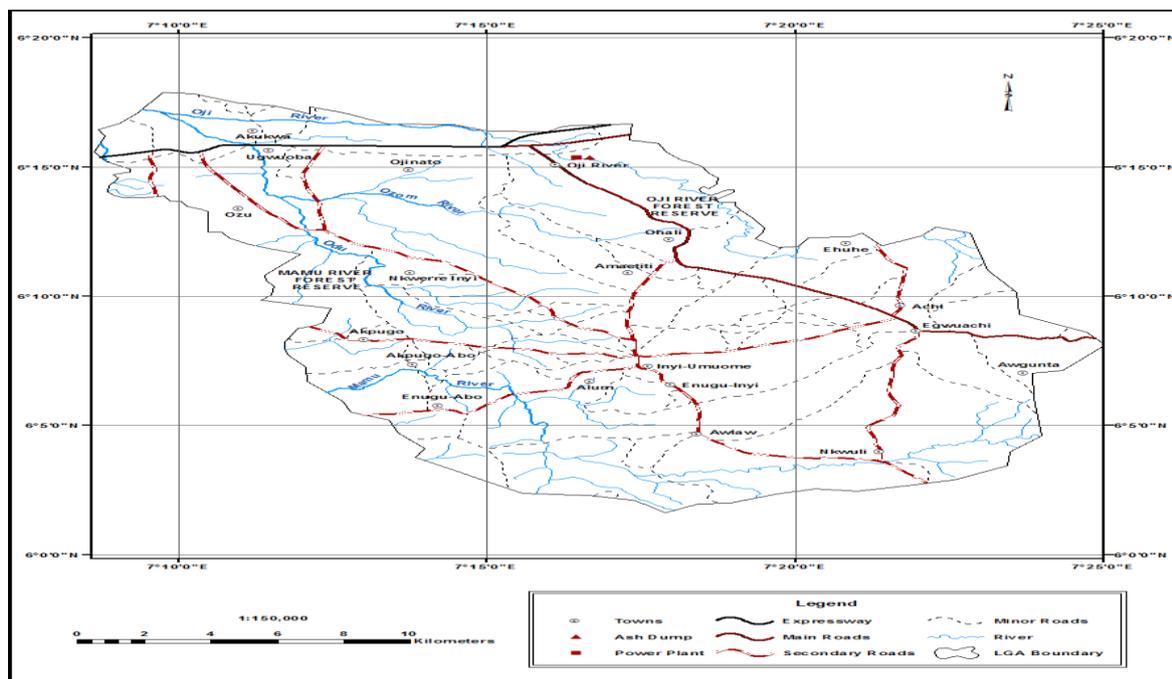
Fig 1: Map of Oji River Local Government Area showing the study area

Materials
Sampling and sample collection
The study area was divided into four cardinal points: East, West, North and South. It covered a distance of 100 m in each of the cardinal points from the coal ash dumpsite, except the east axis which has a distance of 12 m between the dump site and Oji-River. Each of the three axis was divided into five sampling points (1-5) horizontally and five vertical collection points into the soil (a-e) from the $0 - 5$ cm (top soil) to 100 cm depth. Consquently, West, North and South axes had (1a-

1e), (2a-2e), (3a-3e), (4a-4e) and (5a-5e) samples respectively. The East axis has (1a-1e) samples only, giving a total of 80 samples from the study area. Four control samples were also collected,one from each of the cardinal points at a distance of about 2.5km from the dumpsite and power station. The distances of the background sampling were such that the fly ash from the power station and the ash from the dumpsite were not deposited by either wet or dry disposal methods.All the soil samples were collected in polyethene bags and taken to the laboratory for further preparation and analysis.

FUW Trends in Science & Technology Journal, www.ftstjournal.com
e-ISSN: 24085162; p-ISSN: 20485170; August, 2019: Vol. 4 No. 2 pp. 329 – 336

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Sequential extraction

The purpose of sequential selective extraction is to mimic the release of the selective metals into solutions under various environmental conditions (Tessier *et al.,* 1979). In this study, the Tessier sequential extraction protocol was adopted as described below;

Exchangeable fraction (F_1)

For the exchangeable fraction of the soil samples, 1g of the sample was introduced into a Teflon beaker at room temperature (30^0C) and 5 cm^3 sodium acetate (NaOAc) of pH 8.2 was added. The mixture was continuously agitated for 1hr. The resulting solution was filtered using Whatman No.1 filter paper into a 25cm^3 standard flask and made up to mark with deionized water (Tessier *et al*., 1979).

Bound to carbonate/acid extractable (F_2)

The residue from above was leached at room temperature with 8 ml of 1M NaOAc solution adjusted to pH of 5.0 with acetic acid. Continuous agitation was carried out for one hour and the resulting solution was filtered into 25 cm^3 flask and made up to mark with deionized water.

Bound to Fe-Mn oxide/reducible fractions (F_3)

The residue from above was extracted with 20 cm^3 of 0.04M NH$_2$OH*HCl in 25% (v/v) acetic acid at 96^0C with occasional agitation for 5 h. After this, it was filtered into 25 cm^3 flask and made up to mark with deionized water.

Bound to organic matter/oxidizable fractions (F_4)

A solution of 3 cm^3 of 0.02M HNO$_3$ and 5.0 cm^3 of 30% H$_2$O$_2$ adjusted to pH of 2.0 with HNO$_3$ was added to the residue from above and the mixture was heated to 85^0C for 2 h with occasional agitation. A second 3.0 cm^3 aliquot of 30% H$_2$O$_2$ was added and the sample was heated to 85^oC for 3 h with intermittent agitation. The system was allowed to cool and after cooling, 5.0 cm^3 of 3.2M ammonium acetate (NH$_4$OAc) was added and this was diluted to 25 cm^3 with deionized water followed by 30 min of continuous agitation. The addition of NH$_4$OAc was designed to prevent the adsorption of extracted metal into the oxidized sediment.

Residual fraction (F_5)

The residue from above was digested with 5 cm^3 concentrated HF and 5 cm^3 aqua regia and filtered into a 25 cm^3 standard flask and made up to mark with deionized water. All the stored supernatant solutions from (F_1) to (F_4), the residual digest, and the total digest solutions as well as the blanks were instrumentally analyzed for their metal content using Atomic Absorption Spectrophotometer Varian AA240.

Statistical analysis

The results of the heavy metal analysis were accessed statistically using the Pearson correlation analysis to compare the inter-relationship in the respective fractions among the four cardinal points.

Results and Discussion

Table 1 represents the result of the pH of the soil samples from the study area. The results of the pH of the soil of the study area as represented in Table 1 showed that the mean pH of the soil samples are within the 5.5 – 8 range for agricultural soils (Jagadhieshwar, 2017). Unless there is sudden pH change, there may not be any drastic effect on the metals in terms of mobility and speciation.

Table 1: pH of the soil

Soil	pH value
East axis	6.1
West axis	6.5
North axis	6.7
South axis	6.1
Mean pH of the soil	**6.4**

The results of the sequential extraction/heavy metal distribution in the soil samples are presented in Tables 2 – 5. The trend in the fractional distribution of iron (Fe) is the same in the four cardinal points: $F_5>F_3>F_2>F_1>F_4$. The highest level of concentrations of 478.075 mg/kg for East, 634.625 mg/kg for West, 628.125 mg/kg for North and 547.9 mg/kg for South axis were recorded in the residual fractions (Tables 2 – 5). The highest bioavailable fraction of 201.75 mg/kg was recorded in the North axis while the least bioavailable fraction of 159.375 mg/kg was recorded in the South axis (Tables 4 & 5). The result showed that the sources of Fe were basically from the geological composition of the study area and probably little contribution from the coal ash dump.

Table 2: Metal fractions (mg/kg) of the sequential extraction in the east axis of the study area

	Fe	Mn	Ni	Pb	Cd	Co	Zn	Cr	Cu	As	Mo	Se	Hg
F1	88.43	3.78	BDL	50.20	1.28	1.98	0.78	0.93	1.33	125.48	0.70	0.73	BDL
F2	103.43	10.35	0.10	91.05	2.13	6.38	1.90	1.23	1.80	43.38	2.33	0.68	BDL
F3	262.45	35.93	1.53	83.80	4.38	8.38	16.70	2.75	2.45	94.63	21.83	54.25	BDL
F4	39.30	9.38	0.88	83.28	7.53	9.83	10.03	0.28	2.00	76.28	2.33	50.75	BDL
F5	479.70	180.83	17.08	47.93	BDL	40.80	32.58	46.85	15.15	37.70	4.45	79.20	29.68
BAF	191.75	14.25	0.10	141.25	3.45	8.35	2.75	2.23	3.15	173.85	2.88	1.43	BDL
%BAF	20.44	7.5	0.348	39.75	20.68	16.82	7.58	4.65	16.11	45.23	9.16	0.63	BDL

BAF=Bioavailable fraction, BDL= Below detectable limit

Table 3: Metal fractions (mg/kg) of the sequential extraction in the west axis of the study area

	Fe	Mn	Ni	Pb	Cd	Co	Zn	Cr	Cu	As	Mo	Se	Hg
F1	87.38	4.50	0.30	35.98	2.75	1.98	0.45	1.45	0.93	90.45	0.68	0.28	BDL
F2	108.63	14.63	1.75	83.58	3.55	4.55	2.53	1.25	1.55	122.63	0.63	0.30	BDL
F3	358.28	99.88	1.75	86.05	4.58	6.90	28.35	1.75	1.70	106.93	4.85	30.95	BDL
F4	79.73	14.63	8.23	78.98	5.03	9.75	16.03	3.43	1.75	42.28	10.33	65.35	0.98
F5	634.63	302.05	31.63	58.05	BDL	53.10	93.95	73.08	25.90	7.03	6.28	48.15	48.53
BAF	195.98	19.13	2.05	119.55	6.35	6.65	6.75	2.70	5.78	213.10	1.35	0.63	BDL
%BAF	15.53	4.514	4.534	34.954	38.31	8.4	6.79	3.032	8.26	58.044	5.162	0.442	BDL

BAF=Bioavailable fraction, BDL= Below detectable limit

FUW Trends in Science & Technology Journal, www.ftstjournal.com
e-ISSN: 24085162; p-ISSN: 20485170; August, 2019: Vol. 4 No. 2 pp. 329 – 336

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Table 4: Metal fractions (mg/kg) of sequential extraction in the north axis of the study area

	Fe	Mn	Ni	Pb	Cd	Co	Zn	Cr	Cu	As	Mo	Se	Hg
F1	88.80	3.78	BDL	45.85	2.00	2.95	0.83	0.50	1.05	100.10	0.63	1.40	BDL
F2	113.03	13.55	1.28	92.03	2.25	5.75	2.00	1.20	1.43	36.63	0.73	0.75	BDL
F3	279.73	66.33	1.40	75.18	3.70	8.33	9.73	2.85	1.80	111.30	18.08	40.95	BDL
F4	70.08	13.93	0.03	82.25	5.48	10.63	14.50	0.00	1.88	66.63	31.75	71.85	0.88
F5	628.08	211.60	22.88	52.15	BDL	30.03	68.68	54.58	20.23	12.40	23.28	59.40	37.73
BAF	201.75	17.30	1.28	137.85	4.30	8.70	2.90	1.70	2.13	136.75	1.35	2.20	BDL
%BAF	16.9	5.91	5.85	39.70	29.63	19.1	3.072	2.55	9.39	42.14	1.61	1.068	BDL
BAF	201.75	17.30	1.28	137.85	4.30	8.70	2.90	1.70	2.13	136.75	1.35	2.20	BDL
%BAF	16.9	5.91	5.85	39.70	29.63	19.1	3.072	2.55	9.39	42.14	1.61	1.068	BDL

BAF=Bioavailable fraction, BDL= Below detectable limit

Table 5: Metal fractions (mg/kg) of the sequential extraction in the south axis of the study area

	Fe	Mn	Ni	Pb	Cd	Co	Zn	Cr	Cu	As	Mo	Se	Hg
F1	76.90	5.70	0.45	36.83	10.83	0.15	0.35	0.35	0.90	20.68	0.60	0.10	BDL
F2	82.48	9.68	1.43	76.93	8.53	3.58	0.78	0.43	1.18	102.60	0.63	1.05	BDL
F3	325.90	54.93	1.45	78.88	3.43	7.15	19.70	BDL	1.63	130.30	4.15	19.80	BDL
F4	57.00	15.15	0.10	58.03	4.43	10.20	20.83	2.40	1.78	69.48	4.63	36.25	1.93
F5	547.90	189.00	21.05	57.98	26.75	11.55	27.28	74.03	15.80	20.85	11.65	51.05	35.88
BAF	159.38	15.35	1.73	113.85	19.35	3.73	1.15	0.80	2.10	123.28	1.25	1.20	BDL
%BAF	14.83	4.78	8.72	35.38	52.96	13.92	1.55	0.89	11.35	31.19	6.15	0.86	BDL

BAF=Bioavailable fraction, BDL= Below detectable limit

Table 6: Results of the mean metal fractions from the study area

Parameter	F1	F2	F3	F4	F5	BAF	%BA
Fe	85.38±5.68	101.89±13.52	306.59±43.64	61.53±17.50	572.58±243.75	187.23	16.93
Mn	4.44±0.91	12.05±2.41	64.27±26.85	13.27±2.64	220.87±90.53	16.50	5.68
Ni	0.19±0.23	1.14±0.72	1.53±0.15	2.31±3.97	23.16±6.52	1.30	4.86
Pb	42.22±6.95	85.90±7.07	80.98±4.89	75.64±11.88	54.03±13.78	128.13	37.44
Cd	4.22±4.45	4.12±3.01	4.02±0.55	5.62±1.35	6.69±12.76	8.38	35.39
Co	1.77±1.17	5.07±1.25	7.69±0.77	10.10±0.40	33.87±14.98	6.85	14.32
Zn	0.60±0.24	1.80±0.74	18.62±7.71	15.35±4.45	55.62±22.76	3.4	4.75
Cr	0.81±0.49	1.03±0.40	1.84±1.32	1.53±1.66	62.14±29.81	1.85	2.78
Cu	1.05±0.20	1.49±0.26	1.90±0.38	1.85±0.11	19.27±7.98	3.30	11.28
As	84.18±44.84	76.31±42.80	110.79±14.80	63.67±14.82	19.50±14.05	161.75	44.15
Mo	0.65±0.05	1.08±0.83	12.23±9.06	12.26±13.42	11.42±7.88	1.70	5.52
Se	0.63±0.58	0.70±0.31	36.49±14.66	56.05±15.88	59.45±11.85	1.38	0.75
Hg	BDL	BDL	BDL	0.95±0.79	37.96±17.08	BDL	BDL

F1= exchangeable, F2= carbonate bound, F3= Fe/Mn bound, F4= oxidizable, F5= residual

Variations in the level of concentration may be as a result of topography of the study area as small erosion can leach these metals down the topographic gradient of the area. The mean concentration levels of iron (Fe) ranged from 61.525 mg/kg in the non-residual fraction to 572.575 mg/kg in the residual fraction (Table 6). This level of Fe concentration is below the USEPA maximum permissible limit of 5500 mg/kg for agricultural soils. The mean fractional distribution levels followed the trend: F5 > F3 > F2 > F1 > F4 (Fig. 2). This resultis similar to the one reported by Ruqia *et al.* (2015). The result inferred that Fe was probably not a toxic threat to the soil of the study area.

Manganese concentration ranges from (3.775 to 180.825 mg/kg) in the East axis (4.525 to 302.05 mg/kg) in the West axis, (3.775 to 211.16 mg/kg) in the Northand (5.7 to 189 mg/kg) in the South axis, respectively (Table 2 – 5). The trend in the concentrations: F5>F3> F4>F2>F1 was observed for both North and South axis.The observed trend for East and West were F5>F3>F2> F4> F1 and F5>F3> F4 >F2>F1, respectively.

The variation of Mn concentration in the four axis may be related to the topography of the study area. Manganese (Mn) mean concentration ranged from 4.45 to 220.875 mg/kg (Table 6). The fractional distribution followed the trend: F5 > F3 > F4 > F2 >F1 (Fig. 2). Mean bioavailable fraction of Mn was below the permissible limit of 300 mg/kg for agricultural soils (Kabata and Pendias, 2001). Similar results were

reported by Obasi *et al.* (2012). The level of Manganese did not constitute toxic threat since the bio-available fraction was below the standard limit.
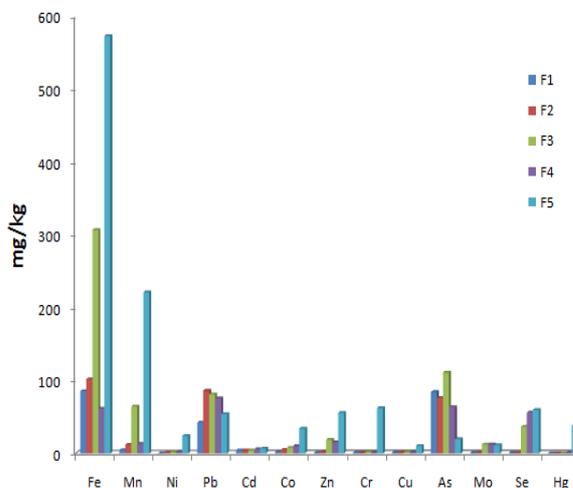
F1= exchangeable, F2= carbonate bound, F3= Fe/Mn bound, F4= oxidizable, F5= residual

Fig. 2: Mean level of metal fractions (mg/kg) in the study area

FUW Trends in Science & Technology Journal, www.ftstjournal.com
e-ISSN: 24085162; p-ISSN: 20485170; August, 2019: Vol. 4 No. 2 pp. 329 – 336

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Fractional distribution of nickel within the four cardinal points of the study area (Tables 2 – 5) ranged from (0.1 to 17.075 mg/kg) in the East, (0.3 to 31.625 mg/kg) in the West, (0.025 to 22.875 mg/kg) in the North and (0.01 to 21.05 mg/kg) in the South.The observed trends were residual>reducible> oxidizable> carbonate>exchangeable for the East axis, residual>oxidizable> reducible> carbonate> exchangeable in the West axis,residual> reducible> carbonate>oxidizable> exchangeable and residual>reducible> carbonate> exchangeable> oxidizable in the South axis. The highest concentration of nickel was found in the residual fraction of the soil in each of the four axes. The geographical position of the study area influenced the results obtained in each axis as there is a correlation between the topography of each axes and metal concentration, more so the dominance of Ni in the residual fraction implied that greater portion of Ni in this study was as a result of the geological composition of the soil environment with little contribution from anthropogenic activities. The levels of Ni concentrations in the four axes were below the permissible limit (Kabata and Pendias, 2001). The results obtained in this study were similar to the ones reported by Rizik (2010), in his study of heavy metal concentrations in soils and leachetes of Mtoni dumpsite bordering the Indian Ocean in Dar es Salaam, Tanzania. Nickel (Ni) mean concentration in the study area (Table 6) ranged from 0.2 to 24.025 mg/kg. Both the mean total and bioavailable Ni were below the maximum permissible range of 20 – 60 mg/kg for agricultural soils (Kabata and Pendias, 2001). Meanwhile, the mean fractional concentrations was in the order F5 > F4 > F3 > F2 >F1. The low level of non-residual fractions means that Ni was not a possible toxic threat to the study area. However, the result did not agree with that of Haluschak *et al.* (1998), who reported that most available nickel in the soil may be that associated with Fe and Mn oxides.

The concentration of lead ranges from (47.925 to 91.05 mg/kg) in the East axis, (35.975 to 86.05 mg/kg) in the West, (45.85 to 92.025 mg/kg) in the North and (36.825 to 78.875 mg/kg) in the South (Tables 2-5). The observed trend for lead (Pb) concentration was carbonate>reducible>oxidizable> exchangeable> residual in the East axis, reducible> carbonate> oxidizable> residual>exchangeable in the West, carbonate> oxidizable >reducible>residual>exchangeable in the North, and reducible>carbonate>oxidizable>residual> exchangeable in the South axis. The trend showed slight dominance of reducible fraction in the East, West and South axis, followed closely by carbonate which was the dominant fraction in the North axis. Correlation of the results from the axes was positive and significant, slight variation in each axis may be a factor of topography. Lead (Pb) mean concentration ranged from 42.225 mg/kg to 85.9 mg/kg (Table 6), while the observed trend followed the order: F2 > F3 > F4 > F5 > F1. Mean extractable lead (Pb) in the soil of the study area was above the USEPA, 1986 and EU set limit of 30 – 300 mg/kg (Kabata and Pendias, 2001). Similar results were reported by Obasi *et al.* (2012). The dominance of non-residual fractions and high value of bio-available fraction implicated anthropogenic activities and possibly the coal ash dump as the major source of Pb in the study area. Interestingly, Pb toxicity threat to the study area is expected.

Fractional distribution of Cd in the four cardinal axes ranged from 1.275 mg/kg to 7.525 mg/kg in the East, 2.75 to 5.025 mg/kg in the West, 2 to 5.475 mg/kg in the North and 3.425 to 26.75 mg/kg in the South (Tables 2 – 5). The observed trend was oxidizable>reducible> carbonate> exchangeable> residual in the East, West and North axis, respectively. The trend observed in the South was residual>exchangeable> carbonate> reducible> oxidizable. Cadmium concentration was dominated by non-residual fractions except in the south

axis, thereby implicating anthropogenic activities as the major source of cadmium in the four axes. Mean cadmium (Cd) concentration ranged between 4.025 and 6.7 mg/kg (Table 6). The trend for the fractions is; F5 > F4 > F1 > F2 > F3 (Fig. 2). Mean bioavailable cadmium was abovethe 3mg/kg and 5mg/kg set limit by some European communities, respectively (Kabata and Pendias, 2001). Similar results were obtained by Obasi *et al.,* (2012). The result inferred that Cd was a potential toxic threat to the study area and probably from the coal ash dump.

Fractional distribution of cobalt in the four cardinal axes ranged from 1.975 mg/kg to 40.8 mg/kg in the East, 1.975 to 53.1 mg/kg in the West, 2.95 to 30.025 mg/kg in the North and 0.15 to 11.55 mg/kg in the South axis (Tables 2 – 5). The trend followed the order: residual> oxidizable>reducible> carbonate>exchangeable, in all the four cardinal points (Fig. 2). The dominance of the residual fractions showed that most of the Cobalt in all the axes may be as a result of geological composition of the study area. Cobalt mean concentration ranges between 1.775 and 33.875 mg/kg (Table 6) while the mean fractional concentration levels followed the trend F5 >F4 > F3 > F2 >F1 (Fig. 2). Similar results were obtained by Micó *et al.* (2006), the result showed that Co was not a possible contaminant in the study area since the non-residual fractions were below the standard limit.

Fractional distribution of zinc in the four cardinal points of the study area ranged from 0.775 to 32.575 mg/kg in the East axis, 0.45 to 93.95 mg/kg in West axis, 0.825 to 68.675 mg/kg in the North axis and 0.35 mg/kg to 27.275 in the South axis (Tables 2 – 5). The observed trend: residual>reducible> oxidizable> carbonate> exchangeable isthe same for both East and West, while the trend: residual> oxidizable> reducible> carbonate> exchangeable was the same for both the North and the South axis. The dominance of the residual fraction followed by reducible fraction and the low level of bio-available fraction indicated that the source of Zn in the four axes were from parent soil material and probably little contribution from coal ash dump. Zinc (Zn) mean concentration ranged from 0.6 to 55.625 mg/kg in the study area (Table 6). The fractional distribution trend was F5 > F3 >F4 > F2 >F1 (Fig. 2). The level of Zn concentration in the study area did not pose any danger since the bio-available phase was below the standard limit (USEPA, 1986). The results of the mobile fraction is similar to the one reported by Obasi *et al.* (2012). Since zinc is more soluble in the soil than other metals, the mobile phase which may be related to the impact of coal ash deposit might have been converted to soluble zinc and taken away through different sources, hence the low mobile phase (Kabata and Pendias, 2001).

Fractional distribution of chromium in the East, West, North and South axes of the study area are shown in Tables 2–5. The metal concentrations ranged from (8.325 to 46.85 mg/kg) in the East, (1.45 to 73.075 mg/kg) in the West, (0.5 to 54.575 mg/kg) in the North and (0.35 to 74.025 mg/kg) in the South. The observed trend: residual> reducible> carbonate> exchangeable> oxidizable was the same for both East and North axes. While the trend: residual>oxidizable>reducible> exchangeable>carbonate was observed in the West axis and residual>oxidizable> carbonate> exchangeable> reducible was observed in the South axis. Chromium concentration was below detectable limit of the instrument in oxidizable and reducible fractions of the North and South axes respectively. The dominance of the residual fraction in the entire axes showed that most of the Cr was native to the study area and probably little contribution from coal ash dump. Chromium (Cr) mean concentration in the study area ranged between 0.8 mg/kg in the non-residual and 62.125 mg/kg in the residual fractions, respectively (Table 6). The observed trend follows the order: F5 > F3 > F4 >F2 >F1 (Fig. 2). The result showed

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that both the residual and non-residual fractions were below the standard limit, therefore Cr was not a possible contaminant from the coal ash dump in the study area. The result is also in agreement with the report of Kabata-Pendias and Pendia (1992), that chromium is resistant to weathering and only slightly soluble under very acid condition.

The concentration of the sequentially extracted copper ranged from (1.325 to 15.15 mg/kg) in the East (0.925 to 2.59 mg/kg) in the West (1.05 to 20.225 mg/kg) in the North and (0.9 to 15.8 mg/kg) in the South axes (Table 2 – 5). The trend:residual>reducible>oxidizable>carbonate>exchangeable was observed in the East axis, while residual>oxidizable> reducible> carbonate> exchangeable was the same for East, North and South axis. The dominance of the residual fraction in the entire axis showed that most of the Cu was native to the study area and probably little contribution from coal ash dump. Variations of Cu in the axis were attributed to the topography of the area. The mean concentration level of copper (Cu) in the study area ranged between 1.05 mg/kg in non-residual and 10.275 mg/kg in the residual fractions respectively (Table 6). The observed trend followed the sequence: F5 > F3 >F4 >F2 >F1 (Fig. 2). The result indicated that Cu was not a possible contaminant since both the residual and the non-residual fractions were below the permissible limit of 100 – 300 mg/kg set limit by USEPA, 1986 for agricultural lands. Similar results were reported by Obasi *et al.* (2012, 2013).

The concentration of the sequentially extracted arsenic ranged from (37.7 to 125.475 mg/kg) in the East (7.025 to 122.625 mg/kg) in the West (12 to 111.3 mg/kg) in the North and (20.85 to 130.3 mg/kg) in the South axes respectively (Table 2- 5). The trend: exchangeable>reducible>oxidizable> carbonate>residual was observed in the East axis, carbonate> reducible>exchangeable>oxidizable>residual in the West axis, reducible>exchangeable>oxidizable> carbonate>residual in the North axis and reducible>carbonate>oxidizable> residual>exchangeable in the South axis. The results from the axes correlated significantly. The observed slight variations may be related to the topography of the area. Arsenic (As) mean concentration ranged from 19.5 to 110.8 mg/kg (Table 6). Also, the sequential extraction results followed the trend: F3>F1>F2>F4>F5 (Fig. 2). Dominance of non-residual fractions especially the bio-available fraction implied that most of the arsenic concentrations in the four axes were attributed to anthropogenic sources possibly the coal ash dump. The bioavailable arsenic in this study were abovethe maximum allowable concentration of 15 – 20 mg/kg for agricultural soils, thereby, posing toxic threat to the environment(Kabata and Pendias, 2001). The results were similar to the one obtained by (Halluschak *et al.*, 1998). Solubilty of arsenic is affected by pH, unlike most trace elements, the inorganic forms of arsenic are more mobile and more toxic than the organic forms (Kabata and Pendias, 1992).

Fractional distribution of molybdenum in the four cardinal points of the study area, ranged from (0.7 to 21.825 mg/kg) in the East, (0.625 to 10.325 mg/kg) in the West, (0.625 to 31.75 mg/kg) in the North and (0.6 to 11.65 mg/kg) in South axis, respectively (Table 2-5). Thetrend follows the order: reducible>residual>oxidizable>carbonate>exchangeable in the East axis, oxidizable>residual>reducible>exchangeable> carbonate in the West axis, oxidizable>residual>reducible> carbonate>exchangeable in the North and residual> oxidizable>reducible>carbonate>exchangeable in the South axis. The results from the axes had positive and significant correlation with each other. The observed variations may be attributed to the topography of the study area. Molybdenum (Mo) mean concentration in the study area ranged from 0.65 to 12.25 mg/kg (Table 6), while the observed trend followed

the order: F4 > F3 > F5 > F2 >F1 (Fig. 2). This result showed that though the bio-available fraction of Mo was below the standard limit (USEPA, 1986); the high level of Mo in Fe-Mn oxide and organic phases indicated that most of the Mo in the four axes originated from anthropogenic sources, probably the coal ash dump. This might be dangerous, especially if there is slight change in pH. The results were less than the ones obtained by Halluschak (1998), Obasi (2012, 2013).

The result of the sequentially extracted selenium ranged from (0.725 to 79.2 mg/kg) in the East (0.275 to 65.35 mg/kg) in the West (0.75 to 71.85 mg/kg) in the North, and (0.1 to 51.05 mg/kg) in the South axis, respectively (Table 2–5). The observed trend followed the order: residual>reducible> oxidizable>exchangeable>carbonate in the East axis, oxidizable> residual> reducible> carbonate> exchangeable in the West, oxidizable> residual> reducible> exchangeable> carbonate in the North while residual> oxidizable> reducible> carbonate>exchangeable was observed in the South axis. Correlation of Se in the four axes were positive, the observed variations may be attributed to the topography of the study area. Mean levels of selenium in the study area ranged from 0.625 to 59.45 mg/kg (Table 6), the observed trend was F5 > F4 > F3 > F2 >F1 (Fig. 2). The high level of Se in the residual fraction contrary to the non-residual fractions implied that most of the Se originated from the parent soil materials and probably little contribution from anthropogenic sources. Invariably, Se pollution may not be expected as long as the pH remains stable and the level of Se is below the permissible limit (USEPA, 1986).

Mercury (Hg) concentration levels were below detectable limit in the exchangeable, carbonate and reducible fractions. However, concentrations range of 0.95 to 37.95 mg/kg was recorded in oxidizable and residual fractions respectively (Table 6). The non detection of Hg in bio-available fraction and the dominance of residual fraction showed that Hg was not a potential toxic threat to the environment, as long as, the natural equilibrium of the ecological system is maintained (Kabata and Pendias, 2001).

The observed trend in the distribution pattern of the mean of heavy metals in the study area was Fe >As > Pb > Mn >Se > Zn > Cr >Co > Hg > Cu > Mo > Ni > Cd (Table 6). The metals were categorised into five fractions: exchangeable phase, acid soluble phase (bound to carbonate) reducible phase (bound to Fe – Mn oxides), Oxidizable phase (bound to organic matter), and residual phase (bound to silicates), represented by series F_1- F_5 (Fig. 2).

Statistical analysis

The effects of the heavy metal concentrations in each axis of the study area were accessed statistically using the Pearson correlation analysis. The results revealed that the metals in the four axes have positive relationship with each other except for arsenic with negative relationship in the east and south axis. Also the relationship was significant for the metals Fe, Mn, Ni, Pb, Cd, Co, Zn, Cr, Cu and Hg at the p-value of either 0.01 or 0.05. The result inferred that the heavy metal concentration in the four axes of the study area were basically from one source; the abandoned coal ash dumpsite.

Conclusion

Evidence abounds that coal ash contain varying levels of metals and metalloids depending on the geological composition of the coal's immediate environment. The pH of the soil environment under study were determined and found to be between 6.1 and 6.7. The results showed that the average pH of the soil were within the normal range. The concentration of the total and bioavailable heavy metals determined in this study were in the order of Fe > As > Pb > Mn > Se > Zn > Cr > Co > Mo > Hg > Ni > Cd > Cu and Fe > As > Pb > Mn> Co > Zn > Cu > Cr > Mo > Se > Ni > Hg.

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The result of the sequential analysis of the soil revealed that only the bioavailable fractions of arsenic and cadmium were above the standard limit for agricultural soils. Meanwhile the non residual fractions of the metals Mn, Pb, Mo, Se, As and Cd were above 50% of the total concentration. Therefore, the dominance of the non residual fractions of the metals Mn, Pb, Mo, Se, As and Cd served as indicators of environmental pollution, thereby implicating the coal ash deposit in the study area.

Recommendations
Soil amendment should be applied if the place must be cultivated. The drinking water sources from the area should undergo proper treatment before being used for both drinking and other domestic purposes. As the Federal Government of Nigeria is planning to resuscitate the coal industry, heavy metal remediation program should be incorporated into the original plant design of the Oji River Power Station.

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