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Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (*Chromolaena odorata*) of Agbabu Bitumen Deposit Area, Nigeria

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Abstract: Fe, Cu, Mn, Cr, Zn, Hg, Pb, Cd, N_i and V were analyzed in soil and plant (*Chromolaena odorata*) samples in the dry season and rainy season of year 2008 using AAS. Mercury was not detected in all soil and plant samples. The mean concentrations of metals in soils, ranging from 0.28±0.04ppm to 10,371.67±252.24ppm considering both seasons, were lower than the maximum allowable limits in soil used in many countries. The mean concentration of heavy metals in plants ranged between 0.10±0.01ppm and 44.80±3.31ppm. Concentrations of the metals were lower in plants than in soil apart from Cd which showed biomagnifications. Enrichment Factor (EF) of the heavy metals in soil showed that Zn (EF = 2.50) in the dry season and Pb (EF = 3.83) in the rainy season had the highest enrichments which were moderate. The low values of EF indicate that the heavy metals probably originated from natural source. Results of Geo-accumulation Index (Igeo) in soil showed low levels of contamination for the heavy metals. Analysis of variance with SAS showed that the mean concentration of metals in soil in the two seasons (" level=0.05) were not significantly different implying that the metals were held firmly in the matrix of soil.

Key words: Heavy metal % Soil % *Chromolaena odorata* % Enrichment factor (EF) % Geo-accumulation Index (Igeo)

INTRODUCTION

Agbabu is one of the farm settlements in Ondo State hosting vast deposit of bitumen (Figure 1).

Heavy metal contamination in soil is a major concern because of their toxicity and threat to human life and the environment [1]. Heavy metals and other pollutants such as polycyclic aromatic hydrocarbons are major components of petroleum hydrocarbons including bitumen [2]. Toxic heavy metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications. They get accumulated in time in soils and plants and would have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption) determining the reductions in plant growth, dry matter accumulation and yield [3]. Heavy metals get into plants via adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals of metals into the inner matrix. Both mechanisms can also occur [4]. In small concentrations,

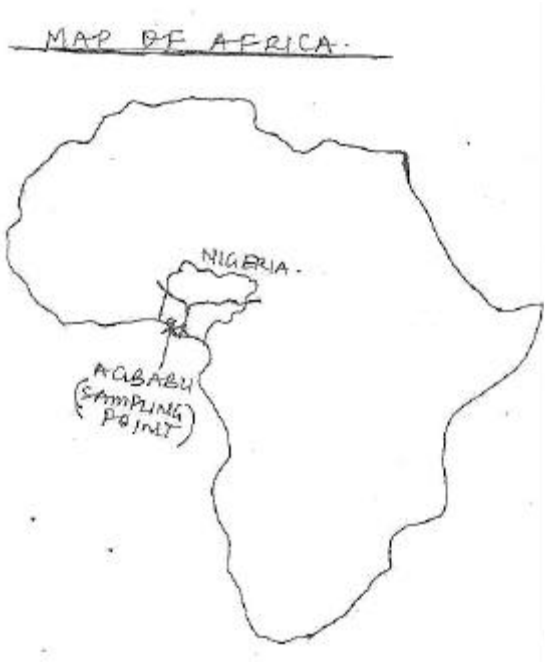

Fig. 1: Map of Africa Showing Sampling Point

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the traces of the heavy metals in plants or animals are not toxic [5]. Lead, Cadmium and Mercury are exceptions; they are toxic even in low concentrations [6]. Monitoring of the contamination of soil with heavy metals is of interest due to their influence on ground water and surface water and also on plants, animals and humans [3].

A common approach to estimate how much the soil is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels [7]. Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material [8, 9]. The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn [9]. The EF of a heavy metal in soil can be calculated with the following formula: [7]

EF = [Cmetal/Cnormalizer]soil/[Cmetal/Cnormalizer]control

where Cmetal and Cnormalizer are the concentrations of heavy metal and normalizer in soil and in unpolluted control. Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the enrichment factor as follows: [10]

- EF < 2 is deficiency to minimal enrichment
- EF 2-5 is moderate enrichment
- EF 5-20 is significant enrichment
- EF 20-40 is very high enrichment
- EF > 40 is extremely high enrichment

As the EF values increase, the contributions of the anthropogenic origins also increase [10].

Index of Geo-accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment [11]. The Igeo of a metal in soil can be calculated with formula: [9, 12]

$Igeo = Log_2 Cmetal/1.5Cmetal\ (control)$

Where Cmetal is the concentration of the heavy metal in the enriched sample and Cmetal(control) is the concentration of the metal in the unpolluted sample or control. The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the soil [9].

The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows: [7]

- Igeo <0 = means unpolluted
- 0<=Igeo<1 means unpolluted to moderately polluted
- 1<=Igeo<2 means moderately polluted
- 2<=Igeo<3 means moderately to strongly polluted
- 3<=Igeo<4 means strongly polluted
- 4<=Igeo<5 means strongly to very strongly polluted
- Igeo>=5 means very strongly polluted.

In West Africa, there are virtually no data available on the contributions of natural resources of environmental pollution. Not much is known about biogeochemical cycles of heavy metals in tropical ecosystems [13]. This study was therefore aimed at evaluating the status of heavy meal pollution of soil and plant of Agbabu bitumen deposit area.

MATERIALS AND METHODS

Samples were collected from Agbabu bitumen deposit area in Nigeria (Appendix A: Figure 1) as follows: In the dry season: 32 soil samples and 5 plant samples. Samples were collected as follows in the rainy season: 32 soil samples and 4 plant samples.

Procedure [14, 15]: Soil samples were digested after drying in the oven and ground into fine powder using pestle and mortar. 5g of sample was weighed into a 250ml beaker. An empty beaker was included in the analysis as reagent glassware blank.

50ml distilled water, 0.5ml concentrated HNO_3 and 5.0ml concentrated HCL were added to each sample and the blank. Each beaker was covered with s watch glass and digestion carried out on a hot plate in a fume chamber avoiding splattering all through. Digestion was continued until the entire volume was reduced to about 15ml. The beakers were allowed to cool to room temperature. The digests were then filtered into a 50ml volumetric flask and made up to volume with distilled water.

Plant samples were digested by thoroughly washing with water to remove all adhered particles. Samples were cut into pieces and air dried.

A representation sample (2.5g) of the plant was accurately weighed and subjected to $HClO_4$, HNO_3 and H_2SO_4 digestion (wet oxidation). The entire digest was then made up to 25ml for analysis.

Analysis was carried out with AAS using GBC Avanta PM. Ver 2.02. To validate the procedure, the

instrument is programmed and it carries out metal detection by displaying three absorbance readings and what is reported is the average. Blanks were also used for correction of background and other sources of error. Apart from calibration before use, quality checks were also performed on the instrument by checking the absorbance after every ten sample runs.

Analysis of variance (ANOVA) and Duncan's multiple range tests were used to find out statistical differences among various parameters.

RESULTS

The concentrations of heavy metals in soil and the averages in the dry and rainy seasons are shown in Appendix B (Tables 1 and 2). The concentrations of heavy metals in plant (*Chromolaena odorata*) and the averages in the dry and rainy seasons are also shown in (Appendix B (Tables 3 and 4). The graphical representations of the mean concentrations are shown in the line charts (A-Figure 2).

Table 1: Heavy Metal Analysis of soil (Dry season)

S/N	SAMLE ID	Fe (ppm)	Std. Dev.	Cu (ppm)	Std. Dev.	Mn (ppm)	Std. Dev.	Cr (ppm)	Std. Dev.	Zn (ppm)	Std. Dev.	Pb (ppm)	Std. Dev.	Cd (ppm)	Std. Dev.	Ni (ppm)	Std. Dev.	V (ppm)	Std. Dev.
1	AG-MILE2-BOT	19177.0	734.5	5.6	0.7	140.5	12.2	50.8	5.5	55.3	4.2	0.9	0.1	0.7	0.0	9.9	1.2	0.8	0.1
2	AG-MILE2-TOP	11107.0	375.3	5.7	0.4	157.0	11.6	35.5	5.9	59.4	6.4	0.5	0.1	0.6	2.0	6.0	0.7	0.4	0.1
3	OK-CONTR-BOT	8520.7	412.4	3.9	0.5	127.9	5.2	25.6	4.2	42.5	10.7	3.7	1.3	0.3	0.1	1.9	0.6	0.3	0.1
4	OK-CONTR-TOP	7562.0	380.6	4.1	1.1	119.7	12.5	22.6	4.7	50.6	6.7	2.8	0.9	0.3	0.1	1.5	0.1	0.2	0.1
5	T0-BOT	14617.0	349.0	8.2	0.5	59.8	5.9	45.6	6.2	72.2	5.9	1.9	0.3	0.4	0.0	3.4	0.5	0.3	0.0
6	T0-TOP	11517.0	82.4	7.7	0.4	68.4	5.4	28.4	3.9	87.5	7.2	3.2	0.2	0.2	0.0	3.3	0.5	0.3	0.1
7	T1E-BOT	7277.0	103.5	6.7	0.3	54.7	7.0	34.5	5.3	99.4	6.9	3.5	0.8	0.4	0.0	3.3	0.6	0.2	0.0
8	T1E-TOP	6427.0	136.9	10.8	0.3	183.3	13.8	29.2	4.3	191.0	8.8	2.3	0.1	0.6	0.1	3.7	0.3	0.3	0.0
9	T1N-BOT	7767.0	372.9	5.4	0.2	102.1	10.1	26.3	4.4	119.7	8.6	1.0	0.1	0.4	0.1	2.8	0.3	0.3	0.0
10	T1N-TOP	9827.0	561.2	6.5	0.4	104.7	14.2	32.9	4.8	141.8	7.2	0.9	0.1	0.4	0.1	2.7	0.6	0.3	0.1
11	T1S-BOT	8367.0	734.4	12.1	0.2	154.7	13.8	34.9	5.3	166.1	8.3	1.7	0.3	0.5	0.0	5.0	0.4	0.4	0.1
12	T1S-TOP	7177.0	76.7	11.3	0.2	149.5	12.8	32.9	2.1	179.2	10.2	1.5	0.1	0.5	0.0	3.4	0.6	0.2	0.1
13	T1W-BOT	7397.0	133.7	3.4	0.3	51.0	4.2	31.9	3.8	10.2	1.7	0.7	0.1	0.3	0.0	2.4	0.3	0.2	0.0
14	T1W-TOP	10867.0	176.4	4.8	0.2	77.4	5.3	41.6	2.2	105.8	7.5	0.9	0.1	0.4	0.0	1.8	0.4	0.2	0.0
15	T2E-BOT	16177.0	438.8	5.7	0.1	109.7	7.9	70.3	3.2	167.8	5.9	0.6	0.0	0.5	0.0	3.0	0.6	0.3	0.0
16	T2E-TOP	17517.0	239.6	5.8	0.1	169.1	8.6	77.6	5.3	182.4	7.3	0.7	0.1	0.4	0.0	3.0	0.7	0.2	0.0
17	T2N-BOT	10637.0	157.5	7.6	0.1	83.0	6.9	43.1	3.3	140.8	6.3	1.0	0.1	0.7	0.1	1.3	0.3	0.1	0.0
18	T2N-TOP	16887.0	288.1	15.9	0.2	129.0	15.3	52.1	4.3	186.8	5.8	12.0	0.1	0.8	0.1	4.4	0.7	0.4	0.0
19	T2S-BOT	8267.0	178.5	2.4	0.1	32.1	6.3	31.8	4.7	54.0	5.4	0.6	0.1	0.3	0.1	1.1	0.3	0.1	0.0
20	T2S-TOP	5467.0	35.9	4.5	0.1	82.3	5.3	24.8	3.4	356.0	10.7	0.8	0.1	0.3	0.1	1.9	0.4	0.2	0.0
21	T3E-BOT	10907.0	87.7	10.1	0.3	354.9	18.6	40.6	6.3	504.0	12.9	1.6	0.0	1.0	0.1	3.8	0.7	0.4	0.1
22	T3E-TOP	13477.0	176.5	7.2	0.2	121.3	8.1	45.6	4.2	180.3	8.8	0.9	0.0	0.6	0.1	1.9	0.4	0.2	0.0
23	T3N-BOT	9517.0	187.8	13.7	0.3	204.4	6.9	37.6	5.3	242.6	12.5	1.9	0.1	0.6	0.0	4.8	0.9	0.5	0.0
24	T3N-TOP	5987.0	232.4	12.6	0.3	226.6	11.8	32.5	4.3	310.2	9.6	2.2	0.5	0.7	0.1	3.1	0.7	0.4	0.1
25	T3S-BOT	24237.0	877.7	3.9	0.1	26.3	6.0	52.7	6.2	51.2	5.4	1.0	0.1	0.5	0.1	2.0	0.3	0.2	0.0
26	T3S-TOP	15527.0	128.5	3.6	0.1	37.3	7.1	48.2	4.2	75.4	6.8	0.9	0.1	0.3	0.0	2.0	0.2	0.2	0.0
27	T4E-BOT	4277.0	86.5	1.2	0.0	24.5	5.1	13.7	3.9	15.0	3.2	0.3	0.0	0.3	0.0	1.3	0.2	0.1	0.0
28	T4E-TOP	2927.0	122.5	1.8	0.1	48.7	5.1	15.6	2.6	22.7	2.7	0.3	0.1	0.3	0.0	1.1	0.3	0.1	0.0
29	T4N-BOT	8527.0	165.6	27.2	0.3	213.3	12.7	39.4	4.4	235.4	15.6	1.8	0.3	0.9	0.1	5.6	0.8	0.5	0.1
30	T4N-TOP	6027.0	78.2	20.3	0.4	239.2	16.3	25.8	4.1	252.4	10.2	1.3	0.3	0.7	0.1	4.9	0.8	0.5	0.1
31	T4S-BOT	8007.0	163.7	3.6	0.1	49.4	7.2	33.2	5.2	86.0	7.8	2.4	0.5	0.3	0.0	2.4	0.5	0.2	0.0
32	T4S-TOP	5257.0	84.2	5.9	0.0	72.3	6.1	22.5	3.3	154.0	8.3	10.9	0.7	0.3	0.1	2.2	0.4	0.2	0.0
	MEAN	10371.7	252.2	8.0	0.2	117.5	9.3	37.7	4.4	150.2	7.6	2.0	0.2	0.5	0.1	3.2	0.5	0.3	0.0

Table 2: Heavy Metal Analysis of Soil (Rainy season)

S/N	SAMLE ID	Fe (ppm)	Std Dev	Cu (ppm)	Std Dev	Mn (ppm)	Std Dev	Cr (ppm)	Std Dev	Zn (ppm)	Std Dev	Pb (ppm)	Std Dev	Cd (ppm)	Std Dev	Ni (ppm)	Std Dev	V (ppm)	Std Dev
1	AG-MILE2-BOT	2,225.0	72.0	4.2	0.3	13.6	1.9	5.8	0.7	13.0	1.8	14.2	1.7	0.2	0.0	2.3	0.0	0.3	0.0
2	AG-MILE2-TOP	1,930.0	87.0	3.7	0.3	16.3	2.4	5.6	0.6	18.5	2.8	8.3	1.2	0.2	0.1	2.3	0.0	0.4	0.0
3	CONTR-BOT	7,730.0	348.0	4.4	0.2	119.1	3.8	14.2	0.7	38.6	4.7	6.3	0.8	0.4	0.0	2.8	0.4	0.3	0.0
4	CONTR-TOP	6,494.0	375.0	4.3	0.4	112.2	5.4	13.4	0.8	39.2	2.6	5.8	0.7	0.3	0.0	2.5	0.1	0.4	0.0
5	T0-BOT	20,707.0	876.0	4.1	0.4	43.8	1.9	22.0	1.2	27.8	3.4	11.8	1.2	0.6	0.1	2.8	0.0	0.3	0.1
6	T0-TOP	9,026.0	268.0	6.2	0.3	170.6	7.3	10.8	0.8	146.4	5.7	23.2	2.5	0.9	0.0	4.8	0.1	0.5	0.0
7	T1E-BOT	7,997.0	265.0	7.8	0.3	66.5	3.7	11.7	1.6	111.6	4.7	133.0	4.4	0.5	0.0	4.6	0.1	0.5	0.0
8	T1E-TOP	6,085.0	231.0	11.9	0.4	81.6	4.3	8.4	0.8	153.4	6.9	341.9	5.7	0.7	0.0	6.1	0.1	0.7	0.1
9	T1N-BOT	18,635.0	156.0	10.2	1.5	131.9	5.3	21.0	2.2	106.0	7.8	14.6	1.6	1.4	0.1	4.9	0.0	0.5	0.0
10	T1N-TOP	18,054.0	235.0	13.5	1.6	198.9	8.1	16.3	2.6	321.6	16.2	17.1	1.6	1.1	0.1	5.3	0.0	0.6	0.1

Table 2: Continued

9	T1S-BOT	4,367.0	165.0	12.1	0.3	193.9	4.6	9.4	0.6	196.0	6.2	17.2	1.8	0.8	0.1	3.7	0.1	0.4	0.0
10	T1S-TOP	5,845.0	264.0	15.0	0.3	231.7	5.4	10.4	0.8	162.0	5.4	27.0	1.6	0.8	0.0	5.0	0.1	0.6	0.1
11	T1W-BOT	8,060.0	56.0	5.3	0.5	45.7	3.5	12.0	1.2	42.9	5.3	15.6	2.4	0.3	0.0	2.4	0.0	0.4	0.0
12	T1W-TOP	7,065.0	341.0	3.9	0.2	55.3	2.8	11.2	0.5	53.0	3.2	13.3	1.9	0.4	0.1	2.2	0.0	0.4	0.0
13	T2E-BOT	8,851.0	164.0	8.2	0.5	193.2	10.3	18.7	1.8	156.0	6.4	20.1	1.7	0.6	0.0	3.7	0.0	0.5	0.0
14	T2E-TOP	9,072.0	165.0	7.8	0.8	118.7	8.6	19.7	2.4	133.1	6.7	19.8	1.9	0.7	0.0	3.5	0.0	0.5	0.0
15	T2N-BOT	10,651.0	124.0	11.0	0.9	79.6	6.6	13.6	0.7	129.4	9.8	12.4	1.4	0.7	0.1	4.6	0.1	0.4	0.0
16	T2N-TOP	10,318.0	232.0	10.4	0.9	131.5	8.4	15.6	1.8	180.3	11.3	16.1	1.8	0.8	0.0	4.2	0.0	0.5	0.1
17	T2S-BOT	7,519.0	312.0	6.1	0.9	77.3	2.7	12.9	1.5	100.0	4.3	5.3	0.5	0.6	0.0	2.7	0.0	0.5	0.0
18	T2S-TOP	6,373.0	238.0	4.8	0.6	62.4	2.3	12.1	0.9	61.8	6.4	13.5	0.8	0.5	0.0	2.4	0.0	0.4	0.0
19	T2W-BOT	10,406.0	157.0	25.9	1.3	33.7	2.5	16.2	1.5	63.9	4.5	20.0	2.5	0.5	0.0	3.6	0.0	0.4	0.0
20	T2W-TOP	10,585.0	78.0	19.2	0.8	68.2	4.4	18.1	1.4	111.9	7.2	30.5	3.2	0.6	0.1	3.4	0.0	0.5	0.0
21	T3E-BOT	11,775.0	572.0	16.2	0.7	202.3	9.8	20.2	1.9	204.6	5.2	10.8	0.8	0.9	0.0	5.4	0.0	0.6	0.0
22	T3E-TOP	11,074.0	273.0	12.6	0.4	62.1	5.5	18.4	2.2	105.3	5.2	27.3	1.7	0.7	0.0	7.2	0.1	0.8	0.1
23	T3N-BOT	7,520.0	68.0	21.9	2.4	197.6	11.3	12.7	1.6	161.9	11.2	35.6	2.8	0.9	0.1	4.6	0.1	0.3	0.0
24	T3N-TOP	12,185.0	267.0	5.6	0.5	54.2	3.5	18.0	1.8	41.3	6.3	16.2	2.0	0.4	0.1	2.7	0.0	0.5	0.0
25	T3S-BOT	8,883.0	166.0	3.7	0.2	26.6	1.6	12.7	1.4	28.4	3.4	9.7	0.4	0.2	0.1	2.0	0.0	0.3	0.0
26	T3S-TOP	10,388.0	412.0	7.9	0.6	42.8	3.7	14.3	0.7	33.1	2.9	11.3	0.6	0.4	0.1	2.6	0.0	0.3	0.0
27	T4E-BOT	3,809.0	167.0	3.1	0.4	33.0	1.0	6.8	0.8	29.3	2.8	9.7	0.6	0.1	0.0	1.3	0.0	0.2	0.0
28	T4E-TOP	3,006.0	178.0	1.9	0.1	31.4	1.2	5.9	0.6	11.6	1.2	6.9	0.7	0.3	0.0	1.2	0.0	0.2	0.0
29	T4N-BOT	9,220.0	174.0	22.5	2.7	281.3	10.5	12.6	1.4	208.2	18.5	2.3	0.8	0.9	0.0	6.0	0.1	0.6	0.1
30	T4N-TOP	6,346.0	128.0	18.5	2.8	258.0	13.3	9.9	0.7	272.4	16.5	21.3	2.6	0.6	0.0	4.9	0.1	0.5	0.1
31	T4S-BOT	8,457.0	88.0	5.0	0.8	52.5	2.9	13.5	0.9	105.4	8.7	2.0	0.2	0.5	0.0	2.8	0.0	0.3	0.0
32	T4S-TOP	9,426.0	172.0	6.3	0.9	70.7	2.8	14.1	1.6	144.2	5.9	2.7	0.2	0.7	0.1	3.4	0.0	0.4	0.0
	MEAN	8,933.1	223.4	9.9	0.8	104.0	5.1	13.4	1.2	113.6	6.7	29.1	1.7	0.6	0.0	3.7	0.0	0.4	0.0

Table 3: Heavy Metal Analysis of Plant (*Chromolaena odorata*) (Dry season) (DRY SEASON)

S/N	SAMLE ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
1	PLANT TO	23.5	±2.24	2.3	±0.56	3.2	±0.43	0.6	±0.08	7.2	±0.66	1.4	±0.2	13.6	±1.15	2.4	±0.06	0.2	±0.05
2	PLANT T2N	33.9	±2.66	2.4	±0.65	8.8	±0.35	0.7	±0.06	6.4	±0.45	1.0	±0.06	1.5	±0.06	1.8	±0.04	0.2	±0.03
3	PLANT T4E	31.5	±1.5	2.4	±0.38	1.8	±0.06	1.2	±0.06	5.6	±0.7	1.6	±0.3	1.7	±0.04	2.8	±0.08	0.2	±0.02
4	PLANT T4N	66.4	±4.25	3.0	±0.26	17.5	±2.1	1.2	±0.05	15.5	±1.4	1.7	±0.05	1.4	±0.05	3.1	±0.14	0.3	±0.04
5	PLANT AG-MILE2	68.8	±5.88	2.6	±0.22	6.9	±0.55	1.2	±0.08	9.7	±0.74	1.5	±0.04	1.5	±0.04	2.4	±0.16	0.2	±0.03
	MEAN	44.8	±3.31	2.6	±0.41	7.6	±0.7	1.0	±0.07	8.9	±0.79	1.4	±0.13	3.9	±0.27	2.5	±0.01	0.2	±0.03

Table 4: Heavy Metal Analysis of Plant (*Chromolaena odorata*) (Rainy season)

S/N	SAMLE ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
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1	PLANT TO	NA		NA		NA		NA		NA		NA		NA		NA		NA	
2	PLANT T2N	24.8	±2.68	1.3	±0.04	6.6	±0.2	0.5	±0.04	4.9	±0.3	0.7	±0.06	1.1	±0.08	1.3	±0.14	0.1	±0.02
3	PLANT T4E	NA		NA		NA		NA		NA		NA		NA		NA		NA	
4	PLANT T4N	42.8	±3.82	1.9	±0.03	10.3	±0.61	1.4	±0.02	12.3	±1.2	1.1	±0.04	0.9	±0.06	1.8	±0.06	0.1	±0.01
5	PLANT AG-MILE2	39.7	±4.55	1.4	±0.02	4.8	±0.06	1.0	±0.02	7.7	±0.45	1.1	±0.03	0.9	±0.04	1.7	±0.08	0.1	±0.01
6	PLANT AG-CONTR	188.7	±5.34	2.7	±0.04	14.8	±1.3	1.2	±0.03	10.7	±0.82	0.9	±0.05	0.8	±0.04	1.6	±0.07	0.1	±0.01
	MEAN	35.8	±3.68	1.6	±0.03	7.2	±0.29	1.0	±0.03	8.3	±0.65	1.0	±0.04	1.0	±0.06	1.6	±0.09	0.1	±0.01

Table 5: Values of Maximum Allowable Limits (M. A. L.) for Heavy Metals in Soil (mg/kg) used in Different Countries

Chemical element	Austria	Canada	Poland	Japan	Great Britain	Germany
1	2	3	4	5	6	7
Cd	5	8	3	-	3	2
Co	50	25	50	50	-	-
Cr	100	75	100	-	50	200
Cu	100	100	100	125	100	50
Ni	100	100	100	100	50	100
Pb	100	200	100	400	100	500
Zn	300	400	300	250	300	300

Ref.: [19].

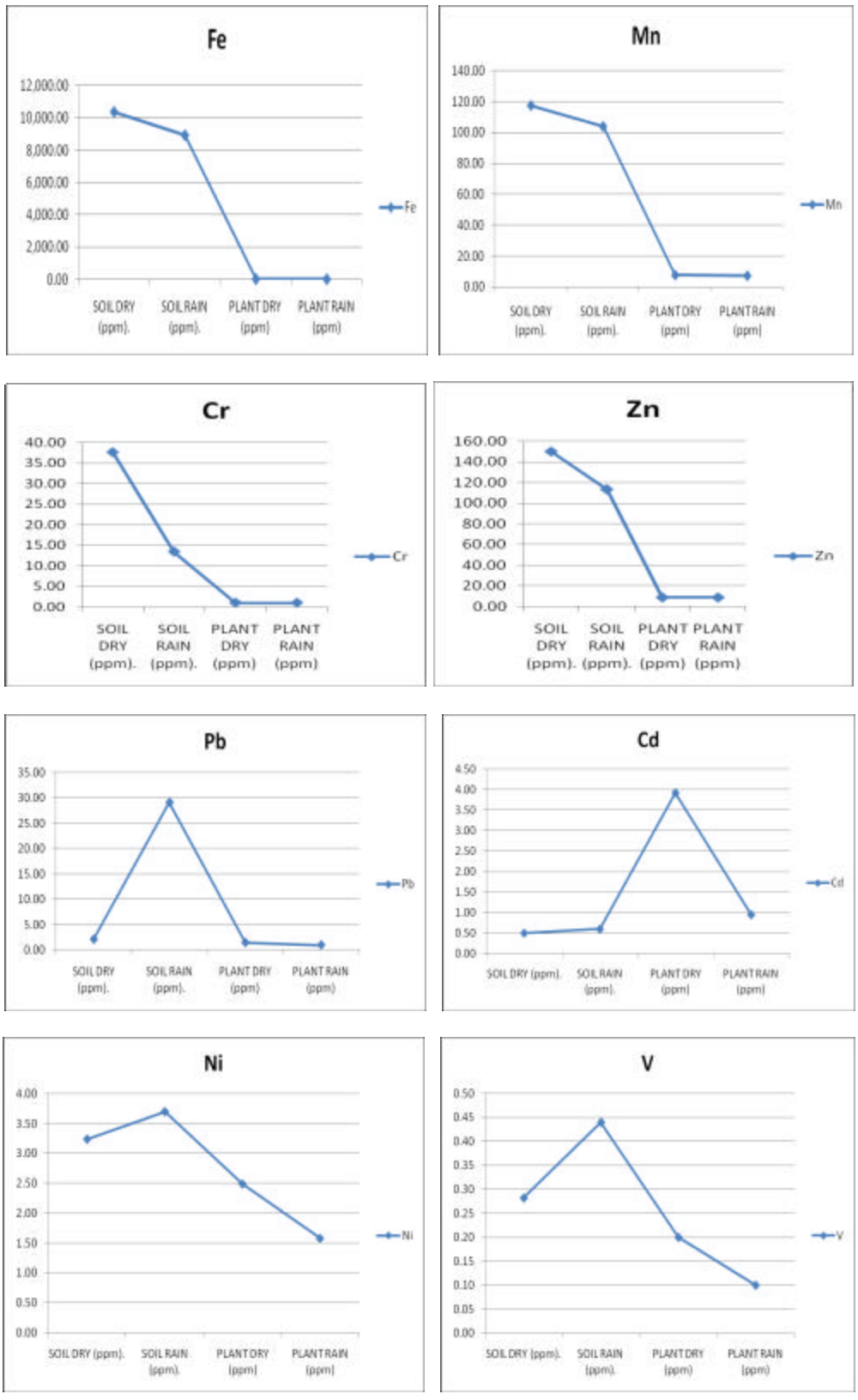

Fig. 2: Line graphs of Heavy Metal conc. (ppm) in Soil and Plant

Table 6: Enrichment Factor (EF) and Geoaccumulation Factor (Igeo) of Heavy Metals in Soil (Dry Season)

	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (ppm)
C(M-s)	10,371.67	8.03	117.52	37.72	150.15	2.00	0.50	3.24	0.28
C(FE-s)	10,371.67	10,371.67	10,371.67	10,371.67	10,371.67	10,371.67	10,371.67	10,371.67	10,371.67
C(M-c)	8,041.33	3.97	123.77	24.10	46.52	3.25	0.29	1.70	0.23
C(Fe-c)	8,041.33	8,041.33	8,041.33	8,041.33	8,041.33	8,041.33	8,041.33	8,041.33	8,041.33
EF	1.0000003	1.5704483	0.7361955	1.2134834	2.5025022	0.4784107	1.3547641	1.4815641	0.9705818
I(geo)	0.001105984	0.5053618	0.037042	0.1448757	0.1036155	0.2057899	-2.352707	0.6668824	-5.416116

Table 7: Enrichment Factor (EF) and Geoaccumulation Factor (Igeo) of Heavy Metals in Soil (Rainy Season)

	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (ppm)
C(M-s)	8,933.13	9.88	103.97	13.45	113.57	29.08	0.60	3.70	0.44
C(FE-s)	8,933.13	8,933.13	8,933.13	8,933.13	8,933.13	8,933.13	8,933.13	8,933.13	8,933.13
C(M-c)	7,112.00	4.34	115.65	13.81	38.90	6.05	0.33	2.68	0.33
C(Fe-c)	7,112.00	7,112.00	7,112.00	7,112.00	7,112.00	7,112.00	7,112.00	7,112.00	7,112.00
EF	0.99999944	1.8128065	0.7157041	0.7756285	2.3243916	3.8298973	1.4475228	1.0999905	1.067896
I(geo)	0.00123031	0.5076544	0.0386221	0.1810681	0.1170088	0.5361961	-1.488819	0.4700163	-2.45704

In all the samples, mercury was not detectable while the mean concentrations of Pb, Ni and V were low in the two seasons. The concentrations of Fe (10,371.67±252.21ppm in dry season, 8,933.00±223.47ppm in rainy season), Cu (8.03±0.22 in dry season, 9.88±0.79ppm in rainy season), Mn (117.52±9.25 in dry season, 104.00±5.10ppm in rainy season), Cr (37.72±4.38ppm, 13.47±1.26ppm) and Zn (150.15±7.60ppm, 103.97±5.13ppm) were high in the soil samples.

DISCUSSION

Fe has been found to occur at high concentrations in Nigeria soil [16]. The high concentrations of these metals in the soil samples may also be due to the deposit of bitumen in the area. Adebiyi F.M. *et al.* [17] in an elemental characterization of the Nigerian bitumen by total reflection x-ray fluorescence showed Fe, Cr and Mn to be part of its components. Trace elements such as transition metals get into bitumen in form of porphyrin complexes at its early stages of formation. The Nigerian bitumen components (asphatene, oil and resins) were subjected to trace metal analysis and were found to contain high concentrations of Zn, Ni, V and Fe, [18]. However, the concentrations of most of the heavy metals were high in the soil but not beyond the maximum allowable limits as used in different countries [19] as shown in Table 5.

Fe (8,933.00±223.47ppm), Mn (103.97±5.13ppm), Zn (113.57±6.68ppm) and Cr (13.45±1.29ppm) were lower in the rainy season probably due to dilution by rainwater which influences concentration and heavy metal dynamics. However, higher concentrations of Cu (9.88±0.79ppm), Pb (29.08±1.71ppm), Cd (0.60±0.04ppm), Ni (3.70±0.04ppm) and V (0.44±0.04ppm) in soil during the rainy season were probably due to rainfall and run off.

The mean concentrations of Fe, Mn, Zn and Cr (soil) were lower in the rainy season probably due to dilution by rainwater which influences concentration and heavy metal dynamics. This agreed with the report of Onweremadu *et al.* [20]. However, it has been reported that mobility of heavy metals depends not only on the total concentration in the soil but also on the soil properties, metal properties and environmental factors. Higher concentrations of Cu, Pb, Cd, Ni and V in soil during the rainy season were probably due to rainfall and run off. This agrees with the findings of Lokeshwary H. and Chandrappa G.T [4].

The mean concentration of Cd was 0.50ppm in the dry season and 0.60ppm in the rainy season in soil but it was biomagnified in the plant (*Chromolaena odorata*) with mean concentrations 3.92ppm in the dry season and 0.95ppm in the rainy season. The magnification coefficient of a metal in plant can be calculated by dividing the concentration of the metal in the plant by the concentration of the metal in soil [21]. Therefore the magnification coefficient is 7.84 in the dry season and 1.55 in the rainy season. This observation of magnification of Cd is in agreement with the finding of Amoo *et al.* [22] which says that plants bioaccummulates Cd more efficiently than other studied heavy metals in the ecosystem. The maximum mean concentration of heavy metals in plants was 44.80±3.31ppm (Fe) in the dry season and 35.77±3.68 (Fe) in the rainy season. Apart from the concentrations of Cd, these were lower than the mean concentrations in soil. This shows that, excluding Cd, the mobility of the heavy metals were very low in soil.

The most polluted station was To with a mean heavy metal concentration of 1473.59ppm in the dry season and 1678.31ppm in the rainy season. This is probably due to proximity to bitumen well MBC-7. The least polluted station was T_4E with a mean heavy metal concentration of 408.39ppm in the dry season and 386.55ppm in the rainy season. Heavy metal pollution at this station was low probably due the long distance to the bitumen well.

The results of the calculation of Enrichment Factor (EF) of heavy metal in soil in the dry season and rainy season are shown in Table 6 and 7 respectively.

Enrichment factors were calculated from the mean concentrations of the heavy metals in the sampling points in the study area. The control sampling point was considered to be the unpolluted or background point. The normalizing element used in study was Fe due to low occurrence variability. Enrichment Factor (EF) of the heavy metals in soil showed that V (0.97), Pb (0.48), Mn (0.74) and Fe (1) had no enrichment; Cu (1.57), Cr (1.21), Cd (1.35) and Ni (1.48) had minimal enrichment; Zn (2.50) had moderate enrichment in the dry season. In the rainy season, Mn (0.72), Cr (0.78) and Fe (0.99) had no enrichment; Cu (1.81), Ni (1.09), V (1.06) and Cd (1.45) had minimal enrichment; Zn (2.32) and Pd (3.83) had moderate enrichment. Normally, as the EF values increase, the contributions of the anthropogenic origins also increase. Therefore, the low values of EF (0.48 to 3.83) show that the slight heavy metal pollution of Agbabu bitumen deposit area was not likely to originate from anthropogenic activities. The heavy metals probably originated from natural procedure due to the presence of bitumen in the environment.

The result of the calculation of Geo-accumulation Index (Igeo) in soil is shown in Table 7. The negative values of Cd and V and zero for Fe, in both dry and rainy seasons, according to contamination classification of Huu *et al*, 2010 [7], showed that the soil was not polluted by Cd, V and Fe. The remaining Igeo values in both dry and rainy seasons were less than 1 indicating that the soil was only moderately polluted by Cu, Mn, Cr, Zn, Pb and Ni. The Igeo factor is not readily comparable with EF due to the nature of Igeo calculation which involves a logarithm function and a background multiplication factor of 1.5.

Analysis of variance was carried out with Statistical Analysis System (SAS) and Duncan's multiple range tests. The mean concentration of metals in soil in the two seasons (" level=0.05) were found not to be significantly different. This implies that the metals were firmly bounded within the crystal structure of the minerals comprising the soil and were not largely affected by dilution due to rain. This may also imply that the heavy metals in the soil of Agbabu bitumen deposit area were immobile. However, the mean concentrations of the metals in different locations were found to be significantly different. This shows that the metals probably originated from many sources. These sources include contamination by bitumen, run-off due to rain fall and anthropogenic activity such as agriculture.

CONCLUSION

Data available in this study can be used as the exploitation base line data at Agbabu bitumen deposit. The environment presently has been imparted slightly by the presence of bitumen in the soil. The mean concentrations of Cd were low in the soil but were biomagnified in the plant samples. The concentrations of the heavy metals were high in the soil but not beyond the maximum allowable limits as used in different countries. The enrichment factors calculated for the heavy metals showed that the enrichment of the heavy metals ranged from no enrichment to moderate enrichment. The low EF values obtained also indicate that the moderate heavy metal pollution observed in the soil of Agbabu bitumen deposit area probably originated from natural process. Apart from Cd, the heavy metals were relatively immobile. Further research has to be carried out to determine the concentration of heavy metals in the various organs of the aquatic animals in the environment. The biomagnifications of the heavy metals in plants and animals in the environment will also need to be studied.

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