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Elemental Analysis and Risk Assessment of Soil and Vegetables from a Crude Oil-Polluted Area in Lagos State, Nigeria

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Abstract

Energy Dispersive X-rays Fluorescence (EDXRF) spectrometry was used to determine the concentrations of nineteen potentially toxic metals in soil and vegetable samples collected from an oil-polluted area of Lagos State. The Enrichment Factors (EF) were calculated to identify the pollution load index of these heavy metals in the soil and vegetable samples Telfairia occidentalis (fluted pumpkin) and Vernonia amygdalina (bitter leaf). The mean concentrations ranged from 36.765-39460 mg/kg, 1.436-14010 mg/kg, and 0.928-29520 mg/kg for the soil and the two vegetables samples respectively. The vegetable samples were enriched with heavy metals such as Fe, Cr, V, and Ti, (EF=1.000-1.43) with the source traceable to the oil-polluted soil. The mean concentrations of these heavy metals in the vegetable samples were higher than the recommended standards set by the Food and Agriculture Organization of the United Nations/World Health Organization and control. The results obtained in this study gave the baseline levels of these heavy metals in the samples and also indicated the risk of exposure of these environmental media to Fe, Cr, V, and Ti.

Keywords: Enrichment factors; Heavy metals; Risk of exposure; EDXRF

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Introduction

Oil has become one of the most important resources in every society today. Unfortunately, activities involving the exploration, extraction, transportation, and distribution of oil have been undermined by challenges that usually led to environmental problems. Oil pollution can have detrimental effects on the ecosystem which may be visible and sometimes devastating [1]. According to Khan, pollution is said to occur when there is a release into the environmental landscape (such as soil, air, bodies of water, streams, and lakes) of substances and energy in quantities that are detrimental to man and other living organisms [2]. Evidence has shown that activities of man enhance the release of these harmful substances into the environment which in turn affect the soil structure, crop performance, and vegetation at large [3,4]. The effect of man's operations on the terrestrial environment includes interference with the land surface and the immediate sub-surface, streams and lakes. Oil and its components that have been released into the environment are degraded into simple compounds of their constituent elements by physico-chemical or biological agencies of the soil with or without human assistance and that had become innocuous after a long period [5]. Oil spillage occurs when pipeline explosions take place due to drilling activity at a new site, accidental bursting of the pipeline when work is taking place around the pipeline or corrosion of old pipeline that has not been checked for maintenance. When this occurs, the effects are usually pronounced on the soil flora and fauna as well as the soil structure. Sometimes, heavy metals could be released into these media or bio-accumulate in living organisms and the human body through various processes, thereby causing adverse effects. In the human body, heavy metals are transported and compartmentalized into body cells and tissues binding to proteins, nucleic acids destroying these macromolecules thereby disrupting their cellular functions [6]. It can also affect the central nervous system leading to mental disorder, damage to the blood constituents, liver, kidney, and other vital organs promoting several disease conditions. Also, long term accumulation of heavy metals in the body may result in slowing the progression of physical, muscular, and neurological degenerative processes that mimic certain diseases such as Parkinson's and Alzheimer's diseases. More so, repeated long-term contact with some heavy metals or their compounds may even damage nucleic acids, cause mutation, mimic hormones thereby disrupting the endocrine and reproductive systems and eventually lead to cancer [7].

Long-term deposition of metals in soils can lead to accumulation, transport, and biotoxicity/zootoxicity caused by mobility and bio-availability of a significant fraction of the metals. Oil spill raises the levels of metals in the soils, plants, and the environment at large [8]. It can also affect plants negatively by creating conditions that make essential elements (like nitrogen, oxygen, phosphorus, calcium, iron, zinc, etc) needed for plant growth unavailable from the oil-polluted soil. Oil pollution in the Gemade Estate area of Lagos state has become a public health concern as a result of its frequent occurrence which has been linked with the leakage of pipelines and vandalization of pipelines. One of the motivations of this work arises from several complaints by residents living in the oil-polluted area of Lagos State. A visit made to the Gemade Estate area before the commencement of the sampling confirms that the majority of the houses do not use water from the borehole/hand-dug well. This is because most of the groundwater sources were polluted by spilled oil, and many people find it difficult to use the water for washing. They would rather buy water from vendors. In this study, the levels and the health risk assessment of nineteen elements were determined in crude oil polluted soil and vegetable samples from Gemade Estate, Lagos State, Nigeria using a multi-elemental EDXRF technique [9].

Materials and Methods

The study was conducted in a residential area popularly called Gemade Estate, a subsidiary of Gowon Estate. Gemade Estate is about 0.79 km from the Ipaja major road of Alimosho local government council of Lagos State, Southwestern Nigeria. The Alimosho local government council has a landmass area of about 57.621 km2, located on a latitude 6º 59′ 79″0 N and longitude 3º 27′ 60″0 E with a steeped terrain in which groundwater is about 27 m below ground surface in hand-dug wells and about 40 m below in bore holes. Just like every other part of Lagos State, Gemade Estate area experiences a wet equatorial tropical climate with a mean annual rainfall of about 1800 mm.

A total of nine soil samples six from the location where the vegetables are usually harvested, three soil samples from an unpolluted or an area where no anthropogenic activity took place as control. Also, nine vegetable samples were collected 3 each of the Telfairia occidentalis (fluted pumpkin), Vernonia amygdalina (bitter leaf) and identical vegetable samples (of each specie) from control site. The soil samples were air-dried in a clean and ventilated room, grounded (in an agate mortar and pestle) and sieved through a 2 mm nylon mesh to achieve a homogenized sample matrix. The stalks of each vegetable sample were removed, weighed and freeze-dried to avoid loss of volatile elements. The homogenized sample was made into pellets with Spec-caps by applying 8-10 torr pressure using a hydraulic pelletizer machine. Each pellet is about 12 mm in diameter and 1-3 mm thick. All samples were analyzed using EDXRF. Quality control was ensured through the proper calibration of the equipment and repeated measurements. Descriptive analysis was carried out using Statistical Packages for Social Scientists (SPSS version 17). The Enrichment Factors (EF) were calculated using

$$EF = \left(\frac{X}{C_{Fes}}\right) \Big/ \left(\frac{Y}{C_{Fes}}\right)$$

Where X is the concentration of the element in the sample, Y is the concentration of the element in the reference, CFes is the concentration of the Fe in the sample, and CFes is the concentration of the element, Fe adopted as reference. EF normalizes the measured heavy metal concentration with respect to the concentration of sample reference metal (Fe or Al). In this study, Fe was used for this purposefully used as result of its relatively high concentration in the earth.

Results and Discussion

The descriptive statistics of the levels of heavy metals in soil samples from the study site and control are given in **Table 1**.

Table 1: Descriptive statistics of heavy metals in soil samples from the study site and control (mg/kg).

Element	Soil samples (site) (n=6)		Soil samples (control) (n=3)	
	Range	Mean ± SD	Range	Mean ± SD
K	743.259-1079.341	911.300 ± 168.041	442.265-799.533	620.899 ± 178.634
Ca	1532.287-1977.917	1755.102 ± 222.815	537.638-636.616	587.127 ± 49.489
Sc	218.145	218.145	129.818	129.818
Ti	11020-11940	11510 ± 430	3861.63-4108.45	3985.04 ± 123.4
V	503.133-730.377	616.755 ± 113.622	135.78-242.649	189.215 ± 53.434
Cr	398.9-552.6	475.76 ± 76.85	94.676-157.626	126.15 ± 31.475
Mn	1037.233-1186.035	1111.63 ± 74.4	637.178-690.04	663.61 ± 26.43
Fe	37750-41170	39460 ± 1710	14920-15160	15040 ± 120
Co	460.817	460.817	249.539-332.049	290.793 ± 41.254
Ni	209.15-278.366	243.759 ± 34.607	124.979-177.44	151.210 ± 26.231
Cu	50.173-72.127	61.15 ± 10.977	97.793-112.233	105.016 ± 7.217
Zn	223.045 – 245.905	234.475 ± 11.430	90.153-114.909	102.53 ± 12.378

Ga	61.467-87.939	74.703 ± 13.236	36.13-52.564	44.347 ± 8.217
As	36.575	36.575	11.902	11.902
Se	68.79-92.01	80.399 ± 11.609	71.103-86.349	78.726 ± 7.623
Br	33.88-56.16	45.02 ± 11.138	9.816-17.224	13.52 ± 3.704
Rb	41.81-73.62	57.716 ± 15.903	41.354-63.616	52.485 ± 11.131
Sr	65.559	65.559	61.132	61.132
Y	145.768	145.768	148.085	148.085

While those of vegetable samples (*Vernonia amygdalina* and *Telfairia occidentalis*) are shown in **Tables 2 and 3**.

Table 2: Descriptive statistics of heavy metals in vegetable (*Vernonia amygdalina*) samples from the study site and control site (mg/kg).

Element	*Vernonia amygdalina* (site) (n=3)		*Vernonia amygdalina* (control) (n=3)	
	Range	Mean ± SD	Range	Mean ± SD
K	28450-30590	29520 ± 1070	20510-22990	21750 ± 1240
Ca	7210.69-7511.57	7361.13 ± 150.44	6291.971-7351.713	7136 ± 214.871
Sc	42.204-83.224	62.714 ± 20.51	66.291	66.291
Ti	135.450-149.296	142.373 ± 6.923	65.625-77.561	71.593 ± 5.968
V	10.197	10.197	18.003	18.003
Cr	31.440-37.428	34.434 ± 2.994	7.979	7.979
Mn	120.669-132.701	126.685 ± 6.016	30.843-32.681	31.843 ± 0.919
Fe	396.128-401.98	399.055 ± 2.927	213.875-214.83	213.354 ± 1.479
Co	4.181	4.181	0.998	0.998
Ni	3.232-3.572	3.402 ± 0.170	2.331	2.331
Cu	5.04-6.198	5.619 ± 0.579	4.738-5.022	4.880 ± 0.142
Zn	9.224-9.406	9.345 ± 0.121	7.857-8.773	8.315 ± 0.458
As	0.002-0.618	0.473 ± 0.145	0.733	0.773
Se	0.928	0.928	0.54	0.54
Br	7.54-9.07	8.305 ± 0.765	1.618	1.618
Rb	17.863-23.361	20.612 ± 2.749	21.637-26.489	24.063 ± 2.426
Sr	12.227-21.479	16.853 ± 4.626	14.209-25.445	19.827 ± 5.618
Y	41.503	41.503	54.799	54.799
Zr	155.037	155.037	873.871	873.871

Table 3: Descriptive statistics of elemental concentration in vegetable (*telfairia occidentalis*) samples from the study site and control (mg/kg).

Element	Telfairia occidentalis (site) (n=3)		Telfairia occidentalis (control) (n=3)	
	Range	Mean ± SD	Range	Mean ± SD
K	12300-13060	12680 ± 380	5302.95-6174.61	5738.781 ± 435.830
Ca	13440-14580	14010 ± 570	4975.616-5179.04	5077.328 ± 101.712
Sc	296.32	296.32	354.967	354.967
Ti	324.487-369.207	346.847 ± 22.360	38.71-55.931	47.322 ± 8.609
V	112.033-146.137	129.085 ± 17.052	13.615	13.615
Cr	85.687-110.989	98.338 ± 12.651	6.618	6.618
Mn	67.027-82.563	74.79 5 ± 7.768	59.763-68.013	63.888 ± 21.899
Fe	484.007-527.805	505.906 ± 21.899	173.988-212.28	193.134 ± 19.146
Co	6.568	6.568	2.504	2.504
Ni	2.451-3.525	2.988 ± 0.537	1.835-3.367	2.601 ± 0.766
Cu	5.429-7.019	6.224 ± 0.795	2.866-3.63	3.248 ± 0.382
Zn	12.958-14.102	13.530 ± 0.572	11.383-13.887	12.635 ± 1.252
As	1.111	6.568	1.129	1.129
Se	1.436	1.436	1.065	1.605
Br	5.552-7.11	6.331 ± 0.799	1.781	1.781

In each table, the range and the average concentrations of nineteen elements (K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Br, Rb, Sr, Y, Zr, and Nb) are presented. In **Table 1**, the mean concentrations (mg/kg) of the elements in the soil samples were in the decreasing order Fe>Ti>Ca>Mn>K>V>Cr>Co>Ni>Zn>Sc>Y>Se>Ga>Sr>Cu>Rb>Br>As.The observed concentrations were found higher for the study site than the control except Cu. For Iron (Fe), arsenic (As) and Copper (Cu), the mean concentrations were 36.765 mg/kg, 39460 mg/kg and 105.016 mg/kg respectively. The high elemental concentration in the study site could be attributed to the effects of oil pollution on the soil. However, the high concentration of Cu in the soil samples (from the control site) may reflect the abundance of Cu being an essential trace element which can result into skin and hair decolouration and other chronic diseases in the human body [2]. **Figure 1** shows the level of enrichment of the elements in the soil samples at the site. The soil samples were slightly enriched in Ca, Ti, V, Cr, Fe, As and Br with EF=1.000-1.437 but not enriched in K, Sc, Mn, Co, Ni, Cu, Zn, Ga, Se and Rb (EF=0.222-0.873).

Table 2 shows the mean concentration of elements (mg/kg) in *vernonia amygdalina* samples for the study site and control. The concentrations (mg/kg) were in the decreasing order Ca>K>Fe>Ti>Sc>Zr>V>Cr>Mn>Sr>Y>Zn>Rb>Co>Br>Cu>Ni>Se> As. The mean elemental concentrations of Se and K in the vegetable specie, *vernonia amygdalina* were 0.928 mg/kg and 29520 mg/kg respectively. These values were found to be higher than the mean concentration of elements in the control. The same trend occurred in other elements except As, Y, V, Sc, Sr, Rb, and Zr. Table 3 shows the mean concentration (mg/kg) of elements in telfairia occidentalis samples for the study site and control. In these vegetable samples, the levels were in the decreasing order K>Ca>Fe>Zr>Ti>Mn>Y>Cr>Rb>Sr>V>Zn>Br>Cu>Co>Ni>Se> As. The mean concentration was in the range 1.436 to 14010 mg/kg. These values were found to be higher when compared with the control except for Y and Se. The observed high levels attributed to the effects of a high index of oil contamination of the soil. **Figure 2** shows the levels of the enrichment of these elements in the two species. The *Vernonia amygdalina* samples were slightly enriched in Ti, Cr, Mn, Fe, Co, and Br with the EF values ranging from 1.00-2.491 but not enriched in K, Ca, Sc, V, Ni, Cu, Zn, As, Se, Rb, Se, Rb, Sr, Y, and Zr (EF=0.0009-0.724. The second vegetable samples (*Telfairia occidentalis*) were also slightly enriched in Ca, Ti, V, Cr, Fe, Co and Br but not enriched in K, Sc, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Y, and Zr. The variation in the enrichment factors of elements in the two vegetable species could be attributed to their different rate of absorption and translocation of the elements.

The results in **Tables 1-3** show that comparatively, some elements (particularly the heavy metals) have higher concentrations in the soil than in the vegetable samples. This is because soils are at the receiving ends of the pollution loads arising from oil pollution or any other anthropogenic source at the sampling site. **Table 4** shows the comparison of the levels of observed heavy metals in vegetables with the recommended limits.

Table 4: Comparison of the mean concentration (mg/kg) of heavy metals in the vegetable samples with FAO/WHO limits.

Elements	*Telfairia Occidentalis* (TO)		*Vernonia Amygdalina* (VA)		Joint FAO/ WHO (2001)
	Site	Control	Site	Control	
Sc	296.32	354.967	62.714	66.291	1000
Ti	346.877	47.322	142.373	71.593	1000
V	129.085	13.615	10.197	18.003	1000
Cr	98.338	6.618	34.434	7.979	2.3
Mn	74.795	63.888	126.685	31.762	6.64
Fe	505.906	193.134	399.055	213.354	420
Co	6.568	2.504	4.181	0.998	NA
Ni	2.451	2.601	3.402	2.331	10
Cu	6.224	3.248	5.619	4.88	40
Zn	13.53	12.635	9.345	8.315	60
As	1.111	1.29	0.475	0.773	1.4
Rb	10.322	6.226	20.612	24.063	25.368
Sr	72.532	56.01	16.853	19.827	34.222
Y	40.689	59.394	41.503	54.799	7.011
Zr	199.664	160.625	155.037	873.871	5.905

NA: Not available

The enrichment of these elements in the soil may also be responsible for the high concentration of the heavy metals found in the vegetable samples. In order words, the elemental concentration in the vegetables can be traceable to the soil. Metal levels are highly variable in vegetation's compared to the host soil [9]. Comparative analysis indicated that both media were enriched in Fe, Cr, V, and Ti. The concentrations of these metals in the vegetables have been compared with the standard set by FAO/WHO **Table 4**. For instance, a high concentration of iron (Fe) in soil and vegetable samples was expected because Fe being the most abundant metal in the earth crust is essential for both plants and animals. On the other hand, if Fe is above 420 mg/kg standard recommended by FAO/WHO [10], it can pose serious environmental and health concerns. High concentration of Fe was reported as a potential cause of tissue damage and some other diseases in humans [11]. Iron (Fe) in this study, the level was below the FAO/WHO recommended standard in the two vegetable species but high in soil. The elevated level may reflect its abundance within the earth's crust or due to the effect of contamination of the soil with oil. In Table 4, chromium (Cr) had a mean concentration of 98.338 mg/kg in Telfairia occidentalis and 34.434 mg/kg in Vernonia amygdalina. These values were higher than the 2.3 mg/kg standard set by FAO/WHO for vegetables. Although Cr is an essential metal in the body as it is needed for the metabolisms of cholesterol, fats, and glucose [11]. Its high concentration (like in this study) could depict the effects of oil pollution in the soil, thereby posing a health risk to the plants grown on such polluted soil. Previous studies have reported a high concentration of Cr build-up in soil contaminated with oil [12, 13, 14]. The mean concentration of vanadium (V) in the soil samples being 616.755 mg/kg is higher than 129.085 and 10.197 mg/kg in Telfairia occidentalis and Vernonia amygdalina, respectively. These values are within the FAO/WHO recommended standard of 1000 mg/kg for vegetables **Table 4**. Other studies have reported a significant concentration of V found in oil-polluted soil [13,15]. The mean concentration of Ti in the soil samples was (11510 mg/kg) significantly higher than 346.877 and 142.373 mg/kg found in the vegetable samples Telfairia occidentalis and Vernonia amygdalina respectively. Despite the high concentration of Ti found in the soil matrix, its levels in the vegetable species are within the FAO/WHO recommended standard **Table 4**.

Figures 1 and 2 depict the levels of enrichment of heavy metals in soil and vegetable samples respectively.

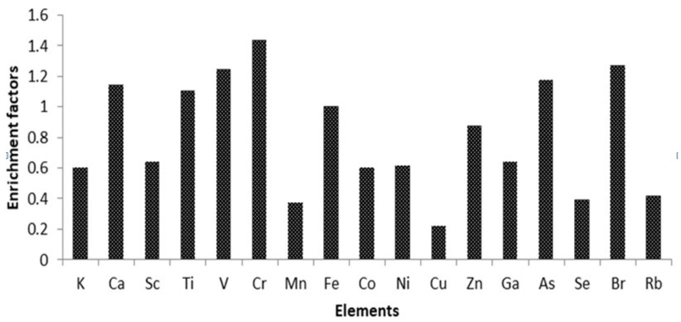

Figure 1: Levels of enrichment of elements in the soil samples.

EF<1=not enriched, EF between 1-10=slightly enriched, EF>10=enriched.

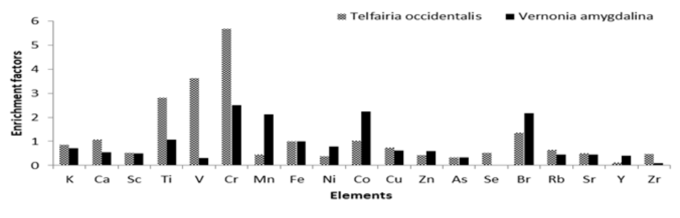

Figure 2: Levels of enrichment of elements in the vegetable samples.

EF<1=not enriched, EF between 1-10=slightly enriched, EF>10=enriched.

Ti is an abundant heavy metal within the earth's crust with a concentration of 6320 mg/kg [16]. The high concentration of Titanium (Ti) may depict the abundance in the soil and not due to the effect of oil pollution. Nevertheless, Ti is an essential element needed for plant growth mostly when Fe is in deficient quantity [17]. Sometimes, Ti can play an antagonistic role in plant growth causing Phytotoxicity. Phytotoxicity occurs when Ti is abundant than Fe in a plant [17]. The two vegetable species were enriched in Cobalt (Co) but not in the soil samples. The breakdown of organic materials and weathering of minerals are two major pathways for Co enrichment in the soil. To the best of our knowledge, Co has not been reported as an elemental composition in either Telfairia occidentalis or Vernonia amygdalina specie. The non-enrichment of Co in the soil may indicate another source of pollution other than the oil. The vegetable species could have picked up Co from an anthropogenic source like lithium-ion batteries and not from the oil-polluted soil. It is also possible that the vegetable species is composed of Co as an essential element. Co is an essential element required in the formation of vitamin B12 cin the human body [18]. However, Co can be toxic especially when found in higher concentrations in the human cells, preventing cellular respiration [19]. Mn enrichment in Vernonia amygdalina has a mean concentration of 74.795 mg/kg higher than the standard set by FAO/WHO in **Table 4**. The composition of Mn in Vernonia amygdalina could as well be traced to the oil-polluted soil because of its high enrichment in the soil samples. Mn is required for photosynthesis but continuous absorption (exceeding the permissible limit) can result in bio-accumulation in the body and damage the lungs and the brains. However, it is important to mention that the samples were not enriched in Sr, Y and Zr but the mean concentration of Sr (72.532 mg/kg) in Telfairia occidentalis was worrisome and higher than the FAO/WHO recommended standard in **Table 4**. Sr is a dangerous radioactive heavy metal carcinogenic to humans. Its high concentration could be linked to another anthropogenic source like radioactive fallouts. The concentration of Y and Zr cannot be concluded as a threat because it was only detected in a few samples.

Conclusion

The Energy Dispersive X-rays Fluorescence spectrometry technique (EDXRF) has been used to determine the elemental concentration of nineteen elements in soil and vegetable samples in an oil-polluted area of Lagos State. Enrichment factor calculations were carried out to identify the pollution load index of heavy metals in the soil and vegetable samples. The vegetable samples (Telfairia occidentalis and Vernonia amygdalina species) were enriched with heavy metals such as Fe, Cr,V, and Ti, source traceable to the oil-polluted soil. Co enrichment in the vegetable samples was traced to another anthropogenic source other than the oil-polluted soil. Only Telfairia occidentalis was enriched in Mn and traceable to the oil-polluted soil. The concentration of heavy metals in the vegetable samples was higher when compared with the FAO/WHO recommended standard. This was an indication that the vegetables grown on such soil were significantly contaminated with heavy metals and the continuous consumption (of the plants) could be detrimental to human health. Other heavy metals determined but not enriched in the samples included Sr, Y, and Zr with concentrations higher than the FAO/WHO recommended standards. Further studies could be carried out to characterize water samples from the hand-dug well and borehole in the area as soon as access is granted.

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