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Phytoremediation of Iron and Antimony Polluted Waste Dump Sites in Anyigba Kogi State, Nigeria: A Multivariate Statistical Technique

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ABSTRACT

Soil degradation by anthropogenic means is increasing day after day all over the globe, particularly in Nigeria. This research became necessary to show how plants grown surrounding waste dumps are able to mitigate soil pollution by Fe and Sb. Both media (plants and soils) were collected, and leached, and analyses were performed to assess the quantum of Iron and Antimony found within sampled media. The EDX3600B X-ray fluorescence spectrometer was used to analyze for soil and plants sampled. The bioconcentration factor (BCF), translocation factor (TF), bioaccumulation coefficient (BAC), and metal uptake efficacy (%) ME for both media were calculated. The evaluated data revealed that *Colocasia esculent* and *Amaranthus viridis* showed the maximum capacity as Fe hyperaccumulators. Also, *Colocasia asculenta*, *Physalis angulate*, and *Zea mays* were suitable plants as hyperaccumulators of Sb. Only *Loportea aestuans* suffices as phytoextractor for Antimony. *Amaranthus hybridus*, *Colocasia asculenta*, and *Corchorus aestuans* have capacities to stabilize Sb in soils. Species collected showed the required ability as phytominers of Sb. The quantities of Iron and Antimony in acquired media were higher than allowable benchmarks in leaves (vegetables). From this investigation, the acquired plants showed evidence of good specimens with abilities to remove Iron and Antimony from the soil. The collected species also showed attributes and characteristics of good reservoirs of Iron and Antimony.

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Most third-world countries face serious soil degradation problems because of anthropogenic activities. Soil degradation has become a major environmental problem with grave consequences for the inhabitants [1, 2]. Reclamation and returning fouled environment by toxic elements to its pristine conditions are on the front burner of national discussion worldwide. With the escalation of anthropogenic occupations, the quantity of toxic metal content is increasing at an alarming rate in our ecosystem. These toxic elements were found to have originated from geogenic and man-made sources like industries, agriculture, and metal extraction.

Metals are resilient and hardly break down in the ecosystem, either by plants or animals. These metals remain in our surroundings for years, thereby posing a danger to the ecosystem [1]. Conventional techniques available for the remediation of soils are mostly mechanical or physio-chemical methods like incineration, excavation, landfill, soil washing, and solidification. Because of the high cost, inefficiency when contaminants have minimal concentrations, the irredeemable effects on the soil attributes, and the generation of secondary pollution sources, the conventional method is being jettisoned for plant-based processes [2, 3]. Therefore, to bring back the metalimpacted soil to its original state, plant-based approach with its varied positive take is being sought after. In addition, plant techniques of soil mitigation are not destructive but rather restore both soil building blocks and allow for recovery of the biological environment [2, 4, 5].

Phytoremediation ways of toxic metal removal no doubt is a huge success. Terrestrial plants do not move from one place to another when planted and as such possesses the ability to resist and adapt to many ecological variables. Mechanisms like eradication and abolition of metals from soils are all useful for regaining fouled soil [4, 6]. The key factor to consider when using plant-based method of soil reclamation is to look for species with the capacity to multiply themselves in the degraded environment [4].

Plants apart from penetration of soil with their roots are also useful in the removal of metals found in impacted soils. This helps in the restoration and enhances the fertility of the soil. The processes involved in metal absorption by plants include increased metal solubility, root absorption, xylem loading, root-to-shoot transportation, cellular compartments, and sequestration. Metals occur as non-soluble and not biologically accessible to plants in the majority of soils. Roots exudates when liberated by plants escalate toxic metal availability through rhizosphere pH alteration and consequently increase solubility [7]. The biologically made available metals are assimilated by the roots and transferred across the membraneous barrier to the root cells. Active diffusion and active transport constitute the most important channels of toxic metal assimilation into the root system. The symplastic pathway is an energy-driven method by metal ion carriers. The precipitated complexes are subsequently immobilized either outside the cellular space or within the cellular spaces in vacuoles [8]. Metal ions after reaching the vacuoles are mobilized into the stele. From here, the metals are moved into the xylem flow with the help of the root symplasm and finally into the shoots via xylem vessels [9].

Plants that can accumulate very high concentrations of metals in any aboveground tissue in their natural habitat are called hyperaccumulators. These are plants that can accumulate > 1000 mg/kg of Cu, Co, Cr, Ni, or Pb; or > 10,000 mg/kg of Fe, Mn and Zn [2, 3]. The main characteristics of hyperaccumulators are as follows: (1) have accumulating capacity of 10,000 mg/kg for Zn and Mn; 1000 mg/kg for Co, Cu, Ni, As, Se and 100 mg/kg for Cd, (2) the ratio of metal concentration in shoot/metal concentration in root, that is translocation factor (TF) is greater than 1, (3) the ratio of metal concentration in plants/metal concentrations in soil, that is bioconcentration factor (BCF) is > 1 [10], (4) enrichment factor (EF), which is the ratio of metal concentration in leaf to metal concentration in soil < 1 is considered a stabilizer while EF value > 1- is an accumulator [4, 11-13].

This research intends to bring to our knowledge the potential of ten plant types that are appropriate for the removal of Fe and Sb from impacted soil. The degraded soils were part of the dump sites in Anyigba, Kogi State.

2. Methodology

2.1. Plants and Soil Sample Acquisition

Amaranthus hybrids, Amaranthus viridis, Abelmoschus esculentus, Cucurbita maxima, Colocasia asculenta, Corchorus aestuans, Laportea aestuans, Physalis angulate, Sida acuta and *Zea mays* species of same physiology, identical size and appearance were acquired [5]. Samples collected were representative of available species (Fig. **1**). Some were acquired twice from two different sites and others three and four times from different sites respectively. Plant specimens were obtained carefully with the help of a plastic hand trowel. The species were gently removed to ensure no part was lost [10]. The plants were washed first with tap water and secondly distilled water. This phase was necessary to eliminate adsorbed soil and other contaminants. The plants were partitioned into three parts and stored temporarily in self-sealing and well-labeled plastic bags. On arrival of samples into the laboratory, they were oven-dried for 72 hours at 70°C until a stable dry matter yield was achieved. The plants were crushed, mixed in a mortar using a pestle, and stored in sealed polyethylene bags ready for analysis [2, 11, 14].

Ten (10) plants were acquired twenty-seven (27) times from ten (10) soil sampled points (Fig. **1**). Soils were obtained from the rhizospheres (0cm-20cm depths) at each previously sampled plant point. All non-soil materials were removed physically. The same subproportion of soils were homogenized thoroughly and a segment was obtained [4]. Soils were oven-dried at 105 °C for total water removal and sieved vide 2mm with the aid of a magnetic sieve shaker. The fine fractions were obtained for later analysis [2].

2.2. Digestion of Acquired Media

1.5gm of pulverized plant each was weighed and put into a digestive vessel. Digestion was perfected in a mix of 4/1 (v/v) HNO₃: HCLO₄ in a hot plate until a clear film of the acid layer was obtained. After cooling, the resultant solution was sieved using a Whatman No.42 paper. The final 50 mL was made with 0.5% HNO₃ in a volumetric flask [15]. An OI-model 7295 microwave digestive apparatus (USA) was employed for soil digestion. 1.5gm of powdered soil was leached in an acid combination of 1:2:2 HNO₃: HCL: HCLO₄ This combination was chosen to get complete leaching plus extraction. The suspension was centrifuged and filtered passed Whatman paper No.42.The final volume of 50mL was achieved with 1% HNO₃ [2, 15, 16].

2.3. Leaching Toxic Metals from Media

Both media were leached and analyzed with an EDX3600B X-ray fluorescence spectrometer in Akure, Nigeria. The analytical range of elements by EDS3600S is between (Mg, $Z = 12$) and Uranium (U, $Z = 92$) (Plate 21). It has a high resolution and accuracy of 0.05%. The detection limit is 0.01 ppm. As part of quality-control measures, duplicates, calibration blanks, and internal standards were carried out to correct for any mass bias. Data obtained for elements of interest from the two sampled media were within **±** 8% of the certified levels. The internal standard and the recoveries of all elements were in the range of 97.50–100%. All acquired results were in mg/kg.

2.4. Data Calculation

- (i) Bioconcentration factor (BCF). BCF=toxic element content in root/ toxic element content in soil [2, 15].
- (ii) Translocation factor (TF). TF= toxic element content in plant shoot/ toxic element content in plant root [2, 17].
- (iii) Biological accumulation coefficient (BAC). BAC= toxic metal content in shoot/ toxic metal content in soil [2, 18].
- (iv) Metal uptake efficacy ME (%): was obtained by dividing toxic elements in shoot/ total toxic elements measure obtained from soil media **×**100 [5].
- (v) Multivariate and ANOVA analyses: Multivariate technique is a data reduction approach. This method brings similar variables together. The average distance method was implemented in the evaluation of how close the parameters were using Ward's method. Smaller Euclidean distances mean greater correspondence and vice versa. Similar variables were found in the same group [2].

The ANOVA and multivariate evaluation were conducted with SPSS v20. Data analyzed by ANOVA under current research were equivalent at 0.05. The correlation matrix using Pearson's correlation coefficient was utilized to show affinities between the parameters. Relationships range of +1 and -1 were accepted for this study [2].

- (vi) The dendrogram was drawn using SPPS vs. 20. The measured variables were plotted against each other to show how similar they were to each other. The dendrogram has been used to show the relationship between variables [2].
- (vii) Tables (**1**-**2**) showing unpolluted vegetable metal contents and sampled plants edible tissues.

Element mg/kg(soil)	Rudnick and Gao, 2003	Papadopoulos et al., 2015	Kabata-Pendias, 2001	Bradford et al., 1996	Element mg/kg (vegetables)	WHO/FAO. 1993	Kabata-Pendias. 2001
Fe		28.50g/kg	$0.5 - 5%$	1.0-8.7%	Fe	48	29-130
Sb	0.3		$0.3 - 9.5$	$0.15 - 1.95$	Sb		0.06

Table 1: Pristine soil and vegetable standard values.

Table **1** is the benchmark for each metal allowed in the vegetable/edible sampled. This table is to allow for a comparison of the fouled soil from the study area with the undegraded and metal quantities in the sampled plants. This was done to show whether each metal has exceeded the benchmark or not.

Table 2: Plants and their edible tissues.

Table **2** shows the edible parts of acquired species from diverse literature sources. This table is the highlights of the acquired species and their edible parts.

3. Results and Discussion

3.1. Iron (Fe)

Iron (Fe) content in soils ranged between 70281.00mg/kg to 107,413.33mg/kg in sites 3 and 6 respectively (Tables **3** and **4**). The standard error was 2506.11 and the standard deviation was 13022.14. The Fe content from the polluted study location was above 370.00mg/kg [19] and 30.89mg/kg [20] for uncontaminated soil background (Table **1**). The accumulation capacities of roots lie between 1336.00mg/kg in *Sida acuta* to 96200.00mg in Colocasia asculenta (Tables **3** and **4**). The absorbed Iron in roots was minimal to that in soils. *Colocasia asculenta* recorded the maximum quantum of Fe in shoot (15,720.0mg/kg) and the lowest (1201.0mg/kg) in *Zea mays* (Table **4**). In general, the quantum of iron was higher in shoots relative to the roots. This suggested that the plants were useful

as stabilizers and means of removal of Fe from the degraded soil surfaces and also as ore of Iron (Fe). This is so because of the steep values of TF. In leaves, the lowest measure of Fe was recorded, and the highest in the roots (Table **3**).

Figure 1: Sample location map [2].

The quantity of Fe in leaves was maximum (950.0mg/kg) in *Amaranthus viridis* and lowest (100.00mg/kg) in *Cucurbita maxima* (Tables **3** and **4**). This revelation countered previous work of [18]. Based on this work, the quantum of Fe was consistently higher in the roots than in other parts of the plants. Another similar study, revealed that *Urtica dioica* accumulated 204 to 892.0mg/kg in roots and 80.1 to 240mg/kg in shoots [21]. Also, in [12], the plants absorbed an average of 393.70 mg/kg and 499.10 mg/kg in roots and shoots respectively. *A.*

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wilkesiana accumulated 5002.4mg/kg in root, 1169.4mg/kg in shoot and 1251.0 mg/kg in leaf from another past investigation [18]. The accumulated Fe in species under investigation was more than the cited works. Going by the definition of hyperaccumulator plants, *Colocasia asculenta*, and *Amaranthus viridis* in sites 3 and 4 were potential Fe hyperaccumulators [4, 11, 13].

Table 3: Mean concentration of Fe (mg/kg) in soils and plant tissues.

Table 4: Fe in soil and plant tissues.

The measure of Fe in leaves was between 100mg/kg to 950mg/kg (Tables **3** and **4**). The baseline quantity of Fe in vegetables is 150.0mg/kg [22] and 48.0mg/kg [23] (Table **1**). Excessive assimilation of Fe from these vegetables can result in hemochromatosis, siderosis, cardiac failure, and cancer [24-26].

3.2. The BCF, TF, and BAC of Root, Shoot, and Leaf

All the (BCF), (BAC) results in plants part were < 1 (Table **3**). Similarly, the root-to-leaf TF was also < 1. The TF (root to shoot) varied from 1.20 in *Amaranthus hybridus* to 5.39 in *Amaranthus viridis* (Table **3**). The TF > 1 revealed the potential of these plants to move Fe from roots to shoots but < 1 BCF showed the inability of species to absorb and translocate Fe [18]. The species sampled, therefore, had shown no affinity for Fe and therefore not appropriate for Fe extraction. The TF of *Amaranthus hybridus, Amaranthus viridis*, and *Cucurbita maxima* from this investigation were all high (Table **3**).

Table 5: Correlations of variables.

*Correlation equivalent at the 0.05 level (2-tailed). **Correlation equivalent at the 0.01 level (2-tailed).

Fig. (**2**) was a union between two clusters. Very strong relationships were revealed between Root-BCF and Shoot-BAC (Table **5**). Weaker associations were also noticeable among Leaf-EFone and Shoot-Soil. The status of resemblance shown reflected the significance of connectivity among the variables measured. From association

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two, a wide gap exists concerning TF-TFone (Table **5** and Fig. **2**). Therefore, the close resemblance that is the high values of correlation in Table **5** is an indication of the greater status of assimilation and solubilization of metals from one part to the other. Little resemblance connotes no correspondence with what was absorbed and thus transferred (low values of correlation values).

3.3. Antimony (Sb)

The quantum of Sb in degraded soil under investigation lay between 6008mg/kg in location 7 to 10548mg/kg in location 4 (Tables **6** and **7**). [19] baseline measure of major and trace metals in benchmark California soils was put at 0.60mg/kg. The upper continental crust figure for Sb was 0.30mg/kg [20]. The quantum of Sb obtained for soils under investigation was more than the California benchmark (Tables **1** and **6**).

The measure of Sb assimilated in roots falls between 6500.0mg/kg in *Physalis angulata* (site 2) to 14006.0mg/kg (site 3) in *Sida acuta*. The optimum assimilation in shoots (13950.00mg/kg) was revealed in *Amaranthus hybridus* (site 3) and the minimum (5520.0mg/kg) was in *Physalis angulata* (site 2). A significant measure of Sb was also assimilated in leaves (Tables **6** and **7**). The highest was 10,000.00mg/kg in *Amaranthus viridis* (site 3) and the lowest value of 2320.0mg/kg in *Physalis angulata* in location 2 (Table **6**). The benchmark figure for Antimony is 36.0mg/kg [22]. The assimilated figures in leaves as reported from this research were quite higher than the admissible limit. This puts the consumers of the vegetables at risk (Tables **1** and **2**) [25, 26]. The roots take in most of the Sb while the leaf holds the lowest measure. The quantity of Sb intake in the species part was in tandem with similar studies. The order of accumulation noticed was roots (12.5mg/kg) > shoots (1.30mg/kg) > leaves (0.299mg/kg) [27]. Also, the relative assimilations in all plant parts under scrutiny indicated elevated figures above the past researches cited in Table **1**.

3.4. The BCF, TF, and BAC for Plant Parts

The BCF was highest (1.39) in *Amaranthus hybridus* (site 1) and least (0.70) in *Physalis angulata* (site 2). The translocation factor for Sb lay about 0.67 in *Colocasia asculenta* to 1.77 in *Cucurbita maxima*. The maximum translocation factor for rice was put at 0.51 in another work [27]. The BAC varied between 0.60 in *Physalis angulata* to 1.63 in *Amaranthus viridis* (Table **6**). Only *Laportea aestuans* showed phytoextraction ability for Sb while *Amaranthus hybridus, Colocasia asculenta*, and *Corchorus aestuans* were stabilizers of Sb. It showed generally that the flow of metals to shoots and accumulations was reasonable over the assimilation of Sb in roots. This connotes that the roots were not tolerant to Sb but can translocate and absorb Sb in shoots. These indices showed suitability on the part of the plants as agents for decontamination of Sb from the impacted soil and as ore for extraction of Sb. It has also been shown that too much Antimony in the edibles could become poisonous to humans when consumed (Table **2**).

Table 6: Mean concentration of Sb (mg/kg) in soils and plant tissues.

Table 7: Sb in soil and plant tissues.

The flow of toxic metals and absorption of Antimony to the leaves were all < 1. This has revealed that very little assimilation and transfer of Sb took place in the leaves (Table **6**). The BCF > 1 and TF > 1 connote the suitability of plants for phytoextraction [4, 11, 28]. Based on this investigation*, Sida acuta; Laportea aestuans, Corchorus aestuans* (site 2), *Abelmoschus* (site 7); *Amaranthus viridis* (site 7), and *Amaranthus hybridus* (site 3) were all instruments for the recovery of Sb. The BCF > 1 and TF < 1 revealed species that have the capacity for phytostabilization [13, 29, 30]. *Colocasia asculenta, Sida acuta*, and *Zea mays*, therefore, have the capacity for phytostabilization of Antimony (Table **6**).

Hyperaccumulators take in > 1000mg/kg of Cu, Co, Cr, Ni or Pb or > 10,000mg/kg of Mn or Zn [30-32]. From the figures obtained, all species were potential hyperaccumulators of Sb (Table **6**).

Table 8: Correlation of variables.

**Correlation equivalent at 0.01 level (2-tailed). *Correlation equivalent at 0.05 level (2-tailed).

Fig. (**3**) consists of two clusters. In association one, Leaf-EFone revealed the highest resemblance (Table **8**). The Root-BCF, Leaf-Root, and soil revealed descending order of resemblance respectively. There was also no connection in terms of the quantum of metals in soil and what was assimilated and later transferred. The Leaf-EFone showed a very good level of linkage (Fig. **3** and Table **8**). From Root-BCF and Root-leaf, this resemblance begins to weaken. The associations in group two were; Shoot-BAC; TF-TFone; and Shoot-TF. The Shoot-BAC revealed peak resemblance and very good chemistry in terms of what was assimilated and subsequently transferred (Table **8**).

Figure 3: Dendrogram of measured variables.

4. Conclusion

Colocasia asculenta and *Amaranthus viridis* could be hyperaccumulators of Fe. The quantum of Fe found in leaves/vegetables was more than the [22, 25, 26] and [23] limits. Sampled plants does not have the capacity as phytominers. Except for *Amaranthus esculantus, Colocasia asculenta, Physalis angulate*, and *Zea mays*, other plants were at variance with the requirements for hyperaccumulation of Sb. The benchmark for Sb in leaves is lower than the values obtained under the current investigation. Only *Laportea aestuans* had the ability as phytoextractors of Sb. *Amaranthus hybridus, Colocasia asculenta,* and *Corchorus aestuans* all had capacities as phytostabilizers of Sb.

More investigations are imperative to recognize the phytomining capacities of these plants. The mechanisms by which Fe and Sb are assimilated and transferred within plant tissues require detailed investigations.

Conflict of Interest

The author declares that there is no conflict of interest.

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