Trace Metal Uptake by Food Cultivars in Coal Mining Environment of Enugu State, Nigeria

L.U Mgbeahuruike¹, E.I Emereibeole¹, F.U Nwobodo¹, C.N Uyo¹, J.C Anyanwu¹, R.F Njoku-Tony¹, K.T Ezirim², F.A Edo¹, C.J Egwim¹, I.M Nmecha¹, C.G Onwuagba¹, H.C Uzoma²

¹Department of Environmental Technology, Federal University of Technology, Owerri, Nigeria
²Department of Chemical Engineering, Federal University of Technology, Owerri, Nigeria
³Department of Mechatronics Engineering, Federal University of Technology, Owerri, Nigeria

*Corresponding author: uyochijioke@yahoo.com

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Abstract The aftermath of unsustainable artisanal mining operated within three communities (Iva valley, Onyeama and Akwukwe) of Enugu State and it’s environ was investigated. Soil and food crops from the selected communities were analyzed for their heavy metal contents using the Atomic Absorption Spectrometry (AAS). The soil samples in the three communities were found to have a higher concentration of Mn, Cr, Pb, and Cd except for Ni when compared to the control sample taken at Oghu in Udi but lower to the WHO permissible limit in soil and plants. However, the value of Transfer Index Factor across the impacted locations affirms that the pumpkin leaf has a higher loading affinity for manganese and chromium values as 2.63 and 0.33 respectively while Pb in Iva Valley has the highest value at 5.67, Nickel has the least loading in all the food crops in the three communities with an insignificant value. Preferences in metal accumulation in crops and soil at Akwukwe location follows the order of decreasing magnitude of pumpkin>scent leaf>cassava> and Mn>Pb>Cr>Cd>Ni respectively. These results suggest that the pollution of the environment by the heavy metals in these areas were as a result of the coal Mining activity and use of chemical fertilizer by the agrarians, thereby increasing the levels of Mn, Cr, Pb, and Cd, concentrations in the soil and food crops. Selective agronomic techniques are suggestive remedial measure to stem down the bioavailable fractions of these trace metals in terrestrial food chain.

Keywords: PTTEs, toxicity, cumulative, transfer factor, pollution index

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1. Introduction

Soil contamination induced by potentially toxic trace elements (PTTEs) is now ubiquitous following the incidences of industrial revolution and urbanization many decades ago, which in turn, created huge changes in the global budget of critical chemicals at the earth’s surface [1]. Indications of this scenario is observed in the higher concentrations (10 to 30 times higher than Fe or Mn) of heavy metals calculated as an ‘index of relative pollution potential’ and expressed as the ratio of annual mining output for a given element to its natural concentration in unpolluted soil [2]. The scale of impact of PTTEs in soil systems can be potentially detrimental in the long term with far reaching consequences due to their mobility, toxicity, and persistence in the environment [3].

The main sources of metallic and non-metallic contaminations are atmospheric deposition, indiscriminate disposal of industrial wastes, mining and smelting operations, and the use of fertilizers, incineration and combustion processes. These activities, especially the leaching of mine tailings and acid mine drainage (AMD) from the mined areas can substantially expose the soil to metal residues thereby altering the haemostasis potentials of the urban soils. The presence of these PTTEs in the soil disrupts the delicate balance of physical, chemical, mineralogical and biological processes upon which the maintenance of soil fertility depends [4]. Interestingly, small amounts of these metals are intrinsically common in our environment and a balanced concentration of a few of them (trace elements) is obligatory and beneficial for good health in the human diet [5]. However, excessive exposure to any of them may cause acute or chronic toxicity as they are non-degradable and often interfere with the terrestrial food chain and pose significant environmental and health risk within the biosphere.

In general, food contamination of PTTEs is exacerbated by both mobility and bioavailability factors resulting in...
significant metal fluxes and cumulative loading beyond the soil threshold dietary toxicity for the soil-crop systems. These bioaccumulations are usually influenced by physicochemical factors (pH, organic matter, clay minerals, CECs and other biochemical properties) and agronomic practices such as fertilizers, water management (irrigation) and crop rotation systems [6]. Following these activities, many authors have reported high levels of PTTEs in soil and groundwater [7], which now serve as an environmental pathway for trace metal contamination. The excessive ingestion and accumulation of PTTEs in the body tissues can be life threatening. The average biological half-life of some of these PTTEs, especially for cadmium has been estimated to be about 18 years, and this is extremely long [8]. PTTEs such as lead (Pb), cadmium (Cd) and copper (Cu) are cumulative poisons and are culpable of certain diseases such as congenital toxins, neurotoxin, phytotoxin and some repercussions [6].

It is against this backdrop, that it becomes imperative to investigate the after effect of the activities of coal mining in some selected communities of Enugu State Nigeria following the unsustainable artisanal mining practices in its operations and the attendant environmental implications it poses to the local habitats.

2. Materials and Methods

2.1. Description of the Study Area

Enugu state, a densely populated metropolitan City in Southeastern Nigeria (Figure 1), has an estimated population of 722,000 in 2006 (National Population Commission, 2006) owes its urban status primarily to the existence of very large deposits of coal (mainly of sub-bituminous grade) estimated at 1.5 million tons [9]. The City has served as the administrative Capital of the old Eastern region of Nigeria. The population of Enugu has continued to rise due to the existence and sitting of large numbers of industries, factories and Government Secretariats that have attracted large number of workers and their dependents to the city. Its physiography is characterized by undulating topography underlain with clay/shale lithologies. The rock unit is made up of dark grey, fissile shale with occasional thin beds of siderite and mudstone [10]. It is on account that these shales wither rapidly to a red or pinkish clay soil or laterite with concretions. Three locations (Iva Valley, Akwuke and Onyeama) within the mining axis have been designated for sampling and a location (Oghu) distant away from the mine area as a control point (Figure 1) to enable the investigation of the extent with which metaliferous toxins have incorporated and interfered with terrestrial food chain.

Figure 1. Study area showing sampling points for sample collection
2.2. Chemicals and Materials

Soil samples were collected from three different locations (Iva Valley, Akwukwo and Onyeama) representing three different local Government areas in Enugu State. The soil samples were dug from a depth of 15-30cm using a metal auger and transferred into prewashed polyethylene nylon bag to avoid contamination. After collection, samples were brought to the laboratory and subjected to the methods recommended by [11]. According to this method, samples were air dried in sun light for a day. Then the samples were finally dried in oven at 105°C till a constant weight was achieved. This was followed by passing half of each of the samples through 0.5 mm nylon mesh sieve to remove exogenous materials and to maintain homogeneity of the sample. Then soil samples were repacked with the complete labelling and preserved for further analysis.

The plant samples were washed with deionized water (18.2 mΩ-cm) and air dried firstly and then in an oven at 70-80°C until a constant dry weight was attained. The dried samples were ground in wooden mortar to make a fine powder. The finely ground samples were passed through 0.5mm nylon mesh sieve and packed in the air tight polythene bags to prevent the absorption of water from the humiud environments.

Soil samples were dried at 105°C and sieved with 100 mesh (152um Bs screen 410). One gram of the dried soil sample was weighed into a labelled 100 mL conical flask and 20 mL of mixture of concentrated HCl and concentrated HNO3 (1:1) were added and well shaken to form a solution. The solution was kept overnight after which it was filtered through with whatman N0.1 filter paper. The clear solution obtained was made up to 100 mL using a standard flask and transferred into a plastic bottle [12]. The sample solutions were analyzed at various wavelengths for each targeted metals using Varian AA240 Atomic Absorption Spectrophotometer according to the method of [13].

For the food cultivars, exactly 1 g of the ground sample was weighed into a beaker. Then, 10 cm3 of 1:1 dilution of the concentrated HNO3 and water were mixed and then covered with a watch glass. The solution was placed on a hot plate to reflux for 10 to 15 minutes without boiling. The beaker was allowed to cool and then 2 cm3 of deionized water and 3 cm3 of 30 % H2O2 were added, covered with watch glass and placed over a hot plate. After the effervescence had subsided, the solution was removed and cooled. Thereafter, HCl (5cm3) and 10 cm3 of deionised water were added and then heated for another 15 minutes without boiling. The solution was then transferred to 100 cm3 beaker and made up to mark using deionised water and taken for AAS determination of lead, chromium, Nickel, cadmium and manganese. Chemicals and reagents used for this analysis were of analytical standard except where otherwise stated.

2.3. Experimental Methods

The constituents (soil and plants) were analysed for their physical and chemical properties, using standard techniques and approaches. pH, Phosphate, Chloride, Sulphate and Nitrate were all determined using standard approaches as described APHA (1998). The baseline metal concentrations of the soil samples and food cultivars were determined using Varian AA240 Atomic Absorption Spectrophotometer [13] after a hot plate digestion of the different substrates. All sample concentrations were corrected for matrix effects by procedural blanks, normalized to sample mass and reported as µg/g dry weight. Matrix-matched calibration (with blank) was performed using a multi-element standard solution (100 mgdm-3) for each element. Then, the determination of the pollution Index (P1) and Transfer Factor (TF) were calculated using the equations 1 and 2 as described by [14].

\[
\text{Pollution Index (P1)} = \frac{1}{n} \left[ \frac{M_1}{(TL)}_1 + \frac{M_2}{(TL)}_2 + \cdots + \frac{M_n}{(TL)}_n \right] 
\]

\[
\text{Transfer Factor} = \frac{\text{concentration of metal in plants}}{\text{concentration of metal in soil}} 
\]

3. Results and Discussion

The physicochemical properties of soil from coal mining communities collected from the different locations in Enugu environs are summarized in Table 1. The Spatial variations observed in the levels of physicochemical parameters was calculated and revealed by one-way analysis (Sig.F value = 0.000) of variance across the sampling locations at p < 0.005 (Table not shown here) and illustrated in Figure 2. At Iva Valley, mean concentrations of pH, SG, BD, NO3-, PO43-, SO42-, Cl- and TOC were 5.25±0.01, 2.11 g/ml, 1.74±0.01 g/cm3, 299±0.01 µg/g, 941 µg/g, 1214 µg/g, 231 µg/g and 4.1±0.01 µg/g respectively while the mean concentration of metals; Mn, Cr, Pb, Cd and Ni were 330±0.01 µg/g, 280.00±0.01 µg/g, 1054±0.01 µg/g and 0.007±0.003 µg/g respectively. However, at Oghu, which serves as control point had their respective mean concentrations as 5.08±0.01, 130.00±0.01 µg/g, 280.00±0.01 µg/g, 1208±0.01 µg/g and 0.007±0.003 µg/g respectively. At Onyeama, the respective mean concentrations were 5.08±0.01, 2.02±0.01 g/ml, 1.10±0.01 g/cm3, 297±0.01 µg/g, 803±0.01 µg/g and 8.0±0.01 µg/g while mean concentrations for Mn, Cr, Pb, Cd and Ni were 330±0.01 µg/g, 280.00±0.01 µg/g, 1054±0.01 µg/g and 0.007±0.003 µg/g respectively. At Akwukwo, the mean concentrations of the respective physicochemical properties were 5.38±0.01, 1.38±0.01 g/cm3, 1.40±0.01 g/ml, 265±0.01 µg/g, 5.50±0.01 µg/g, 1054.00±0.01 µg/g and 6.0±0.01 µg/g while mean concentrations for Mn, Cr, Pb, Cd and Ni were 450.00±0.01 µg/g, 330.00±0.01 µg/g, 330.00±0.01 µg/g, 120.00±0.01 µg/g and 0.007±0.003 µg/g respectively. However, at Oghu, which serves as control point had their respective mean concentrations as 6.0±0.01, 2.20±0.01 g/ml, 1.01±0.01 g/cm3, 297±0.01 µg/g, 940±0.01 µg/g, 1208±0.01 µg/g and 40±0.01 µg/g while mean concentrations for Mn, Cr, Pb, Cd and Ni...
were 250±0.001 µg/g, 95.00±0.01 µg/g, 150.00±0.01, 9.50±0.01, and 0.007±0.003 respectively. These variations across the different sites are expected due to the geology of the area. The range of pH (5.08–5.18) observed at the different sites may have an influence on the retention behaviour and transfer of the metal profiles within the various substrates.

3.1. Concentrations of Metals in Leave Crops

The mean concentration of metal accumulation across the sampling locations were assessed for Pumpkin, Scent and Cassava leaves and the values summarized in Table 2 and illustrated in Figure 3, Figure 4, and Figure 5. The targeted metals showed accumulated variations at different levels of concentrations.

In pumpkin leaves the mean cumulative concentration of metals (Mn, Cr, Pb, Cd and Ni) across the different sampling locations are 212 µg/g, 236 µg/g, 304 µg/g, 166 µg/g for Iva valley, Onyeama, Akwukwe and Oghu respectively (Figure 3). It is observed that the individual metal concentration in pumpkin for Iva valley, Onyeama, and Akwukwe were substantially higher than concentrations at Oghu (Table 2).

In Scent leaves, their respective cumulative concentrations are 136 µg/g, 182 µg/g, 190 µg/g and 70 µg/g for Iva valley, Onyeama, Akwukwe and Oghu respectively (Figure 4). The concentrations of Mn and Pb were significantly higher across the sampling points except for Cr and Ni which showed insignificant traces. However, Cd concentration was relatively same with concentration observed at control point (Table 1).

![Figure 2. Changes in physico-chemical parameters at p < 0.005 as influenced by the different sampling sites](image)

Table 1. Mean separation in concentrations of the heavy metals (µg/g) in Pumpkin Scent and Cassava leaves across the sampling locations

| Metal | Iva valley | Onyeama | Akwukwe | Oghu |
|-------|------------|----------|----------|------|
|       | PF SL CT | PF SL CT | P SL CT | PF SL CT |
| Mn    | 710 430 110 | 850 620 250 | 1170 620 180 | 630 340 100 |
| Cr    | 10 0 0 | 60 10 40 | 110 0 20 | 9 0 10 |
| Pb    | 340 240 350 | 250 270 420 | 210 320 320 | 180 0 220 |
| Cd    | 60 10 10 | 20 10 20 | 30 10 20 | 10 10 10 |
| Ni    | 0 0 0 | 0 0 0 | 0 0 0 | 0 0 0 |

![Figure 3. Influence of different sampling sites on the transfer loadings of heavy metals on Pumpkin leaf. The lower and upper boundaries of the box represent the 25 & 75% of the sample size (n=4)](image)
In cassava leaves, the cumulative concentrations of their respective metals are 94 µg/g, 146 µg/g, 108 µg/g and 68 µg/g for Iva valley, Onyeama, Akwukwe and Oghu respectively (Figure 5). The concentration of Pb across the sampling locations is substantially higher compared to its concentration at Oghu. Cr concentration across the sampling points were significantly different; while Onyeama and Akwukwe showed higher concentrations, Iva valley showed relatively insignificant concentration compared to concentrations observed at Oghu location. Cd concentration showed higher concentration in Iva valley but relatively same for Onyeama and Akwukwe when compared to concentration observed at Oghu. However, Ni concentration remained insignificant across the sampling points (Table 1).

From the above description and analysis, it is obvious that metal accumulation in the crops are in the magnitude of decreasing order of significance Pumpkin > Scent > Cassava with Iva valley location having highest transfer factor followed by Onyeama and Akwukwe swapping interchangeably while Oghu location had the least transfer factor as would be expected from calculation obtained from Equation 2. More so, the transfer factor results for the four communities shows that the pumpkin leaf has a higher loading for manganese and chromium values as 2.63 and 0.33 at Akwukwe respectively while Pb in Iva Valley has the highest value at 5.67 and Nickel has the least loading in all the food crops in the three communities with an insignificant result (Table 2).

Also, the Pollution Index (PI) for the sampling locations is calculated using equation 1 and by inputting the average concentrations of each metals of interest by their tolerable levels in the soil for the different locations and with “n” denoting number of pollution metals. The Table 3 summarizes the Pollution Index (PI) for various locations under review.
However, bulk density for Iva valley was at 1.74 g/cm³ through the roots, and are translocated to the shoots and increased by root exudates. Many studies have affirmed trace metal bioavailability for plants and its solubility is with flowing water. Acidification of the soil increases the capable of forming solutions of net acidity when in contact optimal movement of air and water through the soil [17].

...g/cm³). These values are less than 1.5 g/cm³ suitable for but slightly higher than that observed for Oghu (1.0 below allowable limit of 2.65-2.85. The relatively low communities was lower than the control location and also affect both the bulk density and porosity of the soil. These suggest the porosity of the soil could be attributed to some porous particles and/or organic matter which in turn affect both the bulk density and porosity of the soil. These indicators ascertain the suitability for plant growth and soil permeability and promotes vitality in soil-plat-

The decrease in pH(5.60) levels of Iva valley, Onyeama and Akwukwe soil below the background pH(6.0) at Oghu soil may be attributed to anthropogenic sources resulting from metal tailings containing sulphur-bearing materials potentially capable of forming solutions of net acidity when in contact with flowing water. Acidification of the soil increases the trace metal bioavailability for plants and its solubility is increased by root exudates. Many studies have affirmed that high trace metal contents in food cultivars are accumulated through the roots, and are translocated to the shoots and grains [15]. The specific gravity of soil from the three communities was lower than the control location and also below allowable limit of 2.65-2.85. The relatively low specific gravity of the soil within the impacted areas suggests the porosity of the soil could be attributed to some porous particles and/or organic matter which in turn affect both the bulk density and porosity of the soil. These indicators ascertain the suitability for plant growth and soil permeability and promotes vitality in soil-plat-atmosphere systems [16]. The bulk densities of Onyeama and Akwukwe are 1.1 g/cm³ and 1.38 g/cm³ respectively but slightly higher than that observed for Oghu (1.0 g/cm³). These values are less than 1.5 g/cm³ suitable for optimal movement of air and water through the soil [17]. However, bulk density for Iva valley was at 1.74 g/cm³ much higher than what were observed for the other locations. The increased value may have influenced the transfer factor of metal accumulation observed in the cultivar crops at the location. The concentration of anion exchange capacity (AEC) of the soil has been observed to be higher at Oghu location compared to the impacted locations under review. This increase has been attributed to agronomic practices and the use of fertilizers occasionally used by the agrarians in the area. Anions are dependent on the pH of the soil and increases as the pH decreases. For Iva Valley, Onyeama and Oghu, the anion concentrations are not significantly different compared to Akwukwe having lower concentrations. Although, one should implicitly expect higher SO₄²⁻ in the mining area considering the tailing spoils which is discarded during such activities. Also, the TOC value (40%) observed at Oghu is relatively higher than the other locations. The increased TOC could be attributed to agronomic practices at Oghu.

Higher level of Mn, Pb and Cd observed in Akwukwe soil over other communities could be attributed to anthropogenic and mining activities that took place in this area, and the use of fertilizer sources. The result of the study revealed that the concentrations of these metals in the soil of the three mining communities studied compared to the control soil showed that there is an increase in the heavy metals levels of soil in the mining communities but are within the permissible limit in agricultural soil [18]. High levels of heavy metal in agricultural soil may lead to increased metal uptake in plant which may have adverse health implication in humans via terrestrial food chain. Heavy metal concentrations in plant leaves from the study areas, as shown in Table 3 indicates that heavy metal contents of pumpkin leaves from coal mining impacted areas were significantly higher at p<0.05, when compared to the control plant. The high level of heavy metals in Akwukwe followed by Onyeama and Iva Valley vegetables could be attributed to coal mining activities which resulted in the increase of heavy metal pollution of the farmland. The differences in heavy metal levels in the two leafy vegetable from same location could be attributed to differences in metal uptake by different plant species, atmospheric deposition and leachate deposit of heavy metal on the shoot, size and shape, contact surfaces and heavy metal status on the soil and water systems [19].

The transfer factor of heavy metals in soil and plant food cultivars from Akwukwe, Ngwo and Udi was in the order pumpkin>scent leaf>cassava> and the preponderance of heavy metals in the environment were of the order Mn>Pb>Cr>Cd>Ni. The result is in consonance with that of [20] that the concentrations of heavy metals in plant food crops appears in the order Mn>Pb>Cr>Cd>Ni and were higher in leaves followed by cassava and other food crops. And thus could be attributed to different plant having different uptake and sensitivity to heavy metals as well as such factors like contact surface, organic matter content, atmospheric deposition, textures and morphology [19].

The level of lead (Pb) in the food crops from the three locations were in the order Cassava>scent leaf>pumpkin while lead (Pb) burden of the study areas were Onyeama>Iva Valley>Akwukwe>Oghu. The levels of Pb in plant food crops did not exceed the maximum Pb limit of (2 mg/kg) for human health as has been established for edible plant parts. Elevated levels of lead or even low levels in human body reduce plasma copper concentration, which may lead to irreversible damage of the brain [21]. Exposure to high lead levels can severely damage the brain and kidney and ultimately cause death. Also in pregnant women, high level exposure to lead may cause miscarriage while high level exposure in men can damage organ responsible for sperm production [22].

The levels of transfer factor for Cd in these food crops from Iva Valley is substantially higher compared to those

| Town      | Pollution index of Soil (P1- soil) | Interpretations (P1 > 1 = polluted) (P1 < 1 =Not polluted) |
|-----------|-----------------------------------|------------------------------------------------------------|
| Iva Valley| 0.0065                            | Not polluted                                               |
| Onyeama   | 0.00768                           | Not polluted                                               |
| Akwukwe   | 0.03362                           | Not polluted                                               |
| Oghu      | 0.00494                           | Not polluted                                               |

Table 2. Trace metals Transfer Factors in food cultivars across the four sampling locations

| Metal | Iva valley | Onyeama | Akwukwe | Oghu |
|-------|------------|---------|---------|------|
| Mn    | 2.15       | 1.3     | 0.33    | 1.97 |
| Cr    | 0.08       | 0       | 0.14    | 0.02 |
| Pb    | 1.22       | 0.08    | 1.25    | 1.14 |
| Cd    | 5.67       | 1.33    | 8.67    | 1.33 |
| Ni    | 0          | 0       | 0       | 0    |
| PF    |            |         |         |      |
| SL    |            |         |         |      |
| CT    |            |         |         |      |

Table 3. Pollution Index (PI) of soil from sampling locations under review
of Onyeama, Oghu and Akwukwe and were above the world health organization (WHO) safe standard of 1.50 mg/day (WHO 1996) and 0.03 mg/kg limit of Cd concentration in vegetable for human. This may suggest that the population feeding on these food cultivars from Onyeama, Iva Valley and Akwukwe are at higher risk of cadmium toxicity. The accumulation of cadmium in the system may lead to acute cadmium poisoning which may cause high blood pressure, kidney damage, destruction of testicular tissues and destruction of red blood cells [23]. In pregnant women, normal dietary level exposure to cadmium may cause teratogenic and mutagenic effect to the fetus [24]. This is similar to the report of [22] that Cd and Pb are known human carcinogens and ingesting very high levels of cadmium severely irritates the stomach leading to vomiting and diarrhea.

The transfer factor of nickel (Ni) in the food cultivars was not detectable both in leafy vegetable and cassava in the locations. Although excessive intake of nickel above recommended dietary allowance of 150 µg/day causes allergy, bronchial asthma, dermatitis, larynx, prostate and stomach cancers [22].

4. Conclusion

Trace metal contamination in soil and food cultivars can pose a serious threat to the sustainability of human health due to the metals’ toxicity. The study revealed high concentration of manganese, lead, chromium cadmium and nickel in soil samples and food cultivars grown in these communities; Akwuke, Onyeama and Iva Valley, when compared to a control sample taken at Oghu community, an outskirt of the impacted areas. However, the concentrations of these heavy metals were not high when compared to WHO/FAO Permissible limit in soil and food crops. The uptake and accumulation of these trace metals especially Cd in food cultivars observed at Iva Valley may pose a risk to human health. Transfer potentials of these trace metals as determined by Transfer Index factor shows preponderances of increased Cd accumulation in the food cultivars. There is need to deploy selective agronomic techniques as a remedial measure to stem down the bioavailable fractions continuously interfering with terrestrial food chain.

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