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SPECIATION AND BIOAVAILABILITY OF Cd, Cu AND Cr IN AGRICULTURAL SOILS AMENDED WITH BIOSOLIDS

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ABSTRACT

Agricultural soils amended with biosolids were investigated for Cd, Cu and Cr distributions through modified Tessier sequential extraction protocol. Bioavailability of the metals in *zea mays* and *Amarathus Hybridus* cultivated on the studied soils were assessed. The results showed that the bioavailable Cu ranges between 3% -10% (0.024 ± 0.003 mg/kg and 0.105 ± 0.022 mg/kg) in all locations. Cd concentrations were between 0.016 ± 0.005 mg/kg and 0.246 ± 0.023 mg/kg). Se and Cr in the bioavailable forms ranged between 40% to 60% (0.183 ± 0.031 mg/kg and 2.257 ± 0.205 mg/kg) and 10% to 60% (0.184 ± 0.006 mg/kg and 0.687 ± 0.081 mg/kg), respectively. The transfer factor (TF) values for Cd, Cr, Cu and Se for crops varied among locations. The daily intake of metals was not high except for Cd consumption by a child through *zea mays* (0.402 mg/kg/day) and 0.299 mg/kg/day in *Amarathus Hybridus*. The hazard quotients (HQ) of all the metals were low except for Se. Results of the Principal Component Analysis (PCA) showed that there were strong relationship between Se, Cr and Cd in location A,B, C and D suggesting that Se, Cr and Cd were bounded to the biosolids. The ecological risks of Cu, Se and Cr were low but Cd posed high risk.

Key words: Bioavailability, Ecological risk, *Zea mays, Amaranthus spp*, Speciation, Cadmium.

INTRODUCTION

The emphasis on poultry farming as a means of employment and cheap protein sources has led to a monumental increase in the amount of poultry waste. As the logistic problem associated with the disposal of large quantity of these waste increases, land application of biosolids as fertilizers became an attractive solution[1]. Livestock and poultry manure can be an alternative source of fertilizer in organic farming, where the use of

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anthropogenic chemicals is prohibited[2,3]. However, several problems raised from applications of manure, including the salt toxicity of manure to plants and accumulation of trace metals in plants may pose a health risk when humans or livestock consume them[20]. The use of these biosolids can cause heavy metal accumulation in soils[4,5]. Antoniadis and alloway[5] studied soils that received heavy loads of biosolids and reported that the movement of heavy metals was significant down to the 0.8 m soil depth. Since heavy metals do not break down, they might affect the biosphere for a long time. Wang et al.[6] investigated heavy metal contamination in soils and plants at polluted sites in China, and reported the problems associated to the consumption of rice grown in paddy soils contaminated with Cd, Cr or Zn, because 22 to 24% of the total metal content in the rice biomass was concentrated in the grain.

Heavy metals can also contaminate the food chain and reduce crop yields.[9] The consumption of plants containing high levels of heavy metals might pose a serious risk to human health[7]. Total metal concentrations may indicate the overall level of metal in soils but such values makes available no clue regarding the chemical nature or potential mobility and bioavailability of the metal and its potential toxicity to living organisms[8]. Many sequential extraction protocols exist to evaluate both the actual and potential mobility of metals in the environment. Prominent among them is the five-step procedure of Tessier and co workers[9]. This extraction scheme allows the division of the total metal content into five fractions: exchangeable, carbonate bound, iron/manganese oxide bound, organic matter bound and residual fraction. Other speciation schemes include the European Community Standards, Measurement and Testing Programme., formerly BCR (Bureau Community of Reference)[10]; Maiz et al.[11] Short procedures; Geological Society of Canada (GCS) procedure and its modifications[12,13] and Galán et al. method[14] among others. Conceptually, sequential fractionation categorizes metals associated with chemically homogenous fractions that, ultimately, affect metal availability. Sequential extraction procedures have often been criticised due to lack of speficity of extractants and possible re-adsorption of metals during extraction, sequential fractionation can provide useful information to assess the fate of heavy metals in the environment[15,16].

Excessive accumulation of heavy metals in agricultural soil through biosolid application may not only result in soil contamination but also lead to elevated heavy metal uptake by crops, and thus affect food quality and safety. Hence, the risk of soil contamination by heavy metals must be considered when biosolid is applied especially from intensive farming.

This reported work was aimed to determine the total content; speciate them; assess their plants uptake and accumulation; asses their ecological risks and finally assess the health risk/hazard associated with consumption of the crops grown in the amended soils with respect to copper (Cu), chromium (Cr), cadmium (Cd) and selenium (Se).

EXPERIMENTAL

Materials and method

Equipments and chemicals

Analytical grade chemicals purchased from Sigma Aldrich were used throughout the study without further purification. To prepare all the reagents and calibration standards, double distilled water was used. The metal standards were prepared from stock solution of 1000 mgL^{-1} by successive dilutions. The glass wares were washed with dilute nitric acid followed by several times washing with distilled water. The equipments used are heating mantle, oven, Kjeldahl flask, beakers, pH meter (model), atomic absorption spectrophotometer (Varian AA240).

Area of study

The study was carried out on a one acre vegetable farmland cultivated with *Amarathus Hybridus* and *Zea Mays* located at Nsude-Ngwo Enugu state of Nigeria. It is located at an elevation of 456 meters above the sea level and its coordinates are 6^{o} 24" 0"N latitude and 7^{0} 24" 0"E longitude. The soils have been subjected to heavy application of biosoild from poultry farm for over twelve years. The soils in this area are mainly sandy loam.

Sample collection and treatment

The farmland was divided into four major locations designated A, B, C, and D from which ten soil sample points were created randomly to ensure that all parts of the land were duly represented. The soil samples were taken with a plastic shovel at a soil depth of 15 cm. A non- amended soil used for cultivation was sampled 5 kilometers away from the study area in the same manner as to the study soil to serve as the control. This is designated as sample E. *Amarathus Hybridus* and *zea mays* samples were collected from different parts of the farmland from which the soils were taken. The total of 50 soil samples (i.e. 10 samples from each location)

The soils and the plant samples were brought back to the laboratory in polythene bags. The soil samples were dried, crushed with porcelain mortar and pestle and passed through 2 mm mesh size sieve. Composite samples of the soils were obtained for each of the five study stations by conning and quartering. The latter were stored in an air tight plastic container prior to digestion. The inedible parts of the plant samples were removed and the samples washed with deionized water, air dried and then oven dried at 105°C for 60 mins. The latter were crushed, grinded and stored at 4°C prior to analysis.

Soil characterization

The soil was analyzed for pH, particle size distribution, moisture content and total organic carbon. All the procedures were carried out in line with those described by Allison[17] and the cation exchange capacity (CEC) was determined using the procedure reported by Ibitoye[18].

Determination of total metal content in the soil samples

The determination of the total heavy metals in soils proposed by Ure[19] was adopted. 1 g of each dried soil finely ground, was moistened with deionized water and heated in a 100 mL Teflon beaker with 10 mL conc. HNO_3 and evaporated to small volume. Then 5 mL conc. HNO_3, 5 mL 70% $HClO_4$ and 10 mL conc. HF were added and the whole content heated to perchlorate fumes. After 30 minutes fuming, 10 mL of HCl (1/1, v/v) is added and the mixture boiled for 10 min; cooled and diluted to 100 mL with deionised water. The supernatant was analysed in triplicate with Varian AA240 Atomic absorption spectrophotometer.

For purposes of quality assurance, the limit of detection (LOD) and limit of quantitation (LOQ) of the analytical method were estimated by analyzing three replicate blank solutions and through the following equations:

$$\mathrm{LOD} = \mathrm{Xb} + 3\mathrm{Sb}$$

$$\mathrm{LOQ} = \mathrm{Xb} + 10\mathrm{Sb}$$

where Xb and Sb were mean value and standard deviation of the blank determinations, respectively. Furthermore, the Atomic Absorption Spectrophotometer (AAS) was calibrated before the absorbance readings for each metal were taken. When each metal characteristic wavelength of absorption was selected, distilled water was used to zero the instrument. This was followed by aspirating the serially diluted standard solution in turn at the resonance wavelength from the hollow cathode lamp of the desired metal. Calibration curve for each metal was prepared by plotting the absorbance of standards versus their concentration.

Sequential metal extraction from the soil samples

The speciation of heavy metals in the soil samples were determined through sequential extraction and quantification following five steps modified Tessier protocol[9] outlined below.

Exchangeable phase

1 g of soil was extracted at room temperature for 1 h with 8 mL of $MgCl_2$ solution (1 M $MgCl_2$ pH 7.0) with continuous agitation. The supernatant was kept for analysis while the residue retained for further use.

Bound to carbonate phase

The residue from step 1 was leached at room temperature with 8 mL of 1 M CH_3COONa adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained for 2 h to allow complete extraction. The supernatant was stored for analysis.

Bound to Fe – Mn oxide

The residue from step 2 was extracted with 20 mL of 0.04 M $NH_4OH.HCl$ in 25% acetic acid. The experiment was performed at 96^oC with occasional agitation for 2 h to permit complete dissolution of the free iron oxide. The supernatant was stored.

Bound to organic matter

The residue from step 3 was added 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 and heated to 85^oC for 2 h with occasional agitation. A second 3 mL aliquot HNO_3 and 5 mL of 30% H_2O_2 (pH 2.0 with HNO_3) was added and the sample heated again to 85 = C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M CH_3COONH_4 in 20% HNO_3 was added and the sample was diluted to 20 mL and agitation continuously for 30 mins.

Bound to residual

The residue from step 4 was added 2 mL of concentrated HCl, 6 mL of concentrated HNO_3 and 3 mL of 30% H_2O_2. The mixture was digested on a hotplate in a fume cupboard until almost dry. 3 mL concentrated HNO_3, 10 mL $HClO_4$ and 3 mL 30% H_2O_2 were added. The resulting mixture was digested on hotplate until almost dry. Another 1 mL concentrated HNO_3, 3 mL $HClO_4$ and 1 mL 30% H_2O_2 was added. 20 mL deionized water was added also and the mixture heated until about 15 mL volume. The later mixture was diluted with 25 mL deionized water and centrifuged at 2500 rpm for 20 min. The supernatant was stored for analysis.

The five supernatant from the five steps were analyzed in triplicate with Varian AA240 Atomic Absorption Spectrophotometer.

Plant digestion

1g of each dried plant sample (*Amarathus Hybridus and Zea Mays*) was 5 mL of HNO_3 and 5 mL H_2O_2 and heated for 1 hr at a temperature of 85°C. The mixture was filtered and the supernatant stored for analysis [20].

Data analysis and evaluation

Statistical methods were applied to analyze the data in term of its distribution and correlation among the studied parameters. SPSS software (version 17) for windows was used for statistical analyses of the data. Basic statistical parameters such as mean and standard deviation were computed along with correlation analysis, while multivariate statistics in term of Principal Component Analysis (PCA) was also carried out.

Transfer factor

The plant concentration factor (PCF) was calculated as follow:

$$PCF = C_{plant}/C_{soil} \qquad \ldots(1)$$

where C_{plant} and C_{soil} were the heavy metal concentration plant and soil on dry weight basis respectively.

Oral intake of metal from soil through vegetable

Daily intake of metals (DIM) was calculated using the equation:

$$\text{Daily Intake of Metal (DIM)} = C_{metal} \times C_{factor} \times D_{food\ intake}/B_{average\ weight} \qquad \ldots(2)$$

where C_{metal} is the heavy metal concentration in plant (mg/Kg), C_{factor} is the conversion factor (0.085), D_{food} intake is the daily intake of vegetable, $B_{average\ weight}$ is the average body weight. The conversion factor 0.085 was used to convert fresh green vegetable weight to dry weight, as described by Rattan et al.[21] The average daily vegetable intakes was got through oral interview among the consumers and was considered to be 300 g/day, while the average adult and child body weights were considered to be 70 kg and 16 kg, respectively[22,23].

Health risk index of metal contamination of vegetable

Potential risk to human health by the intake of metal contaminated vegetable are characterized using a Hazard Quotient (HQ)[24]. If the ratio of DIM to R_fD (HQ) < 1 it means the exposed population is assumed to be safe and $1<HQ<5$ means that the exposed population is in a level of concern interval[25]. It must be noted that HQ is not a measure of risk but indicates a level of concern.

$$HQ = DIM/R_fD \qquad \ldots(3)$$

Ecological risk assessment

The potential ecological risk index method by Hakanson[26] was used to estimate the risk and calculated thus:

$$C^1{}_f = C^1{}_{si} / C^1{}_n \qquad \ldots(4)$$

where $C^1{}_f$ is the concentration coefficient of a particular heavy metal. $C^1{}_{si}$ is the measured data of soil heavy metal, $C^1{}_n$ is the reference value. In this study, the soil environmental quality standard was used as the reference value, which proposed Cd, Cr, Cu and Se to have 0.6, 250,100 and 120, respectively[27].

The comprehensive contamination measure is given as

$$C_m = \sum C^1{}_f \qquad \ldots(5)$$

C_m is the summation of $C^1{}_f$

The potential ecological risk index ($E^1{}_r$) of a particular heavy metal

$$E^1{}_r = T^1{}_r \,.\, C^1{}_f \qquad \ldots(6)$$

where $T^1{}_r$ is the toxic response factor.

The toxic response factor using the “elements abundance principle” and the “elements release principle” of Hakanson et al.[26] was adopted. According to the standardized toxic response factor proposed by Hakanson et al., Cd, Hg, As, Pb, Cr, Se, Cu, Zn, and Ni have toxic response factors of 30, 40, 10, 5, 2, 60, 5, 1, and 5, respectively.

The ecological risk index (RI) is given as:

$$RI = \sum E^1{}_r \qquad \ldots(7)$$

These indices (C^1_f, C_d, E^1_r and RI) were interpreted in line with earlier relevant studies[27-29] as shown in Table 1.

Table 1: Physiochemical properties of soils at different locations

Parameter / Location	pH (H_2O)	pH (KCl)	OM%	Moisture content %	CEC (cmol/kg)
A	5.7	4.8	25.19	2.10	6.00
B	5.6	5.1	23.20	3.70	5.85
C	5.7	5.3	33.00	2.30	4.19
D	5.9	5.0	31.17	2.15	7.11
E*	6.0	5.8	3.84	1.90	7.06

E* = Control soil; OM = Organic matter; CEC = Cation exchange capacity

RESULTS AND DISCUSSION

The result of the physiochemical characteristics of the soils were presented in Table 2 while Tables 3 to 7 present the fractions of metals in soil following the sequential extraction. It also presents the results of transfer factor, ecological risk and potential health of the metals, respectively.

Table 2: Heavy metals in fractions of soils in Location A

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
A	Exchangeable	Range	0.19-0.24	4.30-5.02	0.89-1.10
		m ± sd	0.22±0.03	4.57±0.04	1.02±0.01
	Carbonate	Range	0.13-0.29	4.25-0.490	0.80-1.20
		m ± sd	0.21±0.08	4.48±0.04	1.05±0.02
	Fe/Mn Oxide	Range	0.19-0.22	3.99-0.510	0.90-1.09
		m±sd	0.20±0.02	4.42±0.06	0.97±0.01
	Organic Matter	Range	0.18-0.24	4.25-04.95	0.87-1.13
		m±sd	0.21±0.03	4.52±0.04	1.04±0.02

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Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
	Residual	Range	0.17-0.21	4.19-0.498	0.79-1.10
		m±sd	0.19±0.02	4. 47±0.05	0.97±0.02
	Sum of all	Range	0.92- 1.12	21.18- 24.95	0.43- 0.56
	Fractions	m±sd	1.03± .01	22.46± 0.22	0.51± 0.08
	Total metal	Range	1.00-1.20	21.52-25.10	4.48-5.54
	in soil	m±sd	1.10±0.01	22.86±0.20	5.15±0.06
	% Recovery		94	98	98
	Bioavailability		0.43	0.40	0.41
	Mobility factor		43	40	41

Table 3: Heavy metals in fractions of soils in Location B

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B	Exchangeable	Range	0.13-0.17	5.90-7.74	0.78-0.97
		m±sd	0.15±0.02	6.65±0.10	0.09±0.09
	Carbonate	Range	0.12-0.17	6.00-7.60	0.07-0.08
		m±sd	0.14±0.02	6.87±0.08	0.08±0.06
	Fe/ Mn	Range	0.10-0.16	5.50-7.49	0.08-0.09
	Oxide	m±sd	0.13±0.03	6.49±0.10	0.08±0.01
	Organic	Range	0.12-0.17	6.61-7.59	0.077-0.10
	Matter	m±sd	0.14±0.03	7.08±0.06	0.09±0.01
	Residual	Range	0.11-0.16	5.40-7.76	0.07-0.10
		m±sd	0.13±0.03	6.32±0.13	0.08±0.02
	Sum of all	Range	0.62-0.82	2.98-3.82	0.38-0.46
	Fractions	m±sd	0.69±0.11	3.34±0.43	0.41±0.04
	Total metal	Range	0.63-0.82	31.50-38.72	0.39-0.49
	in soil	m±sd	0.71±0.10	35.07±0.36	0.44±0.05
	% Recovery		97	95	94
	Bioavailability		0.42	0.40	0.40
	Mobility factor		42	40	40

Table 4: Heavy metals in fractions of soils in Location C

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
C	Exchangeable	Range	0.15-0.20	5.0-5.78	0.39-0.60
		m±sd	0.17±0.02	5.43±0.04	0.46±0.01
	Carbonate	Range	0.15-0.20	4.50-5.69	0.36-0.47
		m±sd	0.17±0.03	5.19±0.06	0.43±0.01
	Fe/ Mn	Range	0.15-0.21	3.80-5.77	0.38-0.61
	Oxide	m±sd	0.17±0.03	5.04±0.11	0.49±0.01
	Organic	Range	0.150-0.18	4.95-5.00	0.29-0.53
	Matter	m±sd	0.17±0.02	4.98±0.01	0.40±0.01
	Residual	Range	0.15-0.19	3.90-5.60	0.29-0.55
		m±sd	0.17±0.01	4.84±0.08	0.43±0.01
	Sum of all	Range	0.75-0.96	22.20- 27.24	1.71- 2.74
	Fractions	m±sd	0.83±0.11	25.49±0.29	2.22±0.05
	Total metal	Range	0.77-1.00	25.00-28.90	1.98-3.00
	in soil	m±sd	0.86±0.12	27.18±0.28	2.45±0.05
	% Recovery		97	94	91
	Bioavailability		0.41	0.40	0.40
	Mobility factor		41	40	40

Table 5: Heavy metals in fractions of soils in Location D

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
D	Exchangeable	Range	0.23-0.27	5.00-7.91	0.42-0.56
		m±sd	0.25±0.01	6.59±0.148	0.48±0.01
	Carbonate	Range	0.21-0.25	4.50-7.61	0.44-0.57
		m±sd	0.23±0.02	6.17±0.15	0.49±0.007
	Fe/ Mn	Range	0.18-0.24	3.80-8.00	0.39-0.60
	Oxide	m±sd	0.21±0.02	6.17±0.21	0.46±0.012
	Organic	Range	0.20-0.25	5.00-7.90	0.39-0.65
	Matter	m±sd	0.22±0.02	6.60±0.14	0.48±0.014

Cont…

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
	Residual	Range	0.17-0.23	3.90-6.97	0.37-0.57
		m±sd	0.21±0.03	5.92±0.18	0.44±0.01
	Sum of all Fractions	Range	1.07- 1.17	25.80- 38.39	2.04- 2.95
		m±sd	1.10±0.05	32.65±0.05	2.35±0.05
	Total metal in soil	Range	1.22-1.25	29.50-39.59	2.10-2.80
		m±sd	2.00±0.06	34.49±0.505	2.37±0.037
	% Recovery		90	95	99
	Bioavailability		0.43	0.39	0.41
	Mobility factor		43	39	41

Table 6: Heavy metals in fractions of soils in Location E

Loc.	Fraction		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
E*	Exchangeable	Range	0.01-0.03	0.19-0.20	0.02-0.03
		m±sd	0.02±0.01	0.19±0.01	0.03±0.01
	Carbonate	Range	0.01-0.02	0.18-0.19	0.03-0.05
		m±sd	0.02±0.01	0.18±0.01	0.04±0.01
	Fe/ Mn Oxide	Range	0.01-0.03	0.17-0.18	0.03-0.04
		m±sd	0.02±0.01	0.18±0.01	0.03±0.01
	Organic Matter	Range	0.01-0.03	0.17-0.18	0.02-0.04
		m±sd	0.02±0.01	0.17±0.01	0.03±0.01
	Residual	Range	0.01-0.03	0.16-0.18	0.02-0.03
		m±sd	0.02±0.01	0.17±0.010	0.03±0.01
	Sum of all Fractions	Range	0.08- 0.10	0.87- 0.93	0.14- 0.16
		m±sd	0.09 ±0.03	0.89 ±0.03	0.15 ±0.01
	Total metal in soil	Range	0.09-0.11	0.91-0.95	0.16-0.17
		m±sd	0.10±0.01	0.92±0.02	0.164±0.01`
	% Recovery		93	97	92
	Bioavailability		0.35	0.42	0.41
	Mobility factor		35	42	41

E* = Control soil

Table 7: Ecological risk factor and potential ecological risk index of the heavy metals

Metal	C^1f	E^1r
Cadmium	1.535 (light contamination)	46.050 (moderate contamination)
Chromium	0.011 (non- contaminated)	0.022 (low contamination)
Copper	0.004 (non-contaminated)	0.020 (low contamination)
	Cd = 4.636 (low contamination)	RI = 46.042 (low contamination)

C^1f = comprehensive contamination measure; Cd = comprehensive contamination measure; E^1r = potential ecological risk index; RI = ecological risk index

The values of soil pH in the locations ranged from 5.7-5.9 in H_2O and 4.8-5.3 in KCl, which suggest that the soils are moderately acidic. Location C was observed to have the highest organic matter (33%) while location E has the least (3.84%). The cation exchange capacity (CEC) of a soil depends upon its organic matter content among other factors. The CEC in the soils studied ranged from 4.19 to 7.11 meq/100g. The organic matter present in control soil (location E) was low (3.84%) suggesting the absence of biosolid in the soil. However, the pH of the control soil was within the normal soil pH that favours plant growth.

The fraction of metals in soil following the sequential extraction indicated that the exchangeable and bound to carbonate species are called the bio-available as they exhibit mobility relative to the environment and are potentially available for plants. Result showed that the amount of Cu and Cd in the bioavailable form was low. The bioavailable Cu ranges between 3% -10% in location A-E. It is mostly bounded to carbonate in location A (0.105±0.022). Se and Cr in the bioavailable forms range between 40% to 60% and 10% to 60% respectively. However, mean concentration of Se was higher in the exchangeable phase of location D (2.257 ± 0.205).

The fraction of Cd, Cr, and Se associated with oxide was much higher in the soil location D with the levels 0.205 ± 0.028, 0.617 ± 0.215, and 2.229 ± 0.213 mg/Kg, respectively. High amount of Cr (up to 47%) in location B (0.708 ± 0.049) and Se (up to 50%) in location C are bound to organic matter.

Cd, Cr, Cu and Se were present in the residual fraction in all the locations (A-E). The proportion of Se in the residual form is much higher than the other element with location D having the highest level (2.005 ± 0.026). Cu level was found to be the lowest in location B (0.077 ± 0.015).

The concentrations of these metals fractionated from the control soil (location E) were below the level found in the studied soil (A-D). This suggested the absence of biosolids in this soil. The overall sequence of occurrence of these metal in all the locations and fractions of the soils are –

$$Cd < Cu < Cr < Se$$

The transfer factor (TF) values for Cd, Cr, Cu and Se for various crops varied among locations. From the table, a high TF values were obtained for *zea mays* with Cd (0.609) in location A and Se (0.731) in location B while for *Amarathus Hybridus* are Cu (0.784) in location C and Cd (0.736) in location A. The TF for Cu is quite high in *zea mays* (1.278) at location D as this crop is widely consumed by human, through these plant toxic elements can be transferred to human body creating disruption in various biological systems. The lowest TF value was obtained for Cr in *Amarathus Hybridus* (0.008) at location B. It showed the approximate daily intake of metal (DIM) for a 16 kg child and and a 70 kg adult from *zea mays* (corn) and *Amarathus Hybridus* (green vegetable). It was however seen that intake of Cr, Cu and Se were within the permissible limit recommended by USEPA[24] except the daily intake of Cd by a child through *Zea mays* (0.402 mg/kg/day) and *Amarathus hybridus* (0.299 mg/kg/day). The Hazard Quotient (HQ) value for all the metals tested for a child and an adult were below 1 ($HQ < 1$), which was considered safe except for Se. The sequence of HQ for the elements followed the decreasing order for *zea mays*: Se > Cr > Cd > Cu and *Amarathus Hybridus* Se > Cd > Cr > Cu for adult and child.

The result of the analysis of variance of the total metal in soil (TMS), total metal in corn- *zea mays* (TMC) and total metal in vegetable- *Amarathus Hybridus* (TMV) studied in all the locations at 95% probability level ($p < 0.05$) indicated significant differences between the group of Cd in *zea mays* [$F_{3,8} = 1.426$, $p < 0.05$] and the group of Cu in *zea mays* [$F_{3,8} = 0.623$, $p < 0.05$]. This suggested different sources of contamination and rate of input. However the concentration of Se and Cr found in the crops and soils of the different location were not significantly different; suggesting the same source of contamination and rate of input.

Principal Component Analysis (PCA), which was adopted to characterize the distribution of heavy metal in the soils revealed that there were strong relationship between Se, Cr and Cd in location A, B, C and D. This indicates that Se, Cr, and Cd were bound to biosolid whereas the presence of Cu was controlled by natural sources. There were no such association among the metal found in the control soil (location E) suggesting variability in the source of contamination.

The estimated potential ecological risk index of the heavy metals in the soils showed that the risk coefficients of Cd in the soil sample indicated slight contamination while the comprehensive contamination was low. The potential risk index of Cd in the soil was moderately strong while the overall ecological risk index of the four metals was 49.752, which indicated moderate risk. The risk coefficient of Cu, Se, and Cr at the locations were all low, indicating that these heavy metals pose a limited environmental impact on the soil.

CONCLUSION

The assessment of heavy metal levels in the various soil locations indicated that these soils are contaminated with these metals. Evidence of contamination of these soils by Cd, Cr, Cu, and Se were obvious when compared to the control sites, with Se and Cr presenting the highest concentration as shown by the following order of abundance Se > Cr > Cu > Cd. Plants are known to take-up and accumulate metals from contaminated soil and the TF value of Se and Cr found in the crop samples were low (less than 1). The daily intakes of the metals (DIM) were not high except for the intake of Cd by a child through *zea mays* and *Amarathus hybridus* consumption. This calls for concern as long term intake of cadmium accumulates in the kidneys and bones where it causes serious damage, and is probably best known for its association with itai-itai diseases[23]. Also the Hazard Quotient (HQ) value for all the metal tested for a child and an adult were below 1, which is considered safe except for Se.

The ecological risk coefficient of Cu, Se and Cr at the locations were all low, suggesting that these heavy metals pose a limited environmental impact on the soil amended with poultry biosolid.

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