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Comparative Assessment of Sweet (*Zeamays Convar.Saccarata*) and Dent Maize (*Zeamays*) for Phytoremediation of Chromium and Nickel Polluted Agricultural Soils

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Abstract: The consequential effects of heavy metal consumption by man suggest the need for plant assessment for bio-concentration and translocation potentials. This study aimed at comparing the potential of dent maize with sweet maize for phytoremediation of Chromium (Cr) and Nickel (Ni) contaminated soils. Soil samples were taken randomly to a depth of 20 cm. Out of the samples taken; about 500 g of the samples were homogenized, dried, sieved, and used for the determination of soil physicochemical properties. The remaining soil samples were used to fill the polythene bags for the plant growth. The experimental design used was 2^2 by 2 general factorial design consisting of 4 treatments (1 g/dm^3 of Ni $(NO_3)_2.6H_2O$; 3 g/dm^3 of Ni $(NO_3)_2.6H_2O$; 1 g/dm^3 of Cr $(NO_3)_2.9H_2O$ and 3 g/dm^3 of Cr $(NO_3)_2.9H_2O$), 2 replicates of each and the control. The setup was made for each of the maize types. Three seeds of maize were planted on each of the soil samples at a depth of 4 cm and the setup was properly monitored. Soil samples were analyzed at day 1 and every 14 days interval in a period of 70 days after planting (DAP). The result of the initial analysis of the soil samples indicates that the control soil sample contained 0.17$\pm$0.002 mg/kg of Cr and 0.03$\pm$0.001 mg/kg of Ni for soil seeded with both the dent and sweet maize. The mean concentration of Cr and Ni from the soil samples taken from soil contaminated with 1g treatment were 1.24$\pm$0.001 mg/kg and 1.43$\pm$0.002 mg/kg respectively, while that contaminated with 3g treatment has 3.98$\pm$0.02 mg/kg of Cr and 2.96$\pm$0.02 mg/kg of Ni. The results also show a reduction in the heavy metal concentrations of the soil through the 70 days of planting. The Cr and Ni contents of the two maize types increase with the increase in the amount of metals (3 g > 1 g> control) in the soils in which they were seeded. Though, the two types of maize are good phytoplant, sweet maize is more active in Cr removal than dent maize. The two maize types are better in bioaccumulation than in translocation. The growth of the plants was not retarded by the presence of the metal which shows their tolerance and effectiveness in remediating Cr and Ni contaminated soil. The use of this technology will help in attaining sustainable development goals as it addresses the problem of environmental degradation while the subsistence agriculture will be promoted and hence poverty will also be alleviated or eradicated.

Keywords: Chromium, Nickel, Phytoremediation, Heavy metals, Maize, Soil, Nigeria.

1. Introduction

Contamination of agricultural soil within the urban area by pollutants is of great concern due to its hazardous health effects on the biotic and abiotic components of the ecosystem [1]. This Contamination often results from improper chemical handling during production, transportation, storage, usage, or disposal processes [2]. Though, contaminants of diverse nature are being introduced into the environment, heavy metal are receiving particular attention due to their persistence in building up in ecosystem, and ultimately finding their way into the human body primarily through the food chain [3]. While the existence of these metals could be from a natural source, anthropogenic sources such as effluent from oil industries, sewage sludge, metal mining and smelting, electroplating, fossil fuel burning, pesticide application, and use of phosphate fertilizers in agriculture aggravate their occurrence [4][5][6][7].

A number of these metals have been mentioned in different literature with their potential danger to man and his environment, chromium (Cr) and nickel (Ni) made some of the lists [2][8]. The anthropogenic sources of Cr include tanneries, fly ash and steel industries, while the sources of Ni are industrial effluents, surgical instruments, kitchen appliances, automobile batteries, and steel alloys [9]. However, the widespread of Ni in the environment is due to its presence in about a hundred minerals used for industrial and commercial purposes. Ni is considered the most commonly occurring contact allergy and has a correlation with chromium (Cr) and thus people who have developed a Cr allergy tend to be oversensitive to Ni [10]. At high concentrations, while Ni has been noted for its ability to significantly reduce the emergence of some crop's seedlings, damages of skin and mucus membranes of humans are often noted for increased uptake of Cr [11]. The bioavailability of the two metals in soil like any other heavy metals, as well as their absorption and accumulation by plants, depend on some abiotic (soil physicochemical parameters; such as pH, organic matter contents, soil texture, and clay contents) and biotic factors (plant properties; plant species, genotype, phenophase, plant part, and transpiration) [12][13].

Unlike organic pollutants, heavy metals are not biodegradable. However, they can be transformed from one oxidation state or organic complex to another, which thus allows for their bioaccumulation in the plant [14]. According to [2] about 450 plants that range from annual herbs to perennial shrubs and trees (e.g., pennycress, tobacco, maize, sunflower, mustard, brake fern, python tree, rattle bush, willow) have been identified as hyperaccumulator due to their ability to detoxify extremely high levels of metal ions, such as Zn, Co, Pb, Ni, Cd and Mn in their above-ground tissues. Some researchers have argued that the use of edible crops for heavy metal removal would not make phytoremediation a safe technology [15]. However, a review of literature showed that edible crops are the most reported for phytoremediation purposes [16]. This suggests that there is no need to shy away from reality. Most of the crops planted on polluted soil within the urban area are mostly edible; hence, there is a need to assess such crops for the associated health risk of consuming them. Secondly, some of the crops, for instance, maize may not survive if the pollutant load is beyond their tolerant limit. Their survival implies that they could be a phytoplant for the site and most of the metals would not be stored in the edible parts as apparent from the early studies. [11] asserted that at high concentration, Ni has been noted for its ability to significantly reduce the emergence of maize and rice seedlings. Hence, to ensure general acceptance of the technology, the advocacy should be in support of the usage of edible crops and the evaluation of the potential health risk associated with their usage.

The ability of maize to extract and transfer metals from contaminated soils through the roots to shoots has been documented in the literature [17]. The potential use of this crop for phytoremediation has been advocated particularly for developing nations with insufficient funds for environmental remediation [18]. The advantages accrue to the usage of maize for this technology includes its effectiveness in contaminant reduction, low-cost, and its applicability for a wide range of contaminants [18]. More so, grain crops accumulate less heavy metal in their edible parts compare to leafy vegetables **[**19**]**. Even among the grain crops, some are better phytoplants than others. [13] assessed five grain crops for phytoremediation of six heavy metals and concluded that the lowest translocation of the metals into the grains was observed in maize. This suggests that maize is a better biomaterial for remediation as the edible part is least contaminated. According to [18], about 50 species of maize exist and they consist of different colours, textures, grain shapes and sizes. However, they have been broadly classified into six types (flint, flour, dent, pop, sweet and waxy) based on their kernels. In this study, only two types will be considered. Thus, this study aims at comparing the potential of sweet maize with dent maize for phytoremediation of agricultural soil contaminated with Chromium (Cr) and Nickel (Ni).

2. Materials and Methods

2.1 Study Area

The study was carried out at the Farm garden of the Department of Crop Production, Federal University of Technology Minna, Nigeria. Minna lies on latitude 09°36′21.55″N - 09°36′21.55″N and longitude 06°32′E - 06°32′3.54″E. The city is characterized by wet and dry seasons. While the dry season is between November and March, the rainy season is from April to October. Majority of the dweller of the area are farmers and the most cultivated crops include maize, guinea maize, yam, millet, soybean and groundnut [20].

2.2 **Materials**

Two varieties of maize; yellow sweet maize (*Zea mays var saccharata*) and white dent maize (*Zea mays indentata*) were obtained from the Crop Production Department, Federal University of Technology, Minna. Both Cr and Ni used were artificially introduced into the soil by adding chromic nitrate [Cr $(NO_3)_2.9H_2O$] and Nickel (II) nitrate hexahydrate [Ni $(NO_3)_2.6H_2O$] respectively.

2.3 Soil sampling and analysis

Using soil auger, soil samples were taken to a depth of 20 cm within the study area. The samples were used to fill polyethylene bags. Some 500 g of the sample was air-dried, after which they were crushed and sieved using 0. 25 mm sieve mesh to obtain a fine particle. Thereafter, the fine particles were digested and used for the determining the soil physicochemical properties using the standard p rocedure as reported in [21].

2.4 Treatments and Experimental Design

Three seeds of each of the sweet and dent varieties of maize were sown at a depth of 5 cm in polythene bags containing 3 kg of the soil. The experimental design used was 2^2 by 2 general factorial design consisting of 4 treatments (1 g/dm^3 of Ni $(NO_3)_2.6H_2O$; 3 g/dm^3 of Ni $(NO_3)_2.6H_2O$; 1 g/dm^3 of Cr $(NO_3)_2.9H_2O$ and 3 g/dm^3 of Cr $(NO_3)_2.9H_2O$), 2 replicates of each and the control. The setup was made for each of the maize types. Of the polythene bags, three bags were contaminated with 1 g/dm^3 concentration of nickel and another three with 3.5 g/dm^3. The same levels of concentration (1 g/dm^3 and 3 g/dm^3) were made for chromium and another three polythene bags without nickel and chromium were also used for the control (Plate 1). The setup was made for each of the maize types and the crops were irrigated every 2-3 days for seventy days. Analysis of the control and contaminated soil samples were done before planting the seeds. Subsequent to the planting of the seed, samples were also taken and analyzed to determine the amount of heavy metal in the soils at two weeks intervals for duration of ten weeks. At the expiration of the 70th day, the plants were uprooted after the soil samples had been taken, and the root, stem and leaves were also assessed for the heavy metal content.

(a) Sweet maize

(b) Dent maize

Plate 1: Experimental set up

2.5 Plant sample collection and analysis

The plant samples (leaves stem and root) were digested using the approach mentioned in [21]. To remove the dirt and soil particles, the samples were washed and rinsed with distilled water. Thereafter, the samples were oven-dried to a constant weight and ground to powdery form. Some 0.5 g of the sample was weighed into a 50 ml beaker and same quantity of concentrated nitric acid was added. The beaker was heated to a small volume on a hot plate in a fume cupboard. Some 0.5 g of concentrated Perchloric acid was also added and heated again for few minutes. Thereafter, 15.0 ml of deionised water was added and allowed to cool to room temperature. The mixture was then poured into a 100 ml volumetric flask and made up to the mark with deionised water. These solutions were then kept in a storage container and later used for the analysis. Atomic absorption spectrometer (AAS) was used to determine Cr and Ni contents of the samples (soil and the plant parts).

2.6 Data Analysis

To compare the potential of each of the maize types for phytoremediation, the Bioconcentration factor (BCF) and Translocation factor (TF) were estimated. BCF was used in determining the ability of the plant to accumulate heavy metal in the roots and it is computed as the ratio of the content of heavy metal in the roots to the metal in the soil as shown in equation 1 [22]. On the other hand, the Translocation factor (TF) was used to estimate the ability of plant to translocate metals from the roots to above-ground parts and calculated as the ratio of metal concentration in the shoots to that in the roots as shown in equation 2 [22]. Plants that have BCF values of greater than 1 are considered suitable for phytoextraction [23].

$$BCF = \frac{M_{rt}}{M_{sl}} \quad (1)$$

$$TP = \frac{M_{st}}{M_{rt}} \quad (2)$$

Where: M_{rt} is the heavy metal concentration in the roots; M_{sl} is the heavy metal concentration in the soil and M_{st} is the heavy metal concentration in the shoots.

The descriptive analysis of data obtained was carried out using Microsoft Excel 2010. The student's t-test was used to test the significant differences between the two maize types.

3. Results and Discussion

The properties and characteristics of soil may have effects on the heavy metal availability in soil and also on its uptake and translocation by plants [24]. Generally, the study area has a soil sample that is well-drained with a high water infiltration rate. Table 1 shows the physicochemical properties of the soil. Considering the mean values for the particle distribution (9% of silt, 17% of clay and 74% of sand) the soil can be better categorized as sandy loam, though, the soil textural classification ranges from sandy loam to loamy. This is in agreement with the report of [21]. Soil texture plays a significant role in biomass yield and heavy metal uptake of maize [25]. Other physicochemical properties of the soil are also shown in Table 1. The results of the physicochemical parameters further indicate good and healthy status of the soil for agricultural purposes and for low transport of the metals from the soil solution to the plant [21]. For instance pH of 6.8 suggests that the soil is stable and low heavy metal will be absorbed by the plant while some of the metal will be leached due to the presence of a considerable amount (13 g/Kg)) of the organic carbon. The overall combination of soil physicochemical properties influences both the rate and extent of metal uptake [18].

The mean values of the Cr and Ni in the control and contaminated soil samples are as shown in Table 2. At the initial stage, the mean values for the two metal in the control soil sample (Cr = 0.17 mg/kg; Ni = 0.03 mg/kg), as expected are lesser than that of T1 (Cr =1.24 mg/kg; Ni=1.43 mg/kg) and T2 (Cr=3.98 mg/kg; Ni=2.96 mg/kg). It is worth noting that even after contamination, the mean values of all the samples are still within WHO permissible limit for soil (Cr = 100mg/kg; Ni = 35mg/kg) [26]. Table 3 shows the result of the Cr and Ni in the soil samples of the two maize types at the end of the 14^{th}, 28^{th}, 42^{nd}, 56^{th}, and 70^{th} days after planting (DAP).

At the end of the 14^{th} day, the amount of Cr in the uncontaminated soil (i.e. the control) for the dent and sweet maize are 0.13 mg/kg and 0.12 mg/kg respectively while the respective values of Ni for dent and sweet are 0.022 mg/kg and 0.04 mg/kg. The mean values of Cr and Ni in the T1 soil samples are 1.08 mg/kg and 1.21 mg/kg for dent maize and 1.03 mg/kg and 1.19 mg/kg for sweet maize respectively. In the T2 soil samples, the mean values of Cr and Ni are 3.64 mg/kg and 2.21 mg/kg for dent maize and

3.59 mg/kg and 2.17 mg/kg for sweet respectively.

Table 1: Physicochemical parameters of soil in the study area

Parameters	Mean Value
Silt (%)	9
Clay (%)	17
Sand (%)	74
pH	6.8
Available Phosphorus (mg/kg)	21
Potassium (Cmol/Kg)	0.40
Total Nitrogen (%)	1.42
Ca^{2+} (Cmol/kg)	4.50
Mg^{2+} (Cmol/kg)	3.84
K^{+} (Cmol/kg)	0.40
Na^{+} (Cmol/kg)	0.76
Organic Carbon (g/kg)	13.0
Acidity (g/kg)	0.13

The results show a comparative reduction in the two metals in the control, T1 and T2 as compared to the initial soil samples. The results suggest the probable transport of the metals into the plant. The reduction seems to be more with an increase in the concentration levels. This is in line with the submission of [27] that mentioned that the solubility of metals in the soil is largely controlled not only by the pH, the cation exchange capacity, the oxidation state of the mineral components, and the organic carbon content but also by the amount of metal. The more the soluble metals, the more likely is the amount that will be absorbed by the plant. The reduction in heavy metals is comparatively higher in sweet maize.

At the end of the 28th day of planting, the concentration of Cr and Ni in the uncontaminated soil is 0.10 mg/kg and 0.017 mg/kg for dent maize and 0.08 mg/kg and 0.022 mg/kg for sweet maize respectively. These show a further reduction in the mean value of the two metals. The concentrations of Cr and Ni in the T1 and T2 soil samples also reduced when compared to the mean values of the 14th day of planting. The observed reduction in the Cr and Ni content of the soil samples continues to take downward trends with the increase in the number of days after planting. The least mean values were recorded on the 70th day of planting. The pattern of reduction between the two maize varieties was the same over the 70 days, as more reduction was noted in the soil samples seeded with sweet maize. This suggests more heavy metals had probably been absorbed by the sweet maize.

Maize is a high biomass producing crop and as such it has proved effective for heavy metal removal from soil through phytoextraction [8] [28] Herzig et al., 2014). Figure 2(a-d) shows the results of phytoextraction of the Cr and Ni by the Maize. The Cr contents in the root (0.03 mg/kg for dent and 0.05 mg/kg for sweet maize as shown in Figure 2a) and shoot (0.01 mg/kg for dent and sweet shown in Figure 2b) of the maize planted on the control soil were lower than the metal content in the root (1.9 mg/kg and 2.1 mg/kg for the dent and sweet respectively) and shoot (1.3 mg/kg and 1.6 mg/kg for the dent and sweet respectively) of those planted in T1 contaminated soil samples.

Table 2: Concentrations (mg/kg) of Cr and Ni in soil samples at week zero (initial stage)

Treatment	Maize type	Cr	Ni
Control	Dent and Sweet	0.17±0.002	0.03±0.001
1 g/dm^3	Dent and Sweet	1.24±0.001	1.43±0.002
3 g/dm^3	Dent and Sweet	3.98±0.02	2.96±0.002

Results are mean of replicates ± standard deviation

Table 3: Concentrations (mg/kg) of Cr and Ni in soil samples at 14th, 28th, 42nd, 56th and 70th days after planting (DAP)

Treatment	Maize type	14 DAP	28 DAP	42 DAP	56 DAP	70 DAP
Cr (control)	Dent	0.13±0.02	0.10±0.01	0.07±0.01	0.06±0.00	0.05±0.00
	Sweet	0.12±0.01	0.09±0.01	0.06±0.00	0.04±0.00	0.05±0.00
Ni (control)	Dent	0.022±0.00	0.017±0.00	0.013±0.00	0.009±0.00	0.005±0.00
	Sweet	0.04±0.00	0.022±0.00	0.008±0.00	0.007±0.00	0.004±0.00
Cr (1 g/dm^3)	Dent	1.08±0.02	0.87±0.02	0.62±0.01	0.46±0.02	0.34±0.01
	Sweet	1.03±0.02	0.89±0.01	0.61±0.00	0.42±0.01	0.33±0.00
Ni (1 g/dm^3)	Dent	1.21±0.01	1.09±0.01	0.86±0.01	0.66±0.00	0.33±0.00
	Sweet	1.19±0.01	1.04±0.00	0.87±0.01	0.62±0.00	0.35±0.00
Cr (3 g/dm^3)	Dent	3.64±0.02	2.96±0.01	2.28±0.01	1.74±0.01	1.16±0.01
	Sweet	3.59±0.02	2.93±0.01	2.23±0.01	1.67±0.01	1.09±0.01
Ni (3 g/dm^3)	Dent	2.21±0.02	1.89±0.01	1.54±0.01	1.09±0.01	0.78±0.00
	Sweet	2.17±0.02	1.82±0.01	1.51±0.01	1.11±0.00	0.72±0.00

Results are mean of replicates ± standard deviation

The values of the Cr content in the root and shoot of maize planted on control soils were also lower than the metal content in the root (2.7 mg/kg for the dent and 3.9 mg/kg for the sweet) and shoot (1.8 mg/kg for the dent and 2.4 mg/kg for the sweet) of maize planted on T2 soil samples. Similarly, relatively higher values of Ni were observed for T1 and T2 as compared to control (see Figure 2c and 2d). This is in line with the early findings that showed that the amount of heavy metal uptake by plants depends on the metal concentration in the soil [21] [27] [29]. The figure also shows that Cr and Ni are more accumulated in the roots as compared to the shoot. This agrees with the submission of early studies that heavy metals, particularly Cr and Ni are more accumulated at the root of maize [27], [30]. Irrespective of the concentration and plant part (i.e. the root and shoot), the Cr and Ni contents were found to be higher in sweet compared to the dent maize. The result of the t-test shows the total Cr accumulated by sweet is significantly higher ($p = 0.04$) than that accumulated by dent, while the difference was not significant ($p=0.09$) in the case of Ni accumulation. Table 4 shows the bioconcentration and translocation factors of Cr and Ni for the dent and sweet maize. Cr (3.96 for dent; 4.97 for sweet) had higher BCF as compare to Ni (3.01 for dent; 3.74 for sweet) and the values are higher in the sweet maize. However, the two metals have BCF of greater than 1 in the two maize types. This suggests that the two maize types have the potentials for bioaccumulation. This is in agreement with the early finding of [23] which reported Ni having BCF of greater than 1 for maize. Both the Cr and Ni had a TF of less than 1 for the two maize types (0.74 for dent; 0.75 for sweet). This is in disagreement with the findings of [23] which reported that only Ni out of seven metals (Zn, Cu, Fe, Mn, Ni, Cd and Pb) had a TF of above 1 (> 1) in the two maize varieties considered in their study. However, there is an agreement that maize varieties had a better ability to bio-accumulate metals from soil to the root than to translocate them from root to the shoot. Higher Cr and Ni accumulation in the root as compared to the shoot has also been reported in [27].

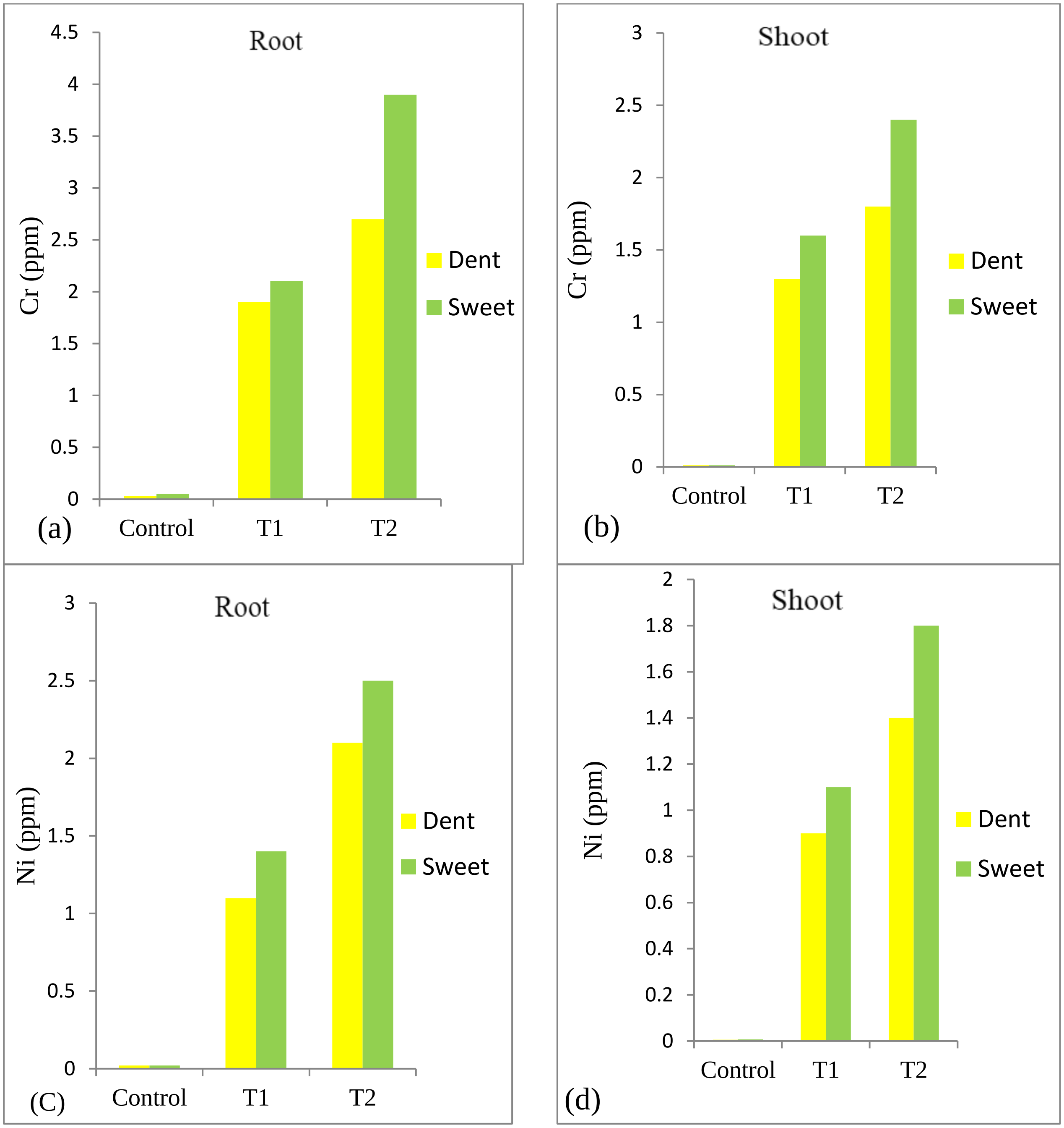

Figure 2: Concentration of Chromium and Nickel in the root and shoot of the maize

Table 4: Bio-concentration and translocation factors of Cr and Ni for the Dent and Sweet maize

Metal	Bioconcentration	
	Dent	Sweet
Cr	3.96	4.97
Ni	3.01	3.74

4. Conclusion

Indiscriminate use of contaminated land for sustenance crop practices could lead to consumption of crops having detrimental effects on human health. Hence, there is a need for the use of plants with higher accumulation at the nonedible parts for remediating the soil. This study shows that dent and sweet maize are good phytoplant, however, Cr accumulated by sweet maize is significantly higher than the dent. The two maize types are more active in bioaccumulation of the metals from soil to root than in translocation of the metals from root to the shoot of the maize plant. Therefore, either of the maize can be used in rotation with other edible plants with less bioaccumulation and high translation for effective remediation, and food security. However, there is a need for caution because the accumulation rate of the plant depends on the metal availability and soil properties. The study will help in attaining sustainable development goals as it addresses the problem of environmental degradation. Mores so, it promotes subsistence agriculture and hence play a vital role in alleviating or eradicating poverty.

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Conflict of Interest
There is no conflict of interest associated with this work.

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