Research Article

The Level of Heavy Metal Contamination in Selected Vegetables and Animal Feed Grasses Grown in Wastewater Irrigated Area, around Asmara, Eritrea

Goitom Kfle, Ghebray Asgedom, Tedros Goje, Felema Abbebe, Lula Habtom, and Hagos Hanes

1Department of Chemistry, College of Science, Eritrea Institute of Technology, Asmara, Eritrea
2SGS, Mineral Assay Laboratory, Bisha Mining Share Company, Asmara 4275, Eritrea

Correspondence should be addressed to Goitom Kfle; nebyat1997@gmail.com

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Soils irrigated with wastewater are by and large contaminated with heavy metals, and consumption of vegetables and animal feed grasses grown in contaminated soils have been a major food chain route for human exposure and pose a health hazard. A study was conducted in three sites to assess the accumulation of heavy metals in farms irrigated with wastewater between two and five decades in and around Asmara, Eritrea. The concentrations of metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, V, and Zn) in soils and plants (Medicago sativa L., Avena sativa L., Cynodon dactylon L., Corchorus olitorius L., and Cynara scholymus L.) grown in the farms were analyzed using an inductively coupled plasma optical emission spectrophotometer (ICP-OES). Multivariate analysis, such as principal component analysis (PCA) and cluster analysis (CA), was performed on the distribution of elements in plant species to identify the source of the heavy metals. The level of the metals in the soil samples was in the order of Mo < Cd < Co < Cu < Pb < V < Cr ≈ Zn < Mn < Fe < Al. The order of the metals in the plants of the different sites has been, in general, Cd < Co < V < Cr < Pb < Cu < Zn < Mn < Al < Fe. The study revealed that the soil samples of the studied sites were unsafe for agricultural purposes with respect to Fe, Mn, and Pb except for Pb in the case of the soil sample from the Kushet area. The levels of most of the studied heavy metals in the vegetation samples from all the sites were found within the FAO/WHO permissible limit. Al and Fe exceeded the FAO/WHO permissible limit with the exception of all plant samples from the Kushet area and M. sativa from Paradizo. The concentration of Al was also below the limit in C. dactylon from Adi-Segdo and Paradizo. Of the five vegetation considered in this study, C. olitorius was found to be a good accumulator and C. dactylon, the lowest accumulator of heavy metals. Based on the results of this study, the grass species C. olitorius should be further investigated for its phytoremediation capability of contaminated soils. The results of the multivariate analysis revealed that Fe, V, Al, Cr, Co, and Pb were controlled by mixed (natural and anthropogenic) sources and Zn, Mo, Cu, Mn, and Cd originated from the anthropogenic source. Very limited and inadequate studies were conducted on the accumulation of heavy metals in plants grown in wastewater irrigated farms around Asmara. Therefore, the results of this study are expected to shed light on the understanding of the community and enable the City Council to monitor the environmental quality and take appropriate actions.

1. Introduction

The use of wastewater for irrigating agricultural soil has been shown to be associated with a number of potential beneficial changes such as an increase in organic carbon, available nitrogen, phosphorus, potassium, and magnesium contents in the soil as compared to the clean ground water irrigated soil [1]. However, these effluents often contain various heavy metals, depending upon the anthropogenic activities from which they originate [2]. Wastewater also contains a range of components including dissolved and particulate organic matter, soluble organic and inorganic anions which can interact with heavy metals, thereby altering their mobility and subsequent bioavailability [3]. Heavy metals are
persistent as contaminants in the environment and are at the forefront of dangerous substances causing health hazards in humans. They are nonbiodegradable substances, and they accumulate in the environment up to a considerable extent. They can be biotransferred, bioaccumulated, and biomagnified in food chains and food webs [4]. Heavy metals can be classified into two categories: essential (biometals) and nonessential (or toxic metals). Essential metals (Co, Cr, Cu, Fe, Mn, V and Zn) can also produce toxic effects on organisms at high levels, while toxic metals (Cd, Pb, and Al) are toxic to human health and environment even at low concentrations. Exposures to toxic metals are associated with severe health problems with varying degrees of severity and conditions: Kidney problems, neurobehavioral and developmental disorders, high blood pressure, and possibly cancer [5].

For many years, aluminium was not considered harmful to human health because of its relatively low bioavailability. In 1965, however, animal experiments suggested a possible connection between aluminium and Alzheimer’s disease [6]. Lead and cadmium ions disrupt the cell transport process by binding with cell membranes and are nonessential metals. Chromium is one of the important components of diet and considered an essential trace element. It is involved in the function of insulin and metabolism of lipids in living organisms [7]. However, its high concentration can cause renal tubular necrosis, dermatitis, lung cancer, and perforation of the nasal system [8].

Zinc is the basic component of a large number of different enzymes and plays structural, regulatory, and catalytic functions in humans. Zinc is also an essential nutrient for plant growth and is involved in important metabolic processes [9]. Copper is an essential trace element and is necessary for many enzymes. It is needed for normal growth and development. For normal development, copper is required in the plants in small quantities (5–20 mg·kg⁻¹), and less than 4 mg·kg⁻¹ is considered as a deficiency [10]. Manganese, an essential element of the human diet, is a naturally occurring component of the Earth’s crust. After Fe, Mn is the second most abundant heavy metal. The adequate daily intake of Mn has been set by the National Academy of Sciences (NAS) at 2.3 mg/day for men and 1.8 mg/day for women [11]. However, elevated Mn levels can cause human neurotoxicity [12]. Iron is the most abundant and essential constituent for all plants and animals. However, at high concentrations, it causes tissue damage and some other diseases in humans [9].

The environmental risk of heavy metals is dependent on various factors, such as their total contents, their chemical speciation, and soil characteristics. However, the speciation of heavy metals is more important than their total concentrations in determining their mobility, bioavailability, and related ecotoxicity [13]. Major sources of heavy metals, in addition to their natural origin, are mines, wastewaters of several metal and paper industries, fertilizers, fossil fuels, pesticides, various chemicals, and domestic wastes [14].

Many studies and researches have been conducted to understand the accumulation of heavy metals in soils and various plants. The accumulation of Ni, Cd, Cr, Cu, As, Hg, Co, Fe, Mn, Zn, and Pb have been determined in potato, red amaranth, spinach, carrot, cabbage, tomato, and brinjal in Bangladesh and the authors recommended for regular monitoring of the study area [15]. Moreover, the effect of heavy metals on plant growth and production has been studied. Plants cultivated on heavy metal polluted soils recorded growth reduction as a result of changes in physiological and biochemical processes. The presence of heavy metals showed growth inhibition, structure damage, and a decline of physiological and biochemical activities, as well as of the function of plants [16]. The continued decline in plant growth reduces the yield, which eventually leads to food insecurity [17].

On the other hand, the study in [18] reported that Vetiver grass (Chrysopogon zizanioides), growing under hydroponic with no supporting medium, can effectively remove organic matter and nutrients from domestic wastewater. Likewise, the study in [19] reported that weed plants tall fescue (Festuca arundinacea) and couch grass (Elymus repens) accumulated high concentrations of heavy metals when planted in contaminated soil indicating a certain degree of tolerance and the possibility of using these plants in the bioaccumulation and phytoremediation process.

The concentrations of seven heavy metals including Cu, Cr, Co, Ni, Ag, Pb, and Sb were determined in plants and soil in districts of Pakistan and were statistically analyzed using multivariate and univariate statistical methods for classification of samples into groups and correlation of metals in different samples [8]. Multivariate analysis was also used in research conducted to study the composition and relationship of oligo elements and heavy metals in species of genus Thymus [20]. In the same way, multivariate analysis, such as principal component analysis (PCA) and cluster analysis (CA), was performed on the distribution of elements in plant species in this study to identify the source of the heavy metals. PCA and CA were used to discover the factors that could explain the correlation model between metals. PCA was performed using the correlation matrix to identify possible associations and evaluate the extent of association between metals. CA was used to identify homogenous groups. The average linkage method was used, and the Euclidean distance was applied for the regrouping and identification of the distribution model of essential metals. Pearson correlation coefficients were also calculated to determine relationships among different metals. Applying multivariate analysis is vital in understanding the correlation among metals and between plants and metals.

Asmara, the capital city of Eritrea, has a population of about half a million. It is common practice to cultivate vegetables around Asmara using wastewater. The wastewater from households and discharges from textile, tannery, metal works, detergent, and battery industries presumably contain heavy metals such as Cr, Pb, Zn, Ni, Fe, and Mn. The use of pesticides and fertilizers in growing the wastewater irrigated vegetables and forages are also frequent. For the reason that high contents of heavy metals may cause adverse effects on cattle health and could also alter the quality of the milk or meat products obtained from them, identification and
quantification of contents of heavy metals in animal feed is thus important. Therefore, the objective of this study is to find out the effect of wastewater irrigation on heavy metal contamination of the soil and some common vegetables and animal feed grasses in the area. The potential application of these grasses as bioaccumulators in the process of soil phytoremediation will also be anticipated.

2. Materials and Methods

2.1. Study Area. The survey was conducted in Paradizo, Adi-Segdo, and Kusht (around Asmara), where animal feed grasses and vegetables are grown using wastewater from the sewerage of the city. Paradizo and Adi-Segdo farms have been irrigated using wastewater for more than four decades, whereas Kusht farm has been cultivated for about 20 years. The soil types used for cultivation in the three sites were clay loams. Paradizo and Adi-Segdo farms use wastewater from the same stream and are located at a distance of 3 km from one another. Kusht is located 8 km southwest of the city and is irrigated with wastewater from a different stream.

2.2. Soil Sampling and Characterization. During the dry season from January to March 2018, soil samples from the farmlands were randomly collected and bulked together to form a composite sample; 1.0 kg soil sample was collected by using polyethylene bags from each site. The soil samples were air-dried and oven-dried at 105°C for 48 hours, and mechanically ground using mortar and pestle and sieved to obtain 212 μm fractions. Then 20–30 g subsamples were drawn from the bulk for digestion and analysis of heavy metals. Samples of soil were collected from the depth of 0–30 cm, considering wastewater irrigation of the soil for decades [8, 21, 22].

Peroxide fusion method was used to digest soil samples [23]. In this study, 0.20 g of each sample and certified reference materials/standards were weighed (catch weight) into a zirconium crucible. Approximately 1.0 g of Na2O2 was added and mixed with a spatula. After that, approximately 0.2 g NaOH was added, and again the surface was covered with approximately 0.5 g of Na2O2. The crucibles were placed in a muffle furnace preheated at 550°C for 30 minutes and then taken out of the furnace and cooled. The contents of the crucibles were transferred into a vial containing exactly 30 mL of deionized water, and the cake was allowed to disintegrate. To this, exactly 10 mL of concentrated HNO3 was added and mixed before the addition of approximately 2 g of tartaric acid. Finally, it was diluted to 100 mL using deionized water. Approximately 20 mL was transferred into a glass test tube arranged in a rack for heavy metal analysis.

2.3. Vegetation Sampling and Characterization. Freshly harvested vegetables and animal feed grass samples of each type (M. sativa, A. sativa, C. dactylon, C. scholymus, and C. olitorius) were collected from four different gardens per sampling site. The plant samples were collected from each corner and from the middle of the plots. Samples from each site were combined to make a composite sample of each grass type. Eventually, they were packaged into labeled paper bags and transported to the laboratory. The scientific name and English name of the studied grasses and vegetables are given in Table 1. The plant species were determined by a taxonomist in Eritrea Institute of Technology (EIT).

In the laboratory, vegetable and grass samples were air-dried, oven-dried at 105°C for 48 hrs [10], and ground using a stainless steel roller and sieved to obtain 300 μm fractions to be used for digestion. The dry ashing method was used to digest the grass samples. In this method, 2.0 g of each vegetable sample was weighed and transferred to crucibles and placed in a furnace (at 550°C) for 3 hrs. After that, the crucibles were taken out of the furnace and cooled. Each sample was transferred to a beaker containing about 60 mL aqua-regia and was placed in a hot plate at 100°C until the volume reduced to 40 mL. Each solution was then transferred to a conical flask and diluted to 100 mL. Approximately 20 mL of the diluted sample was transferred into a glass test tube arranged in a rack and transferred to the ICP room for heavy metal analysis.

2.4. Quality Assurance. Precision and accuracy of heavy metal analysis were assured through repeated analysis of samples against certified reference materials for all the heavy metals. The results were found within ±2% of the certified value. Quality control measures were taken to assess the contamination and reliability of data. Blank and drift standards were run after five determinations to calibrate the instrument. The coefficients of variation of replicate analysis of samples were determined for the precision of analysis, and variations were found to be less than 10%.

2.5. Instrumentation. A dual viewing ICP-OES (Perkin Elmer Optima 8300, made in Singapore) coupled to an ultrasonic nebulizer CETAC 6000AT+ (CETAC, Omaha, NE, USA) was employed for the analysis of the trace and other elements. The Windows 7 compatible S/W provided by Perkin Elmer was used to process the spectral data for calculating sample concentrations by comparing light intensities measured at various wavelengths for standard solutions with intensities from the sample solutions.

2.6. Transfer of Heavy Metals. The bioconcentration factor (BCF) is defined as [Cplant/Csoil], where Cplant is the concentration of the metal in the plant and Csoil is the concentration of the same metal in the corresponding soil [24]. It enumerates comparative variations in heavy metals’ bioavailability to plants.

2.7. Statistical Methods. All the data were statistically analyzed by analysis of variance (ANOVA) as applicable to a completely randomized block design (CRBD) and factorial experimental design (three factors) using STATA version 14. Means were compared using Tukey’s pairwise comparison tests. Statistical significance was defined as $p < 0.05$.

Multivariate analysis, including principal component analysis (PCA) and cluster analysis (CA), was also
performed on the distribution of elements in plants using R programming on a computer. PCA reduces the set of metal concentrations and extracts a small number of components to find the relationship among the metals. In CA, the dataset was treated by the complete linkage method with linkage distance as a measure of similarity. A probability level of $p < 0.05$ was considered statistically significant. Correlation between metal content was established using regression analysis at a 95% significance level ($p \leq 0.05$). The Pearson correlation coefficients were also used to study the relationship of the metals among the plant species.

3. Results and Discussion

3.1. Heavy Metal Content of Soil Samples. The concentration of heavy metals in the studied soil samples is depicted in Table 3 and Figure 2. Mo concentrations in the soil samples collected from the three sites were in decreasing order of Mo $<$ Cd $<$ Cr $<$ Pb $<$ V $<$ Al. The results of this study revealed that soil samples from Paradizo contained the highest level of almost all of the studied heavy metals, followed by soil samples from Adi-Segdo and Kushet. Irrigation for a long period of time with wastewater could be a major contributing factor for the higher levels of heavy metals in the soil sample from Paradizo as supported by studies of [29, 30]. The proximity of Paradizo to the main road and absorption of metals from polluted air could be other factors for the higher levels [31, 32]. The low level of metals in Kushet could be due to the relatively fewer years of irrigation. A study by [21] inferred that there is a linear increase of heavy metal concentrations with irrigation time. Its location being away from the main road and the smaller number of industries/factories contributing to the stream that passes through Kushet could be other factors for the less polluted soil in Kushet.

The average concentrations of Al and Fe in soil samples were 65672.7 mg·kg$^{-1}$ and 56305.4 mg·kg$^{-1}$, respectively, and are much higher than the levels reported for the other metals. The concentration of Fe, Mn, Co, and Cd in all the wastewater irrigated soils, Cr in Adi-Segdo and Paradizo, and Cu and Zn in Paradizo are higher than their respective levels in the reference soil [27]. The higher level of Fe, Mn, Co, Cd, Cr, Cu, and Zn in the wastewater irrigated soils was not only to parent soil but was compounded by wastewater irrigation. However, the concentration of Al in the soil of the present study is lower than the reference soil, and this is attributable to the nature of the parent soil. The levels of heavy metals in the studied soil samples were similar to levels of metals in soils irrigated with wastewater from the same area and its vicinity [27].

3.2. Heavy Metals in Medicago sativa. The concentrations of heavy metals in the studied plant samples are depicted in Table 3 and Figure 2. Mo $<$ Cd $<$ Co $<$ V $<$ Cr $<$ Pb $<$ Cu $<$ Zn $<$ Mn $<$ Al $<$ Fe and is consistent with the order reported for the same plant by [34]. There was no regular trend in the heavy metal concentration of $M$. sativa from the three sites; however, in general, $M$. sativa sample from Adi-Segdo was found to contain higher levels of heavy metals. The amount of wastewater flow decreases around Adi-Segdo and as the farmers collect the wastewater in big wells before application, the contaminants could concentrate and result in higher levels of heavy metals in $M$. sativa sample.

The concentrations of Al and Fe in $M$. sativa from Adi-Segdo exceeded the recommended maximum level of 1000 mg·kg$^{-1}$ in animal feed. The authors of [28, 33] reported the levels of Zn, Cu, Cd, and Pb in wastewater irrigated $M$. sativa in Iran as 28.16, 5.39, 4.4, and 2.04 mg·kg$^{-1}$ [24], respectively, and exceeded the corresponding permissible limit suggested by the Joint FAO/WHO Expert Committee on Food Additive [33]. The concentrations of Zn, Cu, and Pb in this study were higher than those reported by [24] and exceed the permissible level recommended by [36]. However, Cd was below the recommended level. Because of the higher accumulation, the study in [37] suggested $M$. sativa as an option for phytoremediation. Comparing a study conducted by [10] with this work, the concentrations of Cd, Co, Fe, and Zn in $M$. sativa were found higher and significantly different ($p < 0.05$), whereas those of Cu, Mn, and Pb were comparable. Moreover, Mn, Cu, and Zn levels were lower, and the levels of Pb and Cd were higher in $M$. sativa of this study than sewage water irrigated $M$. sativa reported by [28] in Botswana. The results of the study by [28] were in agreement with that of [38], who suggested that alfalfa ($M$. sativa) tend to greatly accumulate heavy metals above allowable standards if irrigation water is contaminated. While the level of Cr was similar, the concentrations of Al and Cu were higher, and Fe, Mn, Pb, and Cd in $M$. sativa samples were lower when compared with their level in vegetables reported by [27] from the same area indicating that the vegetables (cabbage, lettuce) accumulate greater than $M$. sativa.

3.3. Heavy Metals in Avena sativa. As was observed in $M$. sativa, the increasing order of heavy metals in $A$. sativa is as
Table 2: Mean heavy metal content (in mg/kg) of the soil samples from Paradizo, Adi-Segdo, and Kushet and maximum permissible limits (MPL) of some heavy metals in irrigation soils.

| Soil | Al    | Cd    | Co    | Cr    | Cu    | Fe    | Mn    | Mo    | Pb    | V    | Zn    |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|
| P    | 65156.6 ± 184 | 5.51 ± 0.44 | 23.30 ± 0.20 | 339.34 ± 17 | 56.18 ± 9.1 | 60103.92 ± 573 | 1172.98 ± 49 | 5.68 ± 1.3 | 52.59 ± 2.0 | 171.36 ± 0.73 | 349.19 ± 7.60 |
| AS   | 64006.1 ± 140 | 8.51 ± 0.64 | 21.05 ± 1.00 | 207.72 ± 31.45 | 33.84 ± 11.07 | 57771.46 ± 104 | 1140.01 ± 6.32 | 6.53 ± 0.39 | 37.93 ± 1.42 | 162.77 ± 1.04 | 222.95 ± 15.65 |
| K    | 67855.6 ± 149 | 8.95 ± 0.65 | 20.41 ± 0.74 | 105.41 ± 19.48 | 12.03 ± 6.13 | 51041.00 ± 128 | 771.84 ± 6.70 | 7.15 ± 0.62 | 14.17 ± 1.65 | 134.96 ± 1.23 | 140.41 ± 9.03 |
| REF  | 75080.0 ± 33.6 | BDL   | 6.78 ± 0.18 | 112.30 ± 1.12 | 33.80 ± 0.05 | 39782.00 ± 182 | 349.20 ± 4.30 | —     | —     | —     | 236.00 ± 3.80 |
| MPL  | 20    |       |       |       |       |       |       |       |       | 20   | 1500  |

Source for reference [27] and the maximum permissible limit (MPL) [28]. P: Paradizo, AS: Adi-Segdo, K: Kushet, REF: reference soil, MPL: FAO maximum permissible limits, BDL: below detection limit, and —: not reported.
follows:

\[
\text{Cd} < \text{Co} < \text{Mo} < \text{V} < \text{Cr} < \text{Pb} < \text{Cu} < \text{Zn} < \text{Mn} < \text{Al} < \text{Fe}.
\]

Except for Cd and Zn, the concentration of heavy metals in A. sativa from the three sites has shown a regular trend, and the ascending regular trend is Kushet < Adi-Segdo < Paradizo (Table 3 and Figure 3). The presence of greater concentrations of metals in A. Sativa grown in the Paradizo area could be due to high metal concentration in the soil. In addition to variation in soil physicochemical properties, Paradizo’s proximity to the main road and age of the plant could be contributing factors to the higher level of heavy metals in A. sativa from Paradizo. The high BCF value for Mo (0.437) followed by Cu (0.363), Zn (0.119), and Pb (0.114) demonstrated a moderate uptake rate of the metals by A. sativa from the soil; the other metals have low BCF values that range between 0.04 and 0.025. In the present study, the average concentration of Mo in A. sativa was 2.82 mg·kg\(^{-1}\) and was found lower than the 6 mg·kg\(^{-1}\) established as a critical level for forage crops [39], but much lower than the 40 mg·kg\(^{-1}\) permissible level for animal feed [36]. In a study conducted in Pakistan [40], the concentrations of Cd, Cr, and Pb in A. sativa grown in wastewater irrigated soil were reported as 0.26, 53.02, and 40.10 mg·kg\(^{-1}\), respectively and these concentrations were much higher than results of this study. The concentrations of Al, Fe, Cr, and Cu are higher and that of Mn, Pb, and Cd are lower in A. sativa samples when compared with those reported by [27] in vegetables from the same area. The levels of Cu and Cd are similar, the levels of Mn and Zn are lower, and the levels of Pb and Fe are higher in A. sativa compared with sewage water irrigated grass (ryegrass) and M. sativa studied by [28] in Botswana.

Metal concentrations ratio of M. sativa to soil (mean BCF values) shown in Table 4 are in decreasing order of Cu (0.52), Mo (0.30), Zn (0.19), Pb (0.096), Mn (0.047), Co (0.04), Cd (0.025), Fe (0.016), Cr (0.0148), V (0.0143), and Al (0.0114). M. sativa was a moderate accumulator of Cu, Mo, Zn, and Pb and low accumulator of the other metals. BCF values of 1 to 10 indicate hyperaccumulator plant, BCF values of >0.1 to 1 indicate moderate accumulator plant, BCF values of 0.01 to 0.1 indicate low accumulator plant, and BCF values of <0.01 indicate no accumulator plant [35]. The BCF values showed that the concentrations of the metals in the soil and M. sativa were not directly correlated. For example, the BCF value of Fe is a bit greater than Al, as shown in Table 4, indicating M. sativa has greater absorbing ability for Fe, and thus, the concentration of Fe is higher than Al in M. sativa in contrast to its concentration in the soil. The small BCF values, low accumulation of Al and Fe by M. sativa, could be attributed to limited translocation from root to the shoot [28] or the increased concentration of the metals in the soil.

3.4. Heavy Metals in Cynodon dactylon. The order of heavy metals concentrations (Table 3 and Figure 4) in C. dactylon followed the same trend as M. sativa and A. sativa. There was no regular trend in the heavy metal concentrations in C. dactylon samples from the three sites. As shown in Table 4, the five metals with high mean BCF values are in the order: Mn (0.055) < Mo (0.068) < Pb (0.093) < Zn (0.204) < Cu (0.441). These values are similar to the BCF values of M. sativa suggesting the two plants have the same uptaking ability. When the BCF values of the sites are considered, the values for this plant in Paradizo were small compared to the other two sites except for Al, Cd, and Fe. Even though Paradizo soil contained a higher level of heavy metals, C. dactylon sample from Paradizo appeared to accumulate a relatively lower level of heavy metals. This could be due to the tolerance of the plant to a higher level of heavy metals in soil [41]. The concentrations of Al, Cr, Pb, and Cu are higher and Mn, Fe, and Cd are lower in C. dactylon samples when compared with those reported by [27] in vegetables from the same area. Similar results with respect to Cu, Cd, Mn, and Zn and higher levels of Pb and Fe were observed in C. dactylon compared with sewage water irrigated grass (ryegrass) and leguminous forage (lucerne) studied by [28] in Botswana.
Table 3: Mean concentrations of heavy metals in selected animal feed grasses in mg kg⁻¹ and maximum permissible limits (MPL) of some heavy metals in animal feeds.

|       | Al    | Cd    | Co    | Cr    | Cu   | Fe    | Mn    | Mo    | Pb    | V    | Zn    |
|-------|-------|-------|-------|-------|------|-------|-------|-------|-------|------|-------|
| Med_AS| 1157.1 ± 5.91 | 0.22 ± 0.00 | 1.10 ± 0.05 | 4.95 ± 0.00 | 11.31 ± 0.01 | 1384.0 ± 1.17 | 48.68 ± 0.34 | 1.69 ± 0.12 | 4.64 ± 0.29 | 3.59 ± 0.02 | 38.14 ± 1.84 |
| Med_P | 535.43 ± 1.00 | 0.16 ± 0.01 | 0.56 ± 0.01 | 1.85 ± 0.03 | 9.90 ± 1.07 | 652.24 ± 0.03 | 35.39 ± 0.08 | 2.86 ± 0.06 | 1.91 ± 0.10 | 1.78 ± 0.03 | 39.28 ± 1.02 |
| Med_K | 553.99 ± 0.66 | 0.18 ± 0.03 | 0.9 ± 0.01 | 1.61 ± 0.01 | 12.7 ± 0.07 | 602.75 ± 5.01 | 55.06 ± 0.39 | 1.01 ± 0.03 | 3.3 ± 0.61 | 1.43 ± 0.02 | 30.17 ± 2.82 |
| Ave_AS| 1178.8 ± 4.99 | 0.16 ± 0.03 | 0.86 ± 0.06 | 4.08 ± 0.04 | 13.5 ± 0.08 | 1263.9 ± 3.85 | 36.6 ± 0.79 | 2.21 ± 0.03 | 4.53 ± 0.53 | 3.07 ± 0.00 | 35.1 ± 1.50 |
| Ave_P | 1836.2 ± 44.42 | 0.12 ± 0.02 | 1.40 ± 0.04 | 9.96 ± 0.19 | 14.1 ± 0.26 | 2023.3 ± 35.07 | 52.3 ± 1.65 | 3.87 ± 0.10 | 4.74 ± 0.62 | 5.02 ± 0.14 | 34.2 ± 2.01 |
| Ave_K | 746.02 ± 3.94 | 0.06 ± 0.01 | 0.38 ± 0.01 | 1.98 ± 0.01 | 9.49 ± 0.22 | 713.07 ± 2.91 | 24.6 ± 0.70 | 2.38 ± 0.13 | 2.71 ± 0.43 | 1.57 ± 0.04 | 15.3 ± 2.01 |
| Cyd_AS| 950.60 ± 1.14 | 0.05 ± 0.01 | 1.07 ± 0.05 | 4.32 ± 0.06 | 14.26 ± 0.15 | 1138.82 ± 5.79 | 64.02 ± 0.74 | 0.37 ± 0.04 | 3.62 ± 0.65 | 2.68 ± 0.06 | 45.55 ± 0.98 |
| Cyd_P | 865.34 ± 14.45 | 0.13 ± 0.01 | 0.67 ± 0.01 | 4.16 ± 0.06 | 13.88 ± 0.06 | 1131.04 ± 3.11 | 39.40 ± 0.69 | 0.32 ± 0.01 | 4.30 ± 0.17 | 2.55 ± 0.06 | 55.21 ± 0.22 |
| Cyd_K | 363.74 ± 13.27 | 0.08 ± 0.02 | 0.69 ± 0.03 | 1.50 ± 0.06 | 16.87 ± 2.51 | 457.30 ± 9.04 | 66.90 ± 1.12 | 0.62 ± 0.08 | 1.84 ± 0.68 | 1.09 ± 0.06 | 44.6 ± 1.53 |
| Cor_AS| 1391.8 ± 14.18 | 0.18 ± 0.01 | 1.0 ± 0.03 | 5.34 ± 0.27 | 9.81 ± 0.70 | 1587.8 ± 8.24 | 41.97 ± 0.41 | 1.78 ± 0.08 | 4.15 ± 0.24 | 4.25 ± 0.05 | 78.33 ± 1.11 |
| Cyn_P | 1144.9 ± 8.71 | 0.21 ± 0.03 | 0.98 ± 0.01 | 3.98 ± 0.09 | 9.35 ± 0.64 | 1416.7 ± 8.44 | 33.15 ± 0.39 | 0.52 ± 0.03 | 5.89 ± 0.38 | 3.85 ± 0.09 | 24.16 ± 0.39 |
| MPL   | 1000   | 10    | 40    | 1000   | 1000b | 1000 | 1000 | 40    | 40    | 1000 |

Source for the MPL: [33] and [28]. med: M. sativa, ave: A. sativa, cyd: C. dactylon, cor: C. olitorius, and cyn: C. scholymus.
3.5. Heavy Metals in Cynara scholymus and Corchorus olitorius (Table 3 and Figure 5)

C. scholymus was cultivated only in Paradizo and C. olitorius only in Adi-Segdo (Table 1). The trend of heavy metals concentrations observed in M. sativa, A. sativa, and C. dactylon was also reflected in C. scholymus. The trend was slightly different in C. olitorius, and the increasing order of heavy metals was as follows: Cd < Co < Pb < V < Cr < Cu < Mn < Zn < Al < Fe. In C. olitorius, except for Al and Fe, the concentrations of the other studied metals were lower than the maximum permissible limits set by [36] for animal feed. C. olitorius is usually recommended for pregnant women and nursing mothers in Nigeria because it is believed to be rich in iron [42]. The levels of Pb and Zn in C. olitorius which are 4.15 and 78.33 mg·kg⁻¹ in the present study are higher than the 0.310 and 4.85 mg·kg⁻¹ and the amount of Cd which is 0.18 mg·kg⁻¹ is slightly lower than 0.205 mg·kg⁻¹ in C. olitorius leaves cultivated close to the major road, in Ikorodu- Lagos, Nigeria [43].
The levels of Al, Fe, Cu, and Cr in *C. olitorius* grown in Adi-Segdo were found to be 1391.8, 1587.8, 9.81, and 5.34 mg·kg⁻¹, respectively, and these concentrations were significantly different (*p* < 0.05) when compared with the corresponding metal concentrations reported by [27] as 129.52, 452.2, 1.77, and 1.41 mg·kg⁻¹ for lettuce grown in the same area. In the same work, the concentrations of Mn, Pb, and Cd in *C. olitorius* were 41.97, 4.15, and 0.18 mg·kg⁻¹, respectively, and the concentrations of the metals in lettuce grown in the same area were 102.1, 4.18, and 4.14 mg·kg⁻¹ respectively. The results showed that concentrations of Mn and Cd were significantly different (*p* < 0.05), whereas the concentrations of Pb were not, and this showed *C. olitorius* has strong accumulating power. These two leafy vegetables are commonly consumed by the city community.

Comparable concentrations of Cu, lower levels of Mn, and higher levels of Fe, Pb, Cd, and Zn (in *C. olitorius* only) were observed in *C. scholymus* and *C. olitorius* compared with sewage water irrigated grass (ryegrass) and leguminous forage (*M. sativa*) studied by [28] in Botswana. The level of Zn in *C. olitorius* is approximately twice higher than its level in ryegrass and lucerne. The BCF values of Zn (0.0692), Cu
(0.116), and Mo (0.0915) for \textit{C. scholymus} were found lower than the BCF values of Zn (0.315), Cu (0.293), and Mo (0.273) for \textit{C. olitorius}. The result showed there is a high uptake rate of the metals by \textit{C. olitorius} than by \textit{C. scholymus}.

3.6. Comparison of Heavy Metal Content of Vegetables and Grasses from the Same Area. When the heavy metal contents of the grass and vegetable samples within Adi-Segdo are compared, \textit{C. olitorius} was found to contain a greater amount of Cr, V, Zn, Al, and Fe. \textit{M. sativa} contained a greater amount of Cd, Co, and Pb, and \textit{C. dactylon} contained a greater amount of Cu and Mn. Among the grasses and vegetables, \textit{A. sativa} was found to contain a lower amount of heavy metals except Mo which was found in its highest level in \textit{A. sativa} sample from Adi-Segdo. Therefore, based on the results of this study, farmers should be encouraged to cultivate \textit{A. sativa} instead of \textit{C. olitorius}. \textit{C. olitorius} was found to concentrate 5 of the 11 studied heavy metals to a greater extent. \textit{C. olitorius} has a higher capability of absorbing heavy metals, especially when the plant roots expand, i.e., as it becomes aged [43]. Moreover, the study in [44] highlighted that the application of rock phosphate and chemically manufactured phosphate fertilizers had a significant contribution for high levels of heavy metals in \textit{C. olitorius} plants because phosphate rocks and fertilizers contain hazardous elements such as Cd, As, Cr, Hg, Pb, Se, U, and V.

When the heavy metal contents of the grass and vegetable samples within Paradizo are compared, contrary to the observation in Adi-Segdo, \textit{A. sativa} sample was found to contain the highest amount of Co, Cr, Cu, Mo, V, Al, Fe, and Mn. \textit{C. scholymus} contained a greater amount of Cd and Pb, and \textit{C. dactylon} contained a greater amount of Zn. Among the grass and vegetable samples collected from Paradizo, \textit{M. sativa} was found to contain the lowermost amount of heavy metals. Thus, farmers should be encouraged to cultivate \textit{M. sativa} rather than \textit{A. sativa} in Paradizo.

When the heavy metal contents of the animal feed grasses within Kushet are considered, contrary to the observation in Adi-Segdo and in a good agreement with the observation in Paradizo, \textit{A. sativa} sample was found to contain a greater amount of Cr, Mo, V, Al, and Fe. Moreover, \textit{C. dactylon} contained a greater amount of Cu, Zn, and Mn and \textit{M. sativa} contained a greater amount of Cd, Co, and Pb. When compared with the other grasses collected from Kushet, \textit{M. sativa} was found to contain a relatively lower amount of heavy metals. Consequently, based on the results of this study, farmers should be encouraged to cultivate \textit{M. sativa} instead of \textit{A. sativa} and \textit{C. dactylon} in Kushet. Based on the results of this study, although the concentration of heavy metals is low, frequent consumption of the plants by animals may lead to the bioaccumulation of heavy metals on animal organs, thus affecting the nature of their milk and meat which in turn will affect the health of the consumers.

Out of the five studied vegetables and animal feed grasses, \textit{C. olitorius} was found to be a good accumulator (45%) of the studied heavy metals. Specifically, it accumulates Al, Cr, Fe, V, and Zn to a greater extent, and \textit{C. scholymus} was found to be a good accumulator of Pb. Based on the results of this study, consumption of the animal feed grass, \textit{C. olitorius}, has a higher risk of heavy metal contamination. On the other hand, \textit{C. olitorius} should be further investigated for its phytoremediation capability for removing Al, Cr, Fe, V, and Zn from polluted soils. The comparison is made on plants grown in Adi-Segdo as \textit{C. olitorius} is not cultivated in the other farms.

3.7. Univariate Analysis. Two-way ANOVA (RCBD) result revealed that the average concentration of the metals among the three sites is statistically different ($p < 0.05$), and similarly, the metal concentrations are statistically different for the different metals and species of grass (\textit{M. sativa}, \textit{A. sativa}, and \textit{C. dactylon}). Tukey’s Pairwise comparisons conducted among the three sites revealed that the average metal concentration in Paradizo and Adi-Segdo is not significant, but the average metal concentration in Kushet has a statistically significant difference with the two sites (Paradizo and Adi-Segdo). Tukey’s Pairwise comparisons conducted among the three types of grass, also showed that the average metal concentration in \textit{C. dactylon} and \textit{M. sativa} is not statistically different, but the average metal concentration in \textit{A. sativa} has a statistically significant difference with the metal concentration in the two other grass types (\textit{C. dactylon} and \textit{M. sativa}). Tukey’s Pairwise comparisons also revealed that the average concentrations of Fe and Al do not have any significant difference between them, but they have a significant difference with the other metals. Moreover, the concentrations among the other metals (Cd, Co, Cr, Cu, Mn, Mo, Pb, V, and Zn) do not have a significant difference.

3.8. Multivariate Analysis

3.8.1. Pearson Correlation Analysis. Pearson’s correlation matrix of heavy metals elements in the studied plant species is shown in Table 5. The figures are distributed from negative to positive values, the positive figures being dominant, which indicate most of the heavy metals are positively related to each other. If one heavy metal increases, then the other concentrations will increase too, and vice versa [45]. The higher the value is, the stronger correlation of the two heavy metals to each other. Al is strongly correlated with V, Cr, Fe ($p < 0.01$), and with Co and Pb ($p < 0.05$). Co is correlated with Cr, Fe, Pb and V, Cr with Fe, Pb, and V, Cu is correlated only with Mn (at $p < 0.05$).

3.8.2. Principal Component Analysis (PCA) and Cluster Analysis (CA). From the PCA eigenvalues table (Table 6), it can be seen that the first three PCs are enough to explain 83.50% of the pattern variation, 50.04% being explained by PC1, 21.33% by PC2, and 12.13% by PC3. Moreover, the extraction of the commonalities of each element higher than 0.6 (Table 7) showed that PCA was suitable for the dataset in this study. From the PCA analysis, Fe, Al, V, Co, Cr, and Pb have the highest positive loadings on PC1. Only Cu and Mn
have the highest positive loadings on PC2 and Mo and Cd on PC3. The rotated component matrix also showed a similar grouping of the heavy metals.

Positively correlated variables are grouped together on the factor map (Figure 6). Negatively correlated variables are positioned on opposite sides of the plot origin (opposed quadrants). The distance between variables and the origin measures the quality of the variables on the factor map. Based on the factor map Fe, Al, V, Co, Cr, and Pb are important to interpret PC1. It is observed that the Pb loadings are not as high as the loadings of the other elements of the group (Figure 6 and Table 7), which may, therefore, imply a quasi-independent behavior within the group [45]. Cu and Mn loadings, which are closer to the circle of correlations, are important for PC2 (Figure 6).

The heavy metals concentration data were also calculated using the hierarchical clustering (average linkage method) using R programming. Figure 7 shows the CA results as a dendrogram in the study area. The dendrogram shows two big clusters with subclusters. Grouped in cluster one, Fe, V, Al, Cr, Co, and Pb are very well correlated with each other. Fe and V are very closely related to each other and closely related to Al. Fe, V, and Al are also closely related to Cr, all of them being related to Pb. Aluminium is the third most

### Table 5: Pearson’s correlation matrix of heavy metals elements in the studied plant species.

|       | Al    | Cd    | Co    | Cr    | Cu    | Fe    | Mn    | Mo    | Pb    | V    | Zn    |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|
| Al    | 1.00  |       |       |       |       |       |       |       |       |      |       |
| Cd    | 0.25  | 1.00  |       |       |       |       |       |       |       |      |       |
| Co    | 0.77* | 0.30  | 1.00  |       |       |       |       |       |       |      |       |
| Cr    | 0.94**| 0.11  | 0.81**| 1.00  |       |       |       |       |       |      |       |
| Cu    | –0.13 | –0.46 | 0.21  | 0.10  | 1.00  |       |       |       |       |      |       |
| Fe    | 0.98**| 0.31  | 0.79**| 0.94**| –0.12 | 1.00  |       |       |       |      |       |
| Mn    | –0.12 | –0.27 | 0.46  | 0.10  | 0.77* | –0.08 | 1.00  |       |       |      |       |
| Mo    | 0.46  | 0.04  | 0.16  | 0.46  | –0.24 | 0.35  | –0.31 | 1.00  |       |      |       |
| Pb    | 0.75* | 0.52  | 0.64* | 0.63* | –0.21 | 0.80**| –0.21 | –0.07 | 1.00  |      |       |
| V     | 0.97**| 0.40  | 0.79**| 0.91**| –0.20 | 0.99**| –0.10 | 0.35  | 0.80**| 1.00 |       |
| Zn    | 0.18  | 0.10  | 0.19  | 0.21  | 0.15  | 0.24  | 0.27  | –0.20 | 0.00  | 0.26 | 1.00  |

**Significant correlation at \( p < 0.01 \); *significant correlation at \( p < 0.05 \).

### Table 6: Total variance explained (three factors selected) for heavy metals.

| Component | Eigen | Variance (%) | Cumulative (%) | Eigen | Variance (%) | Cumulative (%) | Eigen | Variance (%) | Cumulative (%) |
|-----------|-------|--------------|----------------|-------|--------------|----------------|-------|--------------|----------------|
| PC1       | 5.50  | 50.04        | 50.04          | 5.50  | 50.04        | 50.04          | 5.46  | 49.66        | 49.66          |
| PC2       | 2.35  | 21.33        | 71.37          | 2.35  | 21.33        | 71.37          | 2.36  | 21.49        | 71.15          |
| PC3       | 1.33  | 12.13        | 83.50          | 1.33  | 12.13        | 83.50          | 1.36  | 12.35        | 83.50          |
| PC4       | 0.88  | 8.04         | 91.53          |       |              |                |       |              |                |
| PC5       | 0.63  | 5.68         | 97.22          |       |              |                |       |              |                |
| PC6       | 0.26  | 2.32         | 99.54          |       |              |                |       |              |                |
| PC7       | 0.03  | 0.27         | 99.81          |       |              |                |       |              |                |
| PC8       | 0.02  | 0.14         | 99.95          |       |              |                |       |              |                |
| PC9       | 0.01  | 0.05         | 100.00         |       |              |                |       |              |                |
| PC10      | 0.00  | 0.00         | 100.00         |       |              |                |       |              |                |

### Table 7: Component matrixes.

| Element | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 |
|---------|-----|-----|-----|-----|-----|-----|
| Al      | 0.95| 0.00| 0.03| 0.97| –0.10| –0.15|
| Cd      | 0.17| 0.19| 0.34| 0.34| –0.56| 0.52|
| Co      | 0.69| 0.17| 0.00| 0.87| 0.31 | 0.14 |
| Cr      | 0.86| 0.04| 0.07| 0.95| 0.14 | –0.22|
| Cu      | 0.02| 0.79| 0.02| –0.04| 0.91 | –0.01|
| Fe      | 0.98| 0.00| 0.00| 0.99| –0.08| –0.02|
| Mn      | 0.00| 0.87| 0.00| 0.04| 0.91 | 0.21 |
| Mo      | 0.14| 0.10| 0.57| 0.36| –0.24| –0.79|
| Pb      | 0.67| 0.02| 0.13| 0.78| –0.29| 0.35 |
| V       | 0.98| 0.00| 0.00| 0.98| –0.15| 0.04 |
| Zn      | 0.05| 0.15| 0.16| 0.24| 0.30 | 0.46 |
common element in the Earth’s crust and is naturally present in the environment [46]. The level of Al in the reference soil (Table 2) was found to be higher than its level in the wastewater irrigated soils, which indicates its natural origin. Iron oxide compounds, organic fraction, and argillaceous minerals are main sources of natural V. The average abundance of V (135 mg/kg) in soil ranks this element 5th among all transitional metals and 22nd among all discovered elements in the Earth crust. The concentration of V in the studied soil samples (134.96–171.36 mg·kg\(^{-1}\)) is higher than the Canadian guidelines for soil-quality (130 mg·kg\(^{-1}\)) [47] and the Russian maximum tolerance limit (150 mg·kg\(^{-1}\)) for agricultural soil [48]. The levels of Fe in the wastewater irrigated soils are higher than its value in the reference soil. Moreover, the concentration of Fe in soil samples from the three sites exceeded the maximum permissible limits (1500 mg·kg\(^{-1}\)) for irrigation soils [36]. Common sources of Pb in soils are manure, sewage sludge, lead-arsenate pesticides, vehicle exhausts, and industrial fumes [25]. A higher concentration of Pb (52.59 mg·kg\(^{-1}\)) in soil sample from Paradizo (3.7 times higher than its value in Kushet) in this study could also be attributed to the proximity of the site to the highway because the main source of lead in the environment is known to be vehicle exhaust emissions [26]. A long history of leather tanning till recent times and a number of existing textile industries that release large amounts of chromium containing wastewater are expected to be anthropogenic sources of Cr in this study. This information is supported by the fact that the levels of Cr in Paradizo and Adi-Segdo are, respectively, 3 and 1.85 times higher than its level in the reference soil (Table 2). The farming area has had several decades of intensive untreated wastewater irrigation, long-term fertilizer, and pesticide application, which might be a major source of heavy metals in the study area. Heavy metals may be added to agricultural soils from fertilizers, pesticides, soil amendments (e.g., lime and gypsum), or organic fertilizers (e.g., manures and composts) [49]. Although the major sources of Fe, Al, and V are natural, because of the above-specified reasons, the PC1 loadings (Fe, V, Al, Cr, Co, and Pb) may be classified as a mixed (natural and anthropogenic) group. However, PC2 loadings (Cu and Mn) may be classified as the anthropogenic group. Manganese is ubiquitous in the environment. It comprises about 0.1% of the Earth’s crust. However, municipal wastewater discharges and sewage sludge, Mn-containing agrochemicals such as fungicides and fertilizers, still extensively used in some countries, are also
substantial sources of Mn. Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, and amethyst glass [50]. The concentration of Mn in soil samples from the three sites exceeded the FAO/WHO maximum permissible limits (600 mg·kg\(^{-1}\)) for irrigation soils and also the levels of Mn in Paradizo and Adi-Segdo are approximately 3.3 times higher than its level in the reference soil which are good signs for its anthropogenic source. Pb, Cu, and Zn were reported to mainly come from traffic flow, industry, and pesticides [51]. The level of Cu in Paradizo (site close to the main road) is approximately 2-fold higher than its value in the reference soil. Higher content of Cu might have originated from wastewater and from the application of Cu-contained agrochemicals [25].

The metals Zn, Mo, Cu, Mn, and Cd (Figure 7) are grouped in cluster two. In good agreement with PC2, within the second cluster Cu and Mn are very closely related to one another being correlated to Cd at higher cluster distance (0.7), Zn and Mo are closely related to one another and with the rest of the cluster at a higher distance (1.0). The level of Zn in Paradizo (349.19 mg·kg\(^{-1}\)) is approximately 1.5 times higher than its value in the reference soil (236 mg·kg\(^{-1}\)), an indication of its source from traffic flow and industry [45] and long-term anthropic activity such as pesticides [25]. As can be clearly seen from the dendrogram, Cd is the only element having its own basic cluster for a relatively longer cluster distance. To improve crop yield, farmers often use a large amount of synthetic and organic fertilizers, which leads to excessive cadmium content in soil caused by the long-term accumulation of fertilizers not used by vegetation [51]. The Pearson correlation matrix (Table 1) also reveals that Cd does not correlate to any of the studied heavy metals. Thus Cd may be explained as being controlled by external factors. It can be noted that PCA and CA analyses which are consistent with Pearson’s correlation interpretations help us to give a preliminary conclusion that Fe, V, Al, Cr, Co, and Pb were controlled by a mixed (natural and anthropogenic) sources and Zn, Mo, Cu, Mn, and Cd by anthropogenic source. As very limited and inadequate data about the accumulation of heavy metals in plants grown in wastewater irrigated farms around Asmara are available. Therefore, the results of this study are expected to shed light on the understanding of the community and enable the City Council to monitor the environmental quality and to take appropriate actions.

**Data Availability**

The results of the triplicate measurements data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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