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Heavy Metals Impact on Irrigated Vegetable Food Crops Consumed in Zaria

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ABSTRACT

Research on pollutants level in vegetables in relation to environmental pollution is imperative considering the recent concerns about the pollution in rivers, streams, stagnant waters, and soils on which the vegetables are grown and irrigated in Nigeria. Ten (10) samples each of vegetables, soil and water were collected and analysed for Pb, Cd, Cr and Fe. The order of their occurrence in all the samples is as follows: Cd < Cr < Pb < Fe. The metals were also found to be highest in soil samples, lowest in water sample and in vegetable samples been the intermediary. Results of correlation analysis conducted revealed positive correlation between Fe in vegetable and Pb, Cd, Cr in soil also Fe in Water and Cr, Cd, Fe in vegetable but insignificant at p = 0.05. Transfer factor was also determined and Cd was found to have the highest transfer factor of 0.91 followed by Pb (0.87), Cr (0.83) and iron (Fe) with the lowest transfer factor of 0.18. When the result was compared to food standard set by WHO/FOA, Cd, Pb, Cr and Fe levels in the three media were found to be higher than the maximum permissible limit.

INTRODUCTION

Many organic and inorganic chemicals formed as products of combustion are released to air. These, including those released to air, water, and soil from industrial activities enter humans primarily through inhalation and ingestion of food. Although the inorganic chemicals specifically the heavy metals can exist naturally in soil through parent material, they can also be artificially introduced into soil by processes such as metal production, fossil fuel combustion, waste incineration, emissions from car exhaust, pesticide and fertilizer usage, sewage sludge, mines and smelting factories among others. Addition of organic matter amendments, such as compost, fertilizers and wastes, is a common practice for immobilization of heavy metals and soil amelioration of contaminated soils [1]. Apart from pH, other soil properties, such as cation exchange capacity, organic matter content, quantity and type of clay minerals, content of the oxides of Fe, Al, Mn, and their redox potential determine the soil's ability to retain and immobilize heavy metals. When this ability is exceeded, the quantities of heavy metals available to plants increase, resulting in the appearance of toxicity phenomena.

Accumulation of toxic metals in soils as a result of pollution by industrial and urban activities has generated global health concerns due to the risks of such chemical ending up in the human food chains [2]. Previous studies revealed that the presences of heavy metals like Fe, Pb and Hg reduce soil fertility and agricultural output [3]. Recently, cadmium and lead contents detected from produce harvested in the vicinity of abandoned mines, industrial complexes, and landfills exceeded the cadmium and lead standard rate, raising concerns about the severity of heavy metal pollution in produce [4].Lead and Cd are considered potential carcinogens and are associated with aetiology of a number of diseases, especially cardiovascular, kidney, nervous system, blood as well as bone diseases [5].

Agricultural lands close to highways have been observed to be grossly contaminated with heavy metals due to aerial deposition of metal containing particulates from automobile exhausts, and consequently being taken up by crops [6]. Heavy metals present in soils constitute serious environmental hazards from the point of view of polluting the soils and adjoining streams and rivers [7]. Some agricultural soils are often irrigated with city effluents [8] and this may lead to the introduction of some toxic elements into the soil, which may consequently be taken up by plants and eventually transferred to grazing animals and man. When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues [9].Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues, and milk, if lactating [10]. Humans are in turn exposed to heavy metals by consuming contaminated plants and animal products, and this has been known to result in various biochemical disorders.

Essential heavy metals are generally considered to be less toxic than non-essential metals, [11]. The physico-chemical characteristics and heavy metal profiles of Nigerian rivers, streams and waterways has been studied [12]. The study revealed the levels of Pb, Cd, Cr, Zn and Mn were higher than the standard for World Health Organization [13]. This implies that communities using those surface waters for various purposes such as irrigation and drinking are exposed to health risk posed by heavy metals.

The natural entry route of heavy metals into aquatic environment is through weathering of the earth crust. In addition to geological weathering, human activities have also introduced large quantities of metals to localized area of the sea, in some cases upsetting the natural steady state balance [14]. Metals such as cadmium, chromium, copper, iron, nickel, lead and zinc exhibit aquatic toxicity when present above recommended standard in that they can contaminate surface and ground water bodies, soil, plant, aquatic life and man, through bioaccumulation.

The process of absorption and accumulation of metals in plants is complicated, usually defined by the behaviour of the element, soil characteristics and the properties of the biological reagents. Hence regular investigations of these processes have to be a part of the environmental monitoring [15][16].

The consumption of plants produced in contaminated areas, as well as ingestion or inhalation of contaminated particles are two principal factors contributing to human exposure to metals. Potential health risks to humans and animals from consumption of crops can be due to heavy metal uptake from contaminated soils via plant roots as well as direct deposition of contaminants from the atmosphere onto plant surfaces [17]. Some species of plants have ability to bioaccumulates and bioconcentrate heavy metals, making the level higher in the plants than in the soil where the plants grow [18]. These toxic metals could be transferred from one organism to the other through food chain [19].

Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of trace metals in the edible plant parts with a resulting risk to human and animal health [20]. They can also cause illnesses in humans and animals ingesting the produce through the food chain [21]. The ubiquitous distribution and known toxicity of lead pollution in urban environment are posing great concern, in terms of human health and environment [22]. Lead toxicity leads to anaemia both by impairment of haemobio-synthesis, acceleration of red blood cell destruction and also depresses sperm count [23]. In addition, Pb can also produce a damaging effect on the kidney, liver and nervous system, blood vessels and other tissues [23][24]. Pb like the other elements of Zn, Cu, Fe, Cr and Cd is generally the metal of great concern as well as being phytotoxic [25]. Mobility of Pb is different from soil to soil leading to different amounts of ecological risk

Countries have set heavy metal pollution standards for soil, water and food crops to protect human health from pollution with heavy metals. However, the heavy metal transfer from soil to plant is reported to vary depending on the soil's heavy metal concentration rate, plant characteristics and the soil's physicochemical properties [4]. It is impossible to prevent the possible heavy metal transfer to produce and its damaging effects on human health with such simple standards.

The investigation of pollutants level in the vegetable in relation to environmental pollution was prompted by the recent concerns about the pollution in rivers, streams, stagnant waters, and soil for agricultural practices on which vegetables are produced through irrigation in Nigeria. Thus information about heavy metal concentrations in food products and their dietary intake is very important for assessing their risk to human health. Taking into consideration the dumping of refuse on the coast and into River Kubani, high rate of vehicular emissions, washing of cars and application of compost manure from dumpsite on irrigated farmland, this study was designed to investigate the heavy metal (Pb, Cd,Cr and Fe) concentrations in soils, water and vegetables. Also to estimate the potential health risks of metals to humans through consumption of irrigated vegetables.

MATERIAL AND METHOD

Sampling

A total of ten (10) grab water samples were collected in plastic bottles and were conveyed to the industrial chemical division, National Research Institute for Chemical Technology, Zaria-Nigeria for further treatment. Ten (10) vegetable samples were collected in polyethylene bags at an early hour of the day when market women came to buy from the farmer. Ten (10) Soil samples were also collected at surface level (0-15 cm in depth) from the same irrigated farmland where the vegetable crops were grown.

Sample preparation

Each water sample collected was preserved with 4ml concentrated nitric acid to prevent the precipitation and adsorption of metals and stored in freezer at $4^{o}C$. Soil samples were air dried and ground into fine powder using agate mortar and passed through 2 mm sieve. Well mixed samples of 1 g each were taken in 250 ml glass beakers covered with watch glass and digested with a mixture of nitric acid and perchloric acid in a ratio of 3:1 on hotplate for 2 hours to ensure complete digestion. After evaporation to near dryness, 5ml of ultrapure water was added to the content of the beaker, filtered while hot into volumetric flask and then diluted to 50 ml with ultrapure water. Vegetable samples were thoroughly washed to remove all adhered soil particles. Samples were cut into small pieces, air dried for 5 days in the laboratory. The samples were pulverised and passed through 1 mm sieve. Digestion of these samples (1g each) was carried out using 5 ml of concentrated nitric acid, according to [26] with modification.

Analysis

Heavy metal analyses were carried out using flame atomic absorption spectrophotometer AA-6800 (Shimadzu, Japan) at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis. The chemical composition of water was determined at NARICT and the elements determined included Cd, Cu, Mn and Zn. Transfer factor was calculated for each metal according to the following formula:

TF= concentration of metal in vegetable/concentration of metal in soil [27][28].

Data analysis

Data collected were subjected to statistical tests of significance using the Multivariate tests ($p<0.05$) to assess significant variation in the concentration levels of the heavy metals in the vegetable, water as well as in soils. Probabilities less than 0.05 ($p < 0.05$) were considered statistically significant. Correlation coefficient was used to determine the association between the heavy metals in vegetable, water and soil at $p = 0.05$. All statistical analyses were done by SPSS software 17.0 for windows.

Validation of analytical method

In order to check the reliability of the analytical methods employed for trace metals determination, Lichens coded IAEA-336 was also digested and then analyzed following the same procedure.

RESULT AND DISCUSSION

To evaluate the accuracy and precision of our analytical procedure, a standard reference material of lichen coded IAEA-336 was analysed in like manner to our samples. The values determined and the certified values of the six (6) elements determined were very close suggesting the reliability of the method employed.

Table 1 shows the results of analysis of reference material (Lichen IAEA-336) compare to the reference value

Elements(mg/L)	Cd	Cu	Pb	Mn	Zn
A Value	0.140	4.00	5.25	55.78	29.18
R Value	0.1-1.34	3.1-4.1	4.3-5.5	56-70	27-33.8

A Value = Analysed value R Value = Reference value.

Table 2 shows the ranges of heavy metals concentrations in vegetable at the sampling site. The concentrations ranged from 5.30-55.25ppm, Pb; 0.55-2.41ppm, Cd; 1.00-12.58ppm, Cr; and 88.26-1233.43ppm, Fe. From the results, it can be seen that highest accumulation occurred with Fe followed by Pb then Cr while the least with Cd (Fig. 1, 2 and 3). The average concentrations of the metals in soil sample are illustrated in table 3. The same pattern of occurrence was observed for the elements as in vegetable with Fe having the highst concentration while Cd with the least

concentration. The Pb levels varied from about 24.26-51.21ppm, Cd from 0.76 to 2.55ppm, Cr from 9.31 to about 25.66ppm and Fe from 2237.32 to about 2617.42ppm, respectively.
The mean concentration of the metals in water is presented in Table 2 with the same pattern of occurrence as seen for vegetable and soil. The concentrations of the metals in individual samples varied as follows: Pb from 12.13 to 35.04ppm, Cd from 0.83 to 1.72ppm, Cr from 0.50 to 9.31ppm, and Fe from 191.73 to 263.30ppm. In general the metals are found to be highest in soil than vegetable and water with Fe been the highest in all the sample types analysed.

Table 2 showing Transfer Factor, Mean±SD and range of heavy metals in vegetable, soil and water samples

Element	Transfer Factor	Sample	Mean±SD	Range
Pb	0.87	Vegetable	31.26 ±13.06	5.30-55.25
		Soil	35.98± 9.23	24.26-51.21
		Water	21.36± 8.62	12.13-35.04
Cd	0.91	Vegetable	1.53±0 .67	0.55-2.41
		Soil	1.69±0 .65	0.76-2.55
		Water	1.30±0 .32	0.83-1.72
Cr	0.83	Vegetable	12.12± 20.67	1.00-12.58
		Soil	14.70± 5.84	9.31-25.66
		Water	5.66± 2.73	0.50-9.31
Fe	0.18	Vegetable	456.73± 355.53	88.26-1233.43
		Soil	2507.32± 108.52	2237.32-2617.42
		Water	228.26± 23.32	191.73-263.30

Correlation analysis was conducted to determine the extent of the relationships among metals in vegetable, soils and water over the studied site.
Within media sampled, positive correlations were observed between Pb and Cd, Fe and Cd in water though the correlations are insignificant at p = 0.05. Negative correlation was also found between Cr and Pb, Cr and Cd, Fe and Pb, as well as Fe and Cr in water. Positive correlation suggested that the source contributing these elements or factors responsible for metals presence in water could be the same while negative correlation entails different sources of these metals in water. In vegetable positive correlation was found between Cr and Cd as well between Fe and Cd while negative correlation was seen for other elements. In soil positive correlations were observed between Cd and Pb, Cr and Pb and Fe and Cr. None of this correlation observed was significant at P= 0.05. Negative correlation were observed for other elements tested at p = 0.05. From the result there is likely hood that Pb source in the soil could be responsible for Cd, Cr and Fe presence.
Between media sampled, positive correlations were found for Fe in soil and Pb, Cd, Cr in vegetable indicating similar source of these metals though the correlations are insignificant. The correlation found between Fe in vegetable and Pb, Cd, Cr in soil is also positive but insignificant at p = 0.05. This observation revealed a strong link between the respective metals in the media under study. Similar correlation pattern was seen between Fe in Water and Cr, Cd, Fe in vegetable. Positive and significant correlation was found between Cr in soil and Cd in vegetable. Between Pb in vegetable and Cr in soil, Pb in soil and Pb in vegetable and Cr in water and Cr in vegetable the correlation were negative but significant at P = 0.05.
Results of previous studies [29][30][31][32][28] demonstrated that the food crops grown on contaminated soil posed a health threat to the local inhabitants. The Pb and Cd concentration in

vegetables grown in sampling site were about 7 and 8-fold higher than the maximum permissible level of 5.0 µg/g Pb and 0.2µg/g Cd in plant [33]. The Pb, Cd and Cr concentration of vegetable and soil were higher than reported in related work in the literature [34][30][31][32][28]. Iron was found in all the water samples between 191.73-263.30 ppm with an average value of 228.26±23.32 ppm. The high concentration of Fe in soil, vegetable and water is expected because it has been reported that iron occurs at high concentration in Nigeria soil [35][36].

On the average, the concentration of Pb, Cd, Cr and Fe (Table 2) in the media studied in this work vary with heavy metals detected in similar media from different locations. In a previous work maximum concentration (μg g-1) of 3.4 for Cd, 59 for Pb and 225 for Cr in the waste water irrigated soil of Harare, Zimbabwe was reported [34]. The observed variation could be attributed to geological distribution of minerals that vary from one location to the other [37].

Cadmium when ingested by humans, it accumulates in the intestine, liver and kidney [13]. The health effects of chronic exposure of Cd include proximal tubular disease and osteomalacia. Maximum limit of 0.2 μg/g Cd in plant, 0.01 μg/ml Cd in water, 5.0 μg/g Pb in plant and 5.0 μg/ml Pb in water was prescribed by WHO/FOA [33]. The values for the standard compared to our work indicate Cd and Pb pollution of both water used for irrigation and vegetable grown.

Chromium is considered non-essential for plants, but an essential element for animals. The average abundance of Cr in the earth's crust is 122 ppm; in soils Cr ranges from 11-22 ppm [38]. in this work, Cr was found to ranged between 9.31-25.66 with an average of 14.70±5.84. This value is less than 150 μg/g safe limit giving by EU commission regulation [39] Cr concentration in water is about 56 fold higher than 0.10 μg/ml maximum limit set by WHO/FOA [33]. It is used in alloys, in electroplating and in pigments. Chromium

The average abundance Pb in Earth's crust is 13 ppm, in natural soils background level ranges from 2.6-25 ppm [38] and in this work a range between 5.50-55.25ppm. 24.26-51.21ppm and 12.13-35.04ppm were found respectively in vegetable, soil and water samples analysed Pb in soil is less than 300μg/g and in Vegetable is higher than 0.3 μg/g safe limits giving by EU regulation commission [40]. Lead is the most significant toxin of the heavy metals, and the inorganic forms are absorbed through ingestion by food and water, and inhalation [41]. Lead in water may originate from industrial discharged, mines and smelter discharges and likely from dumping of refuge by the coast and/or inside the water body concerned. Lead poisoning causes inhibition of the synthesis of haemoglobin and in children it leads to poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient [42]

The toxic levels of Cd and Cr ranged from 5-30 and 5-30ppm, respectively [43]. In our study, Cd level falls below the range while Cr levels falls within the range for toxic level. This revealed that the irrigated soil contained high amounts of these metals.

Transfer factor (TF)

Transfer factor (TF) was calculated to understand the extent of risk and associated hazard due to waste water irrigation and consequent heavy metal accumulation in vegetables following [27].

TF= concentration of metal in edible part/concentration of metal in soil.

The food chain (soil–plant–human) pathway is recognized as one of the major pathways for human exposure to soil contamination. Soil-to-plant transfer is one of the key components of human exposure to metals through the food chain.

Our result revealed variations in transfer factor calculated for each element determined in vegetables. Difference in the concentration of metals in the soil and mechanisms of metal uptake by vegetables could be responsible factors [27][28]). Cd has the highest transfer factor of 0.91

followed by Pb (0.87), Cr (0.83) while iron (Fe) has the lowest transfer factor of 0.18. From the above it can be deduce that Cd has the highest mobility rate in the soil while Fe has the lowest mobility rate compare to other elements.

Fig 1 Distribution of concentration of Pb, Cd and Cr in vegetable, soil and water

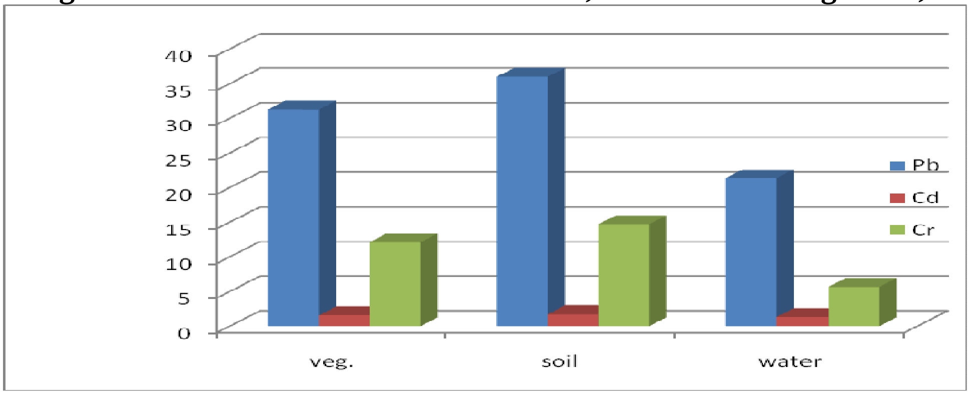


Fig 2 Distribution of concentration of Cd and Cr in vegetable, soil and water

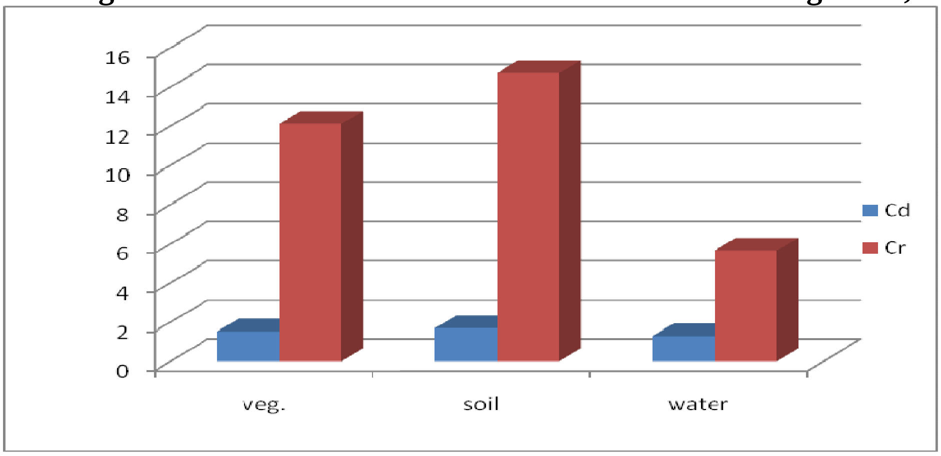
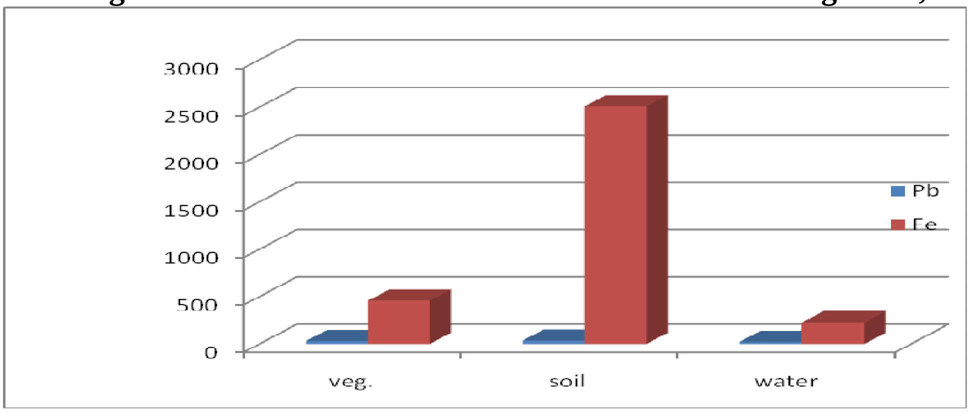


Fig 3 Distribution of concentration of Cd and Cu in vegetable, soil and water



CONCLUSION

The common practice of application of compost manure from dumpsite by farmers in Zaria and irrigation with contaminated water may have led to the accumulation of heavy metals in soil. These metals are found to be transferred from soil to the vegetables and subsequently animals and humans that consume these vegetables thereby increasing their heavy metals burden. Pb and Cd levels were found greater than their prescribed maximum level in vegetable by WHO/FAO. This suggests contamination of the analysed vegetable. For the safety of population that depends on such vegetables as mineral and fibre source, routine assessment of heavy metals contaminants in vegetables grown on irrigated farmland is necessary. In order to reduce the health risk caused by taking the contaminated vegetables, the use of compost to boost yield and dumping of refuse in or along the coast of the river should be discourage by authority.

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