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Transfer Factors and Potential Ecological Risk Index of Potentially Toxic Metals in Soil, Irrigation Water and Vegetables along Gada River Bank of Jigawa State, Nigeria

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ABSTRACT

In recent decades, the concentrations of heavy metals in vegetables are on the increase due to anthropogenic activities. This prompted the current study to assessed the accumulated potentially toxic metals in the soil, irrigation water, and edible part of selected vegetables along Gada Dam of Jigawa State, Nigeria, as well as to evaluate the translocation factor, the Monomial Ecological Risk (E_r^i),and the potential ecological risk index. The results revealed that the concentrations of these potentially toxic metals are in the order of Mn > Pb > Zn > Ni > Cd > Cu in both water and soil samples. The transfer factor revealed that, the metals were within the moderate safe level of $1 \leq C_F^i < 3$for consumption, with cabbage being a better Zn absorber compared to lettuce. The monomial potential Ecological assessed in these vegetables were within the Low Risk values of $E_r^i < 40$ except for Cd in both lettuce and cabbage which are in the range between $80 \leq E_r^i < 160$, regarded as considerably risk. While Ni in cabbage is within $40 \leq E_r^i < 80$ considered as moderate risk. The RI for cabbage is 223.961 and that of lettuce is 172.861, both of which were deemed very dangerous, according to the grade of Potential Ecological risk posed by toxic metals. All the samples analyzed contained certain levels of these metals, indicating an evidence of contamination, which may be due to anthropogenic activity.

Keywords: AAS analysis, Bio-amplification, Toxic Metal, Transfer factor and Vegetables

INTRODUCTION

In most of the developing nations, contamination of farmlands by heavy metals happened due to emission of toxic heavy metals, leading to environmental problem (Ahmed *et al.*, 2019). In recent decades, the concentrations of heavy metals in irrigation water, soil, and vegetables is on the increase on farmlands due to anthropogenic activities (Zhao *et al.*, 2015; Aiman *et al.*, 2016). Irrigation water contaminated with industrial wastewater has resulted into significant heavy metals contamination in soils and crops, particularly the edible parts of the growing plants (Ritter *et al.*, 2002; Khan *et al.*, 2008; David and Kacholi, 2018). These metals are called “heavy metals” because, in their standard state they have a specific gravity of more than 5 g/cm^3 (Chopra *et al.*, 2009; Saatloo *et al.*, 2014). They accumulate in soils and plants over time and can have a detrimental impact on plant physiological activities (e.g. photosynthesis, gaseous exchange, and nutrient absorption. In small concentrations, the traces of the heavy metals in plants or animals are non-toxic, however, heavy metals such as lead, cadmium and mercury are exceptions as they are toxic even in very low concentrations (Sharma and Dubey, 2005; Guan *et al.*, 2014; Kfle *et al.*, 2020). Unlike certain organic pollutants, metals cannot be degraded by chemical or biological processes in the ecosystem and can pass through a food chain, thereby exposing the consumers to concentrations many times greater than in the water, soil, or vegetables. This mechanism (also known as bioamplification, biomagnification, or bioaccumulation) has a number of consequences in the past (Abarnou, 2009).

The fact that, food is essential for healthy growth of living things especially humans, and due to the nutritional values of vegetables, people are encouraged to add vegetables to their meals. Lettuce and cabbage are vegetables that are consumed in almost every house in Kazaure and communities around and are usually consumed in their raw state. However, these vegetables are sometimes contaminated with heavy metals and can results to the malfunction of some human organs. Considering the probable toxicity and persistent nature of heavy metals and the frequent consumption of vegetables, this research is aimed at assessing the concentration levels, translocation factor of some potential toxic metals (Pb, Mn, Ni, Zn, Cd, and Cu), the Monomial

Ecological Risk (E_r^i) of single potentially toxic metal and potential ecological risk index of these potentially toxic metals in cabbage and lettuce samples along Gada irrigation areas of Kazaure Local Government, Jigawa State- Nigeria.

MATERIALS

Agilent Technology 200 series Atomic Absorption Spectroscopy 240FS, Garmin GPS 60^{TM} Personal Navigator, Mi105 Martini Professional portable pH/temperature meter, Hot plate, Analytical weighing balance, Whatman 42 filter paper, Scoop and Fabricated Vendor sampler.

Reagents

All reagents are of analytical grade purity and used without further purification.65% HNO_3, 37% HCl, and 72% HClO were purchased from QRëCTM. Lead nitrate, zinc oxide, anhydrous cadmium chloride, copper nitrate tri-hydrate, nickel nitrate hexa-hydrate, and manganite chloride tetra-hydrate reagents were all purchased from Sigma Aldrich.

Plant, Soil and Water Sampling

Leaves of the vegetable samples (Cabbage and Lettuce) were collected from Gada river bank located between 12° 39′ 10″ N, 8° 24′ 43″E on the globe, using stratified sampling techniques, and were stored in a freezer during the research work. For each plant sampled, the surrounding soil was collected using scoop as described by Onianwa and Fakayode (2000). The coordinate location of each sampling site was read and recorded using Garmin GPS 60^{TM} Personal Navigator site for the months of December, January, February and March. The soil sample were dried in an oven at 40°C for 24h, ground with pestle and motor and sieved using 0.2mm sieve. Representative samples were obtained by coning and quartering techniques as described by Campos-M and Campos-C, (2017).

Water samples were collected at various depth (0.5 m, 1.0 m, and 1.5 m) using modified Van Dorn sampler, then transfer to an amber 250 cm^3polythene bottles. The temperature and pH were read and recorded immediately at the sampling site and acidified with HNO_3 acid to stabilize the metals before transported to the laboratory where the samples was filtered through Whatman No: 42 filter paper and stored in refrigerator at 4 °C as described in Campos-M and Campos-C (2017).

Vegetables samples was washed with distilled water and allowed to drain at room temperature. Then, the edible parts were chopped and dried in a hot air oven at 40 °C for 48 h. Samples were ground into powder using pestle and motor as described by Egwu *et al.* (2019), and was stored in a polythene bags for further analysis.

Digestion of Samples for AAS Analysis

The Vegetable, soil and water samples were digested in *aqua regia*, using a freshly prepared acid mixture of cm^3 65 % HNO_3 and 6 cm^3 37 % HCl (i.e. 1:3 ratio of HNO_3 and HCl respectively) as describe by Jamali *et al.* (2007) and Uddin *et al.,* (2016). The potentially toxic metals (Pb, Mn, Ni, Zn, Cd, and Cu) in the digested aliquot of the samples and control were analysed by Agilent Technology 200 series Atomic Absorption Spectroscopy 240FS and the concentration of each metals in water were calculated using the Equation 1, and soil, and vegetables using equation 2.

$$metal(mg/L) = \frac{C\ x\ V_1}{V_2} \qquad (1)$$

$$metal(mg/Kg) = \frac{C\ x\ V_1}{m} \qquad (2)$$

Where: C is the concentration in mg/L of the metal in the final extract

V_1 is the volume of the final extract (50mL), and

V_2 is the volume of original sample in mL

m is the mass of original sample in grams (1g) (Wang *et al.,* 2019)

Preparation of standards for the AAS Analysis

Standard stock solutions (1000 mg/L) of zinc, manganese, cadmium, lead, copper and nickel metal of high purity were bought from Sigma Aldrich. Then appropriate volumes were diluted to obtain the working standard solutions of various concentrations for plotting calibration curves.

Transfer Factor (TF):

The transfer coefficient was calculated using Equation 3, as described by Kim *et al.,* (2012); Aktaruzzaman *et al.,* (2013); Mirecki *et al.,* (2015).

$$TF\ or\ C_F^i = \frac{C_{plant}}{C_{soil}} \qquad (3)$$

Where:

C_{plant} = metal concentration in plant tissue, mg kg^{-1} fresh weight and

C_{soil} = metal concentration in soil, mg kg^{-1} dry weight.

Potential Ecological Risk Index of heavy metals:

The RI was calculated as follows

$$F_i = \frac{c_n^i}{C_o^i} \qquad (4)$$

$$E_r^i = T_r^i\ x\ F_i \qquad (5)$$

$$RI = \sum_{i=1}^{n} = E_r^i{}_{Zn+} + E_r^i{}_{Mn} + E_r^i{}_{Cu} + E_r^i{}_{Ni} + E_r^i{}_{Pb} + E_r^i{}_{Co} \qquad (6)$$

Where F_i is the single metal pollution index; c_n^i is the concentration of metal in the samples; C_o^i is the reference value for the metal; E_r^i is the monomial potential ecological risk factor; T_r^i is the metal toxic response factor (Aktaruzzaman *et al.,* 2013). The values for each element are in the order Zn =

Mn =1 < Cu = Ni = Pb = 5 < Cd = 30 (Chen *et al.*, 2020).

RESULTS AND DISCUSSION

The temperature and pH of Gada water collected between December and March ranged of between 19.8 to 26.5^{O}C and 6.92 to 7.31 respectively as in Fig 1.This is in line with the finding of OlabimpeIyabo *et al.*, (2017). Temperature affects the amount of dissolves oxygen in water, which is essential for both aquatic life and other oxidation processes that require oxygen, while pH is a measure of acidity or alkalinity, which affects the water's consistency for maintaining aquatic life (Eugene, 2000).

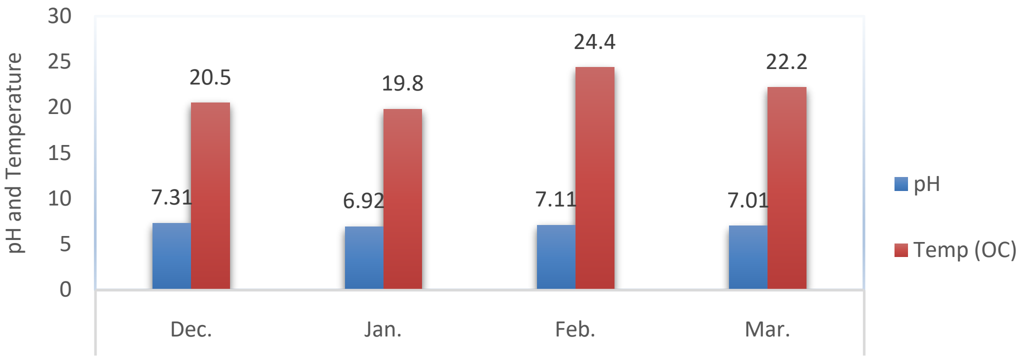

Fig. 1: pH and temperature of water sample between Decembers to March

The results for the potential toxic metals analyses in water and soil are presented in Figs. 2 and 3. It revealed that the highest concentrations of Zn and Mn in the water sample analysed were 0.087 and 0.308 mg/L and that in soil were 52.002 and 413.805 mg/kg in the months of December. The Zn concentrations were below the WHO 1996-recommended allowable level of 5 mg/L for water and 50 mg/kg for soil, while Mn exceeded 0.05mg/L for water and 200 mg/kg for soil. For cadmium, the highest concentration in water is 0.013 mg/L, and 1.153 mg/kg is observed in soil in December. Except for soil, all values were below the permissible limit set by the Dutch 2002, standard for cadmium. The high concentration of Cd may be attributed to location of the soil close to the river where different salts of cadmium are washed, dissolved and carried along into the river, it may also be due to precipitation of various Cd from dust during the harmattan season (Ahmed *et al.*, 2019). The highest lead concentrations in water and soil were 0.077 mg/L and 46.260 mg/kg in the months of December and February, respectively. The Pb in soil are within the WHO 1996 permissible limit of 985 mg/kg, and exceeds the WHO-recommended allowable limit of 0.005 mg/L for water. The possible sources of Pb could be running water from road and vast number of hills surrounding the dams (David and Kacholi, 2018). From the study, Cu was only detected in soil sample, with the highest concentrations of 7.328 mg/kg in February which is below the Dutch 2002 normal acceptable maximum level of 36 mg/kg. Furthermore, the highest Ni concentrations in water and soil are 0.163 mg/L, and 21.938 mg/kg respectively in February and December. The concentrations in water exceeds the WHO 1996 allowable limit of 0.05 mg/L, which may be attributed to the waste containing Ni from various non-point sources, and other commercial structures, as well as industrial discharge, plant smoke stacks, and urban sewage. While the concentrations fall within the WHO 1996 allowable limit of 35 mg/kg for soil.

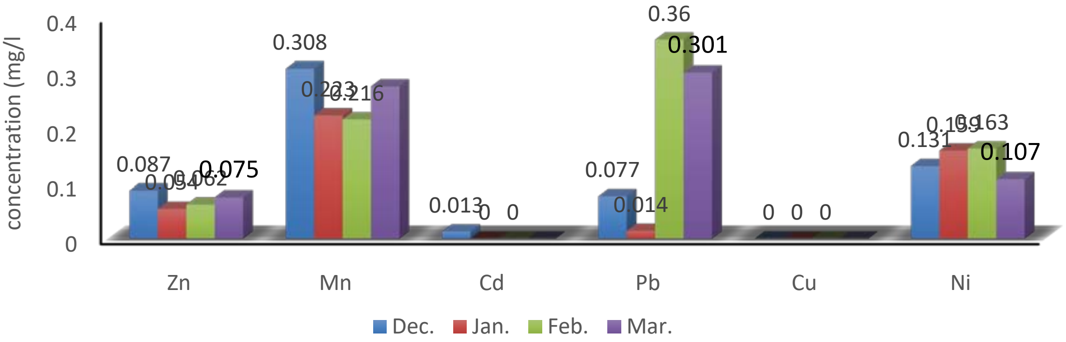

Fig. 2: Concentration of the potentially toxic metals in water sample(mg/kg)

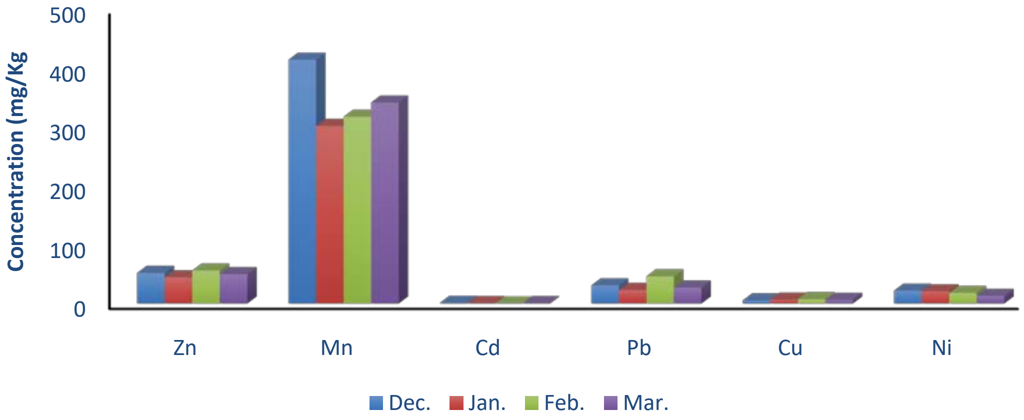

Fig. 3: Concentration of the potentially toxic metals in soil sample (mg/kg)

Additionally, the results for the different metals concentrations in the vegetable samples are presented in Figs. 4 and 5. The highest Zn and Mn levels in lettuce and cabbage samples are 29.585 and 100.883 mg/kg, and 19.173 and 35.462 mg/kg, respectively. This agrees with Ogundele *et al.* (2015) and Limin and Changxu (2019). The Zn concentrations are higher than the WHO 1996 recommended acceptable maximum level of 0.60 mg/kg for vegetables. Although plants only need a small amount of zinc, as essential micronutrient and a component of many enzymes and proteins, it is critical to plant growth because it is involved in a variety of processes. Though zinc deficiency and toxicity are uncommon, they both have an adverse effect on crop growth and quality. It increases the activity of digestive enzymes and aids the plant's ability to survive cold temperatures by assisting in the formation of chlorophyll and certain carbohydrates, as well as the conversion of starches to sugars (Anonymous, 2021). In addition, zinc is required for the formation of Auxins, which aid in growth control and stem elongation. When tissue zinc levels exceed 200 ppm, which is uncommon, zinc toxicity may occur (Anonymous, 2021). Conversely, Mn concentrations are below the WHO 1996 recommended acceptable maximum level of 100 mg/kg. Varying concentration of this metal has been reported in East Ethiopia (Duressa and Leta, 2015). Manganese is a necessary component in nearly all living organisms, acting as an enzyme cofactor or a catalytic metal (Andresen *et al.*, 2018). Its deficiency is uncommon in humans, although Mn poisoning symptoms such as hepatic cirrhosis, polycythemia, dystonia, and Parkinson-like symptoms may occur when *exposed* to high concentrations. Even as Mn is required in limited amounts for plant growth and reproduction, it is just as important as the other nutrients for development (Soetan *et al.*, 2010; Santiago *et al.*, 2020).

Furthermore, the highest Cd level in lettuce and cabbage of 1.568 and 1.375 mg/kg are observed in the months of January and December respectively. The concentrations in both vegetables exceeded the WHO's allowable limit of 0.02 mg/kg and the Dutch norm. This may be due to the river's existence as a point source, as well as dust precipitation during the harmattan session. Cadmium is a potential carcinogen (Sharma *et al.*, 2016) and Cd-rich waste waters results in serious human health problems ("Itai-itai" disease), which was first reported in the 1970s (Mclaughlini and Singh, 1999).

With regards to Pb metal, the highest concentration of 35.532 mg/kg and 56.277 mg/kg are detected in lettuce and cabbage samples, both in the months of February. This finding is in accordance with the work of Aktaruzzaman *et al.*, (2013). The concentrations are higher than the WHO 1996 recommended permissible maximum of 2 mg/kg for vegetables. It may be attributed to significant quantities of Pb in many electronic devices and Lead-acid batteries widely used in automobile batteries, which can end up in soil through erosion (Ogundele *et al.*, 2015).

Besides Cu was detected only in lettuce with the highest concentration of 1.308 mg/kg for the month of March. According to WHO 1996 standards, the concentrations are below the permissible maximum level of 10 mg/kg in plants. Copper is an important micro element for plant growth and occurs naturally in soil and air, however, human activities may cause it to accumulate above the allowable limit, and its content varies depending on soil type and contamination source (Onder *et al.*, (2007).

Further highest Ni concentrations of 12.263 mg/kg and 12.643 mg/kg were recorded in January for both lettuce and cabbage samples, respectively. All the values for both vegetables are above the WHO 1996 prescribed allowable maximum level of 10 mg/kg. This may be due to anthropogenic activities, and is in agreement with the finding of Aktaruzzaman *et al.* (2013), where varying concentrations of these metals were discovered in both water, soil and edible part of vegetables in District Mardan, Pakistan (Hussain *et al.*, 2013). Because it acts as an activator of the enzyme urease, nickel is considered an essential trace element for human and animal health, as well as plant health. Ni is absorbed easily and rapidly by plant (Hjortenkrans, 2003).

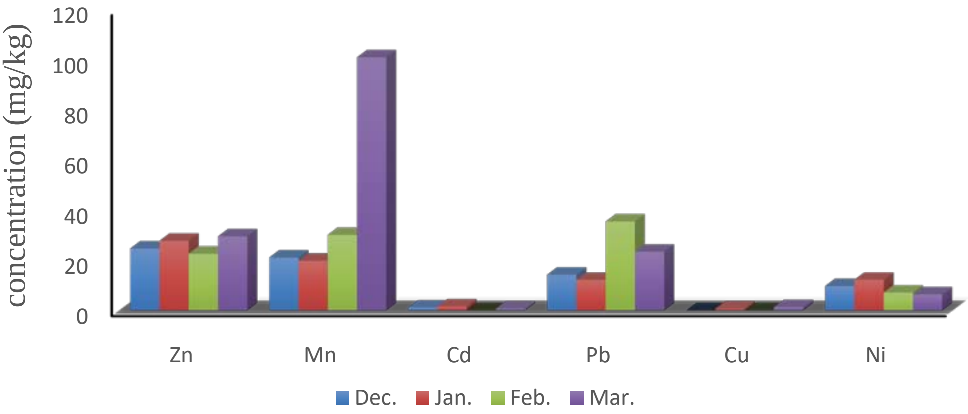

Fig. 4: Concentration of the potentially toxic metals in lettuce sample (mg/kg)

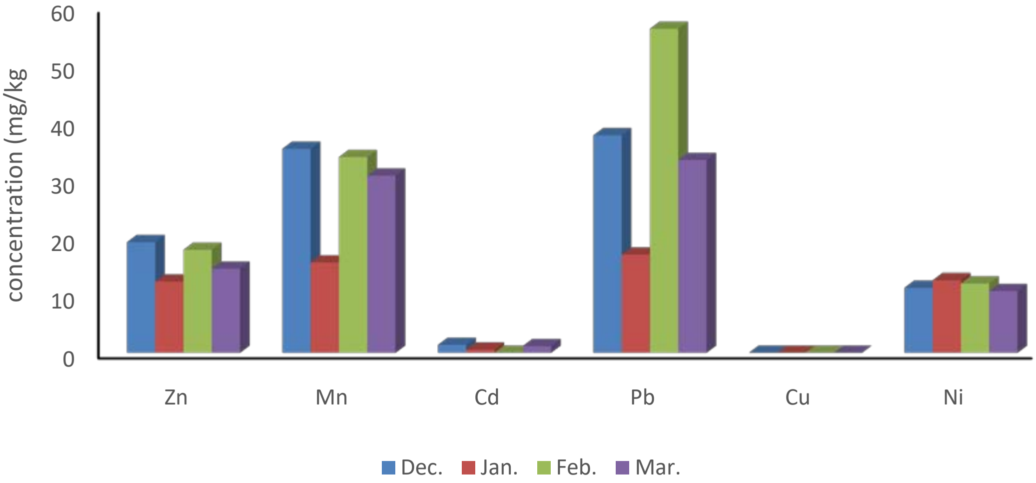

Fig. 5: Concentration of the potentially toxic metals in cabbage sample (mg/kg)

Transfer Factor of the Potentially Toxic Metals in Lettuce and Cabbage Sample

The transfer factor of lettuce and cabbage are depicted in Figs. 6 and 7, with Cd having the highest TF value of 2.704 in lettuce and 0.925 in cabbage. This indicated a possible contamination of Gada farm land as it falls within the moderately contamination recommended level of $1 \le C_F^i < 3$ in both vegetables. Similar TF of Cd in varying plants and sediments were reported by Aktaruzzaman *et al.*, (2013) and Jiang *et al.* (2014). The next metal with the highest transfer factor is Pb, followed by Zn and Mn which are both within the safe level for consumption as described by Limin and Changxu (2019). But lettuce was shown to be a better Zn absorber compared to cabbage, whereas, the absorption capacity for manganese seems to be the same. Similarly, Cu and Ni are within the safe level of $C_F^i < 1$ as described in Limin and Changxu (2019) and the two vegetables seem to have the same absorption capacity for nickel. Although there was no obvious health danger to the local public consuming the vegetables grown in the area, the risk could be multiplied when all of the heavy metals are considered together as plants transfer factor quantifies bioavailability or influential factor on the prediction of uptake of such metals to agricultural products (Kim *et al.*, 2012).

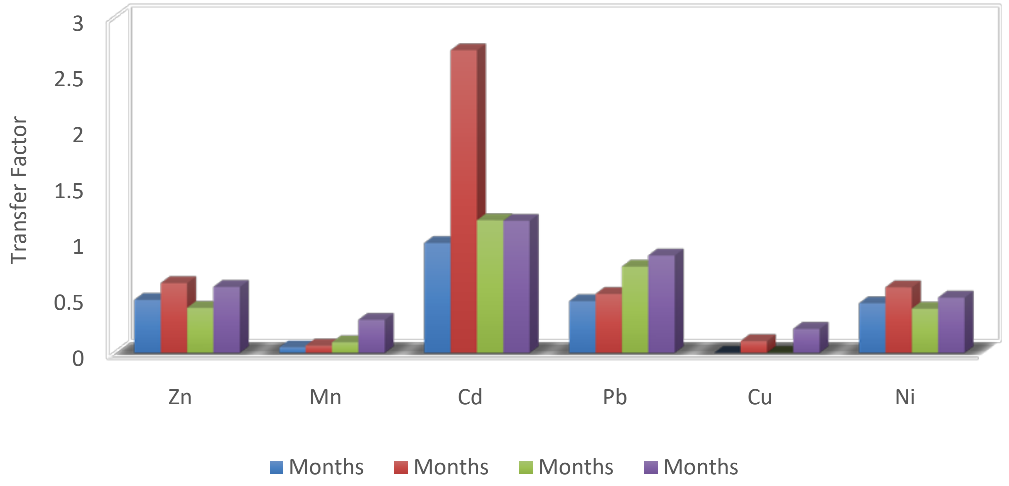

Fig. 6: Transfer Factor of the potentially toxic Metals in lettuce sample (mg/kg)

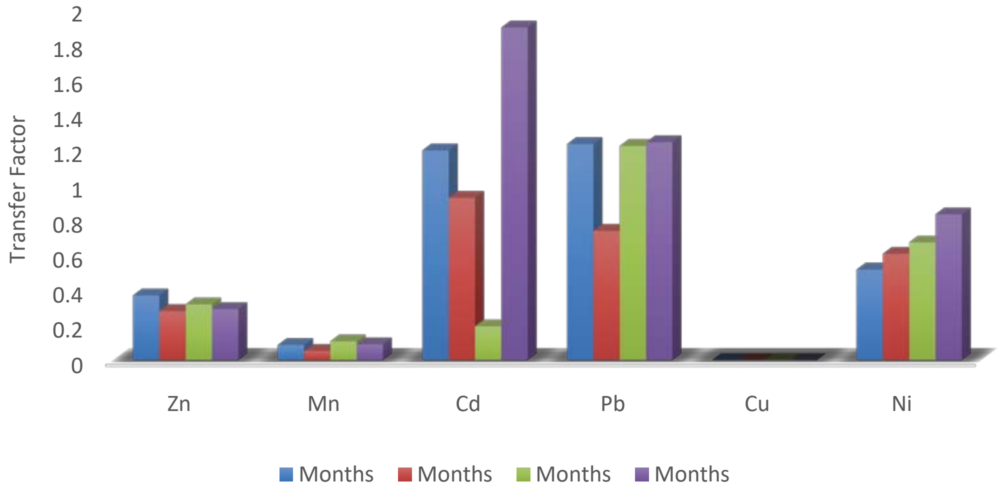

Fig. 7: Transfer factor of the potentially toxic metals in cabbage sample (mg/kg)

Monomial Ecological Risk (E_r^i) and Potential Ecological Risk Index (RI) of the Potentially Toxic Metals in Lettuce and Cabbage Sample

The monomial ecological risk (E_r^i) of the metals analysed are in the order of Cd> Ni> Pb>Mn>Zn>Cu; in both vegetables with the highest value of 181.4077 and 126.0702 Cd in lettuce and cabbage, respectively. Monomial Ecological Risk assessed in these vegetables between December to March are within the Low Risk values of E_r^i<40, with the exception of Cd in both lettuce and cabbage which are in the range between $80 \leq E_r^i < 160$, regarded as considerably Risk, and Ni in cabbage which is within $40 \leq E_r^i < 80$ considered as Moderate Risk.

Finally, the Potential Ecological Risk Index (RI) for cabbage and lettuce are 223.961 and 172.861, respectively. Both values are deemed very dangerous, according to the grade of Potential Ecological risk posed by toxic metals (Aktaruzzaman *et al.*, 2013). The cabbage could be considerably more dangerous, as its RI Values is within the range of $200 \leq \text{RI} < 400$. This means that the inhabitants' intake of these vegetables may pose a high risk to their health.

CONCLUSION

From the research outcomes, the concentrations of these potentially toxic metals are in the order Mn > Pb > Zn > Ni > Cd > Cu in both water and soil. Furthermore, all the samples analyzed contain certain levels of these metals, indicating an evident of contamination, which may be due to anthropogenic activity, such as the disposal of refuge and domestic waste containing these metals. While the monomial potential ecological risk of these metals is in the order of Cd >Pb> Ni > Zn and Mn in lettuce and Cd >, Pb >, Ni >, Mn >Zn in cabbage. Lastly, the RI of the two vegetables indicated that, both were deemed very dangerous, according to the grade of Potential Ecological risk posed by toxic metals.

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