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Impact of Wastewater and Canal Water Irrigation on the Accumulation of Copper in Maize and Millet of Different Districts of Punjab Pakistan

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Cover Page Footnote

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IMPACT OF WASTEWATER AND CANAL WATER IRRIGATION ON THE ACCUMULATION OF COPPER IN MAIZE AND MILLET OF DIFFERENT DISTRICTS OF PUNJAB PAKISTAN

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ABSTRACT

In current work, we examined the absorption of metal Copper in generally grown food crops (Maize & Millet), cultivated in the waste water irrigated different Districts of Punjab, Pakistan. Analyzed samples of Water, Soil, shoot and grain were processed through atomic absorption spectrometric method. Our findings of Copper in water and Shoot were highest for Millet of Sargodha, irrigated with wastewater (1.69 mg/kg and 1.43 mg/kg respectively). In soil and grain samples maximum absorption of Cu was obtained in the waste water irrigated Maize (Sargodha) and Millet (Sheikhupura). Overall, Cu level was within the acceptable parameters set by FAO/WHO (2001). In this study, we also find out different indices such as Enrichment factor, Translocation factor, Pollution Load Index, Bio-concentration factor, Daily intake of metal and Health Risk Index. The study determined that frequently intake of waste watered forages in experimenting zone may carry possible health uncertainties in inhabitants.

Keywords: Maize, millet, copper, wastewater, FAO/ WHO.

INTRODUCTION

Wastewater impacts plant negatively when it's used for the irrigation purposes. Prolonged exposure to waastewater results in accumulation of different heavy metals in soil. When a soil is irrigated for long time with Wastewater it started to accumulate the heavy metal there. Surveys were conducted by (WHO) and it was found heavy metal content were above the tolerable limit and it is very hazardous for the all living beings. As the observations of Kho et al., (2007) and Durkan et al., (2011), human activities took a great part in distribution of heavy metal in soil and consequently lead hazardous effect on the living bodies.

Wastewater is a mixture of different types of substances both organic and inorganic. Among there, organic substances are less hazardous as they decomposed off with the passage of time and leave a less harmful effect on the soil as they broken down into simpler substances and dissolved. But the case of inorganic substances is different as they contain the different components of the heavy metals such as ion metalloids which stay in soil and Wastewater for a long time period. Finally when the crops are irrigated with the Wastewater the all inorganic metal which remains accumulated and dissolved in Wastewater transferred to the soil and stay there for long time (Kabata & Pendias, 2002).

Maize is considered as a very vital crop grown in the world. Maize production in 2012 was 872 million metric tons. It's mainly used in fodder for livestock and used for the production Ethanol, biofuel. Owing to the Importance of the maize in crop family a special sort of comprehensive layout is needed to genetically develop such varieties which are resistant to herbicides and pesticides and increase the production of bio energy (Je et al., 2014).

Millet possesses the very unique properties as it contains the high amount of calcium dietary fiber polyphenols and protein (Devi et al., 2011). Millet, as compared to other cereal contain the sulphur containing amino acids (methionine and cysteine) which make it rich in nutrient amount. Millet contains the fat content whose level is much higher than the maize, rice, and sorghum (Obilana and Manyasa, 2002). Copper is responsible for different processes occurring in plant. Cu pro-enzymes employed its ability to switched between oxidized to reduced state (Atsdr, 2002; Harvey & McArdle, 2008; Stem, 2010).

In this study, we tried to also find out different indices such as Enrichment factor, Translocation factor, Pollution Load Index, Bio-concentration factor, Daily intake of metal and Health Risk Index. The study will help determine that frequently intake of waste watered forages in experimenting zone may carry possible health uncertainties in inhabitants.

MATERIALS AND METHODS

Experimental Part

Study Area

Current study was conducted in various districts of Punjab (Lahore, Sargodha, Kasur, Sheikhupura and Faisalabad) between periods of 2018-19. The climate in these districts was very hot in summer while colder was observed in winter. The maximum and minimum temperatures of these districts are 50^{o}C and 12^{o}C respectively. These districts are well known for production of maize and millet.

Mainly, irrigated water type (canal and sewage water), soil, shoot and grain samples were collected from different districts of Punjab. Four replicates of each sample were collected from different sites of each district and mixed them to make a composite sample (one replicate).

Water Sampling

Both canal and wastewater samples (100 ml each) were collected from various districts. Samples collected into polypropylene flask cleaned up with HNO_3 (1%) and they conveyed to the research centre where stored (4˚C) for later on analysis purpose AFNOR, (1997).

Soil Sampling

In this research work, soil samples (80 replicates) were collected from each district at the depth of 0-15cm and put into air sealed bags to keep them away from internal and external contamination. Further, they were transmitted to research lab for the analysis of studied metals.

About 10 g of each soil sample was gathered from all design of location where the fodders were grownup. Five merged trials were organized, dehydrated in midair and placed in sealed paper bags. Samples were put in oven (72^{0} C) for 48hours and then in incubator (70$^{\mathbf{0}}$ C) for remaining 5 days (Rhue and Kidder, 1983).

Shoot and Grain Sampling

Respective specimens of Maize and Millet were sweep up by means of refined water. Moreover, save them in paper bags after air drying process. Grains are detached from their shoots. Proper identity number was assigned to each sample bag and forced them in the oven.

Sample Preparation

All the oven-dried samples are crushed in mortar & pestle, to obtain a fine powder of samples for digestion purpose. About, one gram weighted each sample was used for digestion process which was performed by ‘‘Wet digestion method’’.

Apparatus used for digestion was digestion flasks of 100 ml, beakers (50 ml and 100 ml), measuring cylinder (50 ml), pipette (10 ml), stirrer, hotplate, filter paper, gloves, sulphuric acid (H_2SO_4) 70 % and Hydrogen peroxide (H_2O_2) 50 % and newly organized condensed water for illustration research.

Digestion (Wet Method)

One gram weighted each sample was taken into the conical flask and digested on the hot plate with a mixture of conc. HNO_3 and H_2O_2 (1:2). Further, H_2O_2 was added to the mixture to attain colorless solution when the fumes fade away. If required then again heated the mixture on hot plate, until the appearance of transparent solution. Digested solution was cooled down to a room temperature and diluted up to a final volume of 50 ml. Finally, diluted volume was filtrated with Whatmann filter paper No. 42.

Metals Concentration

All examined samples were processed through Atomic Absorption Spectrophotometer for Copper (Cu) metal determination. Stock solution was used to gain the standard solution against which standard curve was established.

Quality Control

The analyzed data was compared with the international standards to check out reliability and precision of results. The repeated analysis of sample can also verified the accuracy in examined readings.

Statistical Analysis

Variance and correlation of data was revealed by the SPSS (special program for social sciences) software version No. 20. By the application of ANOVA (Two-way), mean significance of heavy metals concentration was practiced in the samples. According to Steel et al., (2006), the possibility of significant difference (at 0.001, 0.01 and 0.05) was also appraised in analyzed data.

Evaluated Indices

i. Bio concentration Factor (BCF)

For the evaluation of Cu transportation in soil to food crop, a BCF index was practicable (Cui et al., 2004):

$$BCF = \frac{\text{Metal level in food crop}}{\text{Metal level in soil}}$$

ii. Translocation Factor

Ability of a plant to translocate the amount of heavy metal from shoot to grain region was determined by TF index. $A = \pi r^2$Formula given by Li et al., (2012) was:

$$\text{TF} = \frac{\text{Metal conc. in grain}}{\text{Metal conc. in shoot}}$$

iii. Pollution Load Index (PLI)

Liu et al., (2005) declared that PLI ascertained the presence of contaminated heavy metal level in the soil.

$$PLI = \frac{(M)IS}{(M)RS}$$

(M)IS = Concentration of Cu (mg/kg) in investigated soil

(M)RS= Referenced concentration of Cu in soil

Enrichment Factor (EF)

According to Menard & Chesselet (1979), EF was computed by this equation:

Enrichment factor (EF) = Metal conc. in forage / Metal conc. in soil) sample

(Conc. of metal in forage/Conc. of metal in soil) standard

Daily Intake of Metals (DIM)

DIM level of copper was assessed by this specified formula (Sajjad et al., 2009).

$$DIM = C_{metal} \times C_{factor} \times D_{food\ intake} / B_{average\ weight}$$

C_{metal} is the analyzed metal concentration in forages of this study, C_{factor} is a conversion factor whose value 0.085 was utilized to gained the dry weight of forage (Rattan et al., 2005). $D_{food\ intake}$ is a given daily intake of maize and millet. According to Wang *et al*. (2007), its value was 0.242 mg per kg consumed by a person while $B_{average\ weight}$ is referred as prescribed average body weight 55.9 kg of a person (Wang et al., 2005).

Health Risk Index (HRI)

The proportional difference between the DIM of food crops and prescribed Rfd level, determined the HRI value. USEPA (2002) presented the formula as:

Health risk index (HRI) = Daily intake of heavy metal (DIM) / Oral reference dose (Rfd)

When the HRI value>1 was found for any metal, it indicated that the consumer health faces the possible toxic risks of this metal or may be carcinogenic in nature (USEPA, 2013).

RESULTS

Water

The ANOVA of copper in water verified significant impact ($p < 0.05$) in District, District x Forage, Irrigation source and Irrigation source x District x Forage but non -significant demonstrated in Forage, Irrigation source x District (Table 1). The copper in water ranges from 0.102-1.69 mg/l. Maximum value was identified in sewage watered source of Sargodha whereas minimum level was acquainted in the canal water source of Faisalabad (Table 2, Figure 1).

Soil

The results from ANOVA exhibited significant effect in soil from Irrigation source while the non-significant impression in Forage, District, District x Forage, Irrigation source x District, Irrigation source x Forage, Irrigation source x District x Forage (Table 1). In soil the copper in different forages and different districts ranges from 0.07- 1.305 (mg kg^{-1}). Waste water irrigated maize in Sargodha district showed highest value while millet irrigated with canal water at Faisalabad site presents the minimum Cu concentration (Table 2, Figure 2).

Shoot

The results of ANOVA depicted significant effect ($p < 0.05$) in shoot of Irrigation source, Irrigation source x Forage, District x Forage, Irrigation source x District x Forage and non-significantly analyzed in District, Forage, Irrigation source x District (Table 1). The trend of copper concentration in shoot varied from 0.093-1.4. (mg kg^{-1}). Highest value was found in millet of Sargodha watered with sewage water (Table 2, Figure 3).

Grain

The analysis of variance in grain demonstrated significant effect ($p<0.05$) in District x Forage Irrigation source, Irrigation source x District, Irrigation source x Forage, and Irrigation source x District x Forage but non-significant impact of District and Forage (Table 1). The concentration of copper in grain fluctuated from 0.06- 0.502 (mg kg^{-1}) while Cu value 73.3 mg kg^{-1} was specified for grains as per FAO/WHO standards (Table 2, Figure 4).

Bio Concentration Factor

The BCF in soil to grains relation, fluctuated as 0.16-2.014 mg/kg for Cu. Maximum transfer occur in canal watered millet (Sheikhupura) and minimum transfer was observed in forage maize that received sewage irrigation source (Sargodha) (Table 3, Figure 5)

Translocation Factor

The transfer of copper fluctuated from 0.22 to 1.75. Maximum range was found in millet of Sheikhupura of canal water. Minimum amount of translocation was also found in the millet but irrigated with sewerage water of Sargodha region (Table 3, Figure 6).

Pollution Load Index

PLI range for copper was varied from 0.008 to 0.155. Maximum value was appraised by the maize forage in Sargodha irrigated through waste water and minimum concentration was identified in the canal irrigated millet of Faisalabad (Table 3, Figure 7).

Daily Intake of Metal

Cu concentration ranges from 0.00011 to 9.71. Maximum of DIM was observed in the waste watered maize grown on Sheikhupura whereas forage maize when irrigated with sewage water presented the minimum intake of copper (Table 3, Figure 8).

Health Risk Index

Results revealed that HRI for Cu fluctuated from 0.00063 to 0.0046 mg kg^{-1}. The uppermost risk index was showed in millet of Sheikhupura irrigated with Wastewater whereas lowered health risks were associated with the intake of maize forage, grown on canal water irrigated region of Faisalabad (Table 3, Figure 9).

Enrichment Factor

In copper the value of EF fluctuate from 0.03-0.12 mg/kg. Maximum EF values were recorded in millet of Kasoor i.e 0.127 and lowest was recorded in Millet of Lahore in both the source of irrigation was Canal water (Table 3, Figure 10).

DISCUSSION

Our results showed the Cu concentration in water which was similar to findings of (Khan et al., 2015). Our results have indicated greater than permissible limits of FAO (1992). Kacholi and Sahu (2018) study documented higher values of Cu (2.3mg/kg) in soil with respect to current findings. Mean absorption of Cu in soil was found within their respective permissible limit of 100 set by European Commission (2006). It has been observed that the uptake of the Cu from the soil to the plant roots is exaggerated by many plant factors to larger amount. Plant factors have also been stated to have a great impact on the uptake of Cu from the soil by the roots. Dependent on the doings of the roots different plants shows various events and exudates and these have important effect on the phyto availability and solubility of Cu in soil (Stoltz and Greger, 2002).

As the sewage water had the maximum absorption of this metal. Basically, industrial and metal treatment workshops, automobile emissions, waste runoff, fertilizer and fungicidal applications are the sources of copper (Kabata and Pendias, 2001). Lowest value was present in canal watered maize of Sheikhupura. Accumulation of Cu in shoot was higher against the findings of Awokunmi et al., (2015). The Cu concentration falls down than acceptable limit of FAO/WHO (2001).

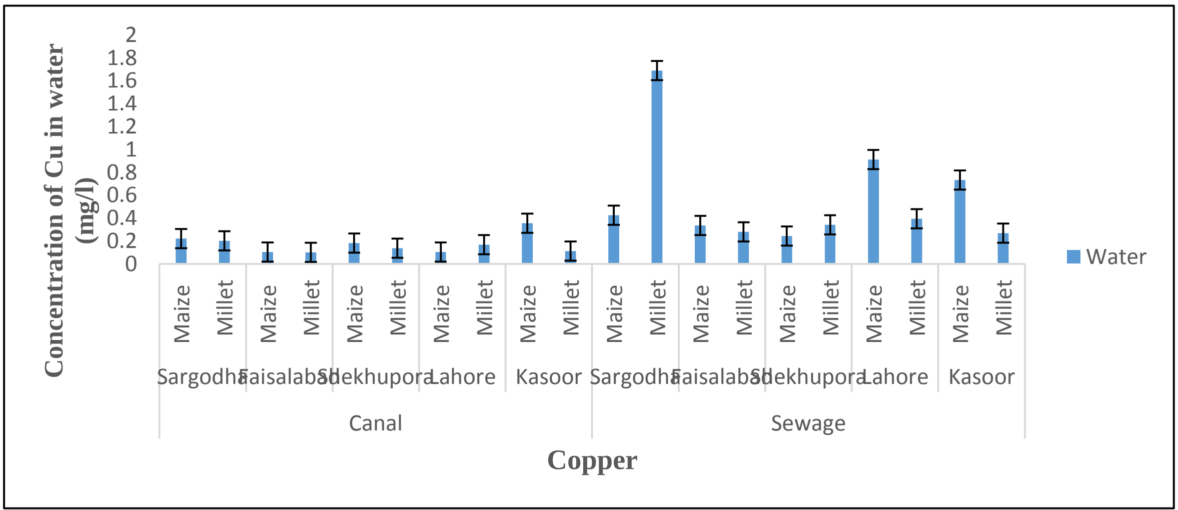

Figure 1: Copper concentration in canal and sewage water (mg/l) of different districts.

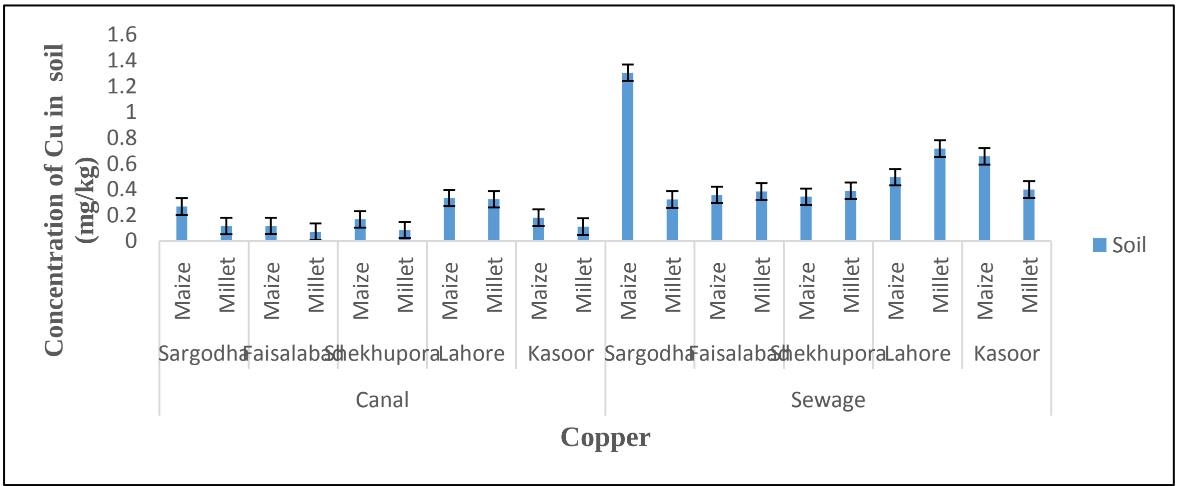

Figure 2: Copper concentration differed in canal and sewage water irrigated soil (mg/kg).

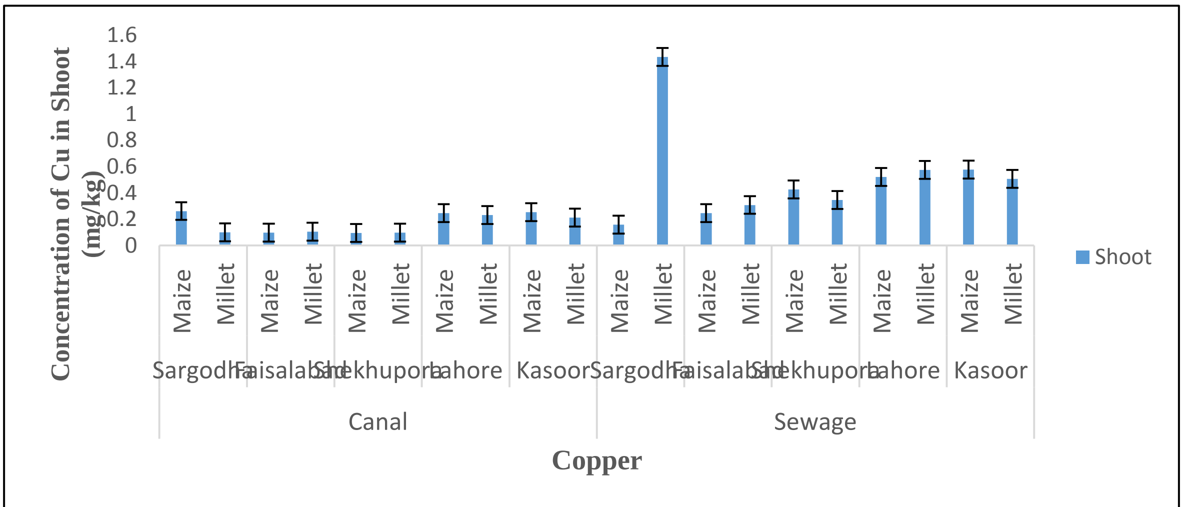

Figure 3: Copper Concentration in shoot samples (mg/kg) of Maize and Millet at various districts.

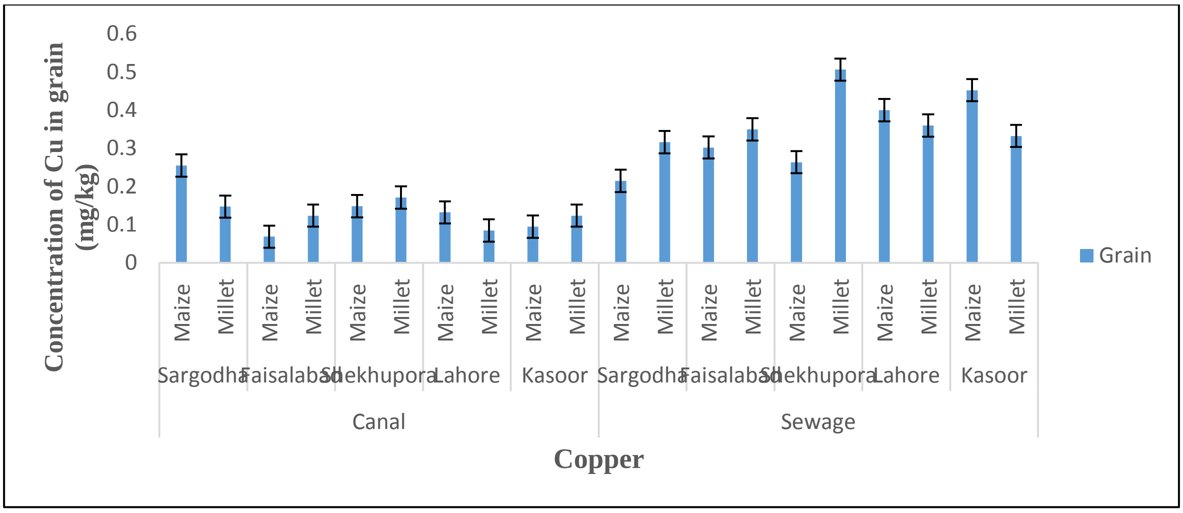

Figure 4: Copper Concentration in Maize and Millet grains (mg/kg) of various districts.

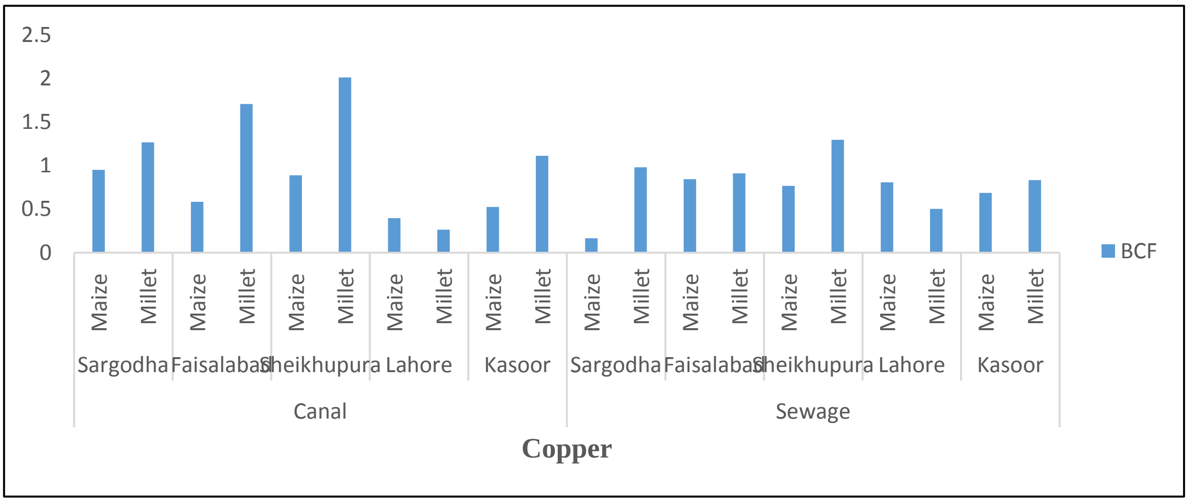

Figure 5: BCF level for Cu in Maize and Millet at different districts.

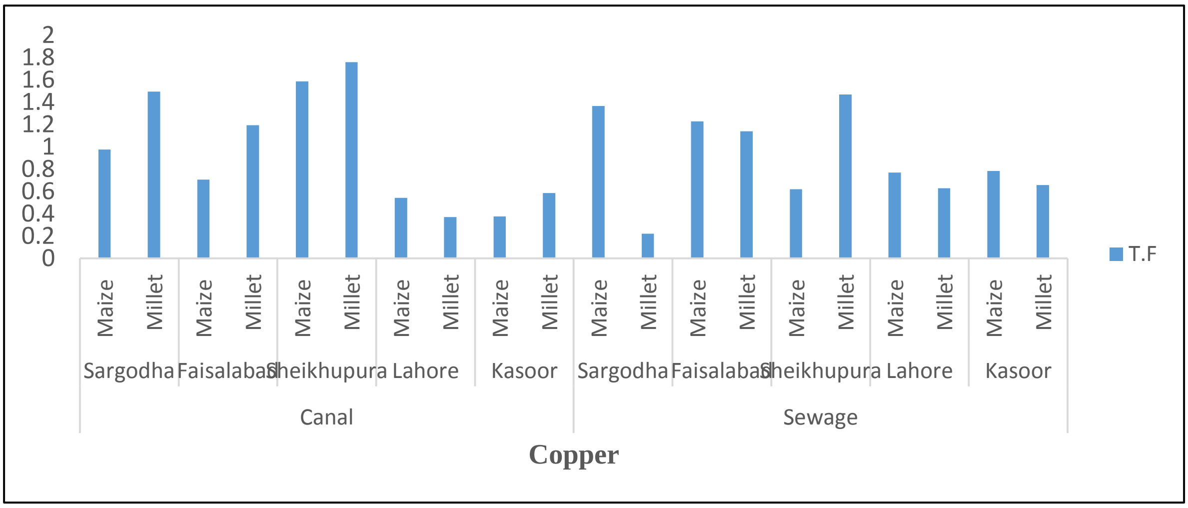

Figure 6: TF level of Cu for Maize and Millet in diverse irrigated districts.

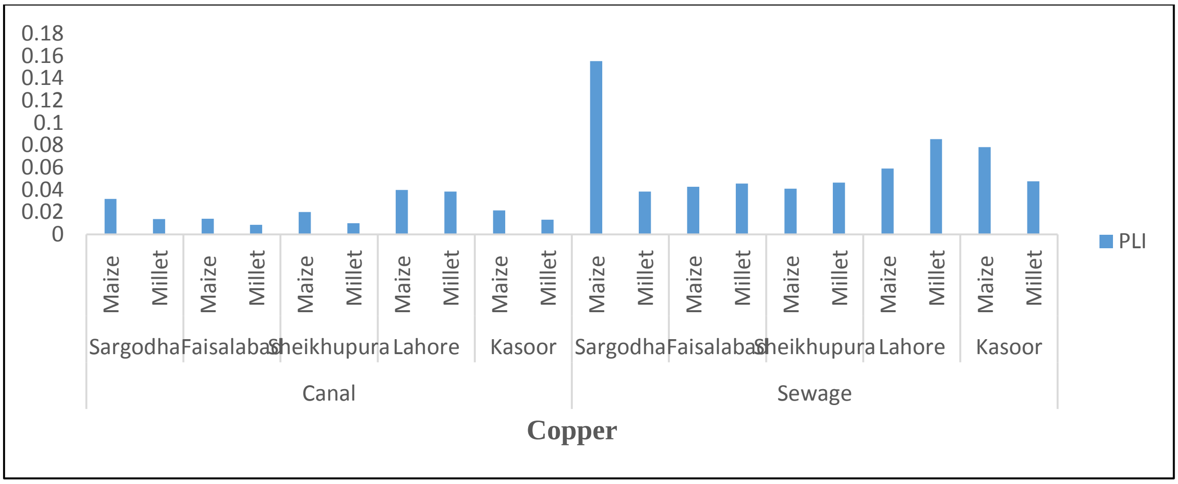

Figure 7: PLI level of Cu in canal and sewage water irrigated various districts.

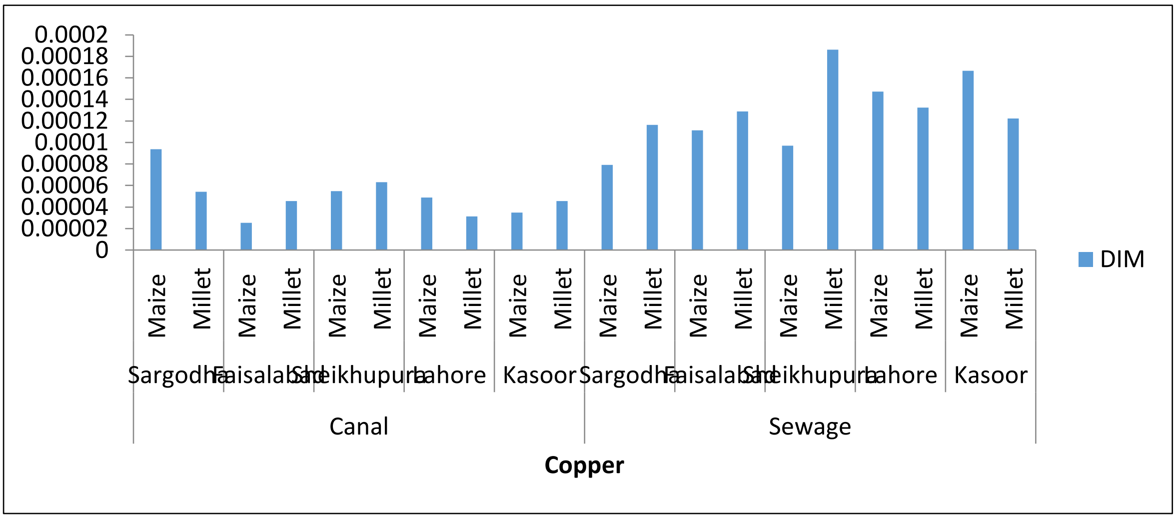

Figure 8: DIM of Cu in Maize and Millet of different districts.

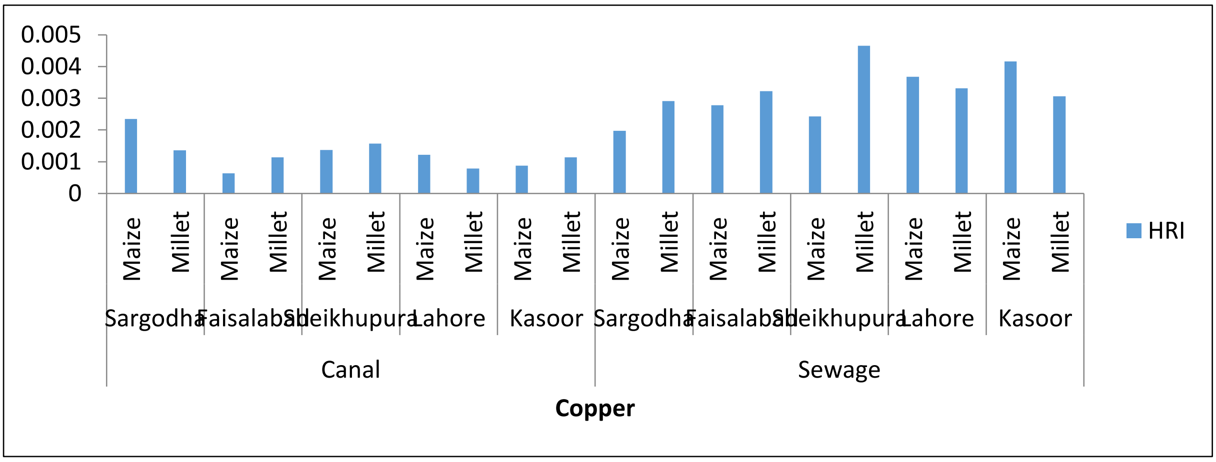

Figure 9: HRI of Cu in Maize and Millet of different districts.

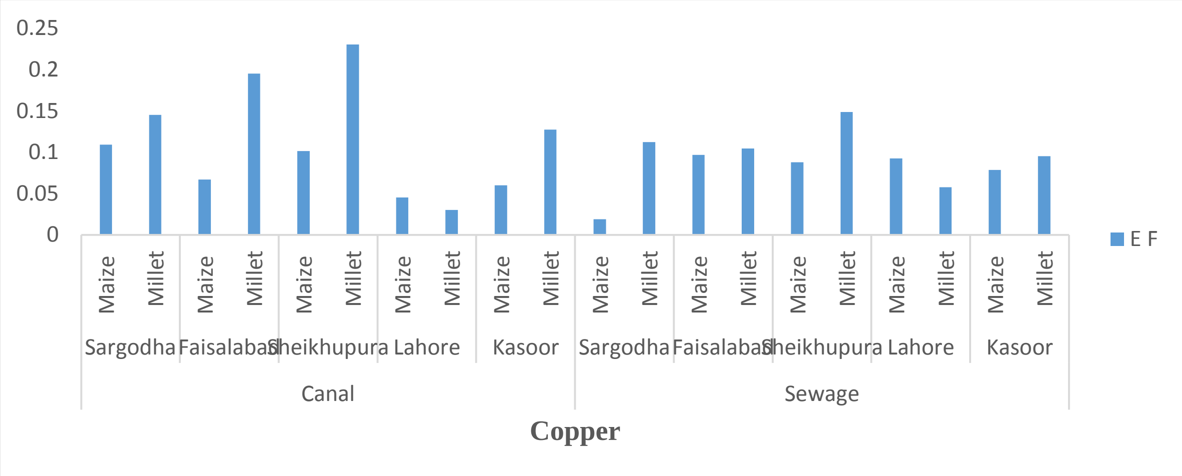

Figure 10: EF of Cu in Maize and Millet of different districts.

Table 1: ANOVA for Cu concentration in Maize and Millet sampled from various districts.

S.O.V	Df	Mean Squares			
		Water	Soil	Shoot	Grain
Irrigation source	1	3.099***	2.583***	2.314***	.922***
District	4	0.473**	0.246ns	0.238ns	0.008ns
Forage	1	0.001 ns	0.341ns	0.212 ns	0.007 ns
Irrigation source x District	4	0.340 ns	0.097 ns	0.107 ns	0.031 ***
Irrigation source x Forage	1	0.065 ns	0.069ns	0.420 **	0.016**
District x Forage	4	0.565 **	0.275 ns	0.263 **	0.023***
Irrigation source x District x Forage	4	0.499**	0.183ns	0.417 *	0.025***
Error	60	0.144	0.180	0.100	0.004

****, **,*, ns= Significant at 0.001, 0.01, 0.05level & non-significant*

Table 2: Mean Cu concentration in the water (mg/l), soil (mg/kg) and different parts of Maize and Millet (mg/kg).

Irrigation sources	District	Forages	Water	Soil	Shoot	Grain
Canal	Sargodha	Maize	0.22125	0.2675	0.26125	0.255
		Millet	0.20125	0.11625	0.09875	0.1475
	Faisalabad	Maize	0.10375	0.1175	0.0975	0.06875
		Millet	0.1025	0.0725	0.10375	0.12375
	Sheikhupura	Maize	0.18125	0.1675	0.09375	0.14875
		Millet	0.1375	0.085	0.0975	0.17125
	Lahore	Maize	0.10375	0.33375	0.245	0.1325
		Millet	0.1675	0.32375	0.23	0.085
	Kasur	Maize	0.35625	0.18125	0.25375	0.095
		Millet	0.1125	0.11125	0.21125	0.12375
Sewage	Sargodha	Maize	0.425	1.305	0.1575	0.215
		Millet	1.69	0.3225	1.43375	0.31625
	Faisalabad	Maize	0.335	0.3575	0.24625	0.3025

		Millet	0.28	0.38375	0.3075	0.35
	Sheikhupura	Maize	0.24375	0.34375	0.42625	0.26375
		Millet	0.34125	0.39	0.345	0.50625
	Lahore	Maize	0.91125	0.495	0.52	0.4
		Millet	0.39375	0.71625	0.57375	0.36
	Kasur	Maize	0.73375	0.6575	0.5775	0.4525
		Millet	0.27	0.39875	0.50625	0.3325

Table 3: Various attributes of Copper in Maize and Millet of different.

Source	**District**		**BCF**	**T F**	**P L I**	**DIM**	**HRI**	**EF**
Canal	Sargodha	Maize	0.953271	0.976077	0.031883	9.38E-05	0.002346	0.109112
		Millet	1.268817	1.493671	0.013856	5.43E-05	0.001357	0.14523
	Faisalabad	Maize	0.585106	0.705128	0.014005	2.53E-05	0.000632	0.066972
		Millet	1.706897	1.192771	0.008641	4.55E-05	0.001138	0.195373
	Sheikhupura	Maize	0.88806	1.586667	0.019964	5.47E-05	0.001368	0.101648
		Millet	2.014706	1.75641	0.010131	6.3E-05	0.001575	0.230605
	Lahore	Maize	0.397004	0.540816	0.039779	4.88E-05	0.001219	0.045441
		Millet	0.262548	0.369565	0.038588	3.13E-05	0.000782	0.030052
	Kasoor	Maize	0.524138	0.374384	0.021603	3.5E-05	0.000874	0.059993
		Millet	1.11236	0.585799	0.01326	4.55E-05	0.001138	0.127322
Sewage	Sargodha	Maize	0.164751	1.365079	0.155542	7.91E-05	0.001978	0.018858
		Millet	0.98062	0.220575	0.038439	0.000116	0.002909	0.112243
	Faisalabad	Maize	0.846154	1.228426	0.04261	0.000111	0.002783	0.096852
		Millet	0.912052	1.138211	0.045739	0.000129	0.00322	0.104395
	Sheikhupura	Maize	0.767273	0.618768	0.040971	9.71E-05	0.002426	0.087823
		Millet	1.298077	1.467391	0.046484	0.000186	0.004657	0.148579
	Lahore	Maize	0.808081	0.769231	0.058999	0.000147	0.00368	0.092494
		Millet	0.502618	0.627451	0.085369	0.000132	0.003312	0.05753
	Kasoor	Maize	0.688213	0.78355	0.078367	0.000167	0.004163	0.078774
		Millet	0.833856	0.65679	0.047527	0.000122	0.003059	0.095444

Copper concentration in grains was found to be within the safe limits. WHO allowed Cu limit in the plants as 10 mg/kg (Zigham Hassan et al., 2012). Results exhibited that copper amount was maximum in millet of Sheikhupura watered through sewage water and minimum in canal watered maize of Faisalabad. Analyzed Cu level in current finding was lower than those given by Tegegne (2015). The values of Cu within the allowable limit of Cu (73.3) suggested by FAO/WHO (2001). Kirchmann et al., (2017) recorded higher range of Cu (8.9 - 27.8) as compared to our work. Anthropogenic actions are the central cause of heavy metal gathering in crops it includes the usage of sewage water, industrial and developed activities and extreme mining (Singh et al., 2004).

Our findings of bio-concentration was higher than that suggested by Asdeo (2014).The consequent uptake of Cu by plants is the result of its accumulation in upper horizon which further prejudiced the copper distribution pattern in various soil horizons (Pendias, 2011).

Asdeo (2014) (0.19) and Chaoua et al., (2018) (0.1) reported the lower TF for Cu, while Rattan et al., (2005) had given the higher values (2.35, 16.7) in the sewage and canal water samples, respectively. The considerable difference in translocation factor takes place, due to the interaction of soil and plant with investigated metal (Alexander et al., 2006).

In current study the contamination was low in contrast to Ahmad et al., (2017). PLI for Cu, given by Khan et al., (2017) (0.23, 0.36) and Ahmad et al., (2018) (0.15, 0.23) respectively, was found lower than the present study. Izah et al., (2017) had given the higher PLI for Cu in dry and wet season (1.08, 1.06 mg/kg respectively).

The concentration of DIM in current study was lie beyond the permitted WHO/FAO (2007) limit (3.0 mg/kg). Daily intake for Cu was high for various types of samples as compared to studied range (0.004 mg/day) of Chaoua et al., (2018). All samples showed the high Daily intake value for Cu against the calculated values (0.004, 0.008 mg/day) of Ahmad et al., (2017). Daily intake for Cu, recommended by Zeng et al., (2015) (0.006 mg/kg/day) was greater for some samples and also found to be lower for others.

HRI for Cu given by Bhatti et al., (2015) was found higher while lowered intake of Cu was reported by Ahmad et al., (2017) in sewage and canal water irrigated samples (0.13, 0.21, respectively). Cu is an essential trace element (Hussain et al., 2011). Its maximum tolerable limit in wheat grains should be (3 mg/kg), as settled by EC and FAO/WHO (2007).

Analyzed data showed that obtained EF level was lowered than the Cu enrichment (3.51, 4.22) suggested in sewage & canal water treatments of Khan et al., (2018) study. Bio-availability of metal determine its Enrichment factor, which further depends upon the chemical form of the metal, their amount in the soil, growth rate which depends on species of plant and the changes in the uptake capability (Tinker, 1981).

CONCLUSIONS

Current result showed that Cu values in soil and forages were within the permissible limits of WHO (2002). Present results concluded that a highest value of copper was measured for DIM and Transfer factor of shoot. Although, analyzed maize and millet samples maintained minimum concentration of copper but it might raises risks of hepatitis and cancer in public via intake of food crops that receives long-term irrigation of wastewater. Present findings suggested that the discharges of municipal waste water must be treated before its appliance on agricultural farms.

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