Heavy Metal Assessment in *Capsicum annum* and *Cyamopsistetragonoloba* Grown around Contaminated Sites in Jaipur City

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Abstract: ***Soil pollution, due to anthropogenic activities like industrial waste water irrigation or unsystematic dumping of solid waste, has severe consequences on the sustainability of ecological equilibrium. This study emphasizes on the effect of contaminated soil on cluster bean and green chilly which are grown in the study areas (Sanganer and Mathuradaspura) Jaipur city Rajasthan, India. The large scale and prolonged cultivation on such soil leads to accumulation of heavy metals in the plants that poses a serious risk to the human health. For this purpose, the human health risk assessment was done by estimating the bioaccumulation factor, daily dietary index, hazard quotient and hazard indices for metals like Fe, Cu, Zn, Pb, Cd, Cr and Ni. The results of the study indicated that the soil of Mathuradaspura dumping ground had elevated concentration Fe, Cu Zn Cr in contrast to the soil of Sanganer industrial area where elevated concentration of Pb, Cd and Ni were found. Because of the tendency of these crop plants to accumulate heavy metals from soil and water provided for irrigation, the vegetables from these areas were found to have increased levels of heavy metals like Pb, Cd and Ni in the Sanganer agricultural areas and Cu, Zn and Ni in Mathuradaspura agricultural fields.***

Keywords: heavy metals, health risk assessment, hazard quotient, daily dietary index

1. Introduction

The problem of heavy metals in the environment is amatter of apprehension. Numerous studies have shown the detrimental effects of heavy metals on the well-being of living organisms. The ever increasing human intervention with the environmental components has disturbed the harmony and delicate balance of the essential and toxic metals in the environment. The improper management of the waste is a major route of entry of the heavy metals in the ecosystem. Even though metals like Cu, Zn, Fe are requisite for a healthy body, but excess of such micronutrients may be harmful. For instance, excessive Zn element suppresses the absorption of Cu and Fe. Free Cu is toxic to human beings[1].Ni, Cd and Pbare a potent carcinogen [2]. High concentration of Mn and Pb affects the health of children.

The identification of entry route of heavy metals is necessary,to assure the quality of food [3]. Waste management face many challenges in the developing nations of the world due to the uncontrolled population, lack of sophisticated technologies and several other reasons. The presence of metals in waste water as well as municipal solid waste has been reported throughout the world though in low concentrations but long term and continuous application may lead to high level of metals in the soil. The metals enter the soil through improper waste management be it waste water irrigation or solid waste dumping. The metals are subsequently transferred to the plants that are raised on metal contaminated soils leading to accumulation of metals in quantities high enough to cause medical problems in human beings and animals [4],[5].

Heavy metals occur in the soil both in soluble and combined forms but only soluble exchangeable and chelated metal species in the soils are available to the plants [6].The present research is an attempt to quantify the metal content in the soil and its effect on the human health mainly in the sites affected with the dumping of municipal solid waste and waste water irrigation. Thus, the current paper focuses on the (i) effect of municipal solid waste and waste water irrigation on the metal content of the soil (ii) the metal content of the plants species grown on such metal rich soil (iii) health risk assessment of the consumption of such contaminated vegetables on the human beings.

2. Material and Methods

2.1 Study Area

The state of Rajasthan is situated between 23º3' and 30º12' N latitude and 69º30' and 78º17' E longitude. It spreads over an area of 132,140 square miles (342,239 square kilometers). The capital city is Jaipur which has a humid subtropical climate, receiving over 650 millimeters (26 in.) of rainfall annually but most rains occur in the monsoon months between June and September. Temperatures remain relatively high throughout the year, with the summer months of April to early July having average daily temperatures of around 30°C (86 °F). Jaipur city covers an area of 11117.8 sq. km. According to 2011 census the population of Jaipur was 66, 26,178 and about 1000-1100 MT of waste is generated here every day.

The vegetables were collected from two polluted sites of Jaipur that supply vegetables to the local marketsfor consumption by the general public. The first site is a municipal solid waste dumping ground, Mathuradaspura village which lies in the north east part of the Jaipur about 20 km away from the main city, situated in Jamwa Ramgarh Tehsil. The total population of study area is 1100 people living in 5- 6 dhanis. The area adjoining the village is used as open dumping ground for non-segregated municipal solid waste. More than 800 tons of municipal solid waste is dumped here every day without segregation. The other site contributing to heavy metal load in the agricultural fields is

Sanganer (Amanishah Nallah) town that lies between 26°49' to 26°51' North latitude and 75°46' to 75°51' East longitude. The total area of Sanganer is about 635.5sq.km. Climate is extremely hot and humid and has population between 10000-25000 people. The area is surrounded by many large and small scale industries which release their effluents in Amanishah Nallah and pollute the water body and the nearby agricultural fields. The sewage effluent also finds its way in the Nallah. Due to lack of surface water sources the waste water of this Nallah is used to irrigate the crops.

The vegetables grown in these areas are supplied to the vegetable markets throughout the city.

2.2 Methodology

Soil samples were collected from the agricultural lands of the two selected sitesusing Grab sampling technique. Collection of soil samples was done from top soil (depth 0-15 cm) with the help of a spatula and transferred to sterilized plastic zip-lock bags. These samples were then sun dried and before sieving large rocks, organic debris, plastic and metallic pieces were removed. The fractions smaller than 1 mm were ground to a fine powder in a pestle mortar.

For plant samples, 8-10 edible parts from different plants of same species were collected randomly. Sampling was done according to the morphological status of the plant species, normal and healthy plant samples were selected for the analysis. The vegetables collected were green chilli (*Capsicum annum*) and cluster bean (*Cyamopsistetragonoloba*).The selected vegetables are largely grown in the study area by the farmers for their own consumption and for supply to nearby vegetable markets of Jaipur. To remove adhered soil particles, the fruits were first washed with running tap water followed by distilled water and then they were air dried. To obtain a constant weight sieved soil and crushed plant samples were then kept in oven at 65 ±2°C for 24 hour. Soil and plant samples (1 gram each) were allowed to digest with a mixture (4:1 V/V) of HNO_3 and $HClO_4$ overnight [7]. After this, these samples were slowly digested on the hot plate at 80-90°C until a clear solution was obtained. The digested samples thus obtained were filtered using Whatman filter paper number 42 and then diluted to 100 ml with distilled water. Heavy metals Fe, Cu, Zn, Pb, Cd, Cr and Ni were analyzed by AAS (Atomic Absorption Spectroscopy, Thermo fisher ICE3300). All analyses were conducted in triplicate.

2.3 Bioaccumulation factor

It enable us to understand the extent of threat and associated perils as a result of waste water irrigation and consequent heavy metal accumulation in the edible portion of selected vegetables [8]:

$$\text{Bioaccumulation factor} = \frac{\text{Concentration of metal in ediblepart}}{\text{Concentration of metal in soil}}$$

2.4 Health Risk Assessment

2.4.1 Daily dietary index (DDI)

Daily intake was calculated by the following equation:

$$DDI(mg/person/day) = \frac{C_{metal} \times D_{food\ intake}}{B_{average\ weight}}$$

where, Cmetal, Dfood intake and Baverage weight are the heavy metal concentrations in edible part of the plants ($mgkg^{-1}$), daily intake of vegetables (gm $person^{-1}$) and average body weight (kg $person^{-1}$), respectively. The average daily vegetable intake rate was estimated by a survey. 100 people having average bodyweight of 60 kg were asked for their daily intake of the selected vegetables from the study area [9].

2.4.2 Hazard quotient (or Health risk index)

The HQ for non-carcinogenic risk was calculated using the following formula [10]:

$$\text{Health risk index (HRI)} = \frac{DIM}{R_fD}$$

Where DIM is daily intake of metal and R_fD is oral reference dose for metals. The value of HRI above 1 for metals indicates high risk to the health of consumers through dietary intake [11].

2.4.3Hazard index

A sum of the hazard quotients of the metals to which an individual is exposed is Hazard Index. In other words, the sum of multiple metal exposures will be proportional to magnitude of the adverse effect.

$HI = \Sigma\ HQ = HQ_{Fe}+HQ_{Cu}+HQ_{Zn}+HQ_{Pb}+HQ_{Cd}+HQ_{Cr}+HQ_{Ni}$

Hence, HI = 0.0 to 1 means no hazard; 1.1 to 10 means moderate hazard while greater than 10 means high hazard or risk [12].

3. Results and Discussion

3.1 Heavy metal concentration in soil

The heavy metals concentrations in the soil of Sanganer agricultural field was in the following order Fe>Ni>Pb>Zn>Cr>Cd>Cu. Iron was the most abundant metal with concentration of 530.66mg/kg while copper was least i.e.14.13mg/kg. Study conducted by Jagariya and Chandel, 2015[13] showed similar results. Cadmium (15.73 mg/kg) was found to be more than Indian and WHO standards[14],[15]. The elevated concentration of Ni (28.72 mg/kg), Pb (17.32 mg/kg), Cr (16.56 mg/kg) and Zn (16.89 mg/kg) is attributed to the presence of various dyes in the irrigation water and itsdirect application to agricultural lands without treatment.

In Mathuradaspura agricultural areathe following sequence of heavy metal concentration in the soil was found: Fe>Zn>Cu>Cr>Ni>Pb>Cd. The most abundant and least abundant metals were iron (6734.21 mg/kg) and cadmium (0.61 mg/kg) respectively. Similar trend in heavy metal content of waste amended soil was obtained byKarim et al, 2014[16]. The dumping of un-segregated waste which includes batteries, metal scrap waste, cable sheeting, pigments in paint and ceramics, the concentration of Ni (16.17 mg/kg), Pb (7.36 mg/kg), Cr (28.67 mg/kg) and Zn (229.05mg/kg) were found to be considerably high. The concentration of most of the metals was high enough to accumulate in the vegetables grown in these areas but was found under the maximum permissible limit.

Table 1: Concentration of heavy metals in the soil collected from the agricultural fields (mg/kg)

Areas	*Fe*	*Cu*	*Zn*	*Pb*	*Cr*	*Cd*	*Ni*
Sanganer	530.66±0.06	14.13±0.21	16.89±0.29	17.32±0.15	16.56±0.18	15.73±0.22	28.72±0.23
Mathuradaspura	6734.21±0.31	59.87±0.09	229.05±0.32	7.36±0.23	28.67±0.15	0.61±0.24	16.17±0.33
Awasthi, 2000		135-270	300-600	250-500	-	3-6	75-170
WHO/FAO 2007	-	100	-	-	-	3	50

Mean± S.E.

3.2 Heavy metal concentration in vegetables

Average metal concentration in the dry matter of cluster bean and green chilly in the study areas are given in the Table 2. In cluster bean highest concentration was seen for iron 464.60 mg/kg in Sanganer and 587.58 mg/kg in Mathuradaspura while lowest was cadmium i.e. 2.36 mg/kg in Sanganer and 0.28mg/kg in Mathuradaspura. In case of green chilly maximum concentration was for iron i.e. 436.73 mg/kg in Sanganer and 446.13 mg/kg in Mathuradaspura while minimum was seen for cadmium i.e. 3.95 mg/kg in Sanganer and 0.23 mg/kg in Mathuradaspura.Yen et al (2013) [17] also reported lowest Cr concentration in all vegetables under study.

On comparing the values with the standards it was found that Fe, Cd, Pb and Cr were nearly exceeding the maximum permissible limit (WHO/FAO, 2007)[15]in both vegetables in both the sites. Zn was found to be more than the permissible limit in both the vegetables from Mathuradaspura. Awode et al(2008) [18]also showed elevated levels of lead and chromium in green chilly as compared to WHO limits. Bashir et al (2009) [19]in their study concluded that green chilly had high levels of all the metals as compared to WHO limits.

Table 2: Heavy metal concentration in different vegetables grown in different polluted areas (mg/kg)

Area	*Vegetables*	*Fe*	*Cu*	*Zn*	*Pb*	*Cd*	*Cr*	*Ni*
Sanganer	Cluster Bean	464.60±0.12	7.83±0.19	6.82±0.09	6.28±0.22	2.36±0.20	4.74±0.16	3.48±0.14
	Green chilly	436.73±0.29	12.09±0.02	7.48±0.15	5.39±0.21	3.95±0.16	4.56±0.21	2.23±0.12
Mathuradaspura	Cluster Bean	587.58±0.31	37.18±0.37	84.12±0.26	3.14±0.05	0.28±0.06	6.04±0.09	2.12±0.08
	Green chilly	446.13±0.08	28.10±0.31	78.14±0.31	7.32±0.33	0.23±0.03	7.47±0.04	3.39±0.28
(Awasthi, 2000)		-	30.0	50.0	2.5	1.5	-	
WHO/FAO (2007)		450	40.0	60.0	5.0	0.2	5.0	

Mean± S.E.

3.3 Statistical Analysis

Simple correlation coefficients were calculatedbetween metal contents in soil and plants of both the study areas. Results were very much in accordance with the previous studies (Rattan et al, 2005; Bashir et al, 2009) [20][19] Zinc was found to be most consistently correlated whereas Fe was found to be non-significantly correlated. The values of the correlation coefficients are given in the Table VII. The amount of metal available to the plant highly depends on the plant species, the type of metal, the method of extraction, and the metal solubility in soil which further depends on the soil pH and organic carbon content.

Table 3: Simple Correlation coefficient (r) between heavy metals in plants and soil

Area	*Vegetable*	*Fe*	*Cu*	*Zn*	*Pb*	*Cd*	*Cr*	*Ni*
Sanganer	Cluster bean	0.1492	0.3172	0.9563#	0.0964	0.3588	0.8161#	0.4067
	Green chilly	0.2298	0.4197	0.9602#	0.2775	0.4093	0.8382#	0.1599
Mathuradaspura	Cluster bean	0.0812	0.4130	0.8539#	0.0780	0.2645	0.4860	0.1609
	Green chilly	0.0721	0.1147	0.9810#	0.2092	0.2119	0.7409*	0.0377

(#) and (*) significant at 5 and 1 % probability levels, respectively.

3.4 Bioaccumulation factor*:* We consume a significant amount of vegetables every day so, transfer of metals from contaminated soil and water to the crops is a matter of concern for human health. Higher the bioaccumulation factor for a vegetable, high is the rate of accumulation of respective metals by that vegetable. The bioaccumulation factor values higher than 0.05 show a higher ability for metal contamination and need to be environmentally monitored.

As indicated in Figure 1, the bioaccumulation factor in Sanganer, for green chillyis maximum for Cu and for cluster bean is maximum for Fe while minimum for Ni in both. In Mathuradaspura, it is highest for Cu in cluster bean and for Pb in green chilly while lowest for Fe in both the plants, as the uptake of metals by plants does not increase linearly with growing concentrations of metals in soils. This is in accordance with the conclusions of Rattan et al. (2005)[20]. Although long term use of contaminated soil and water in agricultural fields may lead to accumulation of metals in soil, but the same concentration may not get transferred to the food chain in the same proportion.

3.5 Health risk assessment: The daily intake rate, hazard quotient and hazard index were estimated in order to determine the health risks associated with heavy metal contamination of the selected plants.

3.5.1 Daily Dietary Index: For both the plants, the maximum value of DDI was found to be for Iron among all the metals in both the sites. In case of Sanganer agricultural field the DDI of cluster bean showed lowest value for Zn that is $1.8x10^{-4}$ mg/person/day. In case of green chilly the lowest DDI was found to be of Ni i.e. $1.5x10^{-4}$ mg/person/day. In case of Mathuradaspura cluster bean and green chilly showed lowest daily dietary index for Cd i.e. $7.9x10^{-5}$ mg/person/day and 1.6 $x10^{-5}$ mg/person/day respectively.

All the values in both the sites for both vegetables were found within the range as given by various environmental agencies.

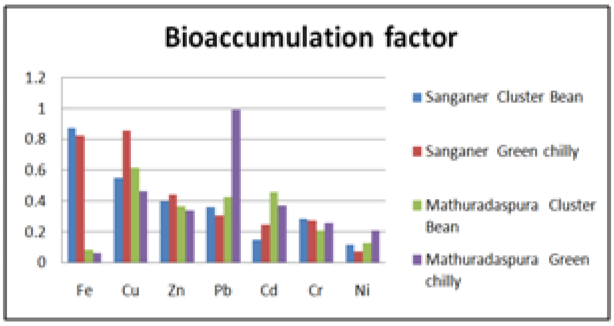

Figure 1: Bioaccumulation factor

Table 4: Daily Dietary Index

Area	vegetable	Fe	Cu	Zn	Pb	Cd	Cr	Ni
Sanganer	Cluster Bean	$12.74 x10^{-2}$	$21.5 x10^{-4}$	$1.8x10^{-4}$	$1.7x10^{-3}$	$6.4x10^{-4}$	$1.3x10^{-3}$	$1.0x10^{-3}$
	Green chilly	$2.99 x10^{-2}$	$8.3x10^{-4}$	$5.1x10^{-4}$	$3.69x10^{-4}$	$2.7x10^{-4}$	$3.1x10^{-4}$	$1.5x10^{-4}$
Mathuradaspura	Cluster Bean	$16.65 x10^{-2}$	$10.5 x10^{-3}$	$23.8x10^{-3}$	$9.0x10^{-4}$	$7.9x10^{-5}$	$1.7x10^{-3}$	$6.0x10^{-4}$
	Green chilly	$3.16 x10^{-2}$	$2.0 x10^{-3}$	$5.5x10^{-3}$	$5.0x10^{-4}$	$1.6x10^{-5}$	$5.3x10^{-4}$	$2.4x10^{-4}$

3.5.2 Hazard quotient (or Health risk index): The value of HQ obtained for the two vegetables for both the sites are summarized in the Figure 2. In cluster bean grown on the Sanganer agricultural land the maximum HQ was for Cd i.e. 0.64 and lowest for Cr, i.e. 0.0009 and in case of green chilly also the maximum value was for cadmium (0.27) and lowest for Cr (0.0002).
In Mathuradaspura agricultural land cluster bean showed the highest value of HQ was for Cu (0.2625) and lowest for Cr (0.0011) and in green chilly highest HQ value was for Cu (0.05) and minimum was for Cr (0.0004).

3.5.3 Hazard index: Hazard index was calculated to find out the possible threat of more than one heavy metals to human health. The value of HI in Sanganer for Cluster bean is 1.335 and for Green chilly is 0.4351whereas in Mathuradaspura HI for Cluster bean is 0.914 and for Green chilly is 0.2668 indicating moderate hazard.

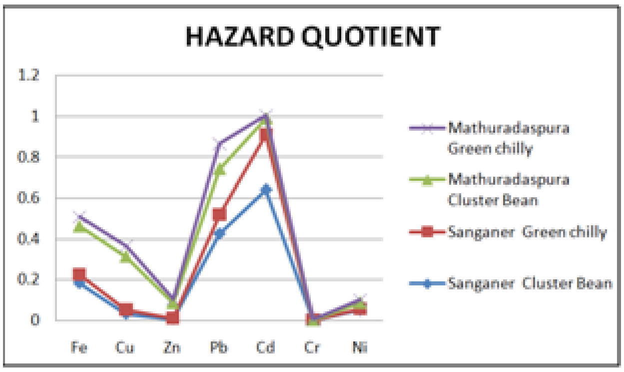

Figure 2: Hazard Quotient

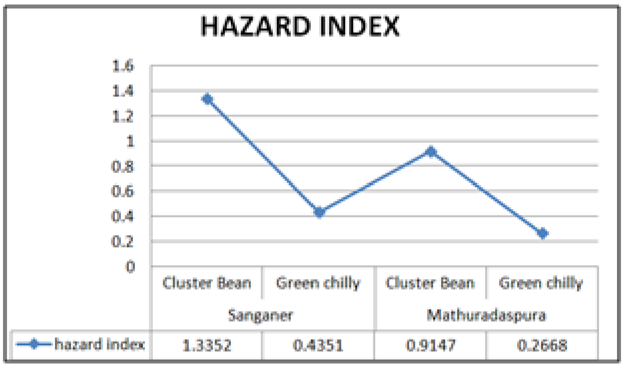

Figure 3: Hazard Index

4. Conclusion

By computing thedaily intake rate (DIR), hazard quotient (HQ) and hazard index (HI)The study has contributed in creating significant information regarding heavy metal uptake and their transfer to food plants in Sanganer and Mathuradaspura areas of Rajasthan (India). The associated health risks were also highlighted to the local residents. From the current study it is concluded that irrigation with waste water and open dumping of municipal solid waste are potential sources of Pb, Cu, Zn, Cd, Cr, Ni and Fe in the soil which further leads to bioaccumulation of these heavy metals in the plants affecting the food chain. Because of the eating habits of the people and their low average body weight,low level of daily dietary index was obtained. Though the level of heavy metals was appreciably high in the soil, but the transfer and accumulation of heavy metals in the crop plants depends on various other environmental factors also. The continuous addition of sewage water or dumping of municipal waste to the soil causesincrease in heavy metal content of the soil and consequent uptake by plants to an alarming level. At present the accumulation of metals in the vegetables because of pollution is not very significant but its consistency may cause serious health implications in future. Hence, it is highly recommended that the entry routs of heavy metals in the soil must be monitored closely, especially around the agricultural lands.

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