Concentration of Toxic Heavy Metals in Some Selected Vegetables and Staples

Narendra Deo
Mewar University, Chittorgarh, Rajastahan

Binay Kumar Singh
Govt. PG College Shadol, Madhya Pradesh

Abstract - The objective of the present study is to determine the impact of heavy metals contaminates of untreated waste water on agricultural produce (Spinach, Cabbage, Beet root, Peas and Bengal Gram whole). Some of heavy metals are very toxic in nature and catastrophic hazards for humans and animals and are mainly Zn, Pb, Cd, Cr and As . Toxicity of heavy metals have been proven to be a major threat and there is several health risks associated with it. The toxic effects of these metals, even though they do not have any biological role, remain present in some or the other form harmful for the human body and its proper functioning.

Key words: Heavy Metals, Health Risk, Toxic, Catastrophic, Hazards, Food Cycle, Effluent, Treatment, Economically motivated, FSSAI (Food Safety and Standards Authority of India), Contaminants.

I. INTRODUCTION

There are numbers of industries those are growing faster and doubling their turnover in half of the decades. But these industries are not strengthening the Effluent water treatment system and discharging the effluent openly illegal fashion without any treatment due to economically motivated concern. The untreated discharged effluent contains heavy metals and other toxic impurities generated from industries .The discharged untreated water reach in cultivated land through open discharged system, the heavy metals gets trapped in to the soil and find the path for entry into food cycle system .The food crops get contaminated with heavy metals .The consumption of Heavy metals contaminated food crops by human leads big health risk. The absorption of heavy metals in human body system varies to certain extent depending on various factors. The study evidences shows that the fractional absorption of Lead with respect to chronic ingestion of diets with less than adequate amounts of Calcium and Zinc. Lead ingested during period of fasting gets absorbed to (FSSAI) prescribes the limits of contaminants under category “Foods not specified” for selected heavy metals only. Different norms and guidelines are given for all the industries depending upon their pollution potentials. Most major industries have treatment facilities for industrial effluents. But this is not the case with small scale industries, which cannot afford enormous investments in pollution control equipment as their profit margin stands lower side.

There are sufficient evidences available related with the mismanagement of industrial wastes. But this is not the case with small scale industries, which cannot afford enormous investments in pollution control equipment as their profit margin stands lower side. There are sufficient evidences available related with the mismanagement of industrial wastes. There are several industries other than Beverage industries these are petrochemical industries, sugar mills, distilleries, leather processing industries, paper mill, agrochemicals and pesticides manufacturing industries and pharmaceutical industries.

The increasing trend in concentration of heavy metals in the environment has attracted considerable attention amongst environmentalist globally during the last decades and has also begun to cause concern in most of the major metropolitan cities. Untreated and Economically motivated industrial effluents and sewage water contains variable amounts of heavy metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium which have the potential to contaminate crops growing under such irrigation. Vegetables and staples constitute an important part of the human diet since they are rich in carbohydrates, proteins as well as vitamins, minerals and trace elements however; they contain both essential and toxic elements over a wide range of concentrations. Metals accumulation in vegetables may pose a direct threat to human health. Heavy metals are one of a range of important types of contaminants that can be found on the surface and in tissue of dry vegetables.

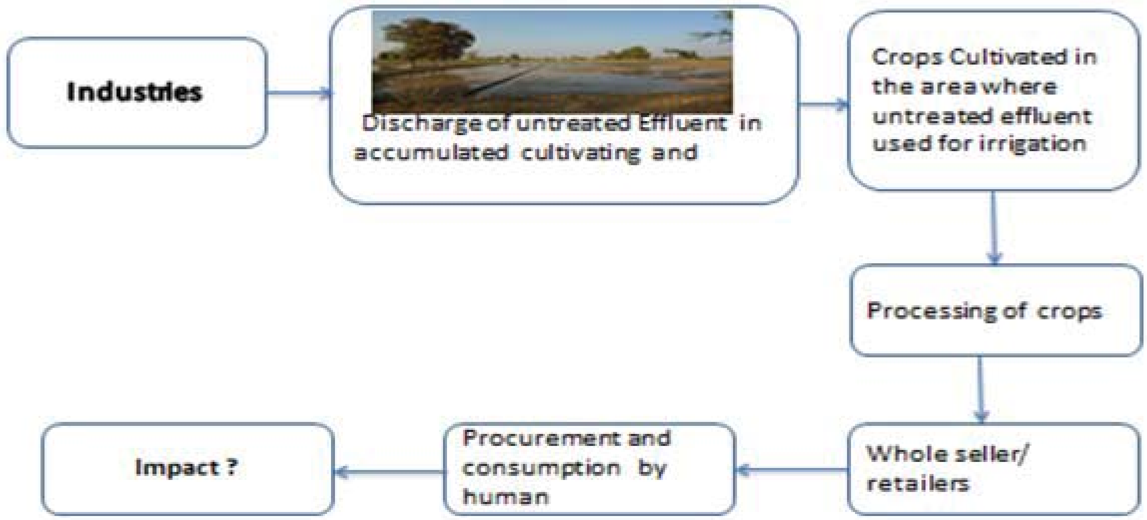

Fig. 1: Untreated effluent in cultivating land

II. AREA OF STUDY

The area (National Capital Region) was selected based on the survey where the untreated effluent water was discharged continuously, through bypass system of industries and associated lands were used for crops cultivation .The agricultural produce vegetable like, Spinach, cabbage Beet roots were grown along with some cereals like Peas & Bengal gram.

2.1. Sampling of untreated Effluent:

The sampling of untreated effluent was collected randomly from the point of discharge. The samples were collected in Polythene bottles 5Ltrx2 .The appropriate quality measures were taken during sampling of untreated effluent .The 08 samples were studied during 2012-2015,(i.e. 02 samples were taken for study per year and in 04 year 8 samples were studied.

2.2. Sampling of selected vegetables (Spinach, Cabbage, Beet Root) and Staples (Peas and Bengal Gram):

The samples were collected randomly from the field irrigated by untreated effluent water, since 2012 to 2015.The sampling cycle was maintained as per crops cycle and collected carefully to avoid the cross contamination. Total 40 samples were studied since 2012 to 2015and statistical methods were used to determine the concentration toxic heavy metals in the samples. Quality and food safety aspects taken care during sampling of vegetables (Spinach, Cabbage and Beet Root) and staples (Peas and Bengal Gram) so that samples could be stored safely till completion of analysis.

S.No.	**Crops**	**2012**	**2013**	**2014**	**2015**
		No. of samples	**No. of samples**	**No. of samples**	**No. of samples**
1	**Spinach**	02	02	02	02
2	**Cabbage**	02	02	02	02
3	**Beet Root**	02	02	02	02
4	**Peas**	02	02	02	02

5	**Bengal Gram**	02	02	02	02
Total Number of samples		**10**	**10**	**10**	**10**

3. Samples Preparation: The samples were prepared using laboratory grade calibrated glassware and analytical grade chemicals and followed by filtration of samples using Whatman No. 41 (0.45 µm pore size). The Filtrate of (500 ml) was preserved with nitric acid to prevent the precipitation of metals. The samples were concentrated to tenfold on a water bath and subjected to nitric acid digestion using the microwave digestion microwave-assisted technique to prepare the sample for analysis.

The vegetable was crushed and grounded well individually to prepare harmonized bulk. The 0.5g sample was taken out by weighing from harmonized bulk to proceed analysis. The sample was kept in clean silica dish and 0.5 ml of 20 % sulphuric acid was added. The sample was mixed well using stirring rod. Post to the mixing sample was shifted in an oven and dried at 110 degree cel., followed by heating on soft flame to remove volatile content of sample. The sample was transferred into muffle furnace and kept for 8 hrs. at 500 degree cel. As a result of heating sample got converted into ash. To make sample free from carbon 0.5 ml nitric acid was added and re heated at 500 degree cel for 30 minutes. After completion of reheating sample was taken out and divided into three parts, the first part of sample was followed by addition of 1ml of nitric acid and 10 ml of water to clean the ash and mixture was heated till the ash get dissolved completely. The dissolved sample was transferred to a 50ml Volumetric flask . The second part of sample dish was heated with 10 ml of hydrochloric acid and sample was transferred in volumetric flask followed by make up with water up 50ml. The third part of sample was used to prepare as blank standard sample. The same quantities of water and reagents were used to prepare blank sample. The 1000ppm stock solution was prepared using analytical grade reagents for each metal ions (Cr, Cd, Pb, Zn)

The adequate amount of sample (100g) of each staple (Bengal gram whole and Peas) sample was drawn from the bulk of sample. A porcelain pestle and mortar was used to grind the seeds the soft samples while a wooden pestle and mortar was employed in the milling of the hard samples. A suitable sieve was used for sieving the samples. A composite sample was obtained from a combination of each sample type before grinding. Three grams of edible portion of each foodstuff (Bengal gram and Peas) was weighed and taken in reflux flask. Wet digestion was carried out using acid mixture (3:2:1 of nitric acid, per chloric acid and sulphuric acid).The mixture of solution was allowed to stand for 48 hrs and after that refluxed at 90 degree cel. for 4 hrs. The sample was then cooled and filtered with whatman no. 42 filter paper and made to the mark with de-ionized water. This process was repeated for all the samples in triplicate including preparation of one set of blank sample.

The glassware and pipettes were first cleaned with tape water thoroughly and finally with de-ionized distilled water, followed by heating for 02 hrs at 60 degree cel, to ensure proper drying of glassware's . The equipment used for analysis and determination of contaminants were calibrated as per approved procedure. The analytical grade reagents were used in the analysis.

4. Analysis of samples using AAS (Atomic absorption) Spectrophotometer and Discussion: The analysis of samples were conducted to determine the concentration metallic contaminants i.e., Chromium (Cr) Cadmium (Cd), Zinc (Zn), lead (Pb) and Arsenic (As.) was done by AA-7000, Shimadzu .The SPC (Statistical Process Control) tools were used for the result interpretation. One blank sample was analyzed parallel to the samples to get the clarity about the result. One reagent blank sample was analyzed and subtracted from the samples to correct for reagent impurities and other sources of errors from the environment. Average values of were taken for each determination.

Untreated effluent waste water:[1]The concentration of heavy metals i.e. Chromium (Cr) Cadmium (Cd), Zinc (Zn), lead (Pb) and Arsenic (As.) were taken in the scope of analysis using sophisticated analytical equipment i.e. AAS (Atomic Absorption Spectrophotometer AA-77000). The analysis results are presented in table-1

Results of Heavy Metals in Effluent water						
year	**Product**	**Chromium (ppm)**	**Zinc(ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (ppm)**
2012	Effluent Water	0	0	0.5	3.2	2.1
2013	Effluent Water	0.15	1.0	0.7	2.6	1.9
2014	Effluent Water	0	0	1.8	5.4	0.9
2015	Effluent Water	0	2.32	0	6.5	3.4

[1] The physical examination of Untreated Effluent waster was conducted, prior to go for analysis of Heavy metal contaminants. Results are as , pH: 10.5 to12.5,Foul odour , BOD:1500,(CPCB permissible limit 30) COD:3500,(CPCB permissible limit, 250)

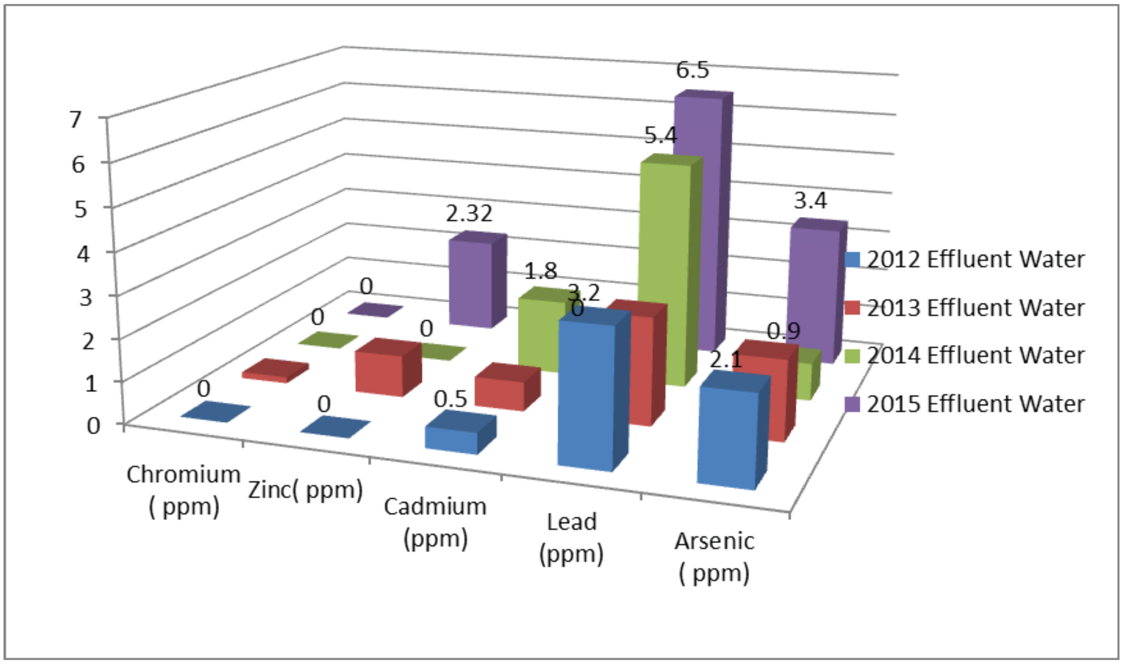

Table -1: Denotes variation in concentration of metallic contaminants of Effluent

The experimental data of Table-1, shows the concentration of heavy metals in waste water effluent[2]. The concentration of each heavy metal varies as, Chromium from 0 ppm to 0.15pp, Zinc from 0 ppm to 2.32 ppm, Cadmium from 0.5 ppm to 1.8 ppm and lead concentration varies from 2.6 ppm to 6.5 ppm. The present metallic concentration was absorbed by the soil and at the time of crop cultivation, it creates adverse effect on crops. The produce obtained such crops become contaminated as they have higher concentration of metallic contaminants.

Heavy Metals in Vegetables: Spinach

Average analysis results of samples						
year	**Product**	**Chromium (ppm)**	**Zinc (ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (PPM)**
2012	Spinach	0.0	1.0	2.1	3.9	0.9
2013	Spinach	0.0	0.4	1.7	2.4	2.2
2014	Spinach	0.1	0.8	1.5	3.2	1.3
2015	Spinach	0.0	0.5	1.9	2.2	1

[2] The permissible limits as per The Environment protection rules 1986, CPCB Limits (into land surface water) for CETP, Lead 0.1ppm, Zinc 5.0ppm, Cadmium: 1.0ppm, chromium2.0ppm, Arsenic 0.2ppm

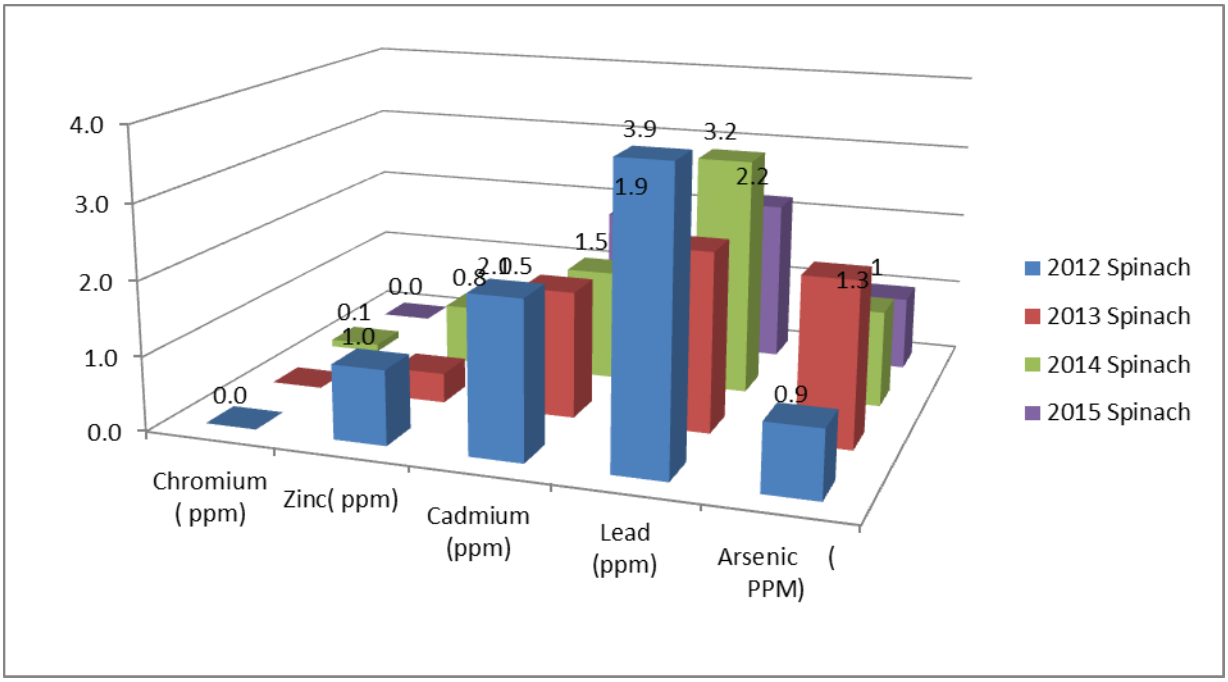

Table -2: Denotes variation in concentration of metallic contaminants in Spinach

The data of table -2 denotes the variation in concentration of heavy metals contaminants in Spinach. The variation in concentration appears as , Chromium (Cr) 0 to 0.1 ppm ,Zinc (Zn) 0.4 ppm to 1.0 ppm , Cadmium(Cd)1.5 ppm to 2.1ppm,Lead (Pb) 2.2 to 3.2 ppm(FSSAR-2011,maximum permissible limit 2.5 ppm) and Arsenic (As) 0.9 to 2.2 ppm(FSSAR-2011,maximum permissible limit 1.1 ppm) The concentration of two heavy metals particulary Lead (Pb) and Arsenic (As) have higher than the permissible limit of FSSAR-2011[3].

Cabbage:

Average analysis results of samples						
year	**Product**	**Chromium (ppm)**	**Zinc(ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (ppm)**
2012	Cabbage	0.0	0.4	2.1	1.1	4.6
2013	Cabbage	0.0	0.1	1.6	1.5	3.1
2014	Cabbage	0.0	0.7	1.4	0.9	2.3
2015	Cabbage	0.0	0.3	2.6	1.3	3.9

[3] *As per FSSAR-2011, the permissible limit stand as ,Chromium(Cr)20 ppm,Zinc(Zn) 50ppm, Cadmium(Cd) 1.5pp, Lead (Pb)2.5ppm and Arsenic (As) 1.1ppm*

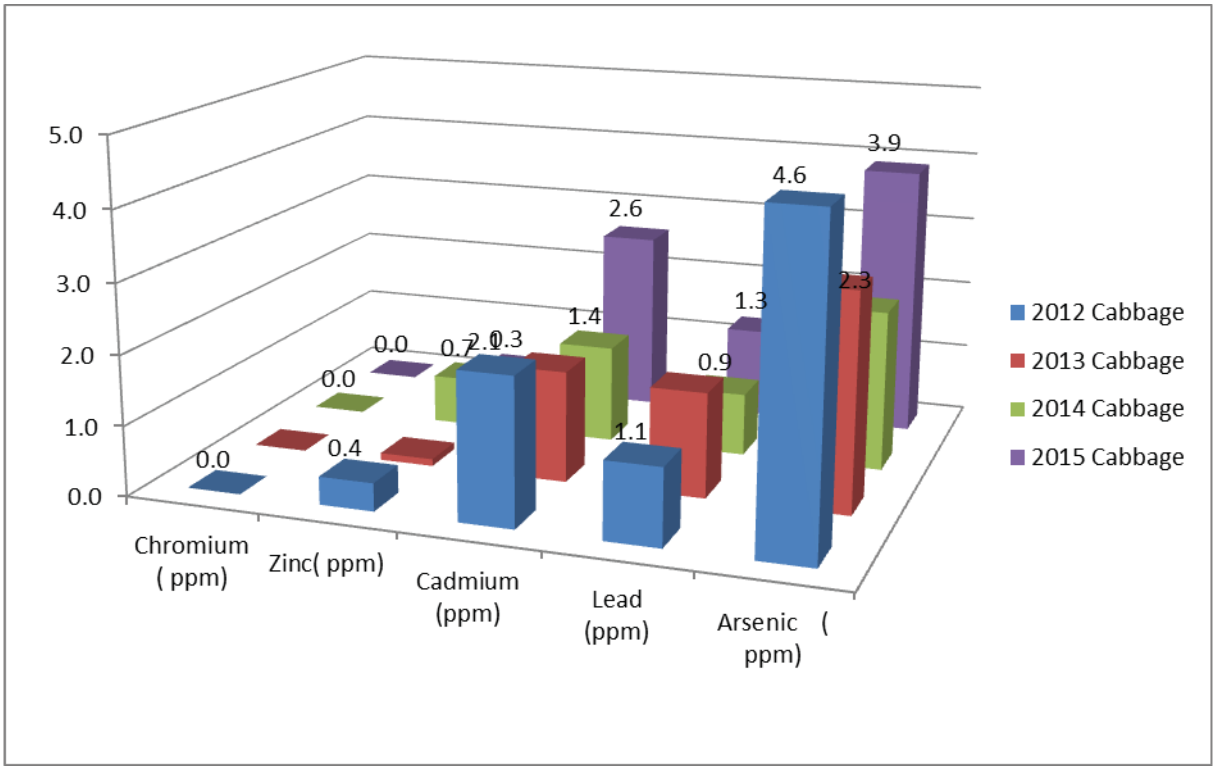

Table -3: Denotes variation in concentration of metallic contaminants in Cabbage

The data of table -3 express the variation in concentration of heavy metals contaminants in cabbage. The concentration varies as , in Chromium (Cr) there is no variation although the presence of chromium not has been reported ,Zinc (Zn) 0.1 ppm to 0.7 ppm , Cadmium(Cd)1.4 ppm to 2.6 ppm(FSSAR-2011,maximum permissible limit 1.5 ppm) ,Lead (Pb) 0.9 to 1.5 ppm and Arsenic (As) 2.3 to 4.6 ppm(FSSAR-2011,maximum permissible limit 1.1 ppm). The concentration of two heavy metals i.e. Cadmium and Arsenic have higher concentration in cabbage, it is above the limit of FSSAR-2011,

Beet Root

Average analysis results of samples						
year	**Product**	**Chromium (ppm)**	**Zinc(ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (ppm)**
2012	Beet Root	0.0	1.0	2.3	1.9	1.5
2013	Beet Root	0.0	0.7	2.7	2.2	2.6
2014	Beet Root	0.0	1.4	2.1	1.6	2.4
2015	Beet Root	0.0	1.1	2.9	1.4	3.3

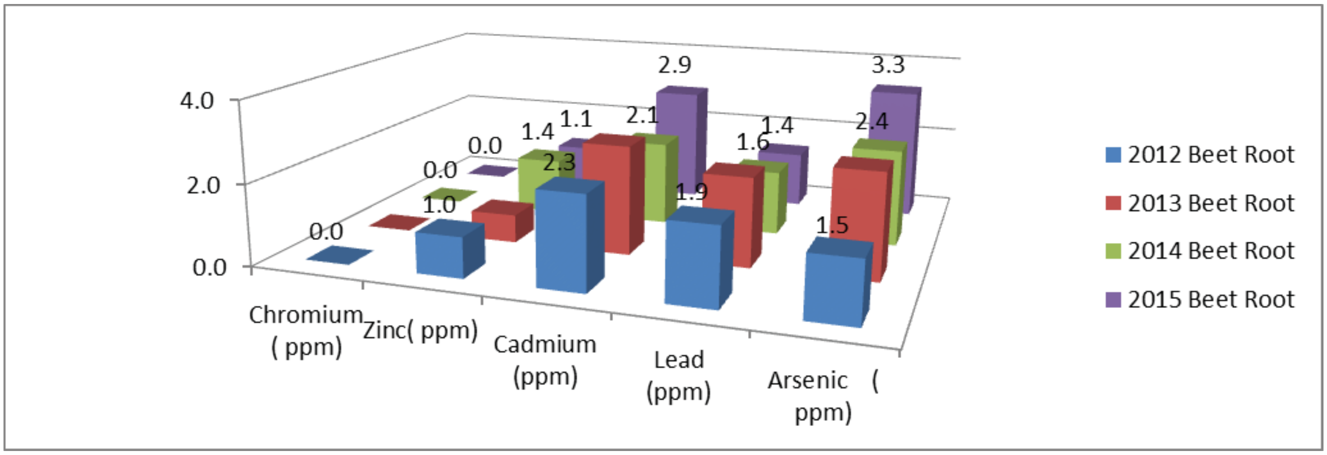

Table -4: Denotes variation in concentration of metallic contaminants in Beet

The data of table -4 express the variation in concentration of heavy metals contaminants in Beet Root. The concentration varies as , in Chromium (Cr) there is no variation although the presence of chromium not has been reported ,Zinc (Zn) 0.7 ppm to 1.4 ppm , Cadmium(Cd)2.1 ppm to 2.9 ppm(FSSAR-2011,maximum permissible limit 1.5 ppm) ,Lead (Pb) 1.4 to 2.2 ppm and Arsenic (As) 1.5 to 3.3 ppm(FSSAR-2011,maximum permissible limit 1.1 ppm). The concentration of two heavy metals i.e. Cadmium and Arsenic have higher concentration in Beet Root, it is above the limit of FSSAR-2011:

Peas:

Average analysis results of samples						
year	**Product**	**Chromium (ppm)**	**Zinc (ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (ppm)**
2012	Peas	0.0	0.9	0.6	1.2	0.0
2013	Peas	0.0	0.2	0.34	2.3	0.0
2014	Peas	0.0	0.0	0.49	1.78	0.0
2015	Peas	0.0	1.0	0.55	2.64	0.0

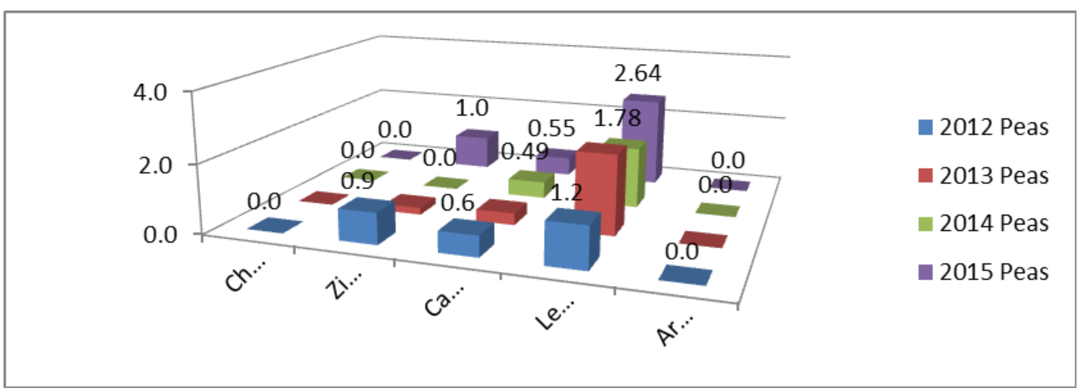

Table -5: Denotes variation in concentration of metallic contaminants in Peas

The data of table-5 states about the variation in concentration of heavy metals contaminants in Peas. The concentration varies as , in Chromium (Cr) there is no variation although the presence of chromium not has been reported ,Zinc (Zn) 0.0 ppm to 1.0 ppm , Cadmium(Cd)0.34 ppm to 0.6 ppm,Lead (Pb) 1.2 to 2.64 ppm and Arsenic (As) 0.0 ppm(FSSAR-2011,maximum permissible limit 1.1 ppm). The concentration of one heavy metal i.e. lead (Pb) higher concentration in Peas, it is above the permissible limit of FSSAR-2011,

Bengal Gram Whole:

Average analysis results of samples						
year	**Product**	**Chromium (ppm)**	**Zinc(ppm)**	**Cadmium (ppm)**	**Lead (ppm)**	**Arsenic (ppm)**
2012	Bengal Gram Whole	0.0	1.0	1.9	0.7	2.9
2013	Bengal Gram Whole	0.2	0.9	2.1	0.3	4.7
2014	Bengal Gram Whole	0.0	0.7	1.8	0.5	3.8
2015	Bengal Gram Whole	0.1	1.2	1.5	1.1	4.8

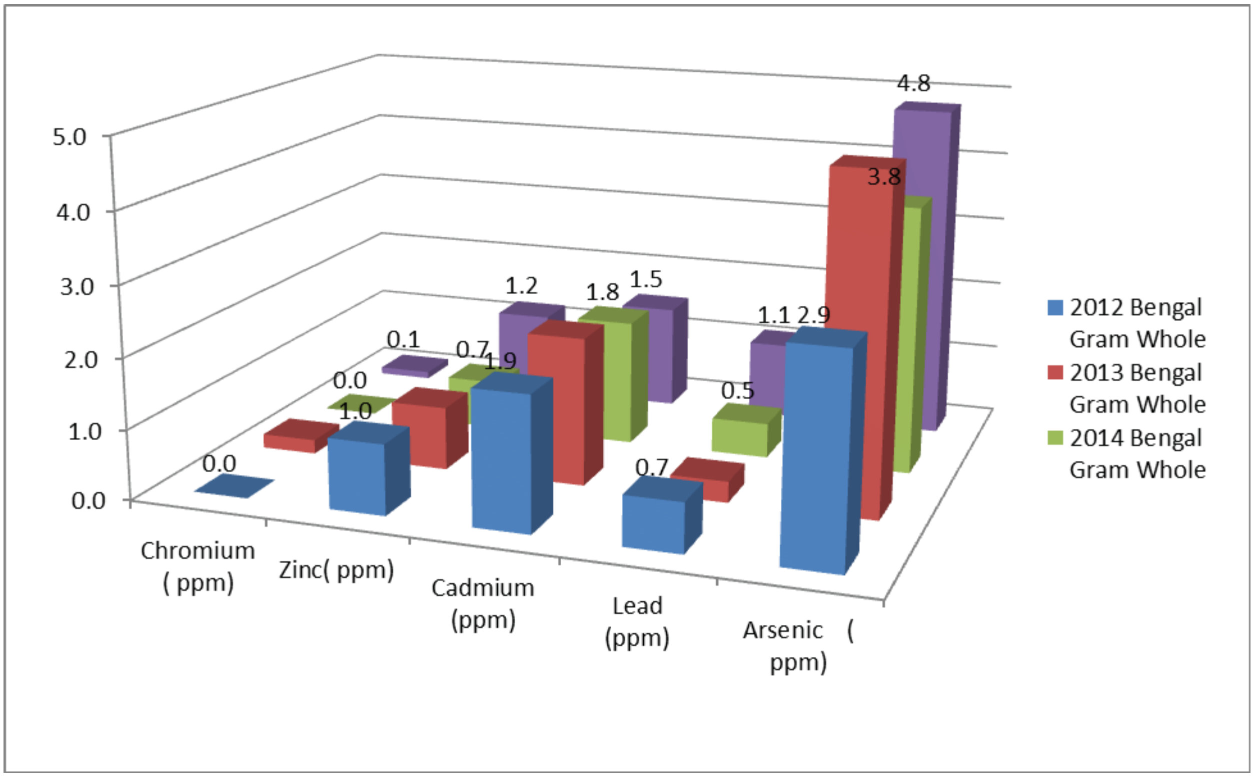

Table -6: Variation in concentration of metallic contaminants in Bengal Gram Whole

The data of table -6 states about the variation in concentration of heavy metals contaminants in Bengal Gram Whole reported as a result of analysis. The concentration varies as , in Chromium (Cr) 0.0ppm to 0.2ppm ,Zinc (Zn) 0.7ppm to 1.2 ppm , Cadmium(Cd)1.5 ppm to 2.1 ppm (FSSAR-2011,maximum permissible limit 1.5 ppm) ,Lead (Pb) 0.3 to 1.1 ppm and Arsenic (As) 2.9 to 4.8 ppm(FSSAR-2011,maximum permissible limit 1.1 ppm). The concentration of two heavy metal i.e. cadmium (cd) and Arsenic have higher concentration in Bengal gram.

III. CONCLUSION

The vegetable accumulate higher concentration of heavy metals (Chromium, Cadmium, Zinc, Lead and Arsenic) contaminants than staples. The lesser accumulation of heavy metals concentrations were reported in staples grains. This shows that the consumption of such vegetable and staple grains is not safe. Important steps must be taken by common people and associated administrative authority to prevent the discharging of untreated effluent in usable land. There is also a need to develop economical methods of treating waste water so that economically motivated concern can be prevented.

Heavy metals are toxic in nature as well as these are non-biodegradable finally its bio-accumulation increases in nutrition. The entry of toxic heavy metals in food chain is a subject of serious concern. The presence heavy metals in food stuffs lead number of incurable diseases in human being. The depreciation of nutrition values and increase of metallic toxicity boost the adverse risk factor for human health. Arsenic is one of the most important heavy metals causing disquiet from both ecological and individual health standpoints. Arsenic toxicity can be either acute or chronic and chronic arsenic toxicity is termed as arsenicosis. Most of the reports of chronic arsenic toxicity in man focus on skin manifestations because of its specificity in diagnosis. Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Lead is a bright silvery metal, slightly bluish in a dry atmosphere. It begins to tarnish on contact with air, thereby forming a complex mixture of compounds, depending on the given conditions. Cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants. Zinc is relatively less toxic. Zinc deficiency causes malnutrition and foods with low bioavailability, aging, certain diseases, or deregulated homeostasis is a far more common risk to human health than intoxication.

REFERENCES

[1] Cartwright, P.S., (1985), "Membranes Separations Technology for Industrial Effluent Treatment - A Review", Desalination, 56, 17.

[2] Babel S. and Kurniawan T.A., (2003), Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. of Hazard Mater, 97,219–243.

[3] Lokhande, R.S., and Kelkar, N., 1999, Studies on heavy metals in water of Vasai Creek, Maharashtra, Indian J. Environ. Protect, 19(9), 664-668

[4] Suneeta Chandorkar and Prachi Deota(2013) Department of Foods and Nutrition, Current World Environment, Vol. 8(2), 291-297 (2013)

[5] Laura M. Plum, Lothar Rink and Hajo Haase, The Essential Toxin: Impact of Zinc on Human Health, Int. J. Environ. Res. Public Health 2010, 7(4), 1342-1365;

[6] Pandey Govind and Madhuri S(2014) Heavy Metals Causing Toxicity in Animals and Fishes, Research Journal of Animal, Veterinary and Fishery Sciences , ISSN 2320 – 6535,Vol. 2(2), 17-23,

[7] Saif S., Haq M. and Memon K.(2005), Heavy Metals, Contamination Through Industrial Effluent to Irrigation Water and Soil in Korangi Area of Karachi (Pakistan). International Journal of, Agriculture and Biology 74: 646 648 .

[8] Panda SK, Choudhury I & Khan MH(2003), Heavy metals induce lipid peroxidation and affect antioxidants in wheat leaves. Biologia Plantgum, 48, 289-294..

[9] S.O. Salihu , John O.J Matthew T. Kolo (2014) Heavy Metals in Some Fruits and Cereals in Minna Markets, Nigeria. Pakistan Journal of Nutrition 13 (12): 722-727,

[10] Duruibe, Ogwuegbu, and Egwurugwu(2007), Heavy metal pollution and human biotoxic effects, International Journal of Physical Sciences Vol. 2 (5), pp. 112-118,

[11] Radwan A. and Salama A(2006)., Market basket survey for some heavy metals in Egyptian fruits and vegetables, Food and Chemical Toxicology 44: 1273–1278.

[12] Tripathi R., Raghunath R. and Krishnamurthy T(1997)., Dietary intake of heavy metals in Bombay city, India, The Science of the Total Environment 208: 149-159

[13] Vinodhini R. and Narayanan, M. (2008).Bioaccumulation of heavy metals in organs of fresh water fish Cyprino carpio (common carp). International Journal of Environmental Science and Technology, 5(2)

[14] Food Standards and Safety Authority of India,2006, (http://www.fssai.gov.in)