

# Accumulation and Distribution of Heavy Metals in Vegetables of Khetri Copper Mine Region, Rajasthan

Anita Punia<sup>1</sup>, N. Siva Siddaiah<sup>2</sup>

Research Scholar, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India<sup>1</sup>

Associate Professor, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India<sup>2</sup>

**ABSTRACT:** We present here the results of a study on the heavy metal accumulation and distribution in several varieties of vegetables grown in the Khetri copper mine region. A total of eight varieties of vegetables (Guar, Spinach, Pepper, Ridged gourd, Brinjal, Bottle gourd, Daikon and Lady finger) were collected neighbouring the mine, tailings and overburden materials, and were analysed for heavy metals (Cu, Zn, Ni, Mn, Fe, Co, Pb and Cd) to understand the impact of mining on their distribution and variation in the vegetables. Among the heavy metals, Cu concentration in all studied vegetables is 2 times higher than the permissible limit of Prevention of Food Adulteration (PFA) act and WHO/FAO. Zn concentration also exceeds the PFA limit in some vegetables while Ni, Co, Mn, Fe, Pb and Cd are present within the permissible limit of PFA. Compared to other vegetables, the Guar (oil seed) and Spinach (leafy vegetable) are highly contaminated with Cu. The rank order of vegetables according to their decreasing heavy metal abundances is as follows Guar > Spinach > Pepper > Ridged gourd > Brinjal > Bottle gourd > Daikon > Lady's finger. The results of the present study will help to assess the impact of consumption of heavy metal bearing vegetables on human health in the region.

**KEYWORDS:** Heavy metals, Vegetables, Pollution, Khetri Copper mines

## I. INTRODUCTION

The ever growing anthropogenic activities such as mining, industrial, transportation and urbanization are the major sources of heavy metals, adversely affecting the different compartments of environment (i.e. soil, air, water and biota) and are major concern of the modern society [1]. Heavy metals such as Fe, Cu, Ni, Mn and Zn are essential for organism's growth, while Cd, Pb, Ag and Hg are not essential biologically but cause adverse health impacts like renal failure, liver damage and chronic toxicity in the humans [2].

India is a mineral rich country and mining activities are going on in many parts of the country since time immemorial. Both metallic and non-metallic minerals are being extracted and huge quantities of mine waste are thrown into the environment annually. Mines and related activities are one of the major contributors of heavy metals in the environment [3-7]. Among metallic mines, the Khetri region is famous for copper mines since historical times. This has resulted in large quantities of sulfide rich tailings and overburden materials. Approximately 25,000 tons/year of tailings are being generated and dumped openly at Khetri [8]. Khetri lies in semi-arid part of the country, during summer season strong winds blow in the region and the finer particles of tailing and overburden materials with fine disseminations of sulfides could easily be carried away to the distant places.

The higher impact of Khetri mining activities on plants is well reported by researchers. Thukral [9] reported a higher concentration of Cu (164-400 µg/g) in the plants of Khetri Nagar. Tiagi and Aery [10] reported maximum Cu concentration (394 µg/g) in the leaves of *Talinum Portulacifolium* followed by *Tephrosia Villoso* (288 µg/g), *Rhus Mysorensis* (234 µg/g) and *Bochea Morubifolia* (147 µg/g). Maharia [11] reported high abundance of Cu, Cr, Cd and Pb in the medicinal plants of Khetri along with the enrichment of Ca and Mg in some plants. The Cu concentration

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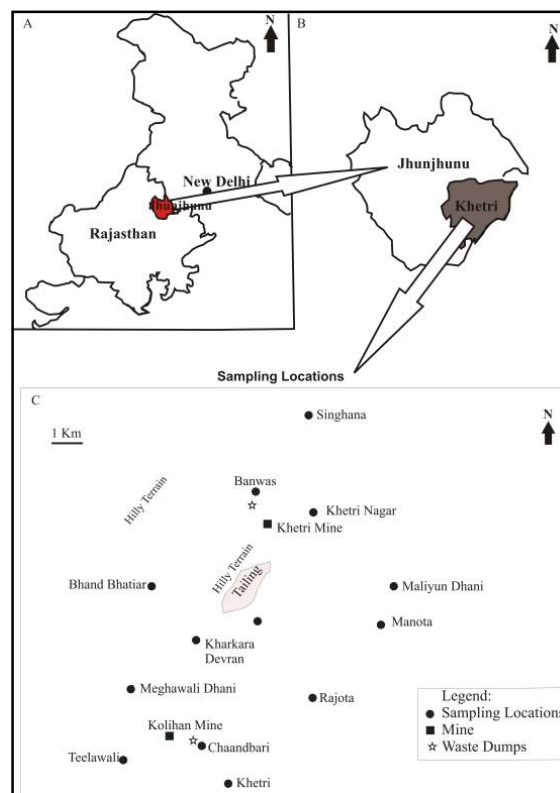
(31.6-76.5 mg/kg) was 3-4 folds higher than the Cu concentration (7.4-15.3 mg/kg) from Hardwar samples. Despite such information no study has been carried out to assess the accumulation of heavy metals in the locally grown vegetables.

The main objective of the present study was to determine the heavy metals (Cu, Zn, Ni, Mn, Fe, Co, Pb and Cd) concentration in locally grown vegetables of Khetri copper mine region and evaluate the contamination level by calculating the heavy metal pollution index.

## II. MATERIAL AND METHODS

### Study area

Khetri is located in semi-arid region of Jhunjhunu district of Rajasthan, India. It is situated in the northwest part of the country and about 200 km southwest of New Delhi, capital of country. It is about 370 metre above mean sea level; latitudes N 28°04.070' and longitudes E 75°49.294'. The average rainfall in Khetri region is ~500 mm per year. During summer maximum temperature reaches to 45°C and minimum is 12°C, while in winter maximum temperature hovers around 25°C and minimum is 2°C. The region is covered with hilly terrain and with lack of surface water bodies. The study area is shown in the Fig. 1.



**Fig. 1** A) Location of Jhunjhunu district in Rajasthan B) Location of Khetri in Jhunjhunu District C) Sampling locations

Khetri copper belt extends about 80 km in length from Singhana (Jhunjhunu district) in the northeast to Sangarva (Sikar district) in the southwest of Rajasthan. Geologically the rocks of northern Khetri Copper Belt are made up of

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feldspathic quartzites with magnetite, banded amphibole quartzites, garnetiferous chlorite schists, mica schists and quartzites, folded into number of regional synclines and anticlines [12].

## Sampling and Analytical method

Vegetable samples were collected in the months of September, 2015 from 13 villages located in and around the mines, overburden materials and tailings. The sampling locations along with the locations of mines and overburden materials are shown in the Fig. 1 C. Reference samples were collected from Singhana market (vegetables were brought from villages distant from copper mines) assuming them to be less effected by the mining activities. Eight species namely *Capsicum annuum* (Chilli pepper), *Solanum melongena* (Brinjal or Eggplant), *Abelmoschus esculentus* (Lady Finger or Okra), *Spinacia oleracea* (Spinach), *Raphanus sativus var. Longipinnatus* (Daikon), *Luffa* (Ridged gourd), *Lagenaria siceraria* (Bottle gourd) and *Cyamopsis tetragonoloba* (Guar) were collected. Approximately 500 gm of vegetables were collected depending upon the availability. The vegetables were collected from home gardens avoiding the commercial farms to minimize the influence of fertilizers or pesticides.

Samples packed in poly zip bags were brought to laboratory for analysis. The vegetables were washed with flowing tap water for approximately 20 minutes to remove the sand and air borne pollutants and dried for 3-4 hours in ambient conditions. Then washed with distilled water for approximately 5-10 minutes and cut into small pieces by stainless knife depending upon the size of vegetables. Samples were dried off in oven at 70°C for 48-72 hours. The dried samples were crushed by using porcelain motor pestle and pass through 60 mesh size sieve. 1 gm of crushed samples were digested by 15 ml of acid mixture (70 % HNO<sub>3</sub>, 65% HClO<sub>4</sub> and 70% H<sub>2</sub>SO<sub>4</sub> in 5:1:1 ratio) and heated at 80°C till the solution become transparent [13]. The heavy metals were analysed by Atomic Absorption Spectroscopy (AAS). During acid digestion reagent blanks were prepared with each batch to monitor the contamination of glassware.

## Pollution assessment

### Heavy Metal Pollution Index

To compare the total heavy metal content in vegetables from different sampling location, the metal pollution index (MPI) is calculated [14].

$$MPI = (C_{f1} \times C_{f2} \dots \times C_{fn})^{1/n}$$

Where C<sub>fi</sub> is the heavy metal concentration i in the sample and n is the total number of heavy metals.

## III. RESULTS AND DISCUSSION

Cu concentration varies from 53 to 131 mg/kg with an average of 72±25 mg/kg. Maximum Cu concentration is found in Guar (131 mg/kg) followed by Spinach (84 mg/kg) and Ridged Gourd (73 mg/kg) while lowest (53 mg/kg) is found in Lady's finger (Table 1). Fe concentration varies from 47 to 373 mg/kg with an average of 143±118 mg/kg. The maximum concentration of Fe is found in Guar (372 mg/kg), Spinach (307 mg/kg) and Brinjal (119 mg/kg) and least is found in Lady's finger (46 mg/kg). Zn concentration in vegetables varies from 26 to 81 mg/kg with an average of 43±21 mg/kg. The order of abundance of individual heavy metals in vegetables is Fe > Cu > Zn > Mn > Ni > Pb > Cd. The detailed description of the heavy metal concentrations in the vegetables of Khetri region are given in the Table 1.

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Table 1 Heavy metal concentration in the vegetables (all concentrations are in mg/kg)

Vegetables	Cu	Fe	Zn	Mn	Pb	Co	Ni	Cd	ΣHeavy metals
Brinjal	65.21	119.79	32.45	17.21	0.11	0.09	0.15	0.01	236
Bottle gourd	62.21	93.77	26.84	17.12	1.08	0.00	0.00	0.00	204
Lady finger	53.40	46.86	33.41	28.59	0.00	0.00	0.00	0.00	162
Ridged gourd	72.67	115.70	47.92	15.99	0.00	0.10	0.50	0.00	253
Daikon	53.49	74.11	25.51	19.65	0.00	0.00	6.03	0.10	179
Pepper	72.66	109.35	80.79	13.89	0.00	0.17	0.23	0.01	277
Spinach	83.63	307.15	70.61	43.95	0.00	0.00	0.58	0.00	506
Guar	130.78	372.95	47.01	28.25	0.00	0.00	1.91	0.00	583
<b>Min</b>	53.40	46.86	25.51	13.89	0.00	0.00	0.00	0.00	-
<b>Max</b>	130.78	372.95	80.79	43.95	1.08	0.17	6.03	0.10	-
<b>Average</b>	74.26	154.96	45.57	23.08	0.17	0.05	1.18	0.02	-
<b>Median</b>	68.94	112.53	40.21	18.43	0.00	0.00	0.37	0.00	-
<b>STDEV</b>	25.02	118.02	20.52	10.06	0.40	0.07	2.06	0.03	-

Different vegetables have different heavy metal accumulation capacity. The sum of all heavy metals in each vegetable is shown in Fig. 2. The sum of all heavy metals are found higher in Guar & Spinach, and lower in Lady's finger. The rank order of vegetables according to their decreasing heavy metal abundances is Guar > Spinach > Pepper > Ridged gourd > Brinjal > Bottle gourd > Daikon > Lady's finger.

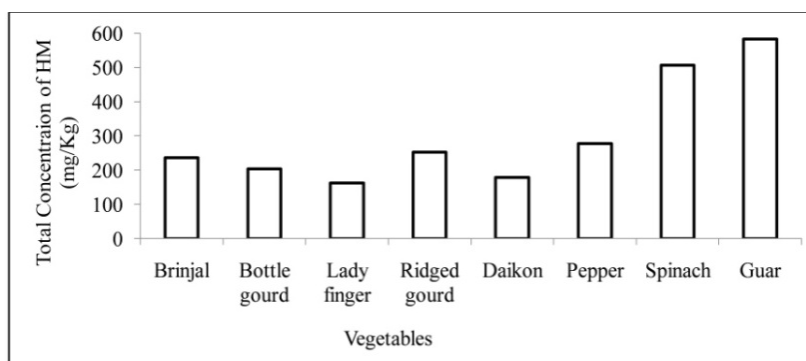


Fig. 2 Total concentration (mg/Kg) of heavy metals in the vegetables of Kheri region

On categorising the vegetables into three categories *first* leafy, *second* fruits and *third* roots. The rank order among the 3 types of vegetables in decreasing order of heavy metal contents is Leafy > fruits > roots. The heavy metal accumulation in vegetables follows two paths *first* through soil and *second* by atmospheric deposition. The heavy metals are accumulated high in the leaves as leaves act as an entry point for the heavy metals from the atmosphere. Leafy vegetable (spinach) also have high capacity to accumulate the heavy metals compared to fruit vegetables due to high surface area. While, in roots the heavy metals are only accumulated through the soil. Hence, roots have lowest heavy metals concentration. It is observed that Fe (307 mg/kg) concentration is relatively high in leafy vegetables compared to fruit & root vegetables. The Fig. 3 shows the high concentration of Cu, Fe, Zn and Mn in the leafy vegetables followed by the fruits and roots.

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Vol. 6, Issue 6, June 2017

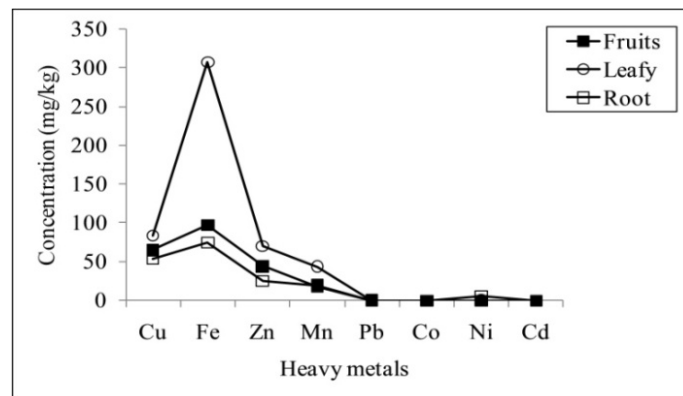


Fig. 3 Heavy metal contents in leafy, fruit & root vegetables

## Heavy metal accumulation with respect to sampling locations

Sampling locations namely Khetri Nagar (near the mines & extraction plant), Banwas (near the underground mines & overburden materials) and Maliyun Dhani (near the tailings dam) have high concentration of Fe, Cu, Zn and Mn as shown in the Fig. 4. Specially, vegetables from Banwas & Khetri Nagar are highly contaminated with Cu & Fe compared to other locations. Compared to Khetri Nagar, vegetables from Banwas have high concentration of heavy metals (Cu, Fe & Zn). This is due to the presence of both mine & overburden materials at Banwas.

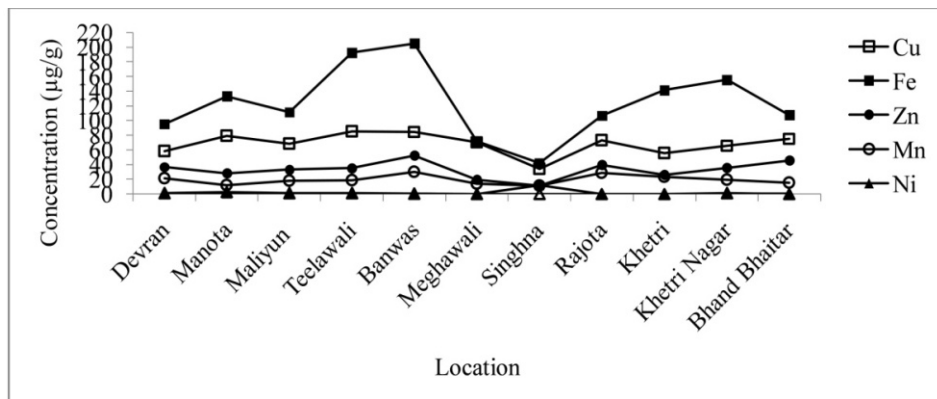


Fig. 4 Heavy metal concentration (mg/Kg) in vegetables at different sampling locations

Statistically, the average heavy metal concentration in vegetables varies widely from location to location. Vegetables from Teelawali & Banwas have maximum Cu concentration i.e. 85 and 84 mg/kg respectively. Vegetables from Singhana have minimum concentration of Cu (34 mg/kg) as these are brought from locations distant from mining activities. The average maximum Fe concentration is found in the vegetables from Banwas, Teelawali & Khetri Nagar i.e. 204, 195 & 155 mg/kg respectively and minimum at Singhana (42 mg/kg). Like Cu & Fe, the average concentration of Zn in all vegetables is highest at Banwas (52 mg/kg) and lowest at Singhana (11 mg/kg).

## Comparison with permissible limits

Heavy metal concentrations in vegetables of Khetri region are compared with the Prevention of food Adulteration (PFA) act [15] and WHO/FAO [16] to assess extent of heavy metal contamination in vegetables. It is found that concentration

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Vol. 6, Issue 6, June 2017

of Cu and Zn in vegetables exceeds the PFA permissible limits. Concentration of Zn exceeds the permissible limits in Pepper & Spinach, while Cu exceeds in all the vegetables. Cu concentration is 2 times higher than the PFA. Hence, the vegetables grown in the Khetri region are contaminated with Cu.

On comparing with WHO/FAO permissible limits the results are similar to PFA limits. Cu concentration exceeds WHO permissible limits in all vegetables while Zn exceeds in Pepper & Spinach as shown in the Fig. 5. Despite of higher concentration of Fe in vegetables it is within the permissible limits (450 mg/kg) of WHO/FAO.

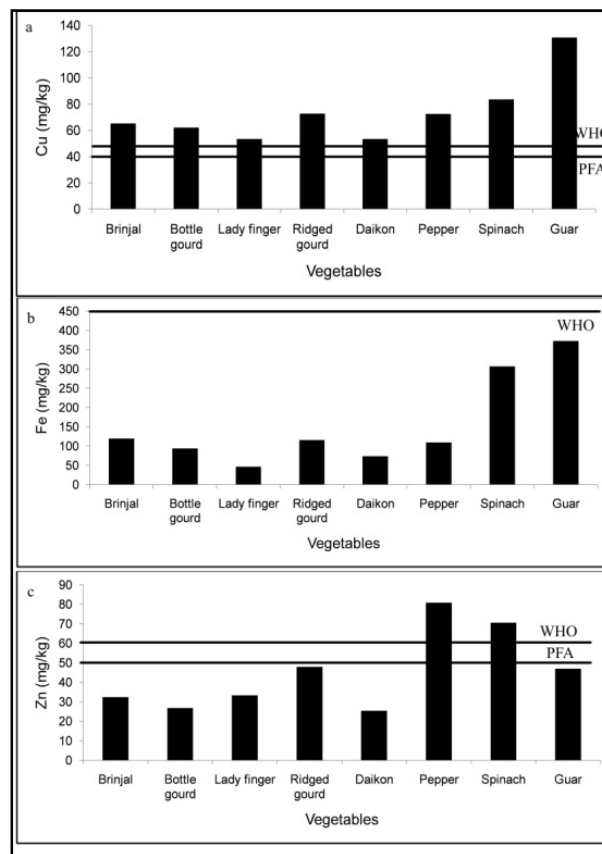


Fig. 5 Comparison of a) Cu, b) Fe and c) Zn concentration with the WHO and PFA permissible limits

### Metal Pollution Index

MPI is calculated to assess the heavy metal accumulation in the vegetables of Khetri region. The calculated MPI varies from 1.76 to 2.03 with an average of  $1.87 \pm 0.10$ . The maximum MPI is calculated for Guar (2.03) followed by the spinach (1.99). The minimum MPI is for lady finger i.e. 1.76. It shows that the heavy metals are highly accumulated in the Guar (Oil seed) and Spinach comparative to lady finger. The MPI values for each vegetable are shown in the Fig. 6.



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Vol. 6, Issue 6, June 2017

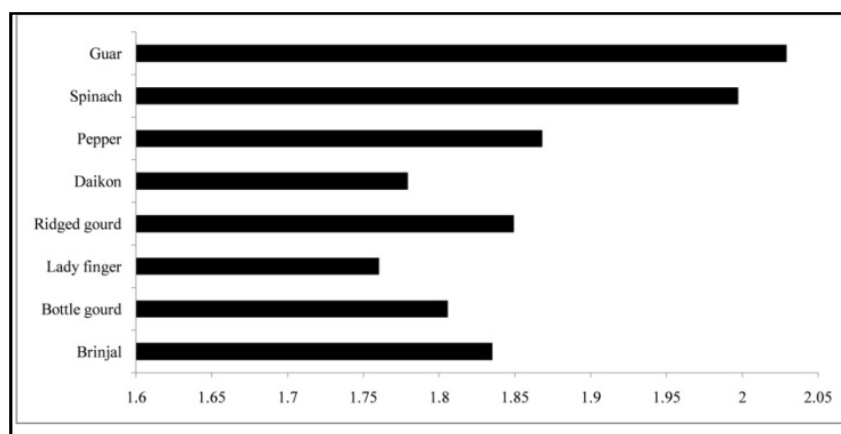


Fig. 6 MPI values for different vegetables collected from Khetri region

In the region, residents are not preferred to grow vegetables in their household gardens due to scarcity of water. According to local residents, the supply of vegetables is from distant locations approximately 30-40 km away from mining. Hence, the impact due to vegetables consumption may not be potential due to low consumption of locally grown vegetables. Cu is present in the aerosol hence the health impacts could be due to inhalation of Cu or through drinking of contaminated groundwater.

## IV. CONCLUSION

Among heavy metals, Fe (143 mg/kg) is the most abundant followed by Cu (72 mg/kg) in all the studied vegetables of Khetri area. The average concentration of heavy metals are higher in leafy vegetables (63 mg/kg) compared to fruit (28 mg/kg) & root (22 mg/kg) vegetables. The concentration of Cu in all the studied vegetables of Khetri area is 2 times higher than the permissible limit (30 mg/kg) of PFA act. Vegetables grown in the Khetri mining area are more contaminated with Cu compared to those far from mining activities. Thus, the heavy metal rich sulfide bearing tailings and overburden material in the area should be stored and managed scientifically to minimize the heavy metal dispersal. The waste should be dumped away from the residential places to reduce the direct impact on humans.

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## REFERENCES

- [1] Lee, Y.H., and Stuebing, R.B., "Heavy metal contamination in the river Toad, Juxtapasper (Inger), near a copper mine in East Malaysia", Bulletin of Environmental Contamination and Toxicology, Vol. 45, pp. 272-279, 1990
- [2] Sathawara, N.G., Parikh, D.J., and Agarwal, Y.K., "Essential heavy metals in environmental samples from western India", Bulletin of Environmental Contamination and Toxicology, Vol. 73, pp.756-761, 2004
- [3] Cui, Y.J., Zhu, Y.G., Zhai, R.H., Chen, D.Y., Huang, Y.Z., Qiu, Y., and Liang, J.Z., "Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China", Environmental International, Vol. 30, pp.785-791, 2004
- [4] Yu, L., Yan-bin, W., Xing, G., Yi-bing, S., and Gang, W., "Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China", Journal of Environmental Sciences, Vol. 18, No. 6, pp.1124-1134, 2006
- [5] Ginocchio, R., Sánchez, P., de la Fuente, L.M., Camus, I., Bustamante, E., Silva, Y., Urrestarazu, P., Torres, J.C., and Rodríguez, P.H., "Agricultural soils spiked with copper mine wastes and copper concentrate: implications for copper bioavailability and bioaccumulation", Environmental Toxicology and Chemistry, Vol. 25, No. 3, pp.712-718, 2006

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Vol. 6, Issue 6, June 2017

- [6] Kachenko, A.G., and Singh, B., "Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia", *Water, Air and Soil Pollution*, Vol. 169, pp.101-123, 2006
- [7] Barenys, M., Boix, N., Farran-Codina, A., Palma-Linares, I., Montserrat, R., Curto, A., Gomez-Catalan, J., Ortiz, P., Deza, N., and Llobet, J.M., "Heavy metal and metalloids intake risk assessment in the diet of a rural population living near a gold mine in the Peruvian Andes (Cajamarca)", *Food and Chemical Toxicology*, Vol. 71, pp. 254-263, 2014
- [8] Mishra, M., Singh, S., Das, T., Kar, R.N., Rao, K.S., Sukla, L.B., and Mishra, B.K., "Bio-dissolution of copper from Khetri lagoon material by adapted strain of *Acidithiobacillusferrooxidans*", *Korean Journal of Chemical Engineering*, Vol. 25, No. 3, pp.531-534, 2008
- [9] Thukral, A.K., Joshi, M.C., and Chand, R., "Copper concentration in some grasses from Khetrinagar and Ajitsagar", *Current Sciences*, Vol. 51, pp.15, 1982
- [10] Tiagi, Y.D., and Aery, N.C., "Biogeochemical studies at the Khetri Copper deposits of Rajasthan, India", *Journal of geochemical exploration*, Vol. 26, No. 3, pp. 267-274, 1986
- [11] Maharia, R.S., Dutta, R.K., Acharya R., and Reddy, A.V.R., "Heavy metal bioaccumulation in selected medicinal plants collected from Khetri copper mines and comparison with those collected from fertile soil in Haridwar, India", *Journal of Environmental Science and Health Part B*, Vol. 45, pp.174-181, 2010. DOI: 10.1080/03601230903472249.
- [12] Das Gupta, S.P., "The structural history of the Khetri Copper Belt, Jhunjhunu and Sikar districts, Rajasthan", *Memoir Geo Survey of India*, Vol. 98, pp.170, 1968
- [13] Allen, S.E., Grimshaw, H.M., and Rowland, A.P., "Chemical Analysis", In: Moore, P.D., Chapman, S.B. (Eds.), *Methods in Plant Ecology*. Oxford : Blackwell Scientific publication, London, pp. 285-344
- [14] Usero, J., Gonzalez-Regalado, E., and Gracia, I., "Trace metals in the bivalve mollusks *Ruditapes decussates* and *Ruditapes phillippinarum* from the Atlantic Coast of Southern Spain", *Environmental International*, Vol. 23, No. 3, pp. 291-298, 1997
- [15] Awashthi, S.K., "Prevention of food adulteration act no. 37 of 1954", *Central and state rules as amended for 1999*, Ashoka law house, New Delhi, (2000)
- [16] WHO/FAO, "Joint FAO/WHO food standard programme codex alimentarius commission 13<sup>th</sup> session", Report of the thirty eight sessions of the codex committee on food hygiene, Houston, United States of America, AL/NORM 07/30/13, 2007