ASSESSMENT OF HEAVY METALS IN VARIOUS PARTS OF PLANTS, SOIL AND AIR OF SOME SELECTED AREAS OF DISTRICT CHARSADDA, PAKISTAN

Hussain GULAB, Mazhar MAHMOOD, Sajid ALI & Fazal Akbar JAN*

Department of Chemistry Bacha Khan University Chrasadda, Khyber-Pakhtunkhwa, 24420 Pakistan Phone# 091-6002934, Email: hussaingulab@gmail.com, Corresponding Author: fazal_akbarchem@yahoo.com

Abstract: Plants and vegetables contamination with heavy metals is one of the burning issues in the recent years. Soil, various parts of the plants and air samples were collected for assessment of some selected heavy metals (Cr, Ni, Zn and Pb) from selected areas of district Charsadda, Pakistan. All the samples were analyzed for the presence and quantification of heavy metals like Cr, Ni, Zn and Pb using atomic absorption spectrophotometer (AAS). Selected heavy metals were found in all samples having diversified concentration. The highest level of Cr was found to be 1.309 mg/Kg in the wheat root sample (near to water entrance) collected from the proximity of service deck and its lowest concentration was found to be 0.140 mg/Kg in the jasmine root sample collected from the Hashtnagar Filling (HNF) station. Similarly the highest concentrations of Ni and Zn were found to be 5.96 mg/Kg and 0.036 mg/Kg in the plant samples collected from oat field situated near vehicles work shop and the soil sample collected from the oat field respectively. The highest concentration of Pb (4.00 mg/Kg) was determined in the root sample of jasmine collected from H.N.F station, which is above the permissible level. The soil samples were found to contain all these heavy metals with profound concentrations. It was found that level of some of these heavy metals was higher than the WHO permissible limit in some of the investigated samples. The study suggests that concentration of these heavy metals must be periodically checked, monitored and controlled in order to avoid or at least minimize the hazardous effects of these toxic metals on fauna and flora of the area**.**

Key words: Heavy Metals, AAS, Plant, Soil and Air Samples, Hashtnagar, WHO.

1. INTRODUCTION

Heavy metals are the members of periodic table having high atomic weight and have high density about 5 times that of water. These metals produce basic oxides by oxidation. Most of them have silver white color. These metals are dissolved in rain water and drained by it to the earth surface due to which the pH is decreased and then absorbed by the plants from soil in the soluble form. The metal present in ghee utensils and oil parts of vehicles are washed mostly by hot water or highly pressurized water by which it goes to the fields and ultimately absorbed by plants. About 17 metals are considered to be very toxic and relatively accessible. They are so toxic that they can cause damaging effects even at very low concentration.

The heavy metals e.g. Hg, Pb, As, Cd, Sc, Cu, Zn, Ni, and Cr are the most common pollutant in developing countries. They are recycling in the environment of the urban areas of the cities of these countries. Heavy metals can effect mankind indirectly and cause damage to metal health, nervous system, kidneys, lungs and other organs (Cunningham & Saigo, 1997). These metals enter to the ecosystem by combustion of engines exhaust and water of washing oily engines or by the washing of hands with many kinds of soaps or by washing of ghee utensils etc. The problem associated with the exposure to heavy metals present in food stuffs had adverse effect on human health. Due to improvements in the food production and processing technology increases the chances of contamination of food with various environmental pollutants, especially heavy metals Intake of these contaminants by animals causes deposition of residues in meat (Sabir et al., 2003). Contamination of

heavy metals is a serious threat because of their toxicity, bioaccumulation and bio-magnifications in the food chain. Zinc concentration was found to be highest in meat, liver, fish and eggs (Wei & Yang, 2010; Demirezen & Uruç, 2006). Automobiles are the agents that cause pollution in soil while the main source of heavy metals for soil and plants is water (Abechi et al., 2010; Mohod & Dhote, 2013). Road dust is of the major source of heavy metals (Ambade & Litrupa, 2012). Heavy metals and metalloids in the environment concerned with analytical and legal problems like neurotoxicity, genotoxicity, or carcinogenicity is widely due to heavy metals (Szyczewski et al., 2009; Flora et al., 2008).

Heavy metal pollution is one of the most important problems in Zambia and causes serious effects to humans and animals (Ikenaka et al., 2010). Soil pH significantly affects the solubility and mobility of heavy metals and all industries discharge their solid as well as liquid waste on land and in water bodies without recommended treatment and pollute the soil, water and air (Parth et al., 2011; Sharma et al., 2011). Biosorbents can be used widely for heavy metal removal (Christiana & Samuel, 2013). Mining activities are also responsible for heavy metal contamination and dissolution of metals during rock-water interaction is relatively due to low flow of ground water in pre-monsoon season (Birsan & Luca, 2010; Rizwan et al., (2010).The uptake of heavy metals by plants through contaminated soil gets accumulated and is a potential threat to animals and human health (Imtiazuddin & Mumtaz 2013). Heavy metal levels of demersal fishes were higher than those of other fishes (Leung & Jiao, 2006). Storm water drains may leak heavy metals to some extent (Lambert et al., (2010). Heavy metals are typically spread out over former industrial sites and may cover acres of land (Mubiana et al., 2005). The literature shows that industrialization and vehicular traffic substantially increase the contents of heavy metals in urban soils and urban road dusts (Janet et al., 1994). The present study is aimed to identify and quantify the Cr, Ni, Zn and Pb in plants, soil and air samples of some selected areas of District Charsadda in order to estimate the probable threats to the plants, animals and human beings of this area due to increasing level of these heavy metals.

2. EXPERIMENTAL

2.1. Materials and Methods

2.1.1. *Sampling area*
The samples have been collected from various areas of District Charsadda, Pakistan (Fig. 1). Most of the cropland of this area is irrigated through the rivers Kabul, Swat and Jindi. The fields are watered by the canals originated from these rivers. These canals pass through the villages and some of the city areas where the waste water from the drainages falls into these canals and this water is contaminated. This contaminated water enters to the fields and contaminates the soil. These polluted soil and water are used by the crops and plants grown in this area.

2.1.2. *Sampling sites*
A total of 50 samples were collected from the study area of which dust samples were 15, soil samples were 15 and vegetables were 20. The soil was collected from a site nearby a petrol pump named as HNF Station situated on Peshawar Road Charsadda. About 30 trucks run by diesel engines stay for overnight in the mentioned filling station. Three samples, one plant "Jasminium officinale" and two soil samples were collected from this site. One soil sample was collected from the surface and one from 10 cm below the surface. Another sampling site is a crop field where oat was cultivated which is adjacent to a vehicle workshop. The canal through which the field is watered passes through the workshop. The mechanics wash various oily parts of vehicles with water of this canal. Two types of samples (soil and plant) were collected from the field irrigated with this water, one from the site near the entrance of water and the other from a site 100 meter away from the water entrance. From the later site one soil sample and three plant samples (root, shoot and fruit) were collected. Another sampling site was a field watered by a canal passing nearby a carwash.

2.1.3 *Preparation of samples*
The soil and plant samples were placed in sun for about 10 days. Then the sun dried samples were transferred to the lab in polythene bags. The soil samples were dried at 100 ˚C for about 1hr in an oven. Plant samples were dried at 80˚C for about 2 hours in oven. Then the soil samples were grinded with mortar and pestle. The plant samples were divided into three parts e.g. root, shoots and fruit (grains). The root, shoot and grains were grinded with the help of a grinder. The samples were passed through a sieve having mesh size of 40. All the samples were properly bottled and stored for onward use.

2.1.4. *Reagents*
Analytical grade HNO_3, HCl and double distilled water were used for sample preparation and analysis. All the solutions were prepared in double distilled water. For each metal working/calibration standards were prepared from the standard solutions.
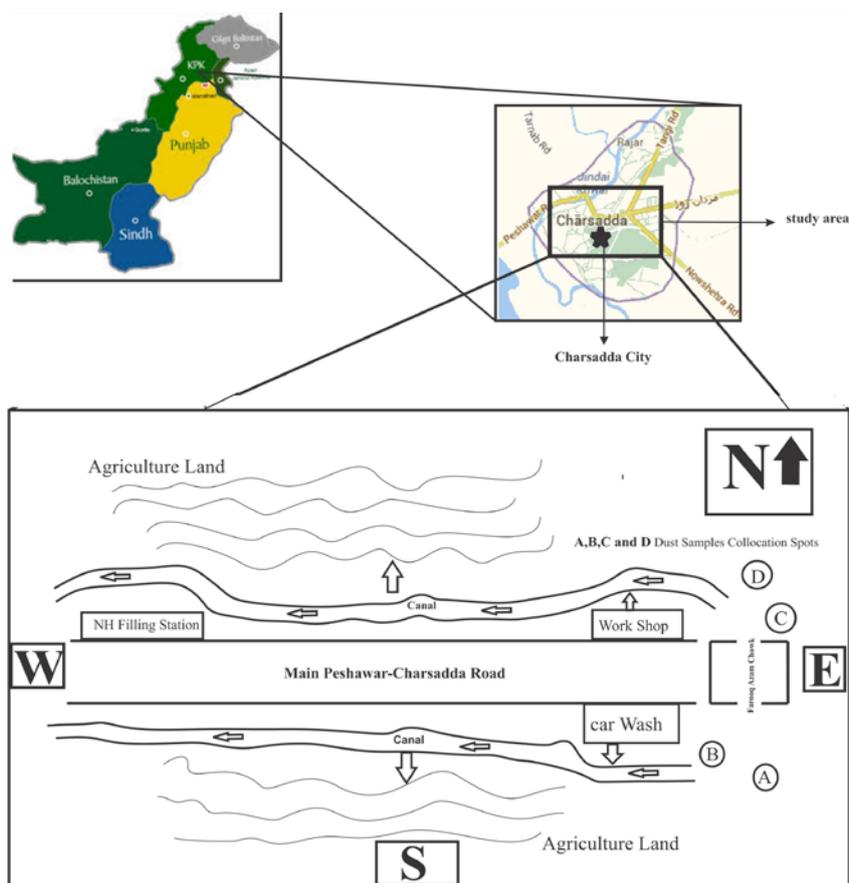
Figure 1. Simplified map of the studied area and sampling points location.

2.1.5. *Digestion of Soil Samples*

One gram of each soil sample was taken in separate beakers and a mixture of 1:3 ratio of HNO_3 and HCl (aqua regia) was used to digest these samples. Then samples were heated gently using heating mantle till all the aqua regia was evaporated. All the samples were diluted in 3 ml of double distilled water and filtered through what man filter paper. The filtrate was washed with distilled water. The sample solutions were prepared up to 20 ml and put in separate cleaned glass bottles.

2.1.6. *Digestion of Plant Samples*

All the plant samples (0.5) g were taken in a beaker and treated with aqua regia and heated gently on a heating plate till all the sample contents were dissolved. The solutions were prepared in double distilled water and filtered through Whatman filter paper. All the solutions were prepared up to 20ml and stored in glass bottles.

2.1.7. *Analysis of Heavy Metals*

The samples were analyzed by Atomic Absorption Spectrometer, model A 900T, made by PerkinElmer, equipped with Flame and Graphite furnace controlled by a PC having A.A. Wind lab software. The flame atomization process was used for analyzing the samples. Hollow cathode lampswere used as line source. All the analyses were carried out in the Advanced Research Lab (ARL) of the Department of Chemistry, Bacha Khan University Charsadda.

3. RESULTS AND DISCUSSION

The collected samples were analyzed for investigation of Cr, Ni, Zn and Pb in order to assess their potential hazardous effect on the living organisms. The level of Cr, Ni, Zn and Pb was determined in all these samples and it was found that all the samples contain a profound amount of these toxic metals. The main source of heavy metals in District Charsadda is municipal waste, workshops waste and contaminated water of service stations through which the ecosystem of this area is directly exposed to these heavy metals.

3.1. *Concentration profile of the selected heavy metals in air samples*

All these four metals were investigated in the air samples collected from three different sites as mentioned in table 1. The highest concentration of Cr was found to be 5.89 mg/m^3 in the air collected from prang road. The probable reason could be that there is plenty of welding workshops on the road sides and

urbanization is increasing day by day. The lowest concentration of Cr was found as 1.36 mg/m^3 in the air sample collected from Farooq Azam (FA) Chowk and the reason could be that there are markets and obviously nominal metal works.

The highest concentration of Ni was found to be 0.442 mg/m^3 in the air sampled from FA Chowk and the possible reason could be that various sprays are used over here for diverse purposes which may contain Ni in a profound ratio. The lowest concentration of Ni was found to be 0.343 mg/m^3 in the air collected from prang road and the reason could be that Ni works are vanishingly low at this site.

The highest concentration of Zn was found as 10.0 mg/m^3 in the air sample from FA Chowk. As it is a market place where paints shops are also available and the painters are painting cars as well through which the Zn may contaminate the air. The lowest concentration of Zn was found to be 0.001 mg/m^3 in the air sampled from Peshawar Road Charsadda where the activities leading to increased concentration of Zn are scarce. The remaining sites were found to contain Zn in between the extremes as per the location and metal practices carried on over there.

The highest concentration of Pb was found to be 0.449 mg/m^3 in the air sample collected from Prang Road. The reason could be that mostly heavy traffic vehicles run by diesel oil are using this road. The concentration of Pb found in the sample collected from FA Chowk was 0.256 mg/m^3. The possible reason is that mostly light vehicles like rickshaws, cars and other LTVs which are commonly run by CNG are the major transport over here. The investigated concentration profile of these heavy metals in the air samples collected from the mentioned sites is given in Table 1.

3.2. Concentration profile of Cr, Ni, Zn and Pb in plant samples

The level of Cr, Ni, Zn and Pb was investigated in the plant samples collected from various sites and the results are given in table 2. Various parts of the plants i.e. roots, stem and fruits were separately investigated for the presence of these metals. The highest concentration of Cr (1.309 mg/Kg) was determined in the oat roots sampled from the oat field situated near a vehicle work shop. This field is watered

with a canal which passes through the workshops and welding shops due to which this water is contaminated.

The lowest concentration of Cr as 0.006 mg/Kg was found in the wheat root sample collected from the site near to water entrance of the same field. The relatively lower concentration of Cr in the fruit sample could be probably due to its indirect exposure and retarded bio-transportation of the Cr. The level of Cr investigated in all the other sites was found to be in between the highest and lowest determined concentrations. Some of these sites have the Cr level above the permissible level, depending upon their proximity and exposure to the Cr sources.

The highest concentration of Ni as 70.12 mg/Kg was determined in the plant sample collected from the oat root which is situated near the workshops. This field is watered with a canal which passes through the houses and the workshops. Thus water of this canal is contaminated due to washing of household ghee utensils and effluent of the service stations. The lowest concentration of Ni was found to be 0.120 mg/Kg in the wheat fruit sampled from the site that was 100 meters away from the water entrance of the same field.

The lower concentration of Ni in this sample could be its larger distance from the metals sources and the mechanism of bio-transportation of the Ni through the roots, stems and fruits. The highest concentration of Zn was determined as 5.40 mg/Kg in the wheat root collected from a site near a car wash. The lowest concentration of Zn was found to be 0.026 mg/Kg in oat stem sample collected from the oat field situated near the work shop. The lower concentration of Zn in this sample could be its lower bioaccumulation in the wheat stem and lower exposure to the Zn source. The highest concentration of Pb was found as 4.00 mg/Kg in the jasmine stem sample collected from HNF station. The reason could be its proximity to the sources of lead i.e. oils and vehicles engines exhausts. The lowest concentration of Pb was determined as 0.52 mg/Kg in the wheat fruit (F) sampled from the field far away from the source. The level of Pb investigated in all the other samples collected from various sites was found to be in between the highest and lowest determined concentrations. Some of these sites have the Pb concentration above the permissible level, depending upon their proximity and exposure to the Pb sources.

Table 1. Concentration of Cr, Ni, Zn and Pb in the Air samples

S#	Air Sample ID	Cr mg/m^3	SD	Ni mg/m^3	SD	Zn mg/m^3	SD	Pb mg/m^3	SD
1	Air of Pesh. R.	2.010	±0.180	0.393	±0.060	2.500	±0.090	0.385	±0.020
2	Air of F. A. C.	1.360	±0.100	0.442	±0.004	10.10	±0.570	0.256	±0.010
3	Air of Pr. R.	5.890	±0.400	0.321	±0.005	0.001	±0.001	0.443	±0.110
Permissible Level		1mg/m^3		1mg/m^3		10 mg/m^3		0.5mg/m^3	

Pesh. R.: Peshawar Road; F. A. C.: Farooq Azam Chowk; Pr. R.: Prang Road

Table 2. The concentration profile of Cr, Ni, Zn and Pb in the plants samples

S. No	Sample ID	Cr mg/Kg	SD	Ni mg/Kg	SD	Zn mg/Kg	SD	Pb mg/Kg	SD
1	Wheat stem (N)	0.040	±0.040	2.88	±0.015	0.400	±0.001	2.800	±0.020
2	Wheat fruit (N)	0.006	±0.160	0.520	±0.002	4.840	±0.002	0.520	±0.030
3	Wheat root (N)	1.309	±0.400	28.80	±0.007	5.400	±0.019	3.680	±0.010
4	Wheat stem (F)	0.920	±0.500	1.440	±0.002	0.720	±0.024	1.680	±0.030
5	Wheat fruit (F)	0.428	±0.077	0.120	±0.002	3.600	±0.034	1.920	±0.003
6	Oat fruit (F)	0.300	±0.007	2.692	±0.021	2.840	±0.080	0.760	±0.260
7	Oat root (F)	0.652	±0.007	70.12	±0.001	0.263	±0.030	3.320	±0.005
8	Oat fruit (F)	0.268	±0.002	15.00	±0.014	1.240	±0.089	2.440	±0.004
9	Leaves (jasmine)	0.292	±0.003	8.720	±0.003	5.960	±0.001	3.920	±0.090
10	Stem (jasmine)	0.140	±0.005	7.280	±0.001	3.872	±0.050	4.001	±0.005
Permissible Level (WHO)		1.30 mg/Kg		10.00 mg/Kg		5.00 mg/Kg		2.00 mg/Kg	

N: Near to water entrance; F: Far from water entrance

Table-3 The concentration profile of Cr, Ni, Zn and Pb in soil samples

S. No	Sample ID	Cr mg/Kg	SD	Ni mg/Kg	SD	Zn mg/Kg	SD	Pb mg/Kg	SD
1	Oat soil (*F)	0.0944	±0.005	5.22	±0.0030	178.6	±0.0012	15	±0.005
2	Wheat soil (F)	0.58	±0.003	20.34	±0.0034	97.8	±0.42	15.8	±0.009
Permissible Level		100 mg/Kg		75 mg/Kg		300 mg/Kg		85 mg/Kg	

N: Near to water entrance; F: Far from water entrance

3.3. The concentration profile Cr, Ni, Zn and Pb in soil samples

All these elements were investigated in two soil samples collected from two different fields and the results are given in table 3. The highest concentration of Cr and Ni was determined to be 20.34 mg/Kg and 0.58 mg/Kg in the soil samples collected from the site situated near the service deck and the site near a vehicles workshop respectively. The Cr contamination could be due to the fact that the canal which irrigates the field is passing through workshops where welding and metal works are in practice. The Ni contamination could be due to the household effluents produced as a result of washing ghee utensils. The lower concentration of Cr and Ni was determined as 0.094 mg/Kg and 5.22 mg/Kg in the soil samples collected from the site nearby the vehicle workshop and service deck respectively. The probable sources of Cr and Ni could be the workshops and household effluents that are drained by the canal water into the crop's fields. The concentration of Zn was found to be highest (178.60 mg/Kg) in the soil sample collected from the oat field situated near the vehicle work shop. The lower concentration of Zn was determined as 97.80 mg/Kg in the sample collected from wheat soil situated near vehicle work shop. The highest concentration of Pb (15.80 mg/Kg) was found in the soil sample collected from wheat field. The reason could be its relatively small distance from the lead sources i.e. oils and engines exhausts. The concentration of Pb determined in the sample collected from oat field (100 meters far) was 0.048 mg/Kg which is below the permissible level. The reason for the lower concentration of Pb in this sample could be its large distance from the Lead sources and common use of CNG in the LTVs instead of the leaded gasoline or diesel.

4. CONCLUSION

The present study shows that the level of Cr, Ni, Zn and Pb is higher in some of the investigated samples collected from various sites. The highest level of Cr was found to be 9.272 mg/Kg in the wheat root sample collected from the proximity of a service deck. The major reason of high concentration of Cr in the investigated sample could be the irrigation of this field with a canal which passes through the welding and metals workshops. Thus water of this canal could be contaminated due to the metal works in proximity of the canal. Similarly the highest concentrations of Ni and Zn were found to be 1.753 mg/Kg and 48.8 mg/Kg in the plant and soil samples respectively collected from the oat field.

The highest level of Pb (4.00 mg/kg) was determined in the jasmine stem which is above the permissible level. The principal cause of the higher Pb level could be the extensive use of leaded batteries, leaded gasoline and other lead pigments as a

commodity of urbanization.

The results show that the levels of certain heavy metals are exceeding their permissible limits in some of the investigated samples while in other cases their levels are so critical that they are touching their ceiling limits. Thus it can be concluded that both the fauna and flora of the explored regions are at risk due to their exposure towards the potential toxicity of these toxic metals. The study suggests that precautionary measures should be taken in order to control and avoid the toxicological effects of these metals on the plants, animals and mankind of the area. The contaminated household wastes, workshops and factories effluents should not be directly delivered into rivers via canals but they must be treated prior to discharge and the solid wastes must be recycled and managed or dumped into the soil in a recommended way. Thus the level of these toxic heavy metals must be monitored and controlled in the environment, crops, vegetables and other food stuffs in order to prevent their hazardous effects on animals and human beings.

REFERENCES

Abechi, E.S., Okunola, O.J, Zubairu, S.M.J, Usman, A.A. & Apene, E., 2010. *Evaluation of heavy metals in road side and major streets, Nigeria*. Environmental Chemistry and Ecotoxicology, 2, 98-102.

Ambade, B. & Litrupa., 2012. *Evaluation of heavy metal in contamination in road dust fallout of billai city*. Advanced Engineering Research and Studies, 1, 81-83.

Birsan, E. & Luca, C., 2010. *Specification of heavy metals in surface water polluted by anthropogenic activities*. Scientific Study and Research 11, 439 – 448.

Christiana, M.A.O. & Samuel, K., 2013. *Investigation of heavy metal levels in roadside agricultural soil and plant samples in Adogo, Nigeria*. Academia Journal of Environmental Sciences, 1, 031-035.

Cunningham, W.P. & Saigo, B.W., 1997. *Environmental Science a Global Concern*.4th Edn. WMC Brown Publisher, New York, pp 389.

Demirezen, D. & Uruç, K., 2006. *Comparative study of trace elements in certain fish, meat and meat products*. Meat Sciences, 74, 255-260.

Flora, S.J.S., Mittal, M. & Mehta, A., 2008. *Heavy metal induced oxidative stress & its possible reversal bychelation therapy*. Indian Journal of Medicinal Research, 128, 501-523.

Ikenaka, Y., Nakayama, S., Muzandu, K.& Choongo, K., 2010. *Heavy metal contamination of soil and sediment in Zambia*. African Journal of Environmental Science and Technology, 4, 729-739.

Imtiazuddin, S.M.& Mumtaz, M., 2013. *Toxicity study of Heavy metals textile pollutants in wastewater effluent on the fishes of Karachi harbour area*. Research WebPub, 1, 16-19.

Janet, C.K., Carl, L.K., James, A.O., Moshes, S.L. & Febiger., 1994. *Modern nutrition in Health and Disease*, 8th Edn. pp 227-228.

Lambert, M., Leven, B.A. & Green, R.M., 2010. *New Methods of Cleaning up Heavy Metal in Soils and Water Innovative solutions to an environmental problem*. Environmental Science and Technology Briefs for Citizens http://www.engg.ksu.edu/HSRC/Tosc/metals

Leung, C.M. & Jiao, J.J., 2006. *Heavy metal and trace element distributions in Ground water in natural slopes and highly urbanized spaces in Mid-Levels area, Hong Kong*. Water Research, 40, 753-767.

Mohod, C.V. & Dhote, J., 2013. *Review of heavy metal in drinking water and there effect on human health*. International Journal of Innovative Research in Science, Engineering and Technology 2: 2992-2996

Mubiana, V.K., Qadah, D., Meys, J. & Blust, R., 2005. *Temporal and spatial trends in heavy metal concentrations in the marine mussel Mytilus edulis from the Western Scheldt estuary, Netherlands*. Hydrobiologia, 540: 169-180.

Parth, V., Murthy, N.N. & Saxena, P.R., 2011. *Assessment of heavy metal contamination in soil Around hazardous waste disposal sites Hyderabad city (India): natural and anthropogenic implications*. Journal of Environmental Research and Management, 2, 027-034.

Rizwan, R., Singh, G. & Manish, J.K., 2010. *Application of Heavy Metal Pollution Index for Ground Water Quality Assessment in Angul District of Orissa, India*. Research in chemistry and Environment, 7, 785-792.

Sabir, S.M., Khan, S.W. & Hayat., 2003. *Effect of environmental pollution on quality of meat in district Bagh, Azad Kashmir*. Pakistan Journal of Nutrition, 2, 98-101.

Sharma, V., Sachdeva, M.V., Sakhuja, N. & Arora, D., 2011. *Impact of heavy metals (Chromium and Nickel) on the health of residents of Jagadhri city due to intake of contaminated underground water*. Archives of Applied Science Research, 3, 207-212.

Szyczewski, P., Siepak, J. & Niedzielski, P., 2009. *Heavy Metals in Poland Polish*. Journal of Environment Study 18: 60-63.

Wei, B. & Yang, L., 2010. *A review of heavy metal contaminations in urban soils and urban road dusts*. Microchemical Journal, 94, 99–107.