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Study on the Concentration of Trace and Heavy Elements in Milk, Maize and Water Samples from Various Regions of Kotli Azad Jammu and Kashmir

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ABSTRACT: Long term exposure to heavy metals in eating material like food and feed can be a severe risk and causes toxic effects on human beings. Therefore we should monitor the number of heavy metals regularly after a regular interval. Actually I had to find the concentration of heavy and trace elements in milk of various animals also find the factors which leads to higher concentrations. Also find out the variations of heavy metals regarding regional differences. I had studied few factors which are responsible for higher concentrations. In light of the above statement, we find the concentration of heavy metals (Pb, Cd) and trace elements like Cu, Cr, Fe, and Mn in maize, water and milk of different animals from different areas and localities. The researcher took the milk from other animals like Cow, Goat, and Buffalo. There were three study regions selected for sample analysis. Tata Pani, Kotli city and Sehnsa. The quantity and concentration (0.5 mg/kg) of milk was found high from set limit of the world health organization. The highest mean quantity or concentration of iron (2.900±0.082 mg/kg) was found or detected in cow milk. The lowest quantity or concentration (0.730±0.041) was found in milk of goat. The buffalo milk contains highest concentrations of lead and was higher from set limit of WHO. The concentration of lead also found higher in goat milk of different regions. The range of lead in buffalo and goat milk was 0.772±1.755 mg/kg. While the concentration of all other elements were found within limit of WHO. In water sample the concentration of iron was found higher from set limit while all other elements like Mn, Ni, Cu were found within set limit of world health organization. The allowable set limit of iron is 1.0 mg/kg but found values were higher in following ranges: 1.534±0.051, 1.409±0.055, 1.152±0.089. The quantity of lead higher from set limit in two regions, Kotli city and Sehnsa while lower in one region, Tata Pani. The values were in Kotli region: 0.265±0.279 mg/kg and quantity found in Sehnsa were: 0.112±0.198 mg/kg. While allowable set limit of lead (Pb) concentration is 0.005 mg/kg and world health organization limit for Cd is 0.01 mg/kg. While selected elements were found within limit in maize sample of all three regions. All assessment were made by using an instrument called Atomic absorption spectrometer Parkin Elmer 400.

Keywords: Atomic absorption spectrometer, Heavy metals, milk, maize, water.

Abbreviations: AAS, atomic absorption spectrometer; SD, standard deviation; BDL, below detection limit,

I. INTRODUCTION

Heavy metals and trace elements having specific properties. Heavy metals have specific ranges, density and standard values. Metals with a density greater than five and atomic values range from 63.54 to 200.59 and have gravity more than four usually air pollutant contains lead and cadmium [1]. Both natural and artificial sources are responsible for air pollutions. The important and essential elements are when exceeding to certain limits because serious problems like heavy metals lead and cadmium. Industries cause the main anthropogenic sources, metallurgical operations and many others [13].

Whenever these elements are present exceed to certain limit than causes serious health issue. These are usually called contaminants. Milk is very important component of diet which is necessary for good health. Milk contains more than one constitutes like proteins, carbohydrates, minerals, lipids and vitamins. The quality of milk depends upon the health of respective animals. The inorganic part present in milk play crucial role for the human health. When its concentrations exceeds to certain limit or decrease to certain limit it hurt in both case. When animals grazing fodders, the heavy metals present in grass enter into animals' body and human obtain through milk [4]. Whenever children and infants consume milk than it cause serious health problems. Therefore, monitoring these heavy and trace elements in milk and dairy products is essential [13]. World health organization set a permissible limit of heavy metals in milk and others food materials. When these concentration disrupt from certain limit cause serious health effects. Trace elements are classified into two categories essential and non-essential elements. Iron, copper and zinc are essential elements, while cadmium and mercury are included in non-essential elements. Non-essential elements are toxic and causes different diseases like kidney failure, skeletal system failure and cardiovascular failure [13]. Due to fast growing papulations and industrializations, the human suffering health issue or problem from last decade. The quality of

environment is reduced by human activity which is directly related to human health. The industries, agriculture activities and mineral process added the contaminants in the environment and causes serious health problems. Mostly urbans areas are effected and mostly people are living in populated areas for taking benefits from facilities. These activities not generating only the environment but also soil and water [8].
Developing countries usually don't take perceptive measurements against the use of natural resources. The death rate is 4-8% annually. The metals, chromium, cadmium, arsenic have their toxic effects and play a significant role [8]. These elements are found in our environment and act as major part of our earth crust. These particles are present in our environment in different forms, like as a suspended particle, gases and as aerosol pollutant likes oxides of Sulphur and oxides of nitrogen disturb the balance of gases system in our environment. These are too toxic and has a harmful effect until 1940 to 1950 century. The two continent America and Europe were rained by these toxic materials. Many developing countries uses the different standard to protect the human health from these pollutants. Two others regions where these toxic material were found, but these were too much away from human activity [10]. The elements lead and cadmium are most concerned elements because these elements are toxic and have harmful effect on plants, animals and environment. Even at low quantity these metals are also toxic. Metals are usually found in positive form and bind with negative ions and form complex chelates. Due to non-biodegradable these elements are remain with soil and water long time [1]. These elements when stuck in soil than also transfer into animals. These heavy metals also effect the human metabolic and enzymatic activity. When the concentrations of these heavy metals exceed to certain limit than cause a serious health issue. When we use this waste water, the quantity of these metals which are present in soil are transferred into milk, fodder and water samples in different areas.

II. MATERIALS AND METHODS

A. Study regions
For sample collection three area were selected from kotli district. This investigation zone lies in the middle longitude 73°6′ to 74°7′ E and scope 33°40 N with height start from 450 to 900 ranges. It situated by Rawalpindi from western side and occupied Kashmir on eastern side, poonch district is from northern side and Mirpur is present on southern side. District kotli have five tehsel viz. Kotli, charhoi, sehnsa and nikyal. The sample location map is shown in following fig. 1.
Sample of milk, plastic bottles, refrigerator, distilled water, nitric acid, hydrogen peroxide, hot plate, centrifuge, per chloric acid and glassware. Atomic absorption spectrometer was used to detect all the heavy and trace elements.

B. Sampling of milk, maize and water samples
Different samples were collected from selected regions. There were three selected regions, Tata Pani, Sehnsa and kotli city. All sample of milk were taken in plastic bottles according to international standards. Water samples were also collected in plastic bottles.

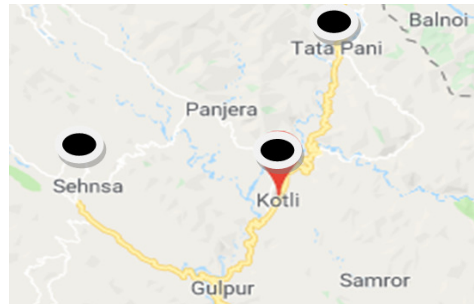

Fig. 1. Dot on map showing sample collecting area.

100 ml of conical flask were taken with fifty ml of water. By using 10% nitric acid and distilled water all glassware were washed.

C. Analysis of water, maize and milk samples
Digestion of sample was performed by using 1:3 ratio of hydrogen peroxide and nitric acid respectively. This technique was specifically performed for milk sample. The sample were kept on hot plate until its volume reduce to 2 ml. after reduction of volume 20 ml distilled water was added to make total of 25 ml solution. The selected metals were detected by using the AAS [1]. Heavy metals and trace elements were Cu, Ni, Cr, Pb, Cd, Fe and Mn. The maize sample was also digested in order to kill the organic content by using the 1% HCl. After that sample of maize was washed and dry at oven at 60-70°C. The digestion of sample was taken place by using mixture of nitric acid and per chloric acid.
In the same way water sample was also digested by using the acid. 50 ml water was taken in flask, added the 7ml nitric acid and 3 ml hydrogen peroxide. In this way total 60 ml solution was made, this kept on hot plate until its volume reduce to 15 ml, the temperature of hot plate was between 80 to 100°C. After that 10 ml distilled water was added into water sample, the total solution become 25 ml. at the end analysis of different metals was performed by using the atomic absorption spectrometer [4].

III. RESULTS AND DISCUSSION

This section may each be divided by subheadings or may further divided into next heads as shown below.

A. Concentration of Trace Elements and Heavy Metals in Milk
The values of trace elements like manganese, nickel, iron and copper were reported in Table 1. The concentration of iron was highest in Tata pani (1.150 mg/kg) in milk of goat and highest means values of nickel (0.118 mg/kg) was found in milk of goat at Tata pani region, while least quantity of iron (0.975 mg/kg) and nickel (0.032 mg/kg) was estimated in cow's milk at Tata pani area. The decreasing order is: Cow < Buffalo < Goat. Goat and buffalo have greater value of iron concentration, which are more than permissible set limit. The permissible set limit is: (0.5 mg/kg). While the concentration of iron is less than set limit. The concentration of nickel was found below the certain limit from set limit. The allowable value of nickel is: (0.43 mg/kg) [1]. Goat milk contains lowest concentration of manganese and copper, the values are 0.062 mg/kg and 0.031 mg/kg respectively. While buffalo milk contain highest mean concentrations of manganese and copper,

the values are ranges from 0.0068 mg/kg and 0.049 mg/kg respectively. The decreasing order of concentrations are as follow: Goat < Cow < Buffalo in Tata pani region. The second region kotli: Cow milk contains highest concentration of iron and copper, values 2.900 mg/kg and 0.062 mg/kg respectively. Buffalo milk contains lowest concentration of iron and copper, 0.875 mg/kg and 0.005 mg/kg respectively. The decreasing order is: Buffalo < Goat < Cow. In second region, the concentration of metals were found below the certain limit. The WHO set limit is: 0.5 mg/kg [1]. Buffalo contains lowest (0.088 mg/kg) nickel concentration and goat contain highest (0.022 mg/kg) mean concentrations. The decreasing order of metals concentration is: Buffalo < Cow < Goat. All values were found within certain limit of world health organization. Buffalo contain highest (0.066 mg/kg) mean concentration of manganese and cow milk contains lowest (0.045 mg/kg) mean concentration of manganese. The decreasing order is: Cow < Goat < Buffalo. The permissible set limit of manganese concentrations is: 55.5 mg/kg [1]. In third selected region the highest quantity or concentration of iron was found in cow milk, which was 0.938 mg/kg while goat's milk contains lowest amount of iron concentrations, which was 0.710 mg/kg. The decreasing order of metals concentration with respect to animals are as: Goat < Buffalo < Cow. Buffalo milk contains greater quantity of nickel, range from 0.103 mg/kg while lowest (0.051 mg/kg) amount was found in goat milk. The decreasing order of nickel metal concentration with respect to animals are as: Goat < Cow < Buffalo. The concentration of all metals were found within the permissible set limit of world health organization [18]. Cow milk contains highest mean concentration (0.088 mg/kg) of manganese while goat buffalo contain lowest or least (0.030 mg/kg) amount of manganese concentrations. The decreasing order as: Buffalo < Goat < Cow. Buffalo milk contains greater amount of copper while cow milk contains lowest amount of copper. The values are 0.030 and 0.007 mg/kg respectively. The decreasing with respect to animals are as: cow < goat < buffalo. All animals contains concentration of copper within the permissible set limit of world health organization. The allowable limit of copper is 24.2 mg/kg [1]. While all animals contains lower concentration of chromium from set limit of world health organization. All the values of metals are shown in Table 1. From all three selected region, Sehnsa contain higher amount of lead. The animal was buffalo. The value of lead was 0.772 mg/kg. While lowest quantity of metals were goat milk of other selected region, Tata pani. The values are as: 0.042 mg/kg. Cow milk of all three selected regions contains lower amount of lead concentration from set limit. The decreasing order of lead concentration from all selected regions as: Goat < Buffalo. Goat and buffalo contains higher amount of metals concentration from permissible set limit. The allowable set limit is: 0.02 mg/kg. Cow milk contains lowest amount of cadmium concentration while goat milk contains highest amount of cadmium concentrations (0.025 mg/kg) from Tata pani region. The decreasing order of cadmium concentration is as: Cow < Buffalo < Goat. From kotli region buffalo contains highest amount of cadmium concentration (0.022 mg/kg) while cow milk contains lower amount of cadmium concentrations (0.004 mg/kg). The decreasing order as: Cow < Goat < Buffalo. From third selected region highest amount was found in buffalo milk and lowest was found in cow milk. The decreasing order as: Cow < Goat < Buffalo. All three selected regions contains lower amount of cadmium values, which are below from allowable set limit of world health organizations. The allowable range as: 0.58 mg/kg [1]. All metals which were selected for assessment, found variations from permissible set limit of WHO as in advance paper [15].

Table 1: Heavy and trace elements from all three regions of selected three animals.

Elements	Tata Pani			Kotli city			Sehnsa		
	Cow	Goat	Buffalo	Cow	Goat	Buffalo	Cow	Goat	Buffalo
Fe	0.973±0.027	1.153±0.065	1.095±0.0045	2.933±0.085	1.078±0.059	0.870±0.032	0.939±0.111	0.711±0.043	0.832±0.900
Mn	0.065±0.014	0.036±0.005	0.0067±0.029	0.047±0.016	0.067±0.007	0.065±0.005	0.087±0.023	0.066±0.014	0.032±0.005
Cu	0.046±0.037	0.033±0.009	0.050±0.006	0.063±0.085	0.035±0.006	0.004±0.007	0.006±0.007	0.020±0.005	0.0032±0.011
Ni	0.035±0.039	0.116±0.065	0.033±0.027	0.067±0.022	0.087±0.029	0.023±0.011	0.082±0.060	0.052±0.082	0.105±0.065
Pb	BDL	0.043±0.175	0.102±0.087	BDL	0.139±0.296	0.165±0.168	BDL	0.076±0.105	0.774±1.758
Cd	0.003±0.004	0.0.26±0.003	0.007±0.007	0.004±0.005	0.016±0.009	0.023±0.009	0.021±0.007	0.023±0.007	0.031±0.006

B. Concentration of Heavy and Trace Elements in Water

The concentration of heavy and trace elements are all shown in Table 2. The decreasing order of iron concentration are shown with respect to regions or selected areas. The order as: Sehnsa < Kotli city < Tata pani. The allowable limit of iron concentration is as: (1.0 mg/kg). Sehnsa region has higher manganese quantity, the second one is kotli city and Tata pani has least quantity of manganese concentration. The decreasing order of manganese concentration as: Kotli city < Tata pani < Sehnsa region. The allowable quantity of manganese concentration is as: 0.5 mg/kg. All three regions, kotli, Sehnsa and Tata pani have lower amount than set limit of world health organization. The concentration or quantity of copper was found higher in first region, Tata pani, while lower amount was found in Sehnsa and kotli city regions. All three selected regions contains lower amount or quantity from set limit of world health organizations. The permissible set limit is as: 0.05 mg/kg.

The allowable limit of nickel is as: 0.2 mg/kg. The decreasing order of metals concentration is as: Tata pani < Kotli city < Sehnsa region. All three regions contains nickel concentration within set limit of world health organizations [19]. The concentration of lead was found higher in kotli and Sehnsa regions. Both regions have higher values from set limit of world health organizations. The allowable limit of lead concentration is as: 0.005 mg/kg [10]. The decreasing order of lead concentration with respect to regions are as: Tata pani < Kotli city < Sehnsa. The third region Tata pani has lower amount of lead concentration from set limit of world health organizations. The second heavy metal cadmium was estimated in water of all three regions. Sehnsa region has higher amount of cadmium than Tata pani and Kotli regions. The allowable set limit of cadmium is as: 0.01 mg/kg [7]. The decreasing order of cadmium concentration is as: Kotli city < Tata pani < Sehnsa. Heavy and trace elements were also find in the same manner as I performed in my researched [14]. Table 2 shows.

Table 2: Heavy and trace elements in water of three selected regions.

Elements	Tata pani	Kotli city	Sehnsa region
Fe	1.535±0.006	1.410±0.054	1.154±0.088
Mn	0.053±0.007	0.024±0.038	0.092±0.003
Cu	0.003±0.006	0.007±0.004	0.003±0.005
Ni	0.0027±0.08	0.039±0.043	0.098±0.065
Pb	0.034±0.068	0.0266±0.0280	0.114±0.195
Cd	0.015 ±0.006	0.004±0.003	0.025±0.06

Mean± standard deviation

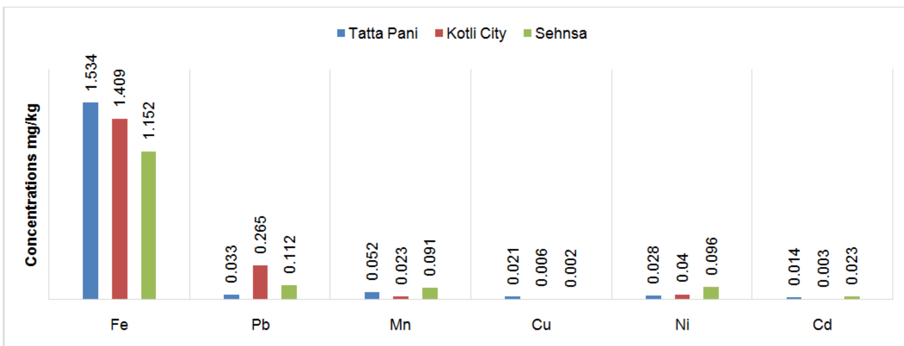

Fig.1. Concentration of all selected metals from three regions.

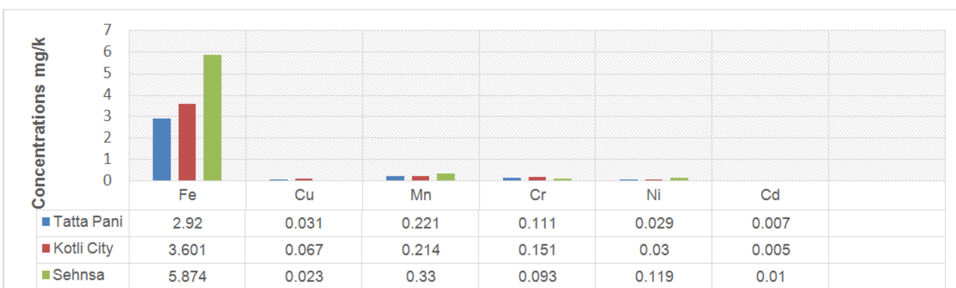

Fig. 2. The concentrations of all selected metals in maize samples.

C. Heavy metals concentration in maize sample

The concentration of iron in maize sample was found higher in Tata pani region where as lower amount was found in third and second regions, Kotli and Sehnsa. The decreasing order of iron concentration in all three selected regions are as: 1.152 < 1.405 < 1.534. From three selected region Tata pani has greater amount of iron while Sehnsa region has lower amount of iron concentrations. The permissible limit of iron concentration according to world health organization is as:8-15 mg/kg. All three regions have lower amount of cadmium from set limit of WHO. The values are from three selected regions are as: 0.010, 0.005 and 0.007 mg/kg in Sehnsa, Kotli city and Tata pani regions respectively. The permissible limit of cadmium (Cd) is as 0.003 mg/kg [8]. The decreasing order of cadmium metal concentration is as: Kotli city < Tata pani region < Sehnsa region. The permissible set limit of chromium is as: 0.1-0.5 mg/kg. The decreasing order of chromium and copper in maize samples are as: Sehnsa < Tata pani < Kotli city regions. The allowable limit of nickel quantity is as: 0.5 mg/kg [9]. The higher quantity of nickel was found in Sehnsa region (0.119 mg/kg). The lower concentrations of nickel was found Tata pani and kotli city regions. The decreasing order of nickel concentration in three selected regions are as: Tata pani < Kotli city < Sehnsa regions. The higher amount of manganese concentration was found in third region, Sehnsa, 0.330 mg/kg, second region which has higher amount of manganese quantity is Tata pani areas and the third region is kotli where manganese quantity is as: 0.214 mg/kg. The permissible set limit of manganese concentration is as: 20-150 mg/kg [5]. Third regions has greater amount of manganese concentration, first has less and second has less than others. Variations of heavy and trace elements are same as studied by Zheng *et.al.* [17]. All values are shown in Table 3.

D. Comparison of trace and heavy metals in maize and water samples

When we compare the concentration of iron in water, we observed that the highest quantity of iron was found in Tata pani region and lowest in sehnsa region. In the same way highest concentration of lead was observed kotli city region and lowest was found in Tata pani region. Menganese and nickel was found higher in sehnsa region. Minute fluactions was found in others metals in all three regions. All the values are shown in Fig. 3. The comparions of heavy and trace elements are shown in Fig. 4. The maize sample from sehnsa region contains higher amounts of iron and lower amount was observed in Tata pani region.

In whole others all values were found in very minute quantities. All values are shown in graph or Fig. 4.

E. Comparison of heavy and trace elements from milk of selected regions

In kotli and Sehnsa region, the highest or higher quantity of manganese, copper and iron quantity was observed particularly in cow milk. Goat milk from Tata pani regions contains higher amounts of nickel. Buffalo milk contains higher amounts or concentration of cadmium and lead from Sehnsa region. From third region, buffalo milk contains lowest amounts of manganese concentrations and goat milk contains lowest amount of iron. From kotli city region, the lowest amount of nickel was found in buffalo milk, while from Tata pani region, the lowest quantity of lead was observed in cow milk. Cow milk from kotli city region contains lowest amount of cadmium. All values are shown in Fig. 3 to 8.

Table 3: Heavy and trace elements in maize samples of given regions (mg/kg).

Elements	Tata pani	Kotli city	Sehnsa region
Fe	2.94±0.047	3.605±0.045	5.876±0.075
Mn	0.223±0.066	0.215±0.078	0.035±0.016
Cu	0.032±0.063	0.068±0.029	0.025±0.006
Ni	0.028±0.064	0.032±0.063	0.117±0.057
Pb	BDL	BDL	BDL
Cd	0.0088±0.004	0.004±0.0003	0.011±0.007

Mean± standard deviation, BDL; Below detection limit

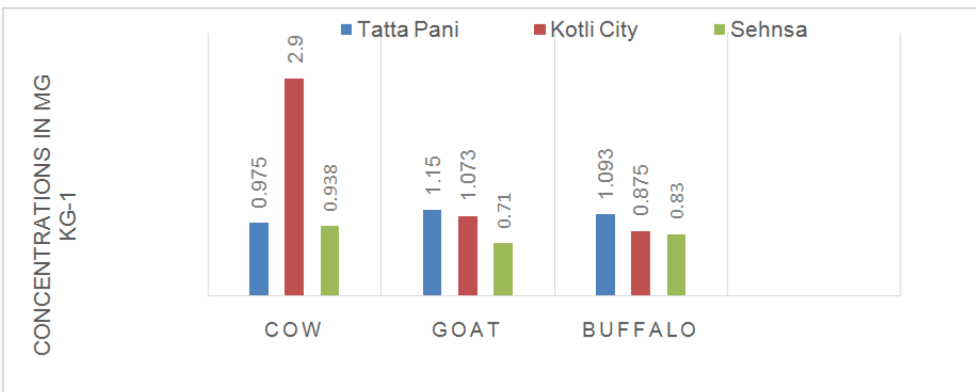

Fig. 3. Quantity or concentration of Fe in milk of selected regions.

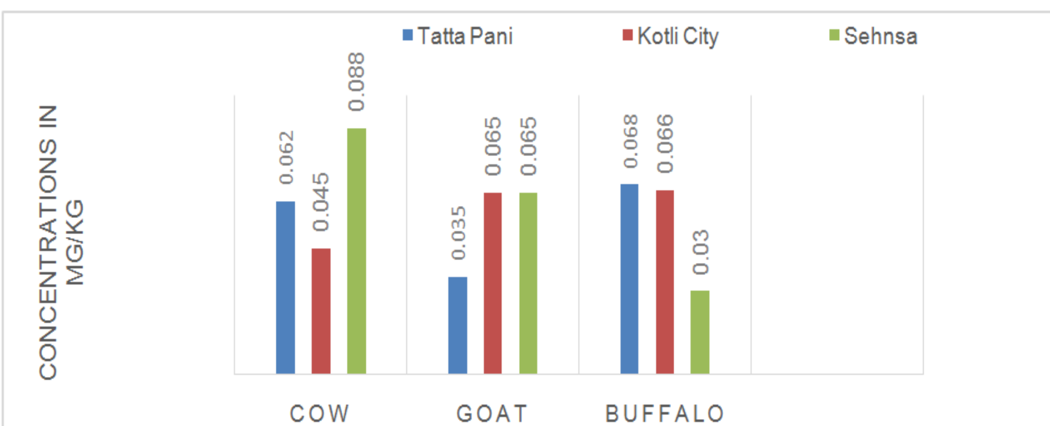

Fig. 4. Quantity of Mn in milk of all three animals.

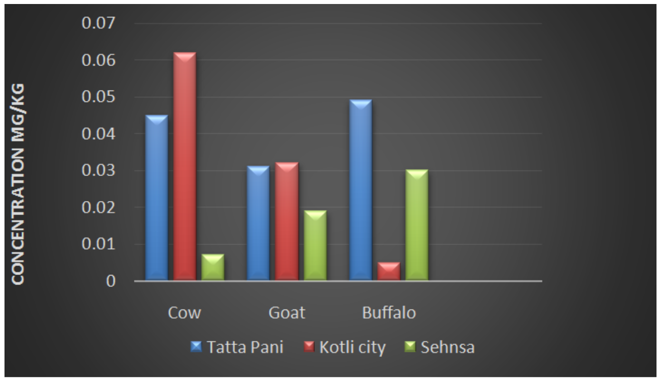

Fig. 5. Quantity of Copper in milk of three animals.

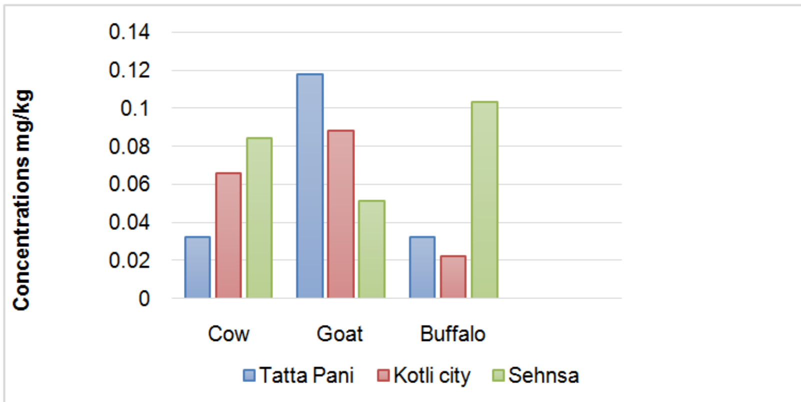

Fig. 6. Quantity of nickel in milk of animals.

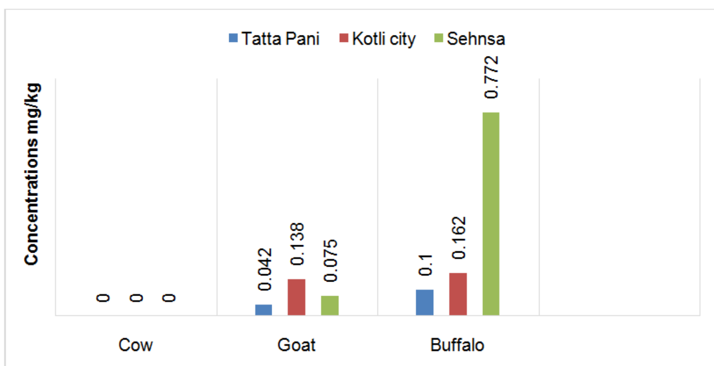

Fig. 7. Concentration of lead in milk of selected regions.

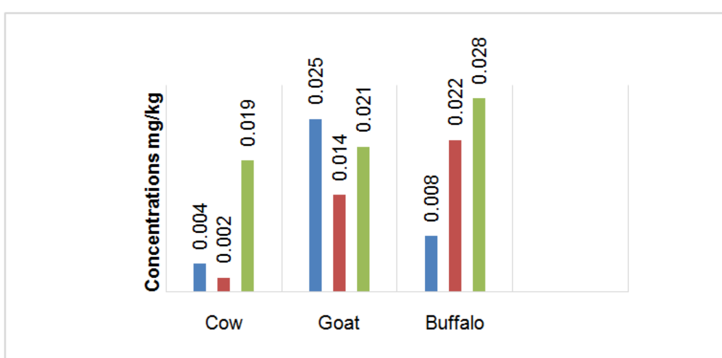

Fig. 8. Quantity of cadmium in milk of all three selected regions.

IV. CONCLUSION

From three selected regions, heavy and trace elements were observed. The selected metals were Pb, Cd, Zn, Cu, Mn, Fe and Cr. In all three regions some elements were found within set limit while some was found higher from set limits of world health organizations. There was found variations in metals from selected regions. From all three selected regions iron was found higher from set limit of world health organizations (0.5 mg/kg). In sehnsa region the lowest amount of iron was observed (0.710 mg/kg). The highest amount of iron was observed in kotli regions (2.9 mg/kg). Milk from some animals contains higher amount of lead (Pb). From three selected regions cow milk contain amount of lead which was lower from set limit of world health organizations. Goat and buffalo milk contains higher amount from set limit of three selected regions. Sehnsa region contain highest quantity of lead (0.772 mg/kg) in buffalo milk and Tata region contains lowest amount. Other metals like Cd, Mn, Ni and Cu were found below the set limit of world health organization from all three selected regions.

From water sample of three selected regions, iron concentration was found higher from set limit of world health organizations (1.0 mg/kg). The lowest amount was found in Sehnsa region and highest was determined in Tata pani regions. All maize samples contains lower amount of selected metals from set limit of world health organizations

This should clearly explain the main conclusions of the work highlighting its importance and relevance.

V. FUTURE SCOPE

Need government intentions regarding the use of water in agriculture and other domestic purposes. Government should declare unhygienic for human consumptions those products from which metals were found higher from permissible limit. Government and private sectors should cooperate each other's to tackle the problems

It is mandatory.

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