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DETERMINATION OF CONCENTRATIONS OF SOME HEAVY METALS IN COW FRESH MILK OBTAINED FROM GUJBA LOCAL GOVERNMENT AREA, YOBE STATE

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Abstract

Milk is a very important component of human diet. The presence of toxic elements in milk may create significant health problems. In this study, some heavy metals levels in fresh cow milk were determined. Fresh milk samples were collected from 20 open grazed areas around Gujba industrial area, Yobe State. Metals concentrations were determined using Epsilon 5, P Analytical Energy dispersive X-ray Florescence Technique (ED-XRF) and the results were analyzed by using Microsoft excel and SPSS (Statistical Package for the Social Science) to evaluate mean, range and Pearson's correlation. The mean concentrations of the analyzed elements such as; Cd, Al, Fe, Cr, NI, Mn, Cu, Pb and Zn are as follows; 0.1369, 1.03645, 1.259, 0.9314, 1.8031, 0.3267, 0.4739, 0.3664 and 0.4384mg/l respectively, which shows a high contamination level of the milk products above the recommended standard values reported by WHO and GEM/FOOD. The concentrations of the heavy metals from fresh Cow milk in almost all areas of Gujba were found to be within the ranges of 0.008-0.295, 0.032-2.111, 0.742-1.841, 0.297-1.754, 0.05-4.357, 0.067-0.841, 0.158-0.772, 0.007-0.868 and 0.019-0.899 mg/l for Cd, Al, Fe, Cr, Ni, Mn, Cu, Pb and Zn respectively, these exceeds the WHO Permissible limits of 0.003, 0.50, 0.30, 0.50, 0.02, 0.2, 1.0, 0.001 and 0.001 for Cd, Al, Fe, Cr, Ni, Mn, Cu, Pb and Zn respectively. The possible implications of the results obtained to public health were briefly discussed. Very high contamination factor values were obtained resulting into high heavy metals pollution indices range from 2.39 to 18.29.This might be due to the mining activities. This study revealed that Fe had significantly (α = 0.05) positive correlation with most of the elements, i.e., Mn(r = 0.574, p <0.01), Ni(r = 0.723, p <0.01), Cu(r = 0.733, p <0.01), Zn(r = 0.869, p <0.01), Al(r = 0.768, p <0.01), Cd(r = 0.575, p <0.01), and Pb(r = 0.707, p <0.01) but no significant correlation with Cr was observed at a 95% confidence level. No significant correlation was between the followings of metals: Cr and Mn, Cr and Cu, Cr and Zn, Cr and Al, Cr and Pb. Therefore, it has been suggested that Cr was not correlated with other metals. However, rest of the metals has significantly positive correlation between each other in different milk samples analyzed, indicating a common source of these metals.

Keywords**:** Heavy Metals, Pollution index, Concentration, Milk, X-Ray Fluorescence and Gujba.

1.0 Introduction

The analysis of milk is important because milk is a significant pathway for toxic metal intake by humans and also a source of essential nutrients. Essential elements required by the human body include the four basic elements H, C, N and O; the quantity elements Na, Mg,K, Ca, P, S and Cl; and the essential trace elements Mn, Fe, Co, Ni, Cu, Zn, Mo, Se and I. Other trace elements include B, Ba, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Sb, Se, Sn, Sr, and Zn.The determination of trace

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element levels in food-stuffs, especially milk could play an important role in understanding a number of deficiency-related diseases[1].

The consumption of milk and milk-products has increased in recent years as they have become the main requirement of daily diet, especially for the vulnerable groups such as infants, school going children and old persons [2, 3].

In recent times, the amount of metals in cow milk is widely studied, particularly in industrialized and polluted areas of the developed and the developing countries of the world, since animals grazing freely on open fields are considered as bio-indicators of environmental pollution [3].Many reports indicate the presence of heavy metals in milk, and often it is needed to assess the levels of heavy metals in food generally [4, 5].

However, in Nigeria, and particularly in Gujba / Yobe the contamination of cow's fresh milk and milk products has not been seriously attended to so far. Few reports are available on this topic using different techniques such as AAS, Graphite Furnace Atomic Absorption Spectrometer (GFAAS) and Inductively-coupled plasma atomic emission spectrometry. The study of toxicity levels in milk and milk products and their relation with various symptoms have not been reportedly carried out in the region as well as using X-ray Florescence technique.

The measurement of the levels of metals in cow milk will depend not only in ascertaining risk to human health but also in the assessment of environmental quality. It is therefore necessary to determine the levels of contaminants in cow milk so that the warning signals, wherever required, can be given to the society. Even otherwise it has become very important to educate the society of the social evils of these contaminants. Many cases of environmental toxicities were recorded from Gujba area of Yobe State such as Hepatitis, infertility, kidney failure, Anemia, miscarriage, children born with cognitive deficiencies and acute struck which may be as a result of ingestions of some heavy metals due to human activities in the area.

The aim of this work is to determine the level of some heavy metals in cow fresh milk obtained from Gujba local Government area, Yobe State using X-ray Florescent Technique (XRF).

The results obtained will be compared with the limits set by Standard Organizations such as World Health Organization (WHO), Global Environmental monitoring system/Food contamination monitoring and Assessment programme [6].

This study will focus only on toxicity assessment of heavy metals such as Cr, Ni, Al, Cd, Pb, Mn, Cu, Zn and Fe in some fresh milk samples obtained from Gujba Local Government area.

2.0 STUDY AREA

Gujba is a local Government in Yobe State north eastern Nigeria, with headquarter in Buni-Yadi, it has an estimated population of about130, 088 people. The area of Gujba local Government is 3,239 km^2 and situated between 11^o 16'08"N and 11^o 55'49"E of the Greenwich meridian. It has two distinct climates, the dry season from November to April and a rainy season from June to Octoberwith an average rainfall of 810 mm.

Gujba local Government is a well-known mining ground of many mineral resources of economic importance for decades. The area has attracted many resource persons for Geographical excursion purposes, the area is highly Agrarian which encourages farming and rearing of Animals for domestic and economic purposes.

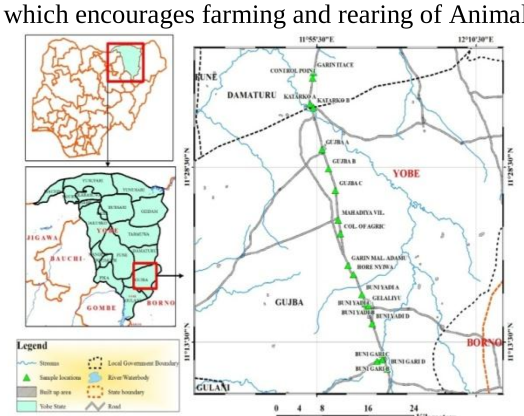

Figure 2.1: Map of Gujba L G A showing Study Sites and Sampling Points.

3.0 MATERIAL AND METHOD

3.1 Sample Collection

Random sampling was adopted and used for the collection of Milk samples from twenty selected areas of Gujba local Government. The sample sites were selected based on their proximity to market places and other activities of interest such as Mining, Grazing and industrial sites. The milk samples was collected from twenty 20 different Cows at Grazing sampling points, and were kept in a plastic containers and properly leveled. The containers that have the fresh milk samples enclosed were kept inside a Flask containing ice at a temperature of about 4℃. In all the twenty 20 selected study areas their geo-referencing points were noted using GPS hand held instrument.

3.2 Sample Preparation

100 ml of the each cow's fresh milk samples were centrifuged by cooling centrifuge machine maintaining the speed 400rpm for 15 minutes to remove fat from the sample. All fat freefresh milk samples, each with a particular identification number were first preserved in a coolers packed with ice blocks at temperature about 4℃ and transported immediately to Laboratory for analysis at Desert Research Monitoring and Control Centre (DRMCC) located at Yobe State University, Damaturu. Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer (Model: Epsilon 5, PANalytical, The Netherlands) was the analytical technique used to determine the concentration of elements in various milk samples.

3.3 Sample Analysis

1ml of each milk samples was pipetted into a pellet-like container of 25 mm diameter, a transparent to X-ray foil cover (Polypropylene with a thickness of 6μm) is used to cover the pellet-like cup with a pellet maker (Automatic Hydraulic Presses, model: 3889-4NEI). The sample pellets like cup were loaded into the X-ray excitation chamber for irradiation with the help of automatic sample changer system. A time-based program, controlled by a software package (PANalytical) provided with the systems was used to irradiate the real samples and the standard materials as well for the construction of the calibration curves for quantitative elemental analysis in the respective samples and afterwards the generated X-ray spectra of the materials were stored into the computer.

3.5 Data Analysis and Evaluation

The trend distribution of the elements can be assessed by calculating some pollution indices and various statistical analysis tools after determining the heavy metals in all the Milk samples collected from the study sites which give a direct quality of the Milk. The pollution indices and statistical analysis includes: Contamination factors, Metal pollution index, Daily intake of metals and Health risk index. While the statistical software SPSS (Statistical Package for Social Science) were used to give a descriptive interpretation on the mean, range and Pearson correlation.

3.5.1 The Correlation Analysis

Correlation is the measure of degree of relationship between two or more variables of interest without any influence of units. Correlation coefficient being a ratio of dimensionless number which normally the spectrum ranges between +1 to -1, it indicates a perfect direct relationship between the variables if the coefficient is +1, while for -1 the indication factor is otherwise. Between the two extremes +1 and -1 there are spectrums indicating the relationship degrees of two variables including zero which indicates lack of any linear relationship [7].

3.5.2 Contamination Factor (CF)

The term contamination factor refers to the degree of presence of strange substances apart from the original composition of the sample of interest (Milk). It can be obtained by taking the ratio of concentration of each metal in the Milk to that of the background (concentration in unpolluted milk). It can be determined based on the below equation 3.1[8].

$$CF = \frac{(C)Heavymetal}{(C)Background} \qquad (3.1)$$

Where, $(C)_{\text{heavy metal}}$ is the concentration of heavy metal in the sample and $(C)_{\text{Background}}$ is the background value for the same metal.

3.5.3 Metal Pollution Index (MPI)

Metal pollution index (MPI) index was calculated following [9], which is the geometrical mean of concentrations of all the metals in the corresponding milk samples. The MPI value of greater than 1 signifies that the sample is polluted, and that of less than 1 indicates that the sample only baseline pollutants level. It is represented by the following the equation 3.2 given below.

$$MPI = \sqrt[n]{CF1 \times CF2 \times CF3 \ldots, CFn} \quad (3.2)$$

Where, CF is the contamination factor, n is the number of heavy metals.

4.0 RESULTS AND DISCUSSION

4.1 Results

The sampling points along with the Geographical coordinates are shown in Table 4.1

Table 4.1: Sampling points with their geo-referencing coordinates.

S/N	LOCATIONS	CODES	LATITUDE	LONGITUDE	ALTITUDE
1	GARIN ITACE	GITC	11° 36’ 38.57”N	11° 55’ 12.98”E	339m
2	KATARKO A	KTR A	11° 33’ 55.44”N	11° 54’ 53.21”E	392m
3	KATARKO B	KTR B	11° 33’ 35.84”N	11° 55’ 11.42”E	390m
4	GUJBA A	GJB A	11° 30’ 1.45”N	11° 56’ 0.37”E	417.9m
5	GUJBA B	GJB B	11° 28’ 22.49”N	11° 56’ 38.06”E	423.7m
6	GUJBA C	GJB C	11° 26’ 29.93”N	11° 57’ 16.28”E	425m
7	MAHADIYA VIL.	MHDY	11° 23’ 58.55”N	11° 57’ 31.73”E	416.8m
8	COL. OF AGRIC	COAG	11° 22’ 48.08”N	11° 57’ 43.5”E	423.5m
9	GARIN ADAMU	GMAD	11° 20’ 6.16”N	11° 58’ 26.72”E	450m
10	HORE NYIWA	HRNW	11° 19’ 18.35”N	11° 58’ 57.52”E	438.8m
11	BUNI YADI A	BYD A	11° 17’ 35.67”N	11° 59’ 46.7”E	429.6m
12	BUNI YADI B	BYD B	11° 16’ 48.14”N	12° 0’ 4.89”E	432m
13	BUNI YADI C	BYD C	11° 16’ 15.17”N	12° 0’ 17.57”E	429.9m
14	BUNI YADI D	BYD D	11° 15’ 6.29”N	12° 0’ 43.75”E	444.4m
15	BUNI GARI A	BGR A	11° 12’ 28.6”N	12° 1’ 42.74”E	439.5m
16	BUNI GARI B	BGR B	11° 11’ 59.8”N	12° 1’ 40.6”E	451.9m
17	BUNI GARI C	BGR C	11° 11’ 51.65”N	12° 1’ 10.93”E	460.9m
18	BUNI GARI D	BGR D	11°11’ 12.7”N	12° 2’ 7.43”E	452.6m
19	GELALIYU	GLYU	11° 16’ 39.72”N	12° 0’ 24.29”E	439.8m
20	CONTROL POINT	CNTL	11° 36’ 8.92”N	11° 55’ 7.85”E	410.4m

The concentrations of Cd, Al, Fe, Cr, Ni, Mn, Cu, Pb, and Zn were determined in twenty (20) milk samples as shown in Table 4.2 below.

Table 4.2: Heavy metals Concentrations determined from different sample sites together with the control sites (mg/l).

		Element								
S/N	Locations	Cd	Al	Fe	Cr	Ni	Mn	Cu	Pb	Zn
1	GITC	0.086	1.97	1.774	0.436	1.974	0.233	0.55	0.117	0.243
2	KTR A	0.072	0.435	1.352	0.297	2.344	0.0675	0.311	0.528	0.039
3	KTR B	0.276	1.477	0.948	1.269	1.677	0.375	0.339	0.815	0.294
4	GJB A	0.097	0.7	0.882	1.045	2.522	0.0815	0.378	0.094	0.511
5	GJB B	0.116	1.214	1.075	1.338	2.555	0.3	0.294	0.032	0.743
6	GJB C	0.302	1.14	1.193	1.211	3.782	0.261	0.384	0.198	0.358
7	MHDY	0.147	0.922	0.892	0.742	4.357	0.552	0.475	0.658	0.284

8	COAG	0.143	2.111	0.742	0.589	3.137	0.187	0.294	0.721	0.228
9	GMAD	0.082	0.521	0.992	0.821	1.865	0.235	0.351	0.741	0.642
10	HRNW	0.036	1.521	1.072	0.871	0.354	0.254	0.273	0.073	0.744
11	BYD A	0.095	0.211	1.841	0.622	0.096	0.261	0.158	0.089	0.863
12	BYD B	0.075	1.243	1.492	0.494	0.079	0.313	0.753	0.069	0.822
13	BYD C	0.045	1.758	1.227	0.911	0.035	0.248	0.486	0.071	0.526
14	BYD D	0.063	1.282	1.0892	0.795	0.055	0.333	0.623	0.058	0.381
15	BGR A	0.155	0.032	1.552	1.754	0.945	0.198	0.772	0.495	0.899
16	BGR B	0.295	0.032	1.822	1.586	1.559	0.587	0.529	0.868	0.275
17	BGR C	0.198	0.912	1.593	1.257	6.322	0.765	0.691	0.762	0.421
18	BGR D	0.175	1.213	1.753	1.073	2.283	0.841	0.738	0.621	0.388
19	GLYU	0.273	1.435	1.079	0.833	0.07	0.225	0.598	0.311	0.089
20	CNTRL	0.008	0.6	0.827	0.683	0.05	0.217	0.482	0.007	0.019

4.2 Discussion

Concentration of Cadmium in all the milk samples areas is higher except Control site which shows 0.008mg/l, this is slightly higher than the WHO baseline standard of 0.003mg/l. Cadmium is a cumulative toxic agent with half-life of several years and their burden of the body increases with age. WHO put the permissible limit for cadmium in food at 0.003mg/l while the Egyptian standards put it at 0.05mg/l. The presence of cadmium above the established limits suggests that there are toxicological risks in the consumption of cow milk from Gujba area. Cadmium and solutions of its compounds are toxic, chronic exposure can cause irreversible damage to the lungs and eventually, death. Eating food or drinking water with high cadmium concentration irritates the stomach causing vomiting and diarrhea. It accumulates in the kidney and liver causing kidney dis-functioning and liver failure, in addition to being a carcinogenic agent [10].

Concentration of Aluminum in all the milk samples areas is higher including the Control site except Buni-Gari A and Buni-Gari B which both shows 0.032mg/l from, this is not too higher than the WHO baseline standard 0.50mg/l. Aluminum is involved in the activities of a small number of enzymes in the body. Excess dose is linked with Alzhermers, a brain disorder that destroys brain cells causing memory loss, problems with thinking and general behavior. It is also linked with a degenerative disorder of the central nervous system that impairs motor skills and speech disorder [11]. The levels of Aluminum in fresh cow milk from this study are quite high and a source of serious concern. The maximum contaminant level (MCL) for Aluminum is given as 0.5mg/l [11].

Iron concentration for all the milk samples from all areas is found to be much higher than the baseline limit set by WHO (0.30mg/l), and other Regulatory bodies. This might also be as a result of the mining activities in the areas. Liver, kidney and the cardiovascular system are the target organs for iron toxicity [12].

Chromium concentration for all the milk samples from all areas is found to be much higher than the baseline limit set by WHO (0.50mg/l) and other Regulatory bodies, except GITC, KTR A, and BYD A. It concentrations are higher in other areas apart from the ones mentioned; it might also as a result of the mining activities in the areas. Chromium is an important mineral the body must have to function properly. The body stores chromium in the blood and in the hair. It's responsible for stimulating the activities of insulin in the body and also help controls blood cholesterol levels. Long term exposure can cause kidney and liver damage as well as circulatory and nerve tissue problems [8].

Concentration of Nickel in all the milk samples areas is higher, than the WHO baseline standard of 0.02mg/l. Small amount of nickel is needed by the body to produce red blood cells. However, excess amount can become toxic. Long term exposure to nickel causes decrease body weight, skin Irritation, heart and liver damage [8].

Concentration of Manganese in all the milk sample areas is not too higher than the WHO baseline standard of 0.2mg/l. But areas of MHDY, BGR B, BGR C, and BGR D indicate a significant variation from WHO baseline as stated above. Manganese is an essential nutrient that is important for normal processes in the human body, though adverse effect have been reported at higher doses. Exposure to high concentration of manganese is associated with impaired neurological and neuromuscular control, mental and emotional disturbances (muscle stiffness, and lack of coordination). Exposure to very high doses results in impaired male fertility, birth defects, and impaired bone development [13].

Concentration of Copper in all the areas is below the WHO baseline standard of 1.0mg/l. Abnormal accumulation of copper in the tissue and blood causes Wilson disease. Most of the absorbed copper is stored in the liver and bone marrow. Acute exposure to copper causes vomiting, bloody diarrhea, hypertension, and cardiovascular collapse [14].

Higher concentration level of lead is found in all areas of this study to be above the recommended level stated by WHO of 0.001mg/l, it might be as a result of frequent mining and Agricultural activities in the areas respectively. Lead is one of the limited classes of element that can be described as purely toxic. Most other elements thought toxic at high concentration are actually required nutrient at lower levels. There is no exposure level below which lead appears to be safe. High level of lead is particularly of great concern especially due to the fact that milk and dairy products are consumed mostly by infants and children who are uniquely susceptible to the effect of lead. Lead absorption constitutes serious risk to public health. It induces reduced cognitive development and intellectual performance in children, increased blood pressure, and cardiovascular diseases in adult as well as liver and kidney dis-functioning [15, 16].

Higher concentration level of Zinc is found in almost all the areas except Control site, Gelaliyu and Katarko A, were the variations are not significant. The remaining areas where Zn concentration found to be significant, it might be as a result of frequent mining and Agricultural activities in the areas respectively. Chronic zinc exposure results in anemia, leucopenia, gastrointestinal diseases and diarrhea [17].

The contamination factor of this work was presented in Table 4.3 below, which shows high level of contamination for Zn, Pb, Ni and Cd for almost all the locations except Gelaliyu and the Control site (where presence of contaminants were not expected), the remaining heavy metals like Al, Fe, Cr, Mn and Cu shows slight-above level of contamination from the recommended baseline level of +1 in almost all the locations. The milk products from area of Buni-Gari show that the contamination level is higher than the other areas. This might be as a result of its closeness to the mining sites.

The background Concentrations (Conc. $_{background}$) of the individual heavy metals Cd, Al, Fe, Cr, Ni, Mn, Cu, Pb and Zn sets by regulatory bodies are 0.003, 0.50, 0.30, 0.50, 0.02, 0.2, 1.0, 0.001 and 0.001mg/l [6,10]. The background concentrations above are used to calculate the contamination factors of each of the elements from the twenty (20) areas.

The MPI value of greater than 1 signifies that the milk sample is polluted, and that of less than 1 indicates that the milk sample only has baseline pollutants. All the milk products from various locations in this study shows high level of heavy metal pollution index which might be due to the mining activities, except the Control site were mining activities are at zero level, the MPI for this study ranges from (2.39 to 18.29) as shown in Table 4.4. This increase in metal pollution index might be as a result of non-proper waste disposal and unplanned sanitation activities in the study area.

The Pearson's correlation matrices among the studied metals (Cr, Mn, Ni. Cu, Zn, As, Cd, Hg, Pb and Fe) in different milk samples were performed using SPSS 22 (IBM Corp., USA) software. This study revealed that Fe had significantly ($\alpha = 0.05$) positive correlation with most of the elements, i.e., Mn($r = 0.574$, $p < 0.01$), Ni($r = 0.723$, $p < 0.01$), Cu($r = 0.733$, $p < 0.01$), Zn($r = 0.869$, $p < 0.01$), Al($r = 0.768$, $p < 0.01$), Cd($r = 0.575$, $p < 0.01$), and Pb($r = 0.707$, $p < 0.01$) but no significant correlation with Cr was observed at a 95% confidence level from Table 4.5. Subsequently this study revealed that there was no significant correlation between Cr and Mn, between Cr and Cu, between Cr and Zn, between Cr and Al, between Cr and Pb (Table 4.5). Therefore, it has been suggested that Cr was not correlated with other metals. However, rest of the metals has significantly positive correlation between each other in different milk samples analyzed in this study, suggesting a common source of these metals.

Table 4.3: Contamination factor (CF) of heavy metals with respect to their sampling points.

S/N	Locations	Cd	Al	Fe	Cr	Ni	Mn	Cu	Pb	Zn
1	GITC	28	3	5.9	0.87	98.7	1.16	0.55	117	243
2	KTR A	23	3	4.5	0.59	117.2	0.34	0.311	528	39
3	KTR B	92	0.003	3.16	2.54	83.85	1.87	0.339	815	294
4	GJB A	32	2	2.94	2.09	126.1	4.07	0.378	94	511
5	GJB B	38	1	3.58	2.67	127.75	1.5	0.294	32	743
6	GJB C	100	2	3.97	2.42	189.1	1.31	0.384	198	358
7	MHDY	48	2	2.97	1.48	217.85	2.76	0.475	658	284
8	COAG	47	1	2.47	1.17	156.85	0.94	0.294	721	228
9	GMAD	27	4	3.31	1.64	93.25	1.17	0.351	741	642
10	HRNW	11	1	3.57	1.74	17.7	1.27	0.273	73	744
11	BYD A	31	3	6.14	1.24	4.8	1.31	0.158	89	863
12	BYD B	25	0.001	4.97	0.98	3.95	1.56	0.753	69	822
13	BYD C	15	2	4.09	1.82	1.75	1.24	0.486	71	526
14	BYD D	21	3	3.63	1.59	2.75	1.66	0.623	58	381
15	BGR A	51	5	5.17	3.51	47.25	0.99	0.772	495	899
16	BGR B	98	0.002	6.07	3.17	77.95	2.94	0.529	868	275
17	BGR C	66	0.001	5.31	2.51	316.1	3.83	0.691	762	421
18	BGR D	58	1	5.84	2.15	114.15	4.21	0.738	621	388
19	GLYU	91	2	3.59	1.66	3.5	1.13	0.598	311	89
20	CNTRL	2	2	2.75	1.36	2.5	1.1	0.482	7	19

Hint: CF >1 =The sample is polluted, CF ≤ 1 = Only natural pollutants present.

Table 4.4: Metal Pollution Index of the heavy metals with respect to their sampling points in this study.

S/N	Locations	Metal Pollution Index (MPI)
1	GITC	9.69
2	KTR A	7.10
3	KTR B	12.79
4	GJB A	11.52
5	GJB B	9.21
6	GJB C	13.25
7	MHDY	14.09
8	COAG	9.94
9	GMAD	12.97
10	HRNW	6.55
11	BYD A	7.22
12	BYD B	6.81
13	BYD C	5.89
14	BYD D	6.55
15	BGR A	16.09
16	BGR B	15.55
17	BGR C	18.29
18	BGR D	15.78
19	GLYU	7.44
20	CNTRL	2.39

Hint: MPI >1 = the area is polluted, MPI ≤ 1 = only natural pollutants present.

Table 4.5: The Person's correlation matrices among the studied metals (Cr, Mn, Ni Cu, Zn, Al, Cd, Pb and Fe) in the different milk samples

	Cr	Mn	Ni	Cu	Zn	Al	Cd	Pb	Fe
Cr	1								
Mn	.241	1							
Ni	.413*	.860**	1						
Cu	.324	.876**	.994**	1					
Zn	.194	.803**	.892**	.906**	1				
Al	.299	.860**	.988**	.992**	.926**	1			
Cd	.498*	.510*	.795**	.773**	.674**	.790**	1		
Pb	.372	.845**	.992**	.987**	.872**	.982**	.744**	1	
Fe	.053	.574**	.723**	.733**	.869**	.768**	.575**	.709**	1

* *Correlation is significant at the 0.05 level (2-tailed).*

** *Correlation is significant at the 0.01level (2-tailed).*

5.0 Conclusion

Important information of toxic elements (Cd, Al, Fe, Cr, NI, Mn, Cu, Pb and Zn) in different cow's milk available in Gujba was presented in this work. The result mean average of concentration of the elements such as; Cd, Al, Fe, Cr, NI, Mn, Cu, Pb and Zn are as follows; 0.1369, 1.03645, 1.259, 0.9314, 1.8031, 0.3267, 0.4739, 0.3664 and 0.4384 mg/l respectively, which shows a high contamination level of the milk products above other studies, together with the recommended baseline standard by WHO and GEMS/FOOD. The concentrations were very high as the metal levels of all the samples obtained from Gujba exceeded the WHO Permissible limits of (0.003, 0.50, 0.30, 0.50, 0.02, 0.20, 1.0, 0.001 and 0.001) mg/l for (Cd, Al, Fe, Cr, Ni, Mn, Cu, Pb and Zn) respectively.

This work also revealed that almost all milk samples were found to contain a higher metal concentration than the concentration sets by the regulatory bodies. More over the Buni-Gari area milk samples show higher metal concentration than the liquid milk collected from other different sampling points, which might be attributed to the fact that in most cases there is a trend that these contaminants effects both water, soil together with the milk samples collected from the cows grazing along that area due to its closeness to the mining site. Among the milk samples, Gelaliyu and Control site collected from Gujba shows lower values of toxic elements than the milk collected from the larger city of Buni-Yadi and Buni-Gari, which may be due to the location of the mining industry from where the milk samples were collected.

From nutritional point of view, the liquid milk collected in this study contains Mn, and Cu, in an amount sufficient to fulfill the requirement of human. Calculated metal pollution index (MPI) indicated that the cow's liquid milk contained more concentrations of the mentioned elements than the liquid milk collected from Gelaliyu and Control site.

6.0 Recommendations

A proper means of waste disposal should be adopted which can favour both the Biological, Physical and chemical settings of the environment so as to be less hazardous.

Further studies are therefore necessary to evaluate the levels of metals on a large number of samples from the region.

Determination of metal levels in fodder and water fed to the animals are also necessary. The use of other techniques such as NAA, INAA and GFAAS etc. is highly encouraged.

References

[1] Almelo K.A., Swaileh K.M., Hussein R.M., Matani M. (2012): Levels of metals (Cd, Pb, Cu and Fe) cow's milk,dairy products and hen's eggs from the West Bank, Palestine. *International food research journal Vol.9* pp1089-1094

[2] Enb A, AbouDonia MA, Abd-Rabou NS, Abou-Arab AAK, El-Senaity MH. (2009). Chemical Composition of Raw Milk and Heavy Metals Behavior During Processing of Milk Products. Global Veterinaria. 2009; 3(3):268–75.

[3] Qin LQ, Wang XP, Li W, Tong WJ TX. (2009): The minerals and heavy metals in cow's milk from China and Japan. *J. Health Sci.* 2009; 55(2):300–5.

[4] Licata P, Trombetta D, Cristani M, GiofreF MD, Calo M, Naccari F. (2004): Levels of "toxic" and "essential" metals in samples of bovine milk from various dairy farms in Calabria, Italy. Environ Int. 2004; 30:1–6.

[5] Tassew B, Ahmed H, Vegi MR. (2014): Determination of Concentrations of Selected Heavy Metals in Cow's Milk. *J. Health Sci.* 2014; 4(5):105–12.

[6] GEMS/Food,(2000): Regional Diets prepared by Global Environmental monitoring system/food contamination monitoring and Assessment programme(GEMS/FOOD).

[7] Seydou, H. (1998): Determination of trace elements in Kubanni river sediment using Energy Dispersive X-ray Fluorescence Techniques. Zaria. Unpublished MSc Thesis in Department of Physics Ahmadu Bello University Zaria.

[8] Lenntech,(2012):Water Treatment and Purification, Lenntech, Rotterdam sewage, Netherland.

[9] Ureso, J., Gonzalez–Regalado, E.,Gracia,L., (1997): Trace element in bivalve. Mollusks Ruditapesdecussates and Ruditapesphillippinarum from Atlantic Coast of Southern Spain. Environ.Int.23 (3), 291–298.

[10] World health Organization (WHO) (2002): Evaluation of certain food additives and Contaminant: Hg, Pb, Cd. 24th Report of Expert committee, WHO Technical Report Series no51.

[11] Samara S. and Richard H, (2009): Heavy metal toxicity, medicine Specialist > Emergency Medicine > Toxicology. New York.

[12] Garcia-Compean, D. ,Jaquez-Quintana, J.O., Gonzalez-Gonzalez, J. A. and Gigahertz Opti Reflection, Transmission, and Absorption". [Online] available from: http://lightmeasurement.com/reflectioabsorption/.[Accessed on 2015-08]. http://www.diabetes.org/heart-disease-stroke.jsp

[13] USEPA IRIS, (2006). United States, Environmental Protection Agency, Integrated Risk Information System.

[14] Lawal A.O., Muhammed S.S. and Damisa D, (2006): Assessment of levels of Cu, Cd and Pb in secretion of mammary gland of cow grazed on open fields. *Science World Journal Volume I. No.01.PP115-119*

[15] Ali J.A., Bukar D.E., Jimoh N, Hauwa N.T., Yusuf N., Umar Z.T. (2011): Determination of copper, zinc, lead and some biochemical parameters infresh cow milk from different locations in Niger State, Nigeria. *Afr. J. Food Sci*. 2011; 5(3):156–60.

[16] Ademola A.K. (2014): Assessments of Natural Radioactivity and Heavy Metals in Consumed Milk in Oke-Ogun Area, Nigeria and Estimation of Health Risk Hazard to the Population. *J Environ Anal Toxicol.2014*; 4:253.

[17] Alem G., Tesfahun K., Kassa B. (2015): Quantitative Determination of the Level of Selected Heavy Metals in the Cows' Milk from the Dairy Farm of the Haramaya University, Eastern Ethiopia. *Int J. Chem* Nat Sci. 2015;3(1):240–8.