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Short Communication

Assessment of Heavy Metals in Milk Samples of Cattles and Buffalos from District Quetta

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Key words
Atomic absorption spectroscopy, Buffalo, Cattle, Contamination level, Metals

ABSTRACT

Milk is a complete liquid food source since it contains rich amount of protein, fat and major minerals. Presence of trace amount of toxic metals in milk products by any means make it unfit for human consumption. The aim of this study was to evaluate metals in raw milk of buffalos and cows from different farms of district Quetta. Fifty-six whole raw milk samples from cows and buffalos were collected and analyzed using atomic absorption spectroscopy for metal contents. Levels of metals (mean±SD) such as mercury (1.97±0.49 ppm), antimony (0.37±0.08 ppm) and aluminum (0.49±0.33 ppm) exceeded the maximum permissible concentration whereas, all other studied metals including arsenic, lead, iron, sodium, cobalt and chromium were below the recommended standard values of World Health Organization (WHO). Mercury and aluminum contents were comparatively higher in buffalo milk (2.02±0.49 ppm and 0.51±0.32 ppm) than in cow milk (1.91±0.48 ppm and 0.46±0.34 ppm). The contents of antimony were higher in cow milk. The presence of metal contents in milk was greatly influenced by environmental factors, fodder contents used for animal's nutrition and water used for animal's water intake use.

Milk is one of the most nutritious foods consumed globally. It provides all essential amino acids and is a rich source of high-quality protein. Cow's milk besides, buffalo, goat, sheep and camel milk is consumed in different parts of the world. Buffalo milk compared to cow milk contains higher content of vitamins, milk proteins, lipids, nutrients and other biologically active substances (Malhat *et al*., 2012; Mikailoglu *et al*., 2005). This study was conducted for the determination of metals, i.e., arsenic, lead, iron, mercury, sodium, cobalt, antimony, aluminum and chromium in raw milk from buffalos and cows of ten different farms in districts Quetta, Balochistan, Pakistan. Varying amounts of these metals or heavy elements are required by living organisms, but excessive levels can pose great risk to living organisms (Sarsembayeva *et al*., 2019). The aim of this study was to evaluate buffalo and cow milk on the basis of composition and presence of metals.

Materials and methods

Quetta, capital city of province Balochistan, Pakistan is situated at an average altitude of 5,500 feet (1,680 meters) above sea level. It is located in northwest of Balochistan covering 2,653 km^2 of land. Quetta has semi-arid climate; the minimum temperature reaches below freezing point in winter and can reach as high as 40 ºC in summer. Livestock raising takes place in urban as well as rural areas of the district.

Fifty-six raw milk samples from 28 buffalos and 28 cows were collected from four different areas (Jan Muhammad Road, Huda, Sariab Road and Eastern Bypass) of district Quetta termed as site 1, site 2, site 3 and site 4, respectively. Seven samples (for cow and buffalo each) were collected from each area in plastic bottles and kept in ice (0 ºC) till the wet digestion took place.

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For determination of heavy metals concentration in the milk, 25 ml of each milk sample was collected in China pot. All samples were digested with the help of oven at 100 °C for 2 h (Abidin *et al*., 2021). After wet digestion, 65% HNO_3 and 35% H_2O_2 were added to each sample and heated in furnace (Model # F30420-33-60-80, Thermolyne™, France) at 700 °C for 3 h. Then 50 ml of de-ionized water in plastic bottles was added to the milk ashes to determine the metals using atomic absorption spectroscopy, using Solaar AA Series S4 system (Tareen *et al*., 2013).

For the preparation of 1000 ppm stock solution, three different concentrations were used for each metal i.e., arsenic (Ar): 40, 80 and 120 mg/l; lead (Pb): 7, 14 and 21 mg/l; iron (Fe): 5, 10 and 15 mg/l; mercury (Hg): 300, 600 and 900 mg/l; sodium (Na): 0.5, 1.0 and 1.5 mg/l; cobalt (Co): 6, 12 and 18 mg/l; antimony (Sb): 25, 50 and 75 mg/l; aluminum (Al): 30, 60 and 90 mg/l; chromium (Cr): 5, 10 and 15 mg/l. All these metals in pure form were dissolved in de-ionized water and were made to volume with de-ionized water in 25ml volumetric flask (Tareen *et al*., 2014).

Results

The average metal concentrations (ppm) in cow and buffalo milk were 0.008±0.043 for arsenic, 0.002±0.007 for lead, 0.138±0.139 for iron, 1.972±0.492 for mercury, 5.180±1.939 for sodium, 0.0009±0.002 for cobalt, 0.370±0.083 for antimony, 0.494±0.331 for aluminum and 0.024±0.023 for chromium. The average levels were higher than the standard levels recommended by the WHO for mercury, aluminum and antimony.

The average values for both cow and buffalo milk samples were also computed for different sampling sites. The highest average values for mercury were observed in site 4, whereas, lower values were observed for site 3. For antimony highest and lowest averages were observed in site 1 and site 4, respectively. For aluminum, the highest average values for mercury were observed in site 2, whereas, lower values were observed for site 4 (Table I).

The mercury contents were compared between buffalo and cow milk; it was found that the concentration of mercury in buffalo milk was higher than cow milk. The average mercury concentration in buffalo milk was 2.02±0.49 ppm which was higher than average mercury concentration in cow milk, 1.91±0.48 ppm. The antimony contents in buffalo milk were slightly lower 0.35±0.10 ppm than antimony contents in cow milk which were 0.38±0.05 ppm. Aluminum contents in buffalo milk were higher 0.51±0.32 than aluminum contents in cow milk, 0.46±0.34 ppm.

Different areas were also compared for their significance on the contents of metals presence in milk. Milk samples collected from certain areas showed elevation in metal concentration; site 4 for mercury, site 1 for antimony and site 2 for aluminum while other areas showed less metal concentration (Fig. 1).

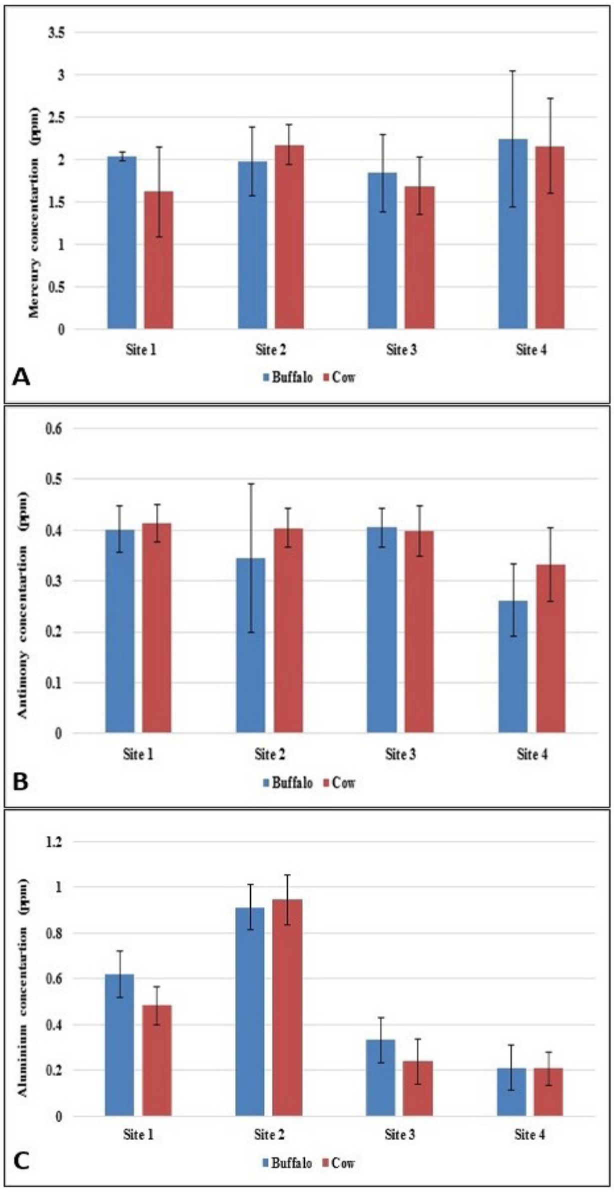

Fig. 1. Area comparison of mercury (A), Antimony (B), and Aluminum (C), concentration in buffalo and cow milk. Site 1: Jan Muhammad Road; Site 2: Huda; Site 3: Sariab Road; Site 4: Eastern bypass.

Discussion

Milk and milk products are the most varied form of the natural food stuffs in composition as it contains over twenty different trace elements. Most of these are vital trace elements including iron, copper, manganese and zinc.

Table I. Concentrations (Mean ± SD) of studied metals (ppm) in cows and buffaloes milk.

Metals	Values for metals recommended by WHO*	Source	Sampling sites			
			Site 1	Site 2	Site 3	Site 4
Arsenic	0.01	Site average	0.0004±0.0007	0.0004±0.0011	0.0016±0.0031	0.030±0.084
	ppm	Cow	0.0001±0.0002	0.0007±0.0016	0.0013±0.0031	0.001±0.001
		Buffalo	0.0007±0.0008	0.0001±0.0002	0.0019±0.0032	0.059±0.116
Lead	0.01	Site average	0.0020±0.0025	0.0010±0.0019	0.0018±0.0041	0.005±0.013
	ppm	Cow	0.0021±0.0020	0.0011±0.0023	0.0034±0.0055	0.003±0.004
		Buffalo	0.0019±0.0031	0.0008±0.0015	0.0001±0.0002	0.007±0.019
Iron	0.3	Site average	0.137±0.016	0.131±0.013	0.119±0.014	0.165±0.285
	ppm	Cow	0.140±0.023	0.136±0.014	0.118±0.007	0.089±0.014
		Buffalo	0.135±0.004	0.126±0.011	0.122±0.020	0.239±0.403
Mercury	0.002	Site average	1.833±0.423	2.078±0.334	1.771±0.395	2.207±0.667
	ppm	Cow	1.624±0.532	2.178±0.233	1.695±0.337	2.165±0.564
		Buffalo	2.041±0.059	1.979±0.405	1.846±0.458	2.249±0.801
Sodium	200	Site average	4.467±2.538	5.446±2.259	4.689±1.459	6.121±0.644
	ppm	Cow	3.519±2.473	5.461±2.234	3.900±1.242	6.158±0.653
		Buffalo	5.416±2.396	5.431±2.463	5.479±1.270	6.0825±0.685
Cobalt	0.005	Site average	0.0004±0.0005	0.0009±0.0011	0.0004±0.0005	0.002±0.004
	ppm	Cow	0.0003±0.0006	0.0004±0.0002	0.0004±0.0004	0.0002±0.0003
		Buffalo	0.0006±0.0004	0.0015±0.0015	0.0003±0.0006	0.0033±0.006
Antimony	0.006	Site average	0.407±0.040	0.374±0.107	0.401±0.043	0.297±0.078
	ppm	Cow	0.413±0.037	0.404±0.038	0.398±0.049	0.333±0.073
		Buffalo	0.401±0.045	0.345±0.145	0.405±0.038	0.262±0.071
Aluminum	0.05-0.2	Site average	0.552±0.149	0.928±0.12	0.286±0.149	0.210±0.258
	ppm	Cow	0.483±0.083	0.945±0.111	0.240±0.099	0.208±0.319
		Buffalo	0.621±0.174	0.913±0.138	0.333±0.183	0.213±0.204
Chromium	0.1	Site average	0.023±0.015	0.035±0.037	0.023±0.013	0.017±0.019
	ppm	Cow	0.025±0.017	0.057±0.041	0.023±0.011	0.022±0.025
		Buffalo	0.021±0.008	0.012±0.012	0.023±0.015	0.012±0.011

The values presented are as mean ± standard deviation. * WHO recommended standards for heavy metals in Part per million (PPM) (WHO, 2007). Site average is the total average of metals detected in both cows and buffaloes milk. Site 1: Jan Muhammad Road; Site 2: Huda; Site 3: Sariab Road; Site 4: Eastern Bypass.

These metals play vital role in various physiological functions of human and animals and are also co-factors in many enzyme activities (Chen *et al*., 2020; Caggiano *et al*., 2005; Zwierzchowski and Ametaj, 2018).

The amount of metals in milk is significantly increased through manufacturing and packaging process and also through environment and different cattle's feed. The metals presence might be attributed to lactating cows'exposure to environmental pollution, contaminated water (fluoride contents in animal water may lead to fluoridated milk and metals containing feeding stuff). The variation in the concentration of metals in the milk of buffaloes and cows is mainly due to their composition. Previous research has shown that buffalo milk is enriched in fat contents and cow milk tends to have lesser amount of fat contents (Domingo, 2021; Chen *et al*., 2020; Kambli *et al*., 2019; Malhat *et al*., 2012).

The amount of metals in un-contaminated milk is certainly minute, but manufacturing and packaging process can significantly alter their quantity. Also, the quantity of these metals is greatly influenced by cattle's feed affected by environmental contaminants i.e., chromium, lead, nickel, cadmium and cobalt. According to Caggiano *et al*. (2005) the toxic metal content in milk and dairy products is due to several factors including but not limited to environmental conditions, diet of animal, manufacturing process and possible contamination during several steps of the manufacturing processes (Kambli *et al*., 2019).

The presence of mercury (in high levels) in milk may be attributed to consumption of polluted water and feeding stuffs by dairy animal. This pollution may be due to the use of mercury and its derivatives in agriculture and industry (Diab *et al*., 2020; Kambli *et al*., 2019). Also, metals (aluminum, antimony, arsenic, calcium, chromium, cobalt, iron, lead, and sodium) presence in drinking water from the current study area was indicated by Khan *et al*. (2017) and in adjacent areas by Tareen *et al*. (2013, 2014).

Different areas were also compared for their significance on the contents of metals presence in milk. Metal contents were greatly influenced by environmental factors, fodder contents used for animal's nutrition and water used for animal's water intake use. Environmental conditions also influenced the metals presence in milk gathered from different areas. The results were also supported by Domingo (2021), where it was reported that environmental conditions have positive impact on the presence of metal contents (Khan *et al*., 2017).

A study conducted on presence of metal concentrations in poultry farm reported that metals (Hg, Cd and Pb) are determined as contaminants in the ambient air and come in contact resulting in formation of human health related hazardous substances. The presence of these metals was attributed to industrial and agricultural activities and subsequently end up accumulating in animals and plants; therefore, make their ways into food chain (Boudebbouz *et al*., 2021).

Metals have an easy admittance to the food chain and are reported exercising various physiological functions in the human body. Upon absorbance, metals accumulate in the human body even for whole span of life (Niu, 2018). These metals can adversely affect various metabolic processes in the body even at low concentrations. It is also reported that lactating animals exposed to high quantities of toxic metals may be hazardous and could pose great risk to consumers (Hooda *et al*., 1997; Llobet *et al*., 2003).

Conclusions

The current study reports high amounts of metals i.e. mercury, antimony and aluminum in milk samples collected from both cows and buffalos. The levels of the metals were higher than the recommended in WHO standards. It was also reported that mercury and aluminum were higher in buffalo milk and antimony content was higher in cow milk.

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Ethical statement

The current study was conducted following ethical guidlines and the study was approved by the Department of Livestock and Dairy Development, Quetta, Balochistan, Pakistan.

Statement of conflict of interest

The authors have declared no conflict of interest.

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