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# Preliminary Study of Metal in Yak (*Bos grunniens*) Milk from Qilian of the Qinghai Plateau

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**Abstract** 63 samples of yak milk were analyzed by the method of ICP-AES of metal elements for aluminum, cadmium, silver and chromium which can reveal the exposed level around yak farm. The metal elements of yak milk were compared to reference data for cow milk, sheep milk, buffalo milk and goat milk. In addition, the concentration was compared to PTWI (provisional tolerable weekly intake) established by the JECFA (WHO/FAO) for metal intake/body weight per week of cadmium, aluminum, and chromium level was compared to EVM (Expert Group on Vitamins and Minerals) guidance level, while the threshold of silver was lacking according to the authority standard. Analysis of regression correlation was calculated between Cd and Co, Cr, Cu, Ag, Al, Mn.

**Keywords** Yak milk · Metal · Regression correlation · Qinghai plateau

At present, the total yak population is estimated to number around 14.2 million, of which 13.3 million are in Chinese territories, about 0.6 million in Mongolia, and the rest in other countries. On the Qinghai plateau, the yak population, about 5.0 million, is the highest in the world. In addition, it is a very important to understand interaction between yak animal and Qinghai plateau ecosystem, as Qinghai plateau is named the roof of the world which is a headstream for three river (Changjiang river, yellow river, Lanchangjiang river).

In China, Qinghai is known for beautiful grassland and vast pasture and gives great contribution to animal products, one of which is yak milk which is rich in nutrients (high protein and unsaturated fatty acids content).With the development of industrialization tend to encroachment yak farms, it is well known that Qinghai plateau has rich mining resources, such as coal, lead–zinc smelter, manganese smelter and copper smelter, have a harmful impact on the yaks' fragile grassland environment.

In paper, the aim of this research is to create a detail database of heavy elements of yak milk collected around a mining area. At present there are limited reference data about yak milk. Researcher Qinghai Sheng presented the results of metal elements for Zn, Fe, Cu, Mn by atomic absorption spectrophotometry (Qinghai Sheng et al. 2008). It is known that milk is a good biomarker of environmental pollution (Anastasio et al. 2006) and with the change of world environment we want to know if our region was affected by the mining industry.

## Materials and methods

Fresh milk samples were collected from 63 lactating yaks from August to September in the region of Yeniu town, Qilian County, Qinghai Province in China. The samples were taken from herds (A, B, C, D, E, F, G, H, N, X) of ten yak farms. The samples were milked directly from the yaks and the vials stored. The samples were brought in ice packs for further processing in the laboratory, where they were kept at −20°C till analysis.

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The metal elements analysis of these samples was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample was nebulized then transferred to argon plasma. The work was performed on a JY ULTIMA 2 with the gas flow at 12 L/min, RF generator power 1000 W. The wavelengths used were 328.068 nm for Ag, 309.271 nm for Al, 214.438 nm for Cd, 283.563 nm Cr, 228.616 nm for Co, 257.610 nm for Mn, 324.754 nm for Cu, 213.856 nm for Zn, 259.940 nm for Fe. Multi-element calibration standards were prepared by appropriate dilution of 1000 mg/L single-element standard solutions.

The detection limit was calculated on unfortified blank samples and calculated at 3 times the signal to noise ratio. The LoD (limit of determination) were 7, 2, 4 and 3 ng/mL for aluminum, cadmium, silver and chromium respectively. The recovery was calculated by analyzing milk samples spiked at 20 ng/mL levels. The recoveries were 94, 97, 92 and 89% for aluminum, cadmium, silver and chromium respectively.

The data were analyzed by the statistical package for social sciences (SPSS) for Windows (version 16.0) software using one-way analysis of variance to find out the statistical difference among the mean values of heavy metals. The regression analysis between heavy metal and nutrient elements were analyzed by 2-tailed test of Pearson correlation.

## Results and Discussion

63 samples of yak milk were analyzed the metal elements (cadmium, silver, aluminum, chromium) of by the ICP-AES method. Table 1 shows the value range of elements in milk of different species. Cadmium concentration in yak milk samples was 462 times higher than in cow milk samples (Hermansen et al. 2005), 5.3 times higher than in sheep milk (Coni et al. 1999), but lower than in goat milk (Guler 2007). Aluminum concentration of yak milk was close to cow milk (Hermansen et al. 2005), but lower than sheep milk (Coni et al. 1999) and goat milk (Guler 2007). Chromium is essential at a low level, but an excess can result in deleterious effects on human health (Ataro et al. 2008). Chromium level in the yak milk (Qilian) ranged from 0.382 to 0.506 μg/g which was much higher than the literature report range from 0.002 μg/g of cow milk (Licata et al. 2004) to 0.006 μg/g of cow milk (Hermansen et al. 2005), but lower than the level 1.14 mg/L of cattle milk and 1.196 mg/L of goat milk (Javed et al. 2009), as well as 0.77 μg/g in goat milk (Guler 2007). There is relatively limited literature about silver in milk, and content of silver observed (Guler 2007) was much higher (2.2 times) than the present analysis result.

The joint FAO/WHO Expert Committee on Food Additives (JECFA) had set the PTWI (provisional tolerable weekly intake) for cadmium at 7 μg/kg of body weight per week (FAO/WHO 2006). Yak milk makes up a large part of the daily diet and frequently a large amount of yak milk products, such as milk, milk tea, milk cake and yoghourt are consumed. PTWI was calculated based on the preliminary diet estimation of yak milk of 1000 g per day and body weight of 60 kg (Haw et al. 2004) and the calculated result of cadmium intake, due to the concentration in yak milk, was 35.6 μg/kg body weight a week, which was an amount distinctly higher than 7 μg/kg from PTWI of JECFA.

A COT (Committee on Toxicity) statement presented the estimates of dietary exposure to chromium (mean- and high-level intakes) for all consumer groups were within the EVM (Expert Group on Vitamins and Minerals) guidance level for trivalent chromium of 150 μg/kg body weight a day. It was calculated that chromium level (8.2 μg/kg body weight a day) of yak milk was lower than EVM guidance level (150 μg/kg body weight/day). The Committee on Medical Aspects of Food and Nutritional Policy (COMA) did not set reference nutrient intakes (RNIs) for chromium but suggested that an adequate level of intake lies above 0.025 mg/day for adults (equivalent to 0.4 μg/kg body weight/day for a 60 kg adult) and between 0.1 and 1 μg/kg body weight/day for children and adolescents (COMA 1991). In short, comparable to the COMA, the dietary exposure of yak milk provides an adequate level of Cr intake for local herdsmen.

The JECFA established the PTWI for aluminum of 1 mg/kg body weight (FAO/WHO 2006), which applied to all aluminum compounds in food, including additives. According to aluminum concentration of yak milk, the diet

**Table 1** The metal elements (μg/g) compared yak to other species milk

| Species | Elements | | | | References |
|---|---|---|---|---|---|
| | Ag | Al | Cd | Cr | |
| Yak | 0.131 ± 0.056 (0.051–0.284) | 0.414 ± 0.087 (0.19–0.607) | 0.305 ± 0.014 (0.278–0.341) | 0.433 ± 0.028 (0.382–0.506) | Present study |
| Cow | _ | 0.340 | 0.00066 | 0.006 | (Hermansen et al. 2005) |
| Sheep | _ | 1.78 | 0.058 | 0.450 | (Coni et al. 1999) |
| Goat | 0.28 | 3.76 | 0.63 | 0.77 | (Guler 2007) |

index aluminum per week (48.3 μg/kg body weight a week) was lower than 1 mg/kg from PTWI (provisional tolerable weekly intake). EFSA (European Food Safety Authority) reported that mean dietary exposure from water and food in non-occupational exposed adults showed large variations between the different countries, and within a country, between different surveys. It ranged from 1.6 to 13 mg aluminum per day, corresponding to 0.2 to 1.5 mg/kg body weight (bw) per week in a 60 kg adult (EFSA 2008).Yak milk level was of 48.3 μg/kg body weight per week, lower than the range level of 0.2 to 1.5 mg/kg body weight (bw) per week of EFSA scientific report.

Data about silver in milk are relatively limited in literature, and content of silver observed by author (Guler 2007) was much higher (2.2 times) than the present investigation regarding yak milk. For yak milk consumers, the silver intake was calculated around 917 μg/kg body weights a week. At present, there is no silver threshold in diet recommendations, however a high level of silver in the diet is considered harmful for the consumer.

We analyzed correlation by the 2-tailed test between Cd and Co, Cr, Cu, Ag, Al, Mn of yak milk samples ($n = 63$) which revealed a significant correlation with Co ($r = 0.740$, $p = 0.000$), Cr ($r = 0.772$, $p = 0.000$), Cu ($r = 0.263$, $p = 0.019$), Ag ($r = 0.344$, $p = 0.003$), Al ($r = 0.284$, $p = 0.012$), Mn ($r = 0.981$, $p = 0.000$). In particular, the metal Cd has almost perfect correlation with Mn, which is a transition metal, both a nutrient and toxicant. The results show that Mn concentration of yak milk was 38 times that of cow milk samples (Hermansen et al. 2005), 2.1 times that of sheep milk (Coni et al. 1999), 264 times that of buffalo milk (Benincasa et al. 2008) and similar to goat milk (Guler 2007). The metal Cd also has almost good correlation with Co, which is in accordance with the research result of R. C. Patra (Patra et al. 2008). Compared to cow milk (Hermansen et al. 2005), the concentrations of Zn, Cu, Fe (data not shown) in yak milk revealed lower levels than those of cow milk samples, in other words, increasing the absorption of Cd and Mn results in the deficiency of Zn, Cu, Fe results. This is due to interactions in metabolism between zinc and cadmium, related to each other, sharing the binding to metallothionein, a low-molecular-weight protein that binds zinc and copper and which may assist in the transport and storage of these essential metals (Goyer 1997). Between Cd and Co, Cr, Cu, Ag, Al, Mn there is significant positive correlation: we assume that perhaps the toxicant element cadmium, an environment pollutant, comes from the ore mining in which the metal elements emission occur. According to investigation, there are rich ore resources in the region of Qilian, and in Qinghai there are about 20 ore extraction companies for lead–zinc, manganese and copper smelter.

In addition, comparing the analysis of ten yak herds, showed that the yak group from farm E had very low concentrations of macro elements Ca, P, S, Mg (data not shown), however there were very high concentrations of micro elements Co, Cr, Mn, Cd, Al distinctly. According to investigation, the yak farm E was possibly polluted by the lead–zinc metal smelter, manganese smelter and copper smelter. Yak farm E has 130 yaks, grazing on the pasture around the metal smelter. Yak farm X is the farthest away from the metal smelter, and has good rearing environment and better management (stable for yak rest at night) for 120 yaks, so the elements concentration of yak milk from yak farm X was higher levels of macro elements for Ca 1378 μg/g, P 1361 μg/g.

In short, the results showed that Cd concentration in yak milk samples was distinctly higher than cow milk, sheep milk, and threshold of the JECFA. Al concentrations of yak milk samples was similar to cow milk, but lower than sheep milk and goat milk, and also lower than PTWI (provisional tolerable weekly intake) of the FAO/WHO threshold. Cr level in the yak milk was higher than the literature report range, but lower than the EVM threshold level. There are relatively limited reference data about silver in milk, and the level of silver observed in the literature was much higher than that of yak milk. There was good regression correlation between Cd and Co, Cr, Cu, Ag, Al, Mn.

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