Heavy Metals Determination in Raw Milk Fed by Contaminated by Cow Feed

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Abstract
One of the key problems in lifestock, Central region, Thailand, was the toxic and heavy metals contaminations in animal feeds produced via harmful environment due to industrial estates. Cow's milk and dairy products are the important foodstuff and beneficial to human health. In this study metal contents in 84 of commercially available in cow's milk (powder and liquid) and dairy product (yoghurt and cheese), samples from different zones in central region were chosen. The heavy metals were determined by Inductively Coupled Plasma-Optical Emission Spectrometry. In accordance with the present survey and studies the amount and level metals has been specified in the cow's milk. Organic matter is digested with nitric acid and perchloric acid; the most suitable acids in wet digestion of milk and dairy products. Mean concentrations of metals (μg/g) in milk and dairy samples analyzed ranged between 0.028-0.061 for Cd, ND-0.89 for Pb, 0.72-0.91 for Cu and 3.1-12.91 for Fe. Results indicated high concentrations of Pb and Cd especially in powder milk samples. The lowest concentrations of metals were found in cheese followed by liquid milk. Finally, further investigations are needed to identify the cause of elevated Pb and Cd levels especially in milk and dairy products.

Keywords: metals, cow's milk, dairy products, Inductively Coupled Plasma-Optical Emission Spectrometry

Introduction

One of the key problems in lifestock, Central region, Thailand, was the toxic and heavy metals contaminations in animal feeds produced via harmful environment due to industrial estates. Cow’s milk and dairy products are the important foodstuff and beneficial to human health. Elements are essential micro-nutrients and have a variety of biochemical functions in all living organisms. Some of them form an integral part of several enzymes. Although they are essential, they can be toxic when taken in excess; both toxicity and necessity vary from element to element and from species to species. Thus, information on the intake of heavy metals through food chain is important in assessing risk to human health.

As trace metals, some minerals are essential to maintain the metabolic systems of the human body. However, at higher levels they can lead to poisoning. Some toxic elements are introduced into animals and human organisms through plants. The mammary glands are the most physiologically active part of dairy cows, and therefore the input and output of toxic elements in these organisms are clearly reflected in the milk. Monitoring the route of toxic elements in relation to the soil–fodder–milk pathway is important since the consequences of their activity have a great impact on both the environment and people’ health [1].

Milk has been part of the human diet for millennia and is valued as a natural and traditional food. Milk and dairy foods are considered to be one of the main food groups important in a healthy balanced diet, and as such feature in the majority of national food-based dietary guidelines from the British Eatwell[2] and Australian plate model[3], to the Chinese Pagoda[4] and the Japanese Spinning top[5], the US pyramid[6], the Guatemalan pot[7]and many others. As milk provides a substantial amount of vitamins and minerals in relation to its energy content, it is considered a nutrient dense food[8].

Cows‟ milk provides a wide range of essential nutrients to the diet. Whilst milk as a source of calcium is often recognized, it is perhaps less commonly known that milk and milk products are also an important source of good quality protein, the B vitamins, B2 (riboflavin) and B12, and the minerals iodine, potassium and phosphorus[9]

Milk and dairy products make an important contribution to the supply of nutrients for the human diet. The ash of cow's milk contains some major elements such as calcium, phosphorus and magnesium, in addition to potassium, sodium and chlorine and a wide range of trace elements including zinc, copper, iron, manganese and iodine. Thus cow 's milk is an important source of protein, minerals and vitamins in the human diet. Thus, contamination of milk and dairy products by toxic metals can be a possible health risk to human population. The presence of toxic metals in the food chain is the result of environmental pollution and their concentrations need to be controlled constantly. The composition of the mineral fraction of milk and milk products has been frequently considered, but only a few published investigations deal with minor but only a few published investigations deal with minor in food.

Milk and dairy products become contaminated with heavy metals either through food stuff and water or through manufacturing and packaging processes[10-12] investigated the concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, Se and Zn in cheese samples packaged in plastic and tin containers. They found that there were considerable differences among of the studied element contents of cheese samples packaged in tin and plastic containers. They concluded that, cheese types and packaging materials play a key role in the content of trace metal

The present study aimed at evaluating the heavy metal quality of cow's milk (powder and liquid) and dairy product (yoghurt and white cheese), samples from different zones in central region were chosen. A total of 84 samples were analyzed after " Wet digestion" for four trace elements using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Aim of Research

The aim of the present study is to heavy metals determination in Raw Milk Fed by contaminated by cow feed

Materials and Methods

Collection of samples

Samples of commercially available cow's milk (powder and liquid), dairy products (yoghurt and white cheese). Sample collection took place twice during 2013. The selection of dairy products was based on estimates on their potential consumption in Pathumtani Province. The samples were collected that they were high probability contamined by heavy metals. The collected white cheese samples were homogenized. White cheese and raw milk samples were kept in clear polyethylene cups. 200 g sample was taken from each product. All samples were stored below −18°C prior to analysis.

Reagents

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) standard solutions for Zn, Cd, Cu, and Pb were purchased from Fisher Scientific Company, USA. Working standard solutions were prepared by diluting the stock solution. Nitric acid and perchloric acid were all of AR quality. De-ionized water has been used when required.

Sample analysis

A microwave system was used for acid digestion of all the samples. All the samples (Milk and Dairy products) were dried at 100°C in a forced stove until dry weight. Thereafter, dry samples were ground to powder using a grinder with stainless steel knife, then stored in clean glass vials for later analysis. Approximately 1.0 g of milk, yogurt and 0.5 g of other dairy products samples were weighed into the TEFLON-vessels, mixed with 5 ml of HNO_3 plus 2 ml of $HClO_4$ and digested by microwave irradiation in steps, increasing power from 250 to 650 W by 5 min increments. Within 15 min, completely clear and colourless solutions were obtained which were subsequently diluted with double-distilled water. Samples were prepared in triplicate runs[13]. Finally, concentrations of Cu, Cd, Pb and Fe were measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

Results and Discussion

The range of linearity of concentration vs. absorbance curve is of great importance in determining the elemental concentration of the milk samples. The calibration curves for Zinc (Zn) and Cadmium (Cd) are shown in Fig. 1 and Copper (Cu) and Lead (Pb) are shown in Fig. 2

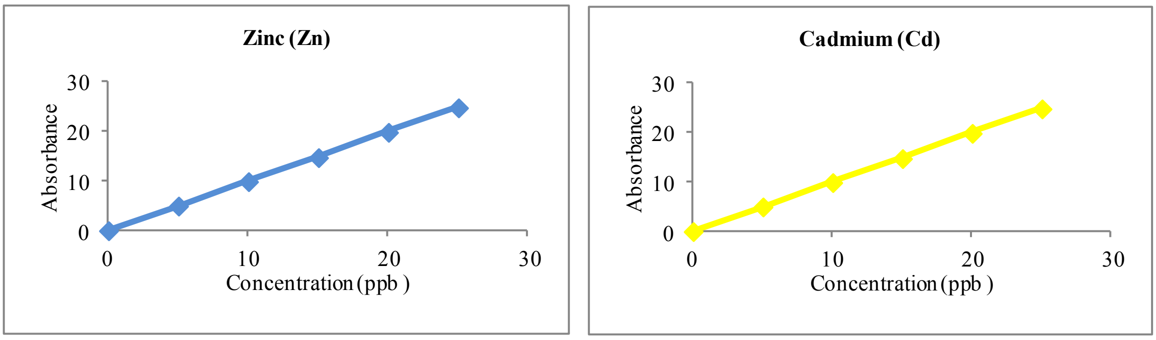

Fig. 1 Concentration versus absorbance curves for Zinc (Zn) and Cadmium (Cd)

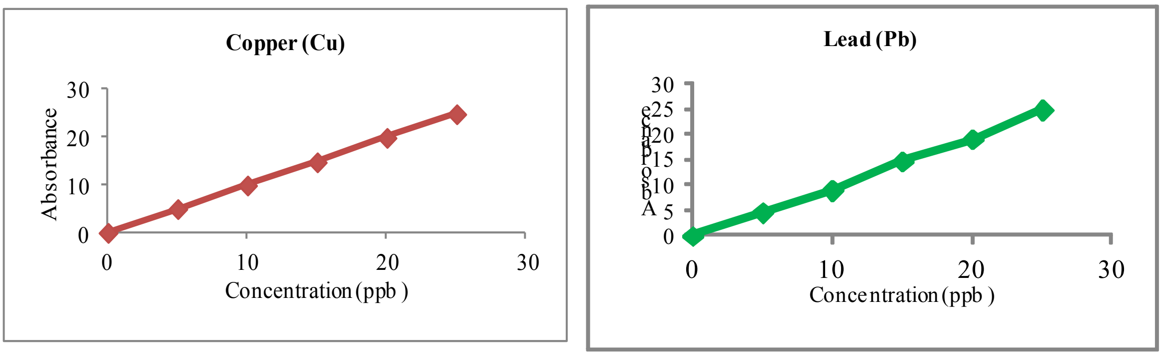

Fig. 2 Concentration versus absorbance curves for Copper (Cu) and Lead (Pb)

Table 1. Concentrations of metals (Means±S.D.) in powder milk consumed in Pathumtani Province. Minimum and maximum values are shown between brackets.

powder milk (pm. District)	Cd±S.D. µg/g	Pb±S.D. µg/g	Cu±S.D. µg/g	Fe±S.D. µg/g
pm.1	31.0 ± 0.0	0.81 ± 0.0	0.51 ± 2.0	18.1 ± 0.1
pm.2	45.0 ± 0.2	0.92 ± 0.2	0.53 ± 1.9	17.1 ± 0.2
pm.3	44.1 ± 0.5	0.74 ± 0.5	0.53 ± 2.1	18.2 ± 0.4
pm.4	32.0 ± 0.4	0.92 ± 0.4	0.43 ± 1.7	18.0 ± 0.0
pm.5	55.1 ± 0.6	0.25 ± 0.6	0.27 ± 1.7	17.0 ± 0.1
pm.6	35.1 ± 0.8	0.15 ± 0.8	0.41 ± 1.6	19.2 ± 1.0
pm.7	23.2 ± 0.4	0.28 ± 0.4	0.44 ± 1.7	17.1 ± 0.3

Metal contents of powder milk and liquid milk are summarized in Tables 1 and Tables 2. In all samples analyzed, concentrations of Fe were the highest and those of Cd were the lowest. Table 1 show metal concentrations in milk powder from 7 district. Cd and Fe levels indicated significant differences between district however ; Cu and Pb levels were similar in powder milk from 1 district. Mean Cd levels in powdered milk from 1 district was significantly higher those from other districts and mean Fe levels in powdered milk from 1 district was significantly higher than other districts. The mean levels of metals were: 14.04, 0.84, 0.53 and 19.1 µg/g for Fe, Pb, Cu and Cd respectively. The high concentration of Fe is caused by the enrichment of powder milk with iron that is practiced by most companies. Lead concentrations in powder milk were found to exceed the maximum allowed limit for Pb in milk powder and cheese that was set as 0.19 µg/g. However, Cd concentrations were below the maximum allowed limit of 0.4 µg/g Cd in powder milk.

Table 2. Concentrations of metals (Means±S.D.) in liquid milk consumed in Pathumtani Province. Minimum and maximum values are shown between brackets.

Liquid milk (lm. District)	Cd±S.D. µg/g	Pb±S.D. µg/g	Cu±S.D. µg/g	Fe±S.D. µg/g
lm.1	29.0 ± 0.0	0.71 ± 0.1	0.21 ± 1.5	6.1± 0.3
lm.2	49.0 ± 0.5	0.72 ± 0.5	0.24 ± 1.2	5.1 ± 0.5
lm.3	57.1 ± 0.5	0.74 ± 0.5	0.21 ± 1.1	5.2 ± 0.6
lm.4	47.0 ± 0.1	0.72 ± 0.2	0.20 ± 1.2	5.0 ± 0.2
lm.5	33.1 ± 0.8	0.75 ± 0.4	0.17 ± 1.3	6.0 ± 0.2
lm.6	32.1 ± 0.5	0.75 ± 0.6	0.21 ± 1.2	6.2 ± 1.1
lm.7	31.2 ± 0.2	0.78 ± 0.2	0.16 ± 1.4	5.1 ± 0.8

Metal concentrations in liquid milk from 7 districts s are summarized in Table 2. No statistically significant differences between liquid milk of districts were observed for Cu, Pb and Fe. The only significant difference was observed for Cd concentrations, where liquid milk from 1 districts contained significantly higher Cd content (98.9 µg/g) than other districts. The mean concentrations of metals in different liquid milk samples were: 6.15, 0.71, 0.27 and 41.21 µg/g for Fe, Cu, Pb and Cd respectively. Levels of metals in liquid milk were having the following order: Fe>Cu>Pb>Cd and were less than those measured in powder milk. However, mean Pb and Cd concentrations in liquid milk exceed the maximum allowed limits of 0.04 and 0.02 µg/g for Pb and Cd in liquid milk respectively.

Table 3. Concentrations of metals (Means ± S.D.) in powder milk consumed in Pathumtani Province. Minimum and maximum values are shown between brackets.

yoghurt (yoghurt. District)	Cd±S.D. µg/g	Pb±S.D. µg/g	Cu±S.D. µg/g	Fe±S.D. µg/g
yoghurt.1	12.0 ± 0.0	0.31 ± 0.1	0.41 ± 1.5	4.2± 0.3
yoghur.2	14.0 ± 0.5	0.58 ± 0.5	0.24 ± 1.2	5.1 ± 0.5
yoghur.3	27.1 ± 0.5	0.42 ± 0.5	0.42 ± 1.1	6.2 ± 0.6
yoghur.4	11.0 ± 0.1	0.91 ± 0.2	0.29 ± 1.2	8.2 ± 0.2
yoghur.5	9.1 ± 0.8	0.27 ± 0.4	0.47 ± 1.3	4.2 ± 0.2
yoghur.6	12.1 ± 0.5	0.93 ± 0.6	0.54 ± 1.2	3.9 ± 1.1
yoghur.7	11.3 ± 0.2	0.88 ± 0.2	0.25 ± 1.4	4.1 ± 0.8

Concentrations of the four metals in yoghurt is shown in Table 3. No statistical differences in Cd, Pb and Fe concentrations were observed for yoghurt from all districts. Significant differences were observed for Cu concentration where yoghurt from all districts contained the highest level of Cu. According to their concentrations in yoghurt, metals were having the following order: Fe>Pb> Cu>Cd. This may be caused by the loss of some metals by the drainage process.

Table 4. Concentrations of metals (Means ± S.D.) in liquid milk consumed in Pathumtani Province. Minimum and maximum values are shown between brackets.

white cheese (white cheese. District)	Cd±S.D. µg/g	Pb±S.D. µg/g	Cu±S.D. µg/g	Fe±S.D. µg/g
white cheese.1	10.0 ± 0.0	0.21 ± 0.1	0.31 ± 1.5	3.1 ± 0.1
white cheese.2	9.0 ± 0.8	0.48 ± 0.6	0.14 ± 1.2	6.4 ± 0.5
white cheese.3	6.1 ± 0.5	0.32 ± 0.5	0.32 ± 1.1	4.2 ± 0.3
white cheese.4	8.0 ± 0.1	0.41 ± 0.1	0.21 ± 1.3	2.1 ± 0.4
white cheese.5	9.9 ± 0.5	0.29 ± 0.4	0.67 ± 1.3	5.3 ± 0.2
white cheese.6	14.1 ± 0.3	0.54 ± 0.4	0.41 ± 1.2	4.1 ± 0.1
white cheese.7	12.5 ± 0.1	0.89 ± 0.1	0.45 ± 1.4	3.8 ± 0.6

White cheese is the main and traditional form of cheese made and consumed in the Pathumtani Province. Results of elemental white cheese analysis from 7 all districts are summarized in Table 4. Generally, cheese is characterized by low concentrations of metals except Cu. Compared to all products analyzed in the present study, white cheese contained the lowest concentrations of Fe and Pb (below detection limits) and the second lowest Cd concentration.

Ranking biological samples according to metal concentration gives a clear idea about metal richness[14]. When ranked according to metal concentrations milk powder was found to have the highest total rank score and cheese the lowest. The 4 products examined had the following decreasing order in total rank score powder milk>yoghurt>liquid milk>white cheese. Milk is the raw material for all other dairy products and the final concentration of metals in any dairy product is affected by the concentration of metals in the milk used and the industrial processing. The results indicate that milk in the present study contains higher levels of metals than most other countries. This is obvious especially in the case of Pb. Although Palestine is not an industrialized country, leaded fuel is still largely used which might be one reason for the high Pb levels recorded. In addition, processing and packaging of milk and dairy products may lead to an elevation in metal concentrations.

Conclusions

Concentrations of Cd, Pb, Cu and Fe in milk, dairy products consumed in the Pathumtani Province showed little variability with districts. Generally, Pb and Cd concentrations in milk and dairy products (white cheese) exceeded the maximum allowed values. The elevated levels could be related to contamination during industry processing and environmental pollution. Powder milk was found to be the richest in metals while white cheese was found to be the poorest. Among the four metals studied, Fe concentrations were always the highest and Cd concentrations were always the lowest. Comparing results of the present study with those of other studies

revealed higher levels of metals, especially Pb, in milk and dairy products investigated in the present study. Finally, the elevated levels of heavy metals (Pb and Cd) need further investigations to identify the cause of these elevated levels.
Increased awareness and controlled manufacture of these products are necessary in order to decrease the contents of elements, in addition to Pb, which showed a wide range of contents. It is vital to inform both farmers and company managers about this issue. The using water for producing and cleaning in milk and dairy factory must be controlled side of trace metals.
Metal migration from the milk containers is important. Therefore, used containers for milk must not contain those toxic metals, or those containers must be isolated with right matter. Dairy factories must using new technology and techniques. The milk and dairy products must not be allowed to sell without package and in open locations.In addition to information, an effective control mechanism (e.g. ISO series) imposed by government would play an important role in the prevention of contamination of milk and dairy products with these metals.

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2. Determination of the Content of Hazardous Heavy Metals on *Curcuma longu* Grown around a Contaminated Area
3. Determination of Heavy Metals in Thai Herbal Plants
4. Determination of Heavy Metals Concentrations in Soil and Plant Samples by Inductively Coupled Plasma-Optical Emission Spectrometry
5. Herbal Extract of Efficiency For Metal Reduced From Vegetables Washing Water
6. Contamination of Microbial in Thai Traditional Medicines